Write your name here

Surname	Other names

Centre Number ☐☐☐☐☐

Candidate Number ☐☐☐☐

Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 27 January 2010 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- 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 Consider the equilibrium

$$Cl_2(g) + PCl_3(g) \rightleftharpoons PCl_5(g)$$

Which of the following is true when the total pressure of the system is increased at constant temperature?

		Value of K_p	Mole fraction of $PCl_5(g)$
☒	**A**	decreases	decreases
☒	**B**	unaltered	increases
☒	**C**	decreases	increases
☒	**D**	unaltered	unaltered

(Total for Question 1 = 1 mark)

2 In which of the following reactions is nitric acid acting as a base?

☒ **A** $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

☒ **B** $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

☒ **C** $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$

☒ **D** $HNO_3 + NaHCO_3 \rightarrow NaNO_3 + H_2O + CO_2$

(Total for Question 2 = 1 mark)

3 Why does phenolphthalein, which is colourless in acidic solutions, turn pink in alkaline solutions?

☒ **A** It is oxidized to a pink compound by hydroxide ions.

☒ **B** It forms a pink anion by loss of H^+ ions.

☒ **C** It forms a pink anion by gain of H^+ ions.

☒ **D** It forms a pink cation by gain of H^+ ions.

(Total for Question 3 = 1 mark)

4 The dissociation of ethanoic acid in aqueous solution is represented by

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Which of the following statements is true for this equilibrium?

☒ **A** CH_3COOH is an acid and its conjugate base is CH_3COO^-.

☒ **B** H_2O is an acid and its conjugate base is OH^-.

☒ **C** At equilibrium, the concentrations of each substance are the same.

☒ **D** At equilibrium, the reaction from left to right and the reaction from right to left have stopped.

(Total for Question 4 = 1 mark)

5 Why are aqueous solutions of sodium ethanoate slightly alkaline?

☒ **A** The sodium ions react with water to give an alkali.

☒ **B** The ethanoate ions react with water to give hydroxide ions.

☒ **C** All sodium salts give alkaline solutions.

☒ **D** The sodium ethanoate is fully ionized in solution.

(Total for Question 5 = 1 mark)

6 When ammonium nitrate crystals dissolve in water, the entropy of the system

☒ **A** remains the same.

☒ **B** falls, because the hydrated ions are more ordered than the solid.

☒ **C** rises, because the ions in the crystal become hydrated in the solution.

☒ **D** rises, because the ions are arranged more randomly in the solution than in the crystal.

(Total for Question 6 = 1 mark)

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

7 Which of the following molecules is a methyl ester?

☒ **A** $CH_3COOCH_2CH_3$

☒ **B** $HCOOCH_3$

☒ **C** $CH_3COCH_2CH_3$

☒ **D** CH_3COCl

(Total for Question 7 = 1 mark)

8 During the preparation of a liquid compound, samples were taken of the product at various stages in the purification procedure. Which of the following techniques would be most suitable for showing the change in composition of these samples during the purification procedure?

☒ **A** Gas-liquid chromatography

☒ **B** Fractional distillation

☒ **C** Filtration

☒ **D** Distillation

(Total for Question 8 = 1 mark)

9 Which of the following compounds would react with lithium tetrahydridoaluminate (lithium aluminium hydride) **and** also with phosphorus(V) chloride (phosphorus pentachloride)?

☒ **A** $CH_3CH_2CH_2COOH$

☒ **B** $CH_3CH_2COCH_3$

☒ **C** $CH_3CH{=}CHCH_3$

☒ **D** $CH_2{=}CHCH_2CH_2OH$

(Total for Question 9 = 1 mark)

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

10 In the synthesis of an ester, the use of an acyl chloride and an alcohol gives a better yield than the use of a carboxylic acid and an alcohol.

This is because the reaction between

☒ **A** an acyl chloride and an alcohol is an equilibrium.

☒ **B** an acid and an alcohol goes to completion.

☒ **C** an acid and an alcohol requires a catalyst.

☒ **D** an acyl chloride and an alcohol goes to completion.

(Total for Question 10 = 1 mark)

11 Not all molecules will absorb infrared radiation. Those that do

☒ **A** change their dipole moment when their bonds stretch or bend.

☒ **B** undergo homolytic fission.

☒ **C** must be polar.

☒ **D** are always organic substances.

(Total for Question 11 = 1 mark)

12 Which of the following methods may be used **in a single step** to make carboxylic acids?

☒ **A** Hydrolysis of an ester with an alkali.

☒ **B** Reaction of acidified potassium manganate(VII) with an alkene.

☒ **C** Hydrolysis of a nitrile with hydrochloric acid.

☒ **D** Reaction of an acyl chloride with ammonia.

(Total for Question 12 = 1 mark)

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

13 A solution of a weak acid cannot be titrated with a weak base using an indicator to find the end-point because

☒ **A** the pH change is too gradual close to the equivalence point.

☒ **B** there are too few H^+ ions to affect the indicator.

☒ **C** there are too few OH^- ions to affect the indicator.

☒ **D** the pH change occurs outside the range of any indicator.

(Total for Question 13 = 1 mark)

14 Which of the following reagents could be used to produce propanamide, $CH_3CH_2CONH_2$?

☒ **A** Ammonia and 1-chloropropane

☒ **B** Ammonia and propanoyl chloride

☒ **C** Methylamine and 1-chloropropane

☒ **D** Methylamine and propanoyl chloride

(Total for Question 14 = 1 mark)

15 The radio waves used in proton nmr

☒ **A** must not be absorbed by the sample.

☒ **B** cause electron transitions in the hydrogen atom.

☒ **C** can only be used with organic substances.

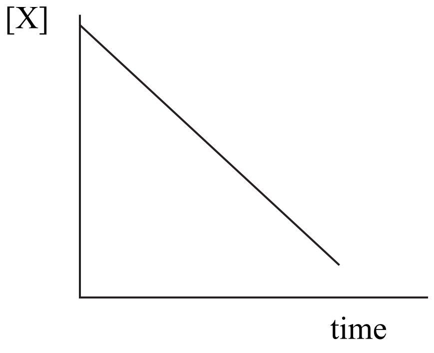
☒ **D** cause the hydrogen nucleus to change its spin state.

(Total for Question 15 = 1 mark)

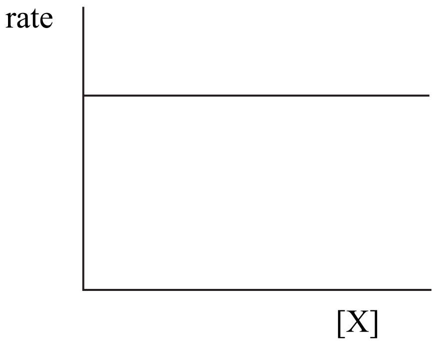
Use this space for any rough working. Anything you write in this space will gain no credit.

16 Which of the following graphs shows that a reaction is first order with respect to reactant **X**?

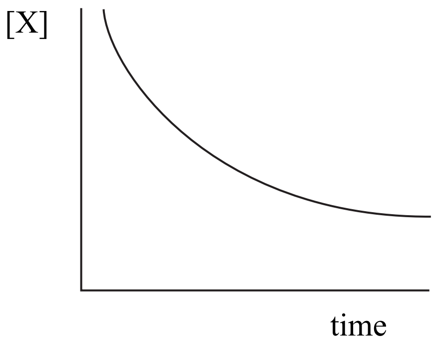
☒ **A**



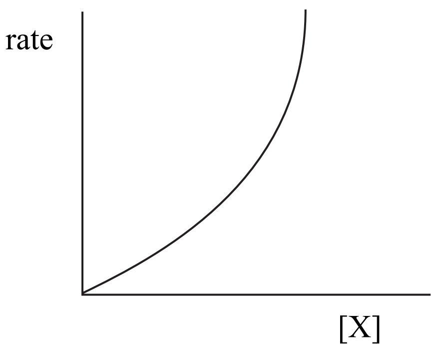
☒ **B**



☒ **C**



☒ **D**



(Total for Question 16 = 1 mark)

17 Which of the following changes will lead to the greatest increase in the **rate** of the following endothermic reaction?

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H \text{ +ve}$$

		Temperature	Initial concentration of N_2 and O_2
☒	**A**	decrease by 15%	decrease by 15%
☒	**B**	increase by 15%	stay the same
☒	**C**	decrease by 15%	increase by 15%
☒	**D**	increase by 15%	increase by 15%

(Total for Question 17 = 1 mark)

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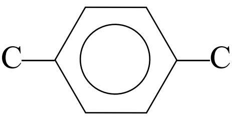
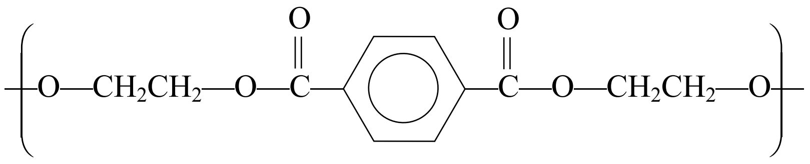
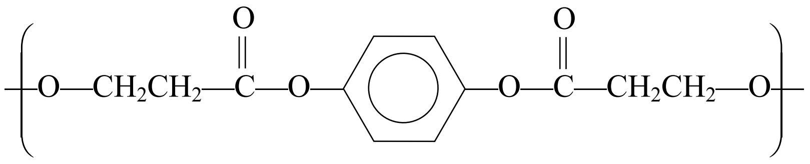
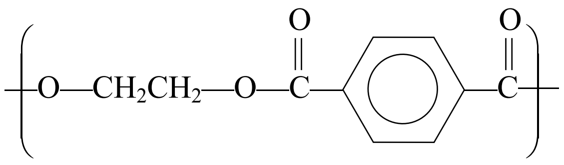
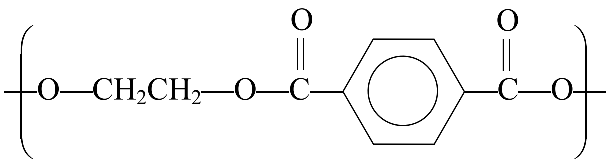
18 The repeat unit of the polyester formed from ethane-1,2-diol, $HOCH_2CH_2OH$, and benzene-1,4-dicarboxylic acid, HOOCCOOH, is

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 18 = 1 mark)

19 Iron and steam at high temperature react in a closed vessel to give an equilibrium mixture

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Which of the following is the correct expression for K_p?

☒ **A** $K_p = \dfrac{P_{H_2}}{P_{H_2O}}$

☒ **B** $K_p = \dfrac{P_{Fe_3O_4} P_{H_2}^4}{P_{Fe}^3\ P_{H_2O}^4}$

☒ **C** $K_p = \dfrac{P_{H_2}^4}{P_{H_2O}^4}$

☒ **D** $K_p = P_{H_2}^4$

(Total for Question 19 = 1 mark)

20 At 100 °C, pure water has a pH of 6, whereas at 25 °C it has a pH of 7. This is because

☒ **A** the dissociation of water is endothermic, so the concentration of hydrogen ions is lower at 100 °C than it is at 25 °C.

☒ **B** the dissociation of water is exothermic, so the concentration of hydrogen ions is lower at 100 °C than it is at 25 °C.

☒ **C** the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100 °C than it is at 25 °C.

☒ **D** at 100 °C, water has a higher concentration of hydrogen ions than of hydroxide ions.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

21 (a) (i) Define **pH**.

(1)

....

(ii) Calculate the pH of 0.0100 mol dm^{-3} hydrochloric acid, which is a strong acid.

(1)

(b) Ethanoic acid is a weak acid with an acid dissociation constant, K_a, of value 1.75×10^{-5} mol dm^{-3} at 25 °C.

(i) Calculate the pH of 0.0100 mol dm^{-3} ethanoic acid at 25 °C, stating any ONE assumption that you have made.

(4)

Assumption ....

....

....

(ii) The pH of hydrochloric and of ethanoic acid at two different concentrations is given in the table.

	pH of 0.00100 mol dm^{-3} solution	pH of 0.000100 mol dm^{-3} solution
Hydrochloric acid	3.0	4.0
Ethanoic acid	3.9	4.4

In the case of hydrochloric acid, dilution by a factor of 10 increases the pH by one unit. Suggest why ethanoic acid behaves differently.

(2)

(c) Orange marmalade usually contains sodium citrate as a preservative. Together with the fruit in the marmalade, it forms a buffer solution which, at a suitable pH, inhibits mould growth.

(i) Define the term **buffer solution**.

(2)

(ii) What is the substance in the fruit that produces a buffer with sodium citrate?

(1)

(iii) Explain how a buffer solution works using this system or any other of your choice. Support your explanation with equations.

(4)

(Total for Question 21 = 15 marks)

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22 *****(a) Ethanol can be oxidized successively to ethanal and to ethanoic acid.

The boiling temperatures of these substances are:
ethanol 78 °C, ethanal 21 °C, ethanoic acid 118 °C.

Explain in terms of the intermolecular forces in the liquids why the order of the boiling temperature is

ethanal < ethanol < ethanoic acid

(3)

(b) State what tests you would perform in each case, and the result you would expect, to show that

(i) ethanal contains a carbonyl group.

(2)

(ii) ethanal is an aldehyde.

(2)

(c) Ethanal reacts with HCN, in the presence of a catalyst of cyanide ions from KCN, to give a cyanohydrin, $CH_3CH(OH)CN$.

(i) Give the mechanism for this reaction.

(3)

(ii) Explain why it is necessary to use HCN and KCN in this reaction, rather than HCN on its own.

(1)

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*(iii) Explain why the product mixture from this reaction is **not** optically active.

(2)

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(Total for Question 22 = 13 marks)

23 Iodine and propanone react in the presence of an aqueous acid catalyst as follows

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

To determine the rate equation for the reaction, propanone is reacted with iodine in the presence of aqueous hydrochloric acid at constant temperature. Samples are withdrawn at known times, quenched with sodium hydrogencarbonate solution, and the iodine remaining titrated with a standard solution of sodium thiosulfate.

The rate equation for the reaction is

$$\text{rate} = k[CH_3COCH_3]^1\ [H^+]^1\ [I_2]^0$$

(a) The graph of $[I_2]$ against time is a straight line, showing that the order of reaction with respect to iodine is zero.

(i) Explain why the propanone and the hydrogen ions must be in large excess in this experiment in order to give this straight line.

(2)

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(ii) What further experiment could be done to show that the order of reaction with respect to propanone is one? State the effect of this change on the graph.

(2)

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(iii) Explain why the minimum number of steps in the mechanism for this reaction is two.

(2)

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(b) Sodium hydrogencarbonate stops the reaction by neutralizing the acid catalyst.

(i) Give the ionic equation for the reaction between sodium hydrogencarbonate and acid.

(1)

(ii) Sodium hydroxide cannot be used for neutralization because under very alkaline conditions a reaction occurs between propanone and iodine.

Write the equation for this reaction. State symbols are **not** required.

(3)

(Total for Question 23 = 10 marks)

24 Hydrogen is used in very large quantities as a fuel, as a reducing agent, and in the production of ammonia. Hydrogen is manufactured by steam reforming of methane from natural gas. Two reactions are involved, both being in equilibrium in closed systems.

Reaction I $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = + 210\ \text{kJ mol}^{-1}$

Reaction II $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -42\ \text{kJ mol}^{-1}$

(a) Write the expression for the equilibrium constant, K_p, for reaction **I**.

(1)

(b) Reaction **I** occurs at a temperature of 1000 K and a pressure of 30 atm over a nickel catalyst.

(i) State and explain the effect, if any, **on the value of K_p** of increasing the pressure on the reaction.

(1)

(ii) Explain, in terms of your answers to (a) and (b)(i), why an increase in the pressure leads to a decrease in yield in reaction **I**.

(2)

(iii) Increasing the pressure on this heterogeneously-catalysed reaction **I** has very little effect on the rate of the reaction. Suggest why this is so.

(2)

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....

(c) The expression for K_p for reaction **II** is

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$$

At a particular temperature and 30 atm pressure, a mixture of equal amounts of carbon monoxide and steam react to give an equilibrium mixture where 75 % of the CO has reacted.

Calculate the value of K_p showing your working.

(3)

(d) Carbon dioxide and hydrogen are separated by washing the gas with potassium carbonate solution to give potassium hydrogencarbonate solution, leaving hydrogen in the gas stream. Potassium carbonate is expensive and is regenerated by heating the potassium hydrogencarbonate and liberating the carbon dioxide.

(i) Hydrogen is often claimed to be a non-polluting fuel as it only produces water on burning.

Explain why its manufacture using reactions **I** and **II** does **not** support this claim.

(1)

....

....

....

(ii) Write the equation for the thermal decomposition of potassium hydrogencarbonate.

State symbols are **not** required.

(1)

(e) Although industrial processes are often discussed in terms of equilibria, they are rarely allowed to reach equilibrium.

Suggest why, apart from insufficient reaction time, this is so.

(1)

....

....

(Total for Question 24 = 12 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

25 The oxidation of iron metal in the presence of oxygen is spontaneous.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

(a) Explain the meaning of **spontaneous** in a thermodynamic context.

(1)

(b) (i) Find the values of the standard molar entropies of iron and of iron(III) oxide from your data booklet.

(1)

(ii) The standard molar entropy at 298 K for oxygen molecules O_2 is +205 J mol^{-1} K^{-1}.

Calculate the standard entropy change of the system for the reaction between iron and oxygen. Include a sign and units in your answer.

(2)

(iii) The standard enthalpy change for the reaction at 25 °C is –1648 kJ mol^{-1}.

Calculate $\Delta S_{surroundings}$.

(1)

(iv) Use your answers to (b)(ii) and (iii) to calculate the total standard entropy change for the reaction. Include a sign and units in your answer.

(2)

*(v) The reaction is thermodynamically spontaneous.

Use your answers to (b)(ii), (iii) and (iv) to explain, in terms of the physical states of the substances in the reaction and the movement of the molecules in the surroundings, why this is so.

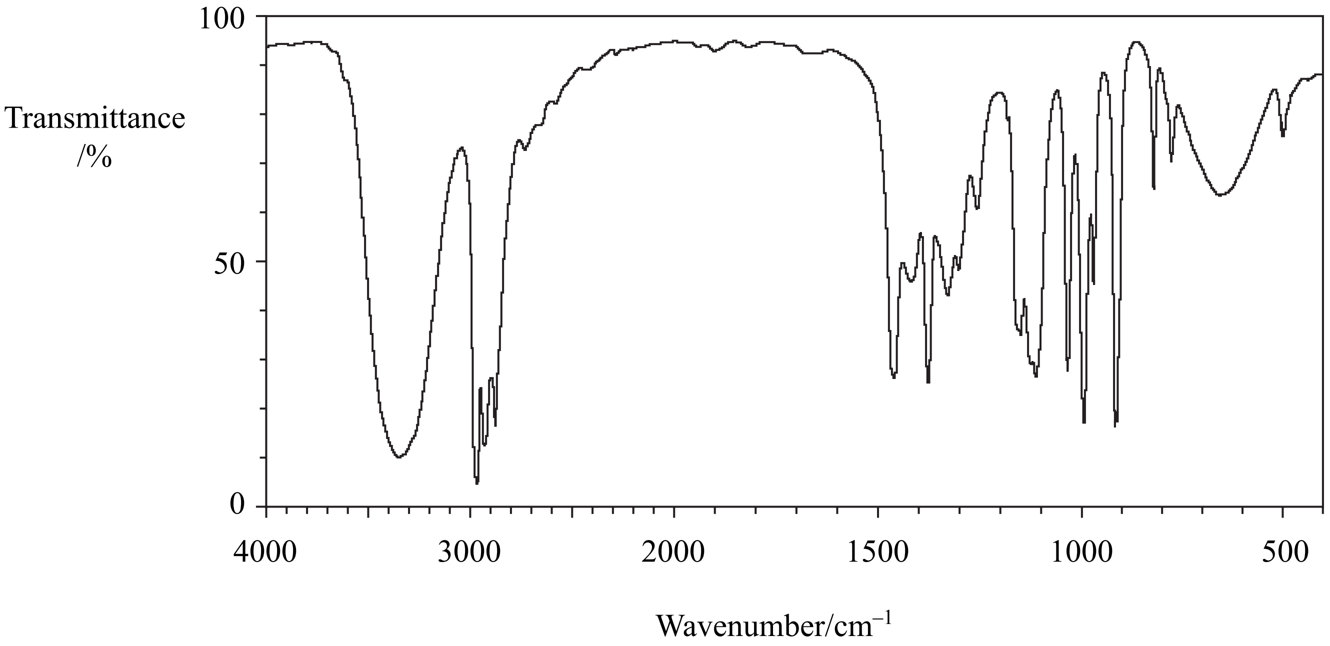
(3)

(Total for Question 25 = 10 marks)

26 This question is about compounds **X**, $C_4H_{10}O$, and **Y**, C_4H_8O.

(a) Compound **X**, $C_4H_{10}O$, can be oxidized to compound **Y**, C_4H_8O. The infrared spectrum of **X** is given below.

Infrared Spectrum of X

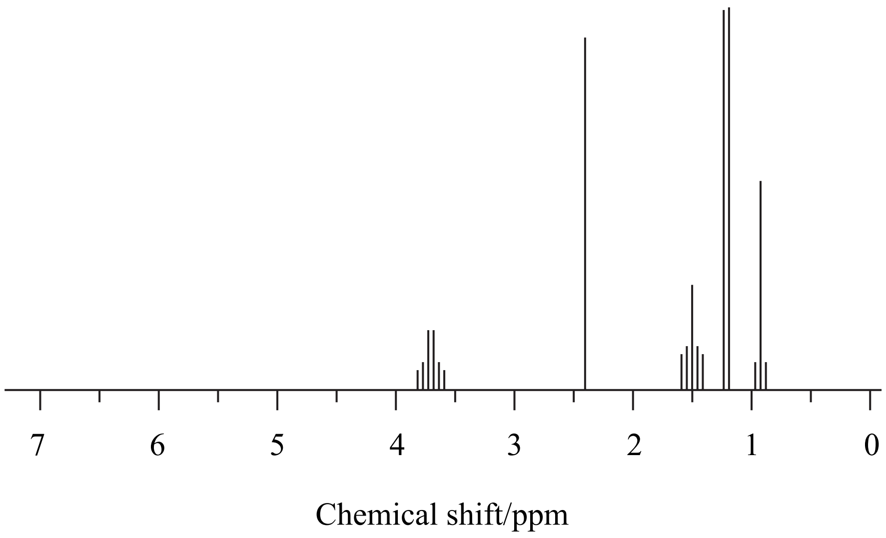


What can be deduced about the structures of **X** and **Y** using all this information and the data booklet? Justify your answer.

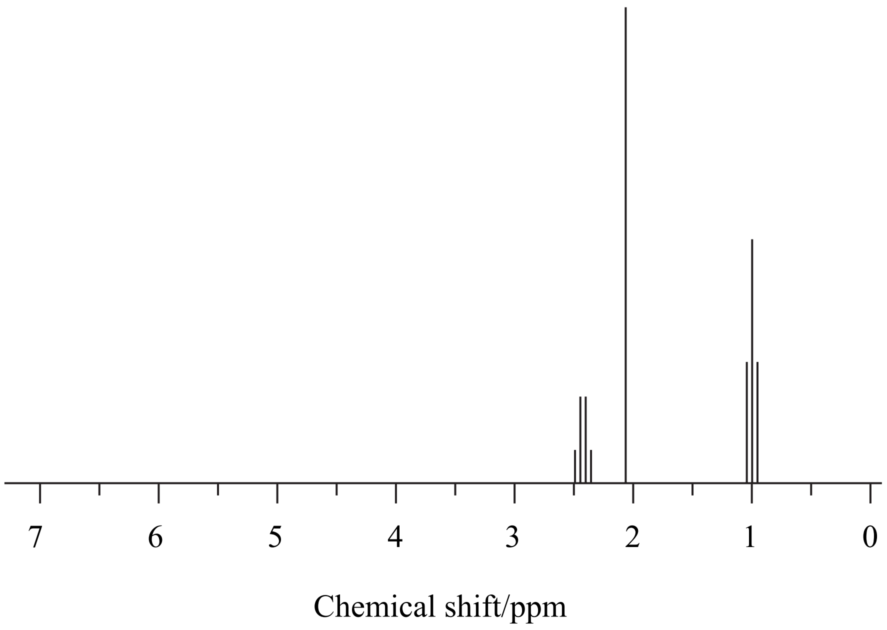
(4)

(b) Below are the nmr spectra of **X** and **Y**.

nmr spectrum of X



nmr spectrum of Y



*Use these nmr spectra and your answer to (a) to deduce the structural formulae of **X** and **Y**. Justify your answer and explain why **both** nmr spectra are consistent with these structures.

(6)

(Total for Question 26 = 10 marks)

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

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
																	(18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
(1)	*(2)*											*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)
January 2010

GCE

GCE Chemistry (6CH04/01)

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Using the Mark Scheme

The mark scheme gives examiners:

- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:

- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A

Question Number	Correct Answer	Reject	Mark
1	B		**1**

Question Number	Correct Answer	Reject	Mark
2	C		**1**

Question Number	Correct Answer	Reject	Mark
3	B		**1**

Question Number	Correct Answer	Reject	Mark
4	A		**1**

Question Number	Correct Answer	Reject	Mark
5	B		**1**

Question Number	Correct Answer	Reject	Mark
6	D		**1**

Question Number	Correct Answer	Reject	Mark
7	B		**1**

Question Number	Correct Answer	Reject	Mark
8	A		**1**

Question Number	Correct Answer	Reject	Mark
9	A		**1**

Question Number	Correct Answer	Reject	Mark
10	D		**1**

Question Number	Correct Answer	Reject	Mark
11	A		**1**

Question Number	Correct Answer	Reject	Mark
12	C		**1**

Question Number	Correct Answer	Reject	Mark
13	A		**1**

Question Number	Correct Answer	Reject	Mark
14	B		**1**

Question Number	Correct Answer	Reject	Mark
15	D		**1**

Question Number	Correct Answer	Reject	Mark
16	C		**1**

Question Number	Correct Answer	Reject	Mark
17	D		**1**

Question Number	Correct Answer	Reject	Mark
18	C		**1**

Question Number	Correct Answer	Reject	Mark
19	C		**1**

Question Number	Correct Answer	Reject	Mark
20	C		**1**

Section B

Question Number	Acceptable Answers	Reject	Mark
21 (a)(i)	(pH =) -log [H^+] OR (pH =) -log [H_3O^+] OR **Accept** Definition in words (For example: “It is minus / negative log(arithm) of the hydrogen **ion** concentration”) Base 10 does not have to be there, but reject “**ln**”	**Just** “concentration of hydrogen ions” { } curly brackets -log H^+	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(ii)	(pH = -log 0.0100) = 2(.00)	If any units given	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (b)(i)	$[H_3O^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$ OR $[H_3O^+]^2 = K_a[CH_3COOH]$ **(1)** *ALLOW* [HA] for $[CH_3COOH]$ and $[A^-]$ for $[CH_3COO^-]$ in rearranged expression **Accept** $[H^+]$ for $[H_3O^+]$ $\therefore [H_3O^+] = \surd 1.75 \times 10^{-7}$ OR $\therefore [H_3O^+] = 4.18(3) \times 10^{-4}$ (mol dm^{-3}) **(1)** pH = 3.38 / 3.4 **(1)** ignore sf except one sf Third mark TE from $[H^+]$ only if pH **less than 7** ***N.B. CORRECT ANSWER, WITH OR WITHOUT WORKING, SCORES (3)*** **Assumption** assumes that degree of ionisation of the acid is very small/negligible OR $[CH_3COOH]_{eqm} = [CH_3COOH]_{initial}$ OR $[H^+] = [CH_3COO^-]$ OR all of the hydrogen **ions** come from the acid / ignore hydrogen ions from the water **(1)** *IGNORE* any references to temperature	3.37 / 3 /3.39 / a correct pH value **with units** just “weak acid” / just “partially dissociates” / acid does not dissociate / $[CH_3COOH]$ **constant** $[H^+] = [OH^-]$ / $[H^+]$ = [salt]	**4**

Question Number	Acceptable Answers	Reject	Mark
21 (b)(ii)	**First mark:** (Dilution/addition of water) shifts the equilibrium $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ / $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ to the **right** OR the above stated in words such as: degree of dissociation increases/ proportion of dissociation increases/ more dissociation (as the ethanoic acid is diluted) **(1)** **Second mark:** so the $[H^+]$ is greater than expected/ so the decrease in $[H^+]$ is less than expected / so that the decrease in $[H^+]$ is less than that for hydrochloric acid **(1)** **Each mark is a stand alone mark.** *ALTERNATIVE ROUTE:* **First mark:** $[H^+] = \surd K_a \times [HA]$ OR $(K_a \times [HA])^{½}$ OR $pH = ½pK_a - ½\log[HA]$ **(1)** **Second mark:** use of mathematical expression given (e.g.$[H^+]$ affected by factor of $1/\surd 10$ on dilution OR substitution of numerical values into the equation) **(1)** *IGNORE:* any comments or calculations relating to HCl(aq)	Reject just a reference to a 0.5 increase in pH for $CH_3COOH(aq)$ compared with a 1.0 increase in pH for HCl(aq)	**2**

Question Number	Acceptable Answers	Reject	Mark
21 (c)(i)	**These marks are stand alone.** Maintains an **almost** constant pH / resists change(s) in pH **(1)** for **small** addition of H^+ or OH^- ions (N.B. both ions needed) / for **small** additions of acid or alkali / for **small** additions of acid or base **(1)** *IGNORE* any references to named buffer mixtures	"resists small change(s) in pH" OR "pH does not change"	**2**

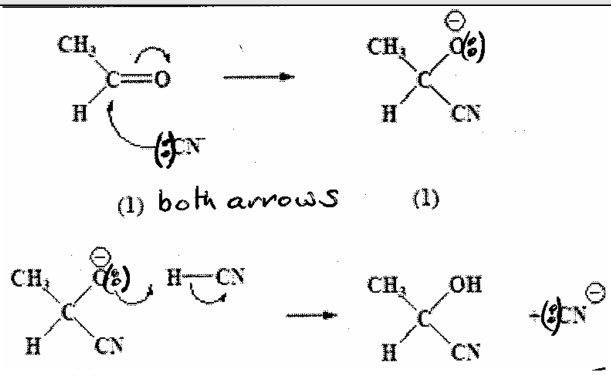
Question Number	Acceptable Answers	Reject	Mark
21 (c)(ii)	citric acid		**1**

Question Number	Acceptable Answers	Reject	Mark
21 (c)(iii)	**First mark:** (buffer contains) reservoir of HA **and** A^- OR (buffer contains) large concentrations of [HA] **and** $[A^-]$ OR **both** equations: $HA \rightleftharpoons A^- + H^+$ **and** $NaA \rightarrow Na^+ + A^-$ **(1)** **Second mark:** (Addition of alkali/base) $HA + OH^- \rightarrow A^- + H_2O$ OR description/equations to show that H^+ reacts with OH^- (to form H_2O) and more acid dissociates (to replace H^+) **(1)** **Third mark:** (Addition of acid) $A^- + H^+ \rightarrow HA$ OR A^- reacting with H^+ in any context described in words (e.g. by reference to weak acid equilibrium) **(1)** **Fourth mark:** the ratio of $[A^-]\div[HA]$ hardly changes / the ratio of $[HA]\div[A^-]$ hardly changes OR $[A^-]$ nor [HA] changes **significantly (1)**	<u>**JUST**</u> $NaA \rightleftharpoons Na^+ + A^-$ and $HA \rightarrow H^+ + A^-$ without correct description **Just** $[H^+]$ remains constant	**4**

Question Number	Acceptable Answers	Reject	Mark
22 (a) **QWC**	**Each mark is a stand alone mark.** **First mark:** hydrogen bonds in **both** ethanoic acid **and** ethanol OR no hydrogen bonds in ethanal **(1)**	any reference to hydrogen bonding in ethanal **just** references to ethanol and ethanoic acid forming H bonds **with water**	**3**
	Second mark: hydrogen bonds are stronger than van der Waals'/ dipole-dipole/London/dispersion/ induced dipole / permanent dipole /intermolecular forces (in ethana**l**) OR hydrogen bonds are the strongest/strong intermolecular forces **(1)**	references to breaking **covalent** bonds	
	Third mark: ethanoic acid has more electrons/ethanoic acid has the most electrons OR ethanoic acid is dimeric OR ethanoic acid forms dimers OR description of ethanoic acid dimers (N.B. In the context of dimerisation, ignore statement that "ethanoic acid forms two hydrogen bonds per molecule") OR ethanoic acid is more polar because of having more oxygen atoms **(1)**	**Just** "ethanoic acid has more hydrogen bonds than ethanol"	

Question Number	Acceptable Answers	Reject	Mark
22 (b)(i)	**(Test):** 2,4-dinitrophenylhydrazine /Brady's reagent/2,4-dnp/ 2,4-DNP/2,4-DNPH **(1)** **(Result):**yellow **precipitate** /orange **precipitate** /red **precipitate** ALLOW: 'solid' or 'crystals' in lieu of precipitate **(1)** **Result** mark for result CQ on correct reagent (or a near miss reagent (e.g. 2,4-DHPN))	**1,2**-DNP etc/ hydrazine / /2,4-dinitrophen**o**lhydrazine /2,4-dinitrophenylhydraz**o**ne	**2**

Question Number	Acceptable Answers	Reject	Mark
22 (b)(ii)	(Warm with) Fehling's (solution) / Benedict's (solution) **(1)** red precipitate/brown precipitate/brick-red precipitate **(1)** *ALLOW* "solid" *ALLOW* "red Cu_2O" *ALLOW* yellow/orange solid for Benedict's test *Penalise omission of "solid"* ***once only*** *in parts (b)(i) and (b)(ii)* **OR** (Warm with) Tollens' (reagent) **(1)** silver (mirror)/black(solid) **(1)** **(N.B. here, solid not required)** **OR** (Warm with) ammoniacal silver nitrate (solution) **(1)** silver (mirror)/ black / dark-grey (solid) **(1)** **(N.B. here, solid not required)** 2nd mark CQ on correct reagent or a near miss *Penalise omission of "solid"* ***once only*** *in (b)(i) and (b)(ii)*	acidified potassium dichromate(VI) / manganate(VII) **(0)** iodoform reaction **(0)** just "red due to Cu^{+}" / "red solid due to Cu^{3+}" **(0)**	**2**

Question Number	Acceptable Answers	Reject	Mark
22 (c)(i)	 **(1)** *IGNORE* any dipoles shown Check curly arrows are all **double-headed** in mechanism. (If all arrows are **single-headed**, can only score intermediate mark.) **Accept:** arrow to an H^+ instead of an H-CN for third mark. [It is **not** necessary to show the lone pairs.] *IGNORE* any equations which generate CN^- ions	 arrow from N in CN^-	3

Question Number	Acceptable Answers	Reject	Mark
22 (c)(ii)	With HCN alone, insufficient CN^- OR KCN provides (sufficient) CN^- OR KCN increases the concentration of CN^- *ALLOW* "nucleophile" instead of CN^- *IGNORE* any subsequent comments about the role of the CN^- ion	Just "HCN is a weak acid" OR HCN "is too weak a nucleophile"	**1**

Question Number	Acceptable Answers	Reject	Mark
22 (c)(iii) QWC	**These are stand alone marks** **First mark:** attack from both sides **OR** attack from above and below **(1)** **Second mark:** (gives) racemic mixture / (gives) equal amounts of each isomer / (gives) equal amounts of each enantiomer **(1)**	attack on a (planar) carbocation OR attack on a (planar) intermediate OR S_N1 OR S_N2 "planar product"	**2**

Question Number	Acceptable Answers	Reject	Mark
23 (a)(i)	**These are stand alone marks** **First mark:** (ensures that) [H$^+$] **and** [propanone] (virtually) constant OR so that the [H$^+$] **and** [propanone] do not affect the rate **(1)** **Second mark:** the [I_2] / iodine concentration changes OR so that the **overall** order (of reaction) is **not** determined OR otherwise a curve (graph) is obtained **(1)** ***NOTE:-*** "**only** the [I_2] changes **scores (2)** **OR** "**only** the I_2 concentration changes" **scores (2)** **BUT** "only the iodine changes" **scores (1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
23 (a)(ii)	**First mark:** **double** the concentration of propanone *OR* change/increase/decrease the concentration of propanone **(1)** **Second mark (mark consequentially):** slope/gradient of line **doubles** *ALLOW* "rate doubles" *OR* slope or gradient changes/increases/decreases by same factor *ALLOW* "rate changes/increases/decreases by same factor" **(1)** ***NOTE:* may suggest a different procedure**:- **First mark:** monitor/measure [propanone] over time **(1)** **Second mark (mark consequentially):** plot [propanone] v. time graph **and** state that $t_{½}$ constant **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
23 (a)(iii)	I_2 not involved in rate-determining step/ I_2 not involved in slow(est) step / H^+ and propanone involved in rate-determining step/ H^+ and propanone involved in slow(est)step **(1)** so there must be another step where I_2 is involved/ so there must be a fast step where I_2 is involved **(1)** ***BUT:-*** I_2 not involved until **after** the rate-determining step/ I_2 not involved until **after** the slow(est) step **(2)** *ALLOW* H^+ involved in rate-determining step **(1)** and is regenerated as it is a catalyst (in another step) **(1)**	I_2 involved **before** rate-determining/slowest step **(0)**	**2**

Question Number	Acceptable Answers	Reject	Mark
23 (b)(i)	$HCO_3^- + H^+ \rightarrow H_2O + CO_2$ OR $HCO_3^- + H^+ \rightarrow H_2CO_3$ OR $HCO_3^- + H_3O^+ \rightarrow 2H_2O + CO_2$ OR $HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$ *ALLOW:* $NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2$ OR $Na^+ + HCO_3^- + H^+ \rightarrow Na^+ + H_2O + CO_2$ *IGNORE* any correct or any incorrect state symbols	$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ OR any equations with HA	**1**

Question Number	Acceptable Answers	Reject	Mark
23 (b)(ii)	$CH_3COCH_3 + \mathbf{3}I_2 + \mathbf{4}NaOH$ $\rightarrow CHI_3 + CH_3COONa + \mathbf{3}NaI + \mathbf{3}H_2O$ *IGNORE* any correct or any incorrect state symbols **CHI_3** on RHS of equation **(1)** remaining species correct **(1)** balanced equation **(1)** ***NOTE:*** balancing mark is CQ on all species correct **Accept** correct ionic equation (i.e. Na^+ omitted) NOTE: If **CH_3I**, can only access second mark above		**3**

Question Number	Acceptable Answers	Reject	Mark
24 (a)	$K_p = \frac{p(H_2)^3\, p(CO)}{p(CH_4)p(H_2O)}$ **(1)** Brackets not required	**[ ]** $K_p = \frac{p(H_2)^3 + p(CO)}{p(CH_4) + p(H_2O)}$	**1**

Question Number	Acceptable Answers	Reject	Mark
24 (b)(i)	No effect (as K_p dependent only on temperature) **(1)**		**1**

Question Number	Acceptable Answers	Reject	Mark
24 (b)(ii)	(Since $K_p = \frac{x(H_2)^3\, x(CO)}{x(CH_4)x(H_2O)} \times \frac{\boldsymbol{P_T}^4}{\boldsymbol{P}_T^2}$ to maintain K_p constant, mole fractions of numerator must decrease OR mole fractions of denominator must increase as × $\boldsymbol{P}_T^2$ overall) **First mark:** *EITHER* mole fractions/partial pressures of numerator decrease *OR* mole fractions/partial pressures of denominator increase **(1)** **Second mark:** any mention of × $\boldsymbol{P}_T^2$ OR × $\frac{\boldsymbol{P_T}^4}{\boldsymbol{P}_T^2}$ **(1)** *ALLOW* ***P*** for $\boldsymbol{P}_T$ **NOTE:** **If Le Chatelier quoted, statements such as:** "Equilibrium shifts to side of fewer moles (of gas molecules)/fewer (gas) molecules" **max (1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
24 (b)(iii)	Reaction takes place on **surface** of the catalyst **(1)** Active sites/(catalyst) surface is saturated with reactant molecules/reactants (at the pressure of the reaction) **(1)** *NOTE:* an answer such as "... depends on the availability of active sites on catalyst surface" scores **(2)**		**2**

Question Number	Acceptable Answers	Reject	Mark
24 (c)	$CO + H_2O \rightleftharpoons CO_2 + H_2$ (table below) • eq'm moles all correct **(1)** • mole fractions all correct **(1)** • partial pressures and answer = 9 **with no units** **(1)** *NOTE:* **3rd** mark not awarded if any units shown *NOTE:* $\frac{11.25^2}{3.75^2}$ = 9 **scores (3)** *NOTE:* Mark each step CQ. **CHECK ALL WORKING**		**3**

initial	**1**	**1**	**0**	**0**
eq'm	**0.25**	**0.25**	**0.75**	**0.75**
mol frac	**0.125**	**0.125**	**0.375**	**0.375**
pp	**3.75**	**3.75**	**11.25**	**11.25**

Question Number	Acceptable Answers	Reject	Mark
24 (d)(i)	production (of hydrogen) forms CO_2 OR production (of hydrogen) forms a Greenhouse gas OR production (of hydrogen) forms CO OR CO_2 is a Greenhouse gas OR CO is a Greenhouse gas ALLOW production (of hydrogen) uses/requires energy *ALLOW* CO is toxic/poisonous	methane **produced (0)**	**1**

Question Number	Acceptable Answers	Reject	Mark
24 (d)(ii)	$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$ *ALLOW* multiples		**1**

Question Number	Acceptable Answers	Reject	Mark
24 (e)	products removed OR not a closed system OR balance between rate and yield OR balance between time and yield OR recycling of reactants OR more product in unit time (so process more economically viable) *IGNORE* any comments relating to cost	references to atom economy dangers of maintaining high pressures	**1**

Section C

Question Number	Acceptable Answers	Reject	Mark
25 (a)	ΔS^o_{total} is positive / $\Delta S^o_{total} > 0$ with or without superscript *NOTE:* **This mark may be awarded from answer to Q25(b)(v)** **Accept** ΔG^o is negative	**Just** "the entropy is positive"	**1**

Question Number	Acceptable Answers	Reject	Mark
25 (b)(i)	(+)27.3 **and** (+)87.4 (J mol^{-1} K^{-1}) *IGNORE* incorrect units		**1**

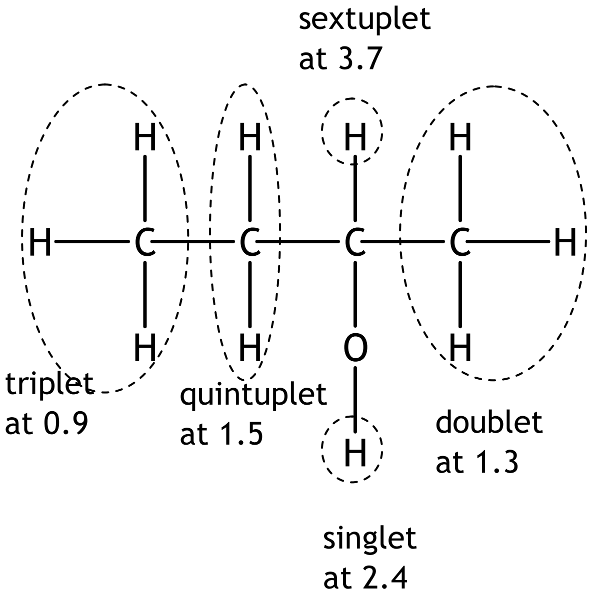
Question Number	Acceptable Answers	Reject	Mark
25 (b)(ii)	ΔS^o_{sys} = (2x87.4) – {(4x27.3 + (3x205.0)} **(1)** = –549.4 / –549(J mol^{-1} K^{-1}) **(1)** Correct answer with or without correct units **(2)** *IGNORE any wrong units* **Accept** TE from (b)(i) *NOTE:* +549/+549.4 scores **(1)** **Check working** *NOTE:* 1st mark: for x2, x4 and x3 2nd mark: for (products – reactants), with correct arithmetic		**2**

Question Number	Acceptable Answers	Reject	Mark
25 (b)(iii)	$\Delta S_{surr} = -\frac{\Delta H}{T}$ $= -(-1648 \times 10^3) \div 298(.15)$ ($J\ mol^{-1}\ K^{-1}$) = (+) 5530 ($J\ mol^{-1}\ K^{-1}$) OR = (+) 5.53 **$kJ\ mol^{-1}\ K^{-1}$** **(1)** *NOTES:* • Correct answer, with or without working, scores **(1)** • If **5530** ($J\ mol^{-1}\ K^{-1}$) given, **IGNORE** any subsequent incorrect attempts to convert it to a value in $kJ\ mol^{-1}\ K^{-1}$ *IGNORE* s.f. except one s.f.	**Just** (+)5.53 with no units OR (+)5.53 **$kJ\ mol^{-1}$**	**1**

Question Number	Acceptable Answers	Reject	Mark
25 (b)(iv)	ΔS_{total} = (-549.4) +(+5530) = +4980.6/+ 4981 **$J\ mol^{-1}\ K^{-1}$** OR +4.981 **$kJ\ mol^{-1}\ K^{-1}$** **(1)** for value **(1)** for correct sign **and** units *IGNORE* s.f. except one s.f. **Accept** TE from (b)(ii) and (b)(iii)	**Just** the formula: $\Delta S_{total} = \Delta S^{o}_{sys} + \Delta S_{surr}$	**2**

Question Number	Acceptable Answers	Reject	Mark
25 (b)(v)	(ΔS_{system} is negative): as loss of disorder as gas → solid OR more order as gas → solid OR as decrease in entropy as gas → solid **(1)** (ΔS_{surr} is positive): (heat) energy released (increases kinetic energy and hence movement of the surrounding molecules) **(1)** ΔS_{total} is positive because ΔS_{surr} is (numerically) greater than ΔS_{sys} OR ΔS_{surr} "outweighs" ΔS_{sys} OR ΔS_{surr} sufficiently large so that ΔS_{total} is positive **(1)**	**Just** "reaction is exothermic" ΔS_{total} is negative **(0)** for third scoring point	**3**

Question Number	Acceptable Answers	Reject	Mark
26 (a)	**(IR spectrum of X)** peak at 3400 (cm^{-1}) **(1)** *MAY BE ANNOTATED ON SPECTRUM* *ALLOW* anything in the Data Booklet range which is 3200 to 3750 (cm^{-1}) **X** has an O-H (group) OR **X** is an alcohol **(1)** **(From the chemical information)** **X** is primary **or** secondary (alcohol) OR **X** is **not** tertiary (alcohol) OR **X** is any two from: butan-1-ol, butan-2-ol, (2)-methylpropan-1-ol **(1)** **Y** is an aldehyde **or** a ketone *ALLOW* " **Y** is a carbonyl" **(1)** *NOTE RE THIRD/FOURTH SCORING POINTS:* If just state that **X** is butan-1-ol with no justification **(0)** but then go on to state **Y** is butanal, give CQ mark **(1)** OR If just state that **X** is butan-2-ol with no justification **(0)** but then go on to state **Y** is butanone, give CQ mark **(1)** OR If just state that **X** is (2)-methylpropan-1-ol with no justification **(0)** but then go on to state **Y** is (2)-methylpropanal, give CQ mark **(1)** ***NOTE:* These Part (a) marks may be awarded from answers to either Part (a) or Part (b)**	**X** is a phenol **(0)**	**4**

26 (b) **QWC**	**First two marks:** **X** is $CH_3CH(OH)CH_2CH_3$ **(1)** **Y** is $CH_3COCH_2CH_3$ **(1)** **These marks are stand alone** *NOTE:* Two correct names, but no structural formulae for both scores **(1)** out of **(2)** If **X** identified as $CH_3CH_2CH_2CH_2OH$ **and** and **Y** identified as $CH_3CH_2CH_2CHO$ **award (1) unless previously credited in (a)** **(NMR spectrum of X)** **Third mark:-** **hydrogen** OR **H** in **five** (different) environments *(IGNORE* reference to butan-1-ol here) OR (so must be butan-1-ol or butan-2-ol and) **not** 2-methylpropan-1-ol which has four peaks/hydrogen environments **(1)** *NOTE:* Candidates may annotate a structural or displayed formula to show that there are five environments. (For this mark, no details of splitting or chemical shifts are needed.)  splitting pattern (2,6,1,5,3) consistent with **butan-2-ol** OR splitting pattern inconsistent with butan-1-ol (which is 3,6,5,3,1) **(1)**		**6**

Fourth mark:-
splitting pattern (2,6,1,5,3) consistent with **butan-2-ol**
OR
splitting pattern inconsistent with butan-1-ol (which is 3,6,5,3,1)
OR
assign peaks correctly quoting chemical shifts from the spectrum

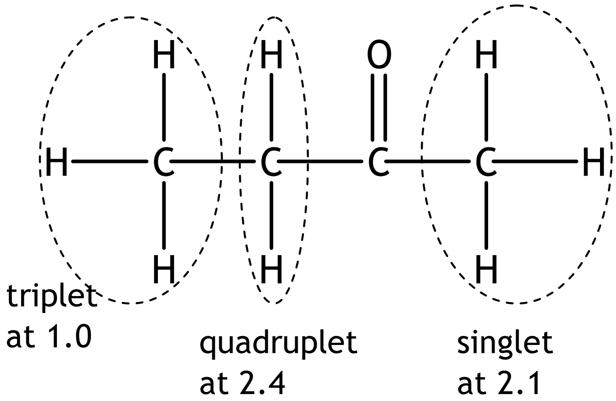
(1)

(NMR spectrum of Y)

Fifth mark:-
hydrogen OR **H** in **three** (different) environments

(1)

NOTE: Candidates may annotate a structural or displayed formula to show that there are three environments. (For this mark, no details of splitting or chemical shifts are needed.)



Sixth mark:-
splitting pattern (1,4,3) is consistent with butanone
OR
splitting pattern is inconsistent with butanal (which is 3,6,4,3)
OR
splitting pattern inconsistent with 2-methylpropanal (which is 2,8,2)
OR
assign peaks correctly quoting chemical shifts from the spectrum

(1)

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Write your name here

Surname	Other names

Centre Number	Candidate Number

Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Thursday 17 June 2010 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- 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 Propanone reacts with iodine in acidic solution as shown in the equation below.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The rate equation for the reaction is

$$\text{Rate} = k[CH_3COCH_3(aq)][H^+(aq)]$$

(a) The most appropriate technique to investigate the rate of this reaction is

(1)

☒ **A** titrating samples of reaction mixture with acid.

☒ **B** measurement of optical activity.

☒ **C** measurement of the volume of gas given off.

☒ **D** colorimetry.

(b) Which statement about the reaction is **not** correct?

(1)

☒ **A** The overall order of reaction is second order.

☒ **B** The units of the rate constant are $dm^3\ mol^{-1}\ s^{-1}$.

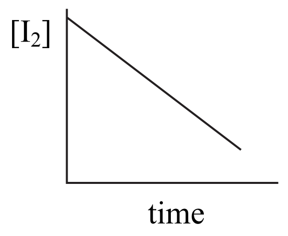
☒ **C** The rate constant increases with temperature.

☒ **D** The rate increases four times when the concentration of propanone and iodine are both doubled**.**

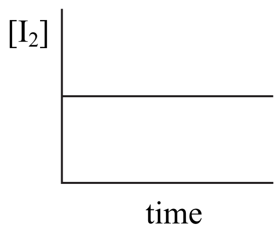
(c) The reaction is carried out using a large excess of both propanone and acid. Which of the graphs below shows the change of iodine concentration with time?

(1)

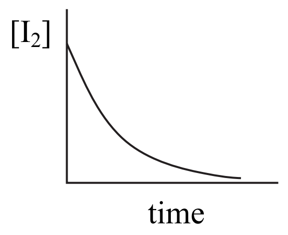
☒ **A**



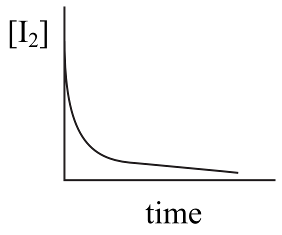
☒ **B**



☒ **C**



☒ **D**



(Total for Question 1 = 3 marks)

2 Which of the following is true for the exothermic reaction shown below?

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

☒ **A**	ΔH	positive
☒ **B**	$\Delta S_{\text{surroundings}}$	positive
☒ **C**	ΔS_{system}	negative
☒ **D**	ΔS_{total}	negative

(Total for Question 2 = 1 mark)

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

3 In which reaction is water acting as a Brønsted-Lowry acid?

☒ **A** $H_2O + HCl \rightarrow H_3O^+ + Cl^-$

☒ **B** $H_2O + SO_3 \rightarrow H_2SO_4$

☒ **C** $H_2O + NH_3 \rightarrow NH_4^+ + OH^-$

☒ **D** $H_2O + CO_2 \rightarrow H_2CO_3$

(Total for Question 3 = 1 mark)

4 Which of the following compounds has both optical and *E-Z* isomers?

☒ **A** $CH_3CH{=}CHCH_2CH_3$

☒ **B** $CH_3CHClCH{=}C(CH_3)_2$

☒ **C** $CH_3CCl{=}CClCH_3$

☒ **D** $CH_3CHBrCH{=}CHCl$

(Total for Question 4 = 1 mark)

5 Which of the following reacts with hydrogen cyanide, HCN, to make a racemic mixture?

☒ **A** Methanal, HCHO

☒ **B** Ethanal, CH_3CHO

☒ **C** Propanone, CH_3COCH_3

☒ **D** Pentan-3-one, $C_2H_5COC_2H_5$

(Total for Question 5 = 1 mark)

6 Which of the following is a redox reaction?

☒ **A** Ethanal reacting with Tollens' reagent.

☒ **B** Ethanoyl chloride reacting with ammonia.

☒ **C** Ethanoic acid reacting with ethanol.

☒ **D** Ethanoic acid reacting with sodium hydroxide.

(Total for Question 6 = 1 mark)

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

7 The following methods can be used to distinguish between pairs of organic compounds without further tests.

A Warm each compound with Fehling's or Benedict's solution.

B Add solid sodium carbonate to each compound.

C Add 2,4-dinitrophenylhydrazine (Brady's reagent) to each compound.

D Add water, drop by drop, to each compound.

(a) Which test would distinguish propanone from propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test would distinguish between aqueous solutions of ethanoic acid and ethanol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test would distinguish ethanoyl chloride from ethanol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 7 = 3 marks)

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

8 When propanone reacts with iodine in the presence of sodium hydroxide, the crystalline solid product has the formula

☒ **A** CH_3I

☒ **B** CHI_3

☒ **C** CH_3COCH_2I

☒ **D** CH_3COCI_3

(Total for Question 8 = 1 mark)

9 When the following reaction mixtures are warmed, which will contain ethanoic acid as one of the products?

☒ **A** Ethyl methanoate and sodium hydroxide solution.

☒ **B** Ethyl methanoate and dilute sulfuric acid.

☒ **C** Methyl ethanoate and sodium hydroxide solution.

☒ **D** Methyl ethanoate and dilute sulfuric acid.

(Total for Question 9 = 1 mark)

10 The spectra of the compounds with the formulae $CH_3CH(OH)CH_3$ and $CH_3CH_2CH_2OH$ can be distinguished by

☒ **A** the value of *m/e* of the molecular ion in the mass spectrum.

☒ **B** the presence of a fragment with *m/e* =15 in the mass spectrum.

☒ **C** the presence of an absorption peak due to O–H in the infrared spectrum.

☒ **D** the number of peaks in the nmr spectrum.

(Total for Question 10 = 1 mark)

11 Which of the following has two singlet peaks in its nmr spectrum?

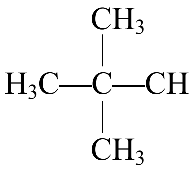
☒ **A** Methanal, HCHO

☒ **B** Methanol, CH_3OH

☒ **C** Chloromethane, CH_3Cl

☒ **D** Dichloromethane, CH_2Cl_2

(Total for Question 11 = 1 mark)

12 The nmr spectrum of 2,2-dimethylpropane, 
$H_3C-C(CH_3)_2-CH_3$, contains

☒ **A** one singlet peak.

☒ **B** four singlet peaks.

☒ **C** one quartet peak.

☒ **D** four quartet peaks.

(Total for Question 12 = 1 mark)

---

13 Which of the following solutions has the lowest pH?

☒ **A** 0.010 mol dm^{-3} hydrochloric acid.

☒ **B** 0.100 mol dm^{-3} hydrochloric acid.

☒ **C** 0.010 mol dm^{-3} ethanoic acid.

☒ **D** 0.100 mol dm^{-3} ethanoic acid.

(Total for Question 13 = 1 mark)

---

14 Which of the following solutions, when mixed, would make a buffer with pH more than 7?

☒ **A** Methanoic acid and sodium methanoate.

☒ **B** Sodium hydroxide and sodium chloride.

☒ **C** Ammonia and ammonium chloride.

☒ **D** Ammonium chloride and ammonium ethanoate.

(Total for Question 14 = 1 mark)

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

15 This question is about the equilibrium reaction

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

Which statement is **not** correct?

☒ **A** The units of K_p are atm^{-2}.

☒ **B** K_p increases as temperature is decreased.

☒ **C** K_p increases when the pressure increases.

☒ **D** K_p increases when the total entropy change, ΔS_{total}, increases.

(Total for Question 15 = 1 mark)

16 1,2-dichloroethane decomposes in the presence of a catalyst.

$$CH_2ClCH_2Cl(g) \rightleftharpoons CH_2{=}CHCl(g) + HCl(g) \qquad \Delta H = +51\ \text{kJ mol}^{-1}$$

Which of the following would result in an increase in the equilibrium yield of chloroethene?

☒ **A** Increasing the temperature.

☒ **B** Increasing the pressure.

☒ **C** Increasing the surface area of the catalyst.

☒ **D** Changing the catalyst to a more efficient one.

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 A bromoalkane has the molecular formula C_4H_9Br. The ionic equation for the hydrolysis of this compound with aqueous sodium hydroxide is shown below.

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

(a) The rate of hydrolysis was investigated by mixing a large excess of the bromoalkane with aqueous sodium hydroxide, and measuring the time taken for **all** the hydroxide ions to be used up. This was carried out with different initial concentrations of the bromoalkane and the hydroxide ions. The results are shown in the table below.

Experiment	$[C_4H_9Br]$ /mol dm^{-3}	$[OH^-]$ /mol dm^{-3}	Time for OH^- to be used up/s	Initial rate /mol dm^{-3} s^{-1}
1	0.017	0.0012	42	2.9×10^{-5}
2	0.034	0.0012	21	5.7×10^{-5}
3	0.034	0.0020	35	....

(i) Complete the missing value of the initial rate in the table.

(1)

(ii) State the order of the reaction with respect to C_4H_9Br and to OH^-. Justify each answer by reference to the concentrations of both reactants.

(3)

Order with respect to C_4H_9Br ....

Reason ....

....

Order with respect to OH^- ....

Reason ....

....

(iii) Deduce the rate equation for the reaction.

(1)

Rate = ...

(iv) Use the results for the first experiment in the table to calculate the rate constant and give its units.

(2)

Units ....

(b) What evidence supports the theory that there is more than one step in the reaction mechanism?

(1)

....

....

....

(c) Write the mechanism for the hydrolysis of C_4H_9Br which is consistent with your rate equation. Show the structure of C_4H_9Br clearly in your mechanism.

(3)

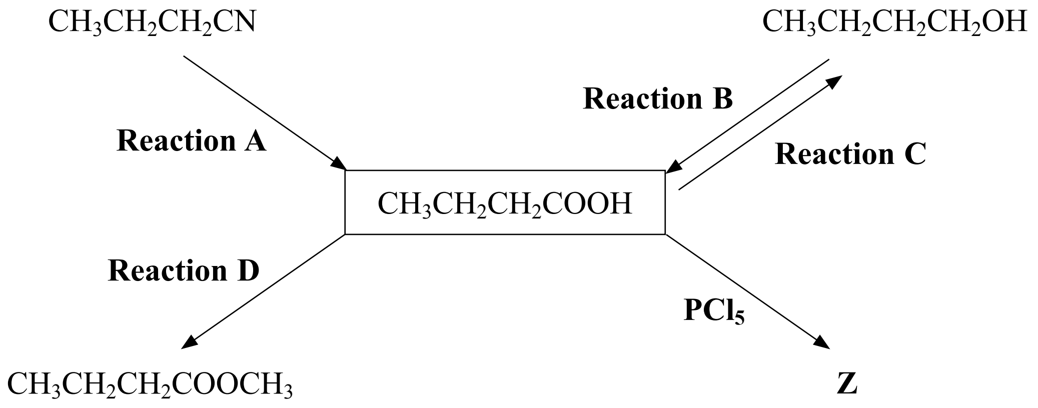
*(d) Explain why primary and tertiary bromoalkanes are hydrolysed by different mechanisms.

(2)

(Total for Question 17 = 13 marks)

18 This question is about butanoic acid, $CH_3CH_2CH_2COOH$.

(a) Some reactions involving butanoic acid are shown below.



(i) What type of reaction is **Reaction A**?

(1)

....

(ii) Identify, by name or formula, the reagent which is used with sulfuric acid to carry out **Reaction B**.

(1)

....

(iii) What reagent is used in **Reaction C**?

(1)

....

(iv) Name the organic product of **Reaction D** and write a balanced equation for its formation.

(2)

Name ....

Equation

(v) Write the **displayed** formula for **Z**, the organic product of the reaction of butanoic acid with phosphorus(V) chloride, PCl_5.

(1)

(b) Butanoic acid and propane-1,2,3-triol are formed when fats in milk are hydrolysed. The presence of milk fat in low fat spreads is detected by hydrolysing the spread, and then analysing the products using gas chromatography (also called gas-liquid chromatography, GLC).

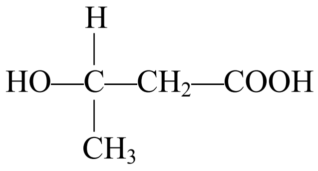
(i) Explain why nitrogen, rather than oxygen, is used as the carrier gas in GLC.

(1)

(ii) What property determines whether butanoic acid or propane-1,2,3-triol would move faster through the chromatography column?

(1)

(c) The formula of 3-hydroxybutanoic acid is shown below.



$$HO{-}\overset{\displaystyle H\atop |}{\underset{\displaystyle | \atop CH_3}{C}}{-}CH_2{-}COOH$$

(i) 3-hydroxybutanoic acid can form a polymer which is used to make “green” packaging as it is biodegradable.

Draw a section of this polymer, showing TWO monomer units. Clearly show any double bonds.

(2)

(ii) The polymer cannot be used in acidic conditions. What reaction would occur when the polymer is in prolonged contact with an acid?

(1)

(Total for Question 18 = 11 marks)

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19 Ethanoic acid can be manufactured by the following reaction, which is carried out between 150 °C and 200 °C.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(a) A mixture of 50.0 mol of methanol and 50.0 mol of carbon monoxide reaches equilibrium at a pressure of 32.0 atm. At 175 °C, the equilibrium partial pressure of ethanoic acid is 22.2 atm.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

(ii) Calculate the partial pressures of methanol and carbon monoxide at equilibrium.

(2)

Methanol ....

Carbon monoxide ....

(iii) Calculate the value of K_p for this reaction at 175 °C. Include a unit in your answer and give your answer to **three** significant figures.

(2)

(b) Another sample of 50.0 mol of methanol and 50.0 mol of carbon monoxide was allowed to reach equilibrium at the same pressure of 32.0 atm, but at a lower temperature. 93.6 % of the methanol was converted at equilibrium.

(i) Complete the table below to show the number of moles of each species in the equilibrium mixture.

(2)

	CH_3OH	CO	CH_3COOH
Number of moles at start	50.0	50.0	0
Number of moles at equilibrium			

(ii) Calculate the partial pressure of ethanoic acid in the equilibrium mixture.

(1)

(iii) Is the reaction exothermic or endothermic? Explain your answer.

(1)

....

....

....

....

(c) How, if at all, does the addition of methanol to the equilibrium mixture affect the following? Justify your answers.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(i) The equilibrium constant for the formation of ethanoic acid.

(1)

(ii) The equilibrium yield of ethanoic acid.

(1)

(d) In industry, catalysts are used even though they are often expensive.

State and explain ONE benefit to the **environment** resulting from the use of catalysts in industrial processes.

(2)

(Total for Question 19 = 13 marks)

20 Vinegar is used as a food preservative. It is an acidic solution containing ethanoic acid, CH_3COOH.

(a) A titration was carried out to measure the concentration of ethanoic acid in a sample of vinegar. 25.0 cm^3 of a vinegar solution was titrated with a solution of sodium hydroxide, concentration 0.250 mol dm^{-3}. The concentration of the ethanoic acid in the vinegar solution was found to be 0.125 mol dm^{-3}.

(i) Calculate the pH of 0.250 mol dm^{-3} sodium hydroxide at 298 K.

[$K_w = 1.00 \times 10^{-14}$ $mol^2\,dm^{-6}$ at 298 K.]

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for ethanoic acid.

(1)

(iii) Calculate the pH of 0.125 mol dm^{-3} ethanoic acid at 298 K.

[K_a for ethanoic acid is 1.7×10^{-5} mol dm^{-3} at 298 K.]

(2)

(iv) When half the ethanoic acid is neutralized, the concentration of the remaining ethanoic acid equals the concentration of the sodium ethanoate which has formed. What is the pH of the mixture at this point? Justify your answer.

(2)

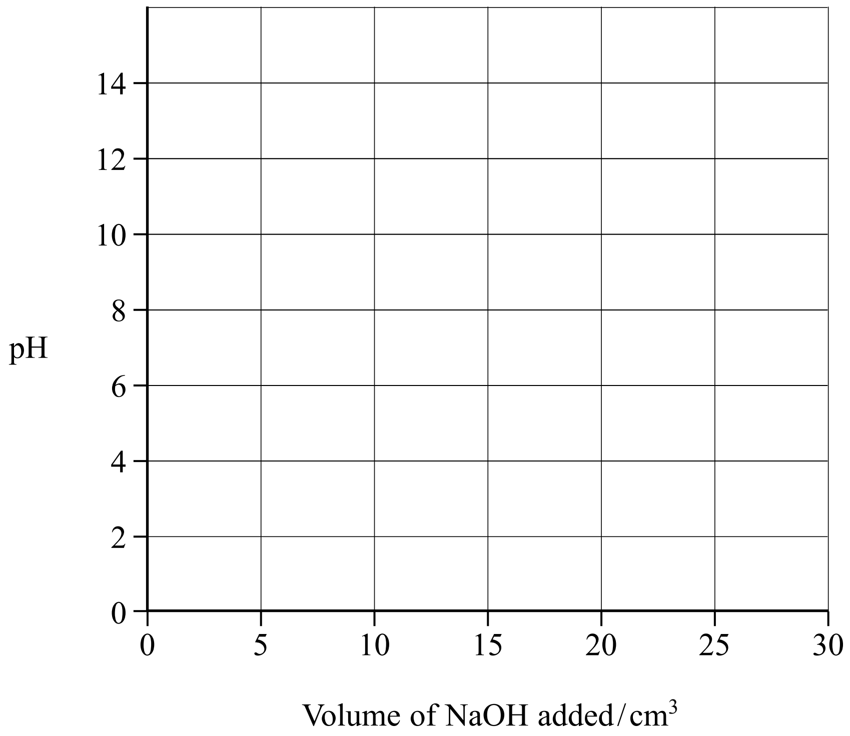
pH ....

Justification ....

....

(v) On the axes below, sketch the titration curve for this reaction when 30 cm^3 of the sodium hydroxide is added to 25.0 cm^3 of the vinegar solution.

(3)



*(vi) The only indicators which were available for this titration were methyl yellow (in ethanol) and thymolphthalein. Explain which indicator is more suitable for this titration and why the other is unsuitable. You will need to refer to your data booklet.

(2)

....

....

....

....

....

(b) In the food industry, ethanoic acid is described as an acidity regulator, additive number E260.

Ethanoic acid can neutralize alkalis. What substance could be mixed with ethanoic acid so that it regulates pH as a buffer in foodstuffs?

(1)

....

(Total for Question 20 = 13 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

21 (a) Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when they are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

(i) Calculate the entropy change of the system, $\Delta S^\ominus_{\text{system}}$, at 298 K. Include a sign and units in your answer. You will need to refer to your data booklet.

(2)

(ii) Explain whether the sign of your answer to (a)(i) is as expected from the equation for the reaction.

(1)

....

....

....

(iii) The standard enthalpy change for the reaction, $\Delta H^\ominus$, is +88.1 kJ mol^{-1}. Calculate the entropy change in the surroundings, $\Delta S^\ominus_{\text{surroundings}}$, at 298 K for this reaction. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^\ominus_{\text{total}}$, at 298 K for the reaction.

(1)

(v) Does your answer to (a)(iv) indicate whether hydrated cobalt(II) chloride can be stored at 298 K without decomposition? Explain your answer.

(1)

....

....

....

(b) A student attempted to measure the enthalpy change of solution of anhydrous cobalt(II) chloride by adding 2.00 g of cobalt(II) chloride to 50.0 cm^3 of water in a well-insulated container. A temperature rise of 1.5 °C was recorded.

The student used a balance which reads to 0.01g, a 50.0 cm^3 pipette, and a thermometer which can be read to 0.25 °C.

(i) Which measuring instrument should be changed to give a result which is closer to the accepted value? Justify your answer.

(2)

....

....

....

....

....

....

(ii) Suggest ONE **other** change the student could make to give a result which is closer to the accepted value. Justify your suggestion.

(2)

....

....

....

*(c) The lattice energies of magnesium chloride, $MgCl_2$, calcium chloride, $CaCl_2$, and strontium chloride, $SrCl_2$ are shown in the table below.

Chloride	Lattice energy / kJ mol^{-1}
$MgCl_2$	–2526
$CaCl_2$	–2258
$SrCl_2$	–2156

(i) Use data on ionic radii, from your data booklet, to explain the trend in these values. Estimate a value for the lattice energy of cobalt(II) chloride, giving ONE piece of data to justify your estimate.

(4)

(ii) Explain how lattice energy values, together with other data, can be used to predict the solubility of ionic compounds.

(3)

*(d) Cobalt forms another chloride, $CoCl_3$, but scientists predict that $MgCl_3$ cannot be made. Suggest a reason for this.

You should consider the enthalpy changes in the Born-Haber cycle, which provide evidence about why cobalt(III) chloride is known but magnesium(III) chloride is not.

(2)

(Total for Question 21 = 20 marks)

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

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	*(18)*
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported
but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)
June 2010

GCE

GCE Chemistry (6CH04/01)

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Summer 2010

Publications Code UA023636

Section A (multiple choice)

Question Number	Correct Answer	Mark
1 (a)	**D**	**1**

Question Number	Correct Answer	Mark
1 (b)	**D**	**1**

Question Number	Correct Answer	Mark
1 (c)	**A**	**1**

Question Number	Correct Answer	Mark
2	**B**	**1**

Question Number	Correct Answer	Mark
3	**C**	**1**

Question Number	Correct Answer	Mark
4	**D**	**1**

Question Number	Correct Answer	Mark
5	**B**	**1**

Question Number	Correct Answer	Mark
6	**A**	**1**

Question Number	Correct Answer	Mark
7 (a)	**C**	**1**

Question Number	Correct Answer	Mark
7 (b)	**B**	**1**

Question Number	Correct Answer	Mark
7 (c)	**D**	**1**

Question Number	Correct Answer	Mark
8	**B**	**1**

Question Number	Correct Answer	Mark
9	**D**	**1**

Question Number	Correct Answer	Mark
10	**D**	**1**

Question Number	Correct Answer	Mark
11	**B**	**1**

Question Number	Correct Answer	Mark
12	**A**	**1**

Question Number	Correct Answer	Mark
13	**B**	**1**

Question Number	Correct Answer	Mark
14	**C**	**1**

Question Number	Correct Answer	Mark
15	**C**	**1**

Question Number	Correct Answer	Mark
16	**A**	**1**

Section B

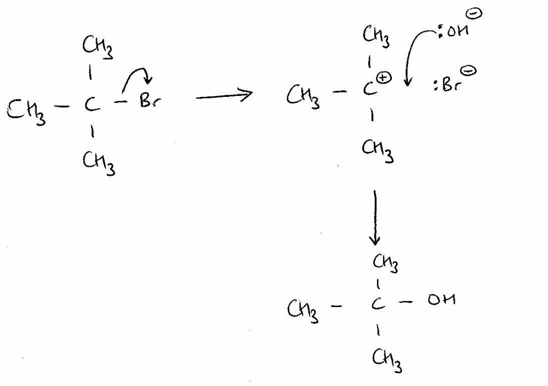
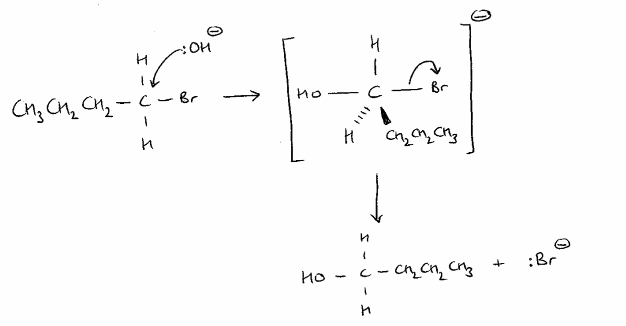
Question Number	Acceptable Answers	Reject	Mark
17 (a)(i)	5.7×10^{-5} /5.71×10^{-5} /5.714×10^{-5} /0.000057 *IGNORE* SF except 1 (ie don't accept 6×10^{-5})		**1**

Question Number	Acceptable Answers	Reject	Mark
17 (a)(ii)	C_4H_9Br: first order / 1 **(1)** (going from first to second experiment) rate doubles when concentration / number of moles doubles (and $[OH^-]$ constant)/ rate and concentration increase in proportion **(1)** *ALLOW* 'time halves' instead of 'rate doubles' OH^- : zero order / 0 **and** (going from second to third expt) as increase in concentration does not affect rate (and $[C_4H_9Br]$ constant) **(1)** *ALLOW* 'doubling in concentration of OH^- instead of 'increase in concentration' *ALLOW* time increases by the same factor as increase in hydroxide concentration (5/3) May refer to experiment number rather than concentrations		**3**

Question Number	Acceptable Answers	Reject	Mark
17 (a)(iii)	Rate = $k[C_4H_9Br]$ OR Rate = $k[C_4H_9Br]^1[OH^-]^0$ *ALLOW* k in lower or upper case Rate equation must be consistent with orders in (a)(ii) If no order is given for hydroxide in (ii) mark cannot be given		**1**

Question Number	Acceptable Answers	Reject	Mark
17 (a)(iv)	$k = \frac{2.9 \times 10^{-5}}{0.017}$ **=** 1.7×10^{-3} / 1.71×10^{-3} / 1.706×10^{-3} s^{-1} *ALLOW* $k=1.68 \times 10^{-3}$ (value obtained from experiment 2 or 3) value of k **(1)** units **(1) stand alone mark** *ALLOW* TE from (a)(iii) *IGNORE* SF except 1 Rate = $k[C_4H_9Br]^2$ gives k= 0.10036 $dm^3\ mol^{-1}s^{-1}$ Rate = $k[C_4H_9Br][OH^-]$ gives k= 1.42 $dm^3\ mol^{-1}s^{-1}$ *ALLOW* k=1.39 $dm^3\ mol^{-1}s^{-1}$ (value obtained from experiment 2 or 3) Rate = $k[C_4H_9Br][OH^-]^2$ gives k= 1184.6 $dm^6\ mol^{-2}s^{-1}$ Rate = $k[C_4H_9Br]^2[OH^-]$ gives k= 83.62 $dm^6\ mol^{-2}s^{-1}$		**2**

Question Number	Acceptable Answers	Reject	Mark
17(b)	$[OH^-]$ is (in chemical equation but) not in rate equation / not in rate determining step (so is in a step other than rate determining step) OR Only C_4H_9Br is in rate equation / rate determining step (so OH^- is in a step other than rate determining step)		**1**

Question Number	Acceptable Answers	Mark
17 (c)	**First mark** Choice of bromoalkane must be consistent with rate equation in (a)(iii). If $[OH^-]$ is not in rate equation, secondary/tertiary bromoalkane. If $[OH^-]$ is in rate equation, primary/secondary bromoalkane. **(1)** **Second and third marks** Either SN1 or SN2 mechanism can score **2 marks** regardless of choice of bromoalkane.  Lone pairs not required Curly arrow from C-Br **bond** to Br (making Br^-) **(1)** Curly arrow from anywhere on OH^- / HO^- to C^+ in correct intermediate (making alcohol) **(1)** **OR**  Both curly arrows from OH^- and from C-Br bond to Br (may both be shown at start) **(1)** Transition state including minus charge (and product) **(1)** Do not penalise if C_2H_5 shown instead of C_3H_7. Bonds in transition state can be dotted. Do not penalise the missing H atoms in alkyl groups in **mechanism**.	**3**

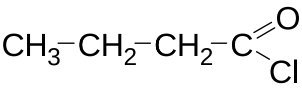
Question Number	Acceptable Answers	Reject	Mark
17 (d) QWC	(Primary and tertiary) carbocation intermediates have different stabilities **(1)** as (inductive effects of) alkyl groups stabilise tertiary carbocation **(1)** **OR** Steric hindrance differs for attack on primary and tertiary carbon (in the molecule) / less space available for attack by OH^- on tertiary carbon / more space for attack by OH^- on primary carbon **(1)** as bulky / three alkyl groups obstruct attack **(1)**	"Tertiary bromoalkanes react by SN1" without further explanation carbocation intermediates have different reactivity steric hindrance in carbocation	**2**

Question Number	Acceptable Answers	Reject	Mark
18 (a)(i)	(Acid) hydrolysis	substitution	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (a)(ii)	$K_2Cr_2O_7$ / $Na_2Cr_2O_7$ / $Cr_2O_7^{2-}$ Potassium dichromate((VI)) / sodium dichromate((VI)) / dichromate((VI)) ions *ALLOW* manganate((VII)) ions, etc	Just "dichromate" chromates Correct formula with wrong name and vice versa Incorrect oxidation number	**1**

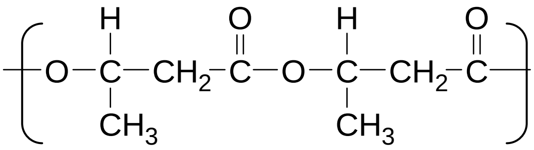
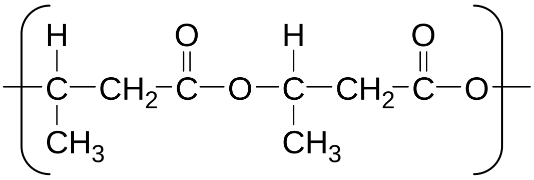
Question Number	Acceptable Answers	Reject	Mark
18 (a)(iii)	Lithium tetrahydridoaluminate/ lithium aluminium hydride/ $LiAlH_4$ (in dry ether)	Just $[H^-]$	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (a)(iv)	Methyl butanoate **(1)** $CH_3CH_2CH_2COOH + CH_3OH \rightarrow$ $CH_3CH_2CH_2COOCH_3 + H_2O$ **(1)** *ALLOW* $\rightleftharpoons$ *IGNORE* state symbols even if wrong	Methyl butoate	**2**

Question Number	Acceptable Answers	Reject	Mark
18 (a)(v)	 $CH_3-CH_2-CH_2-C(=O)Cl$ Don't penalise undisplayed methyl groups as here. COCl must be displayed as above.	C_3H_7 for $CH_3CH_2CH_2$	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b)(i)	Nitrogen inert / unreactive / less reactive (than oxygen) **OR** Oxygen might react with chemicals going through column / sample might oxidise		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b)(ii)	Solubility (in liquid / stationary phase) **OR** Interaction with liquid / stationary phase **OR** Interaction between mobile and stationary phase **OR** Attraction for liquid / stationary phase **OR** **Strength** of (named) intermolecular forces **OR** Adsorption on liquid / stationary phase **OR** Absorption on liquid / stationary phase	Size of molecule / molar mass Polarity, unless with explanation Boiling point / volatility Viscosity Attraction for carrier gas Just a named intermolecular force Just 'retention time' Density	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (c)(i)	 OR  Ester link including C=O **(1)** Rest of polymer with oxygens at end correct **(1)** All H atoms must be shown. *PENALISE* lack of displayed C=O once only *ACCEPT* Without brackets around formula but bonds at end should be shown More than two correct units *IGNORE* n after brackets		**2**

Question Number	Acceptable Answers	Reject	Mark
18 (c)(ii)	Hydrolysis **OR** Splits / breaks ester link **OR** polymer breaks down to monomers **OR** equation showing hydrolysis	Just ‘breaks polymer down’	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (a)(i)	(K_p =) $\frac{pCH_3CO_2H}{pCH_3OH \text{ (x) } pCO}$ Partial pressure symbol can be shown in various ways, eg pp, p_{CO}, (CO)p, etc *ALLOW* p in upper or lower case, round brackets *IGNORE* units	[ ] State symbols given as (l) + in bottom line	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (a)(ii)	P CH_3OH = 4.9 (atm) **(1)** P CO = 4.9 (atm) **(1)** 1 mark for recognition that pressures are equal *IGNORE* units		**2**

Question Number	Acceptable Answers	Reject	Mark
19 (a)(iii)	K_p = ((22.2)/(4.9)^2) = 0.925 **(1)** atm^{-1} **(1) stand alone mark but must match expression used in (a)(iii)** **OR** 9.25 x 10^4 Pa^{-1} / 92.5 kPa^{-1} **(2)** *ALLOW* TE from (a)(i) if inverted and/or (a)(ii)	Answers to other than 3 significant figures	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(i)	CH_3OH: 3.2 CO : 3.2 **(1)** for both values CH_3CO_2H: 46.8 **(1)** *ALLOW* TE for moles of ethanoic acid based on numbers of methanol and carbon monoxide used, as long as moles of methanol and carbon monoxide are equal and moles ethanoic acid + moles methanol = 50		**2**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(ii)	$\left(\frac{46.8 \times 32}{53.2}\right) =$ 28.2 / 28.1504 (atm) *IGNORE* sf except 1 Value = 28.16 if mol fraction rounded *ALLOW* TE from (b)(i)	28.1 $\frac{46.8 \times 32}{50} =$ 29.95 (atm)	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(iii)	exothermic as yield / pp of ethanoic acid / conversion of reactants/ K_p is higher at lower temperature / as equilibrium moves (right) at lower temperature *ALLOW* if partial pressure of ethanoic acid < 22.2 atm in (b)(ii), endothermic as yield / pp of ethanoic acid / conversion of reactants/ K_p is lower at lower temperature		**1**

Question Number	Acceptable Answers	Reject	Mark
19 (c)(i)	No effect **and** other concentrations change to keep K_p constant / K_p is only affected by temperature/ as equilibrium moves (right) to keep K_p constant / **change** in pressure does not change K_p	As K_p is a constant	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (c)(ii)	Yield **increased** to restore fraction / quotient / partial pressure ratio back to K_p *ALLOW* (equilibrium moves) to use up the methanol /answers based on entropy or Le Chatelier Correct prediction in (c)(i) and (c)(ii) with inadequate explanations scores **1 mark** in (c)(ii)	Just 'equilibrium moves to the right'	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (d)	Mark independently Reaction can occur at lower temperature / has lower activation energy / requires less energy **(1)** less fuel needed / fewer emissions (from fuels) / fewer raw materials needed / less natural resources used **(1)** **OR** Enables use of an alternative process with higher atom economy **(1)** fewer raw materials needed / less natural resources used **(1)**	Answer based on car exhaust emissions	**2**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(i)	Correct answer with or without working scores **2 marks** $[H^+]$ = (1 .00 x 10^{-14}/ 0.250) = 4 x 10^{-14} **(1)** pH = (13.39794 =) 13.4 **(1)** **OR** pOH = -log 0.250 = 0.602 **(1)** pH = (13.39794 =)13.4 **(1)** *ALLOW* TE in second mark if error in $[H^+]$ calculation gives pH more than 7 3 or more sf *IGNORE* rounding errors e.g. accept 13.39		**2**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(ii)	$(K_a =)\ \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ **(1)** *ALLOW* H_30^+ instead of H^+ $\frac{[A^-][H^+]}{[HA]}$ if key to symbols given *IGNORE* state symbols	$\frac{[H^+]^2}{[CH_3COOH]}$	**1**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(iii)	Correct answer with or without working scores **2 marks** $1.7 \times 10^{-5} = \frac{[H^+]^2}{0.125}$ **(1)** $[H^+] = 1.46 \times 10^{-3}$ pH = 2.84/2.8 **(1)** no TE from an incorrect $[H^+]$		**2**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(iv)	pH = 4.8 / 4.77 **(1)** pH = pK_a / [H^+] = K_a (when acid is half neutralized) **(1)**	H^+ = K_a	**2**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(v)	Sigmoid curve starting between pH 2 and 4 (2.8), ending between pH 12 and 14 inclusive **(1)** with steep rise (may be vertical or gently sloping) of between 3 – 7 units between pH 6 and 12. Sloping section should not extend over more than 5cm^3. **(1)** When 12.5 cm^3, NaOH added. **(1)** *ALLOW* tolerance for grid Reverse curves lose first mark		**3**

Question Number	Acceptable Answers	Reject	Mark
20 (a)(vi)	**First mark** Thymolphthalein more suitable as it changes (from colourless to blue) in steep region of titration (pH 8.3 to 10.6)/ at the equivalence point / at the end point OR thymolphthalein has pH range in steep region of titration **(1)** **Second mark** Methyl yellow changes (from red to yellow at pH 2.9 to 4) before equivalence point / before the end point / doesn't change in steep section OR Methyl yellow has pH range before / outside steep region of titration **(1)** *ALLOW* 'Thymolphthalein more suitable as it changes at the equivalence point but methyl yellow does not.' This scores **2 marks** **OR** **First mark** pK_{in} ± 1 must lie within vertical region on titration curve **(1)** **Second mark** hence thymolphthalein is suitable and methyl yellow is not **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
20 (b)	Sodium ethanoate/ CH_3COONa Potassium ethanoate / CH_3COOK *ALLOW* other cations as alternatives to sodium	Use of sodium hydroxide (because it's in food)	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(i)	$\Delta S^{\ominus}_{\text{system}}$ = 109.2 + (6x 69.9) – 343 **(1)** =(+)185.6(J mol^{-1} K^{-1}) / (+)186 (J mol^{-1} K^{-1}) **(1)** **OR** (+)0.186 (kJ mol^{-1} K^{-1}) **(2)** IGNORE units even if incorrect correct answer with no working scores 2 Value using 1 for H_2O = -163.9 scores 1 Use of value for $H_2O(g)$ (188.7) gives 898.4 (J mol^{-1} K^{-1}) **(1)** correct value with incorrect sign scores 1	185	**2**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(ii)	Yes as (solid and) liquid forms (from solid) / number of moles increases **OR** If $\Delta S^{\ominus}_{\text{system}}$ in (i) is negative the sign is not as expected as liquid forms from solid / number of moles increases	Disorder increases, with no ref to liquid or number of moles	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(iii)	**First mark** $\Delta S^{\ominus}_{\text{surroundings}} = -\frac{88.1 \times (1000)}{298}$ **(1)** **Second mark** = -295.6375 = -295.6 J mol^{-1} K^{-1} **(1)** correct units must be shown but order not important **OR** -0.2956 kJ mol^{-1} K^{-1} **(1)** correct units must be shown but order not important correct answer with or without working and correct units scores **(2)** ignore sf except 1 correct value with positive sign scores 1		**2**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(iv)	(185.6–295.6) **= -110 (J mol^{-1} K^{-1})** OR **-0.110 (kJ mol^{-1} K^{-1})** could use 186 or 296 etc TE from (a)(i) and (iii) **(+)602.8 (J mol^{-1} K^{-1}) if value for 6H_2O(g) was used in (a) (i)** **-459.5 (J mol^{-1} K^{-1}) if value for one H_2O was used in (a) (i)**	Answers where values in J are added to kJ	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (a)(v)	Decomposition (at 298 K) will not occur as $\Delta S^{\ominus}_{total}$ is negative / Reactions are only spontaneous if total entropy change is positive / decomposition not thermodynamically feasible / (hydrated cobalt chloride) is thermodynamically stable TE if answer to (a)(iv) is positive showing decomposition (at 298 K) may occur **OR** Positive total entropy change doesn't indicate rate of reaction		**1**

Question Number	Acceptable Answers	Reject	Mark
21 (b)(i)	**First mark** Thermometer **(1)** **Second mark** (dependent on first) depends on choosing thermometer as temperature change is small / (%) error in balance smaller than for temperature reading (%) error in pipette smaller than for temperature reading (can be shown by calculation) / as scale with greater degree of precision needed / scale with more graduations needed **(1)** *IGNORE* any references to 'accurate thermometer'		**2**

Question Number	Acceptable Answers	Reject	Mark
21 (b)(ii)	Use more cobalt chloride / less water **(1)** To increase temperature rise **(1)** Mark independently	Just 'use more reactants' Use more cobalt chloride and more water repeat expt add a lid or extra insulation to beaker use distilled water	**2**

Question Number	Acceptable Answers	Reject	Mark
21 (c)(i) **QWC**	Radius (of cation) increases (down group) OR any **two** values of radius: Mg $^{2+}$ = 0.072, Ca $^{2+}$ = 0.100 / Sr $^{2+}$ = 0.113 (nm) data may be shown beside the table **(1)** Radius Co^{2+} = 0.065 nm OR Co^{2+} radius smaller than other ions **(1)** Data on **EITHER** Co^{2+} **OR** data showing increase in radius down Group II required for **BOTH** of first two marks Force of attraction between ions decreases (as radius of ions increases) / charge density of ions decreases / negative ion can come closer to nucleus of positive ion **(1)** *ALLOW* "weaker ionic bonds" Predict lattice energy –2550 to -2900 (kJ mol^{-1}) **(1)** IGNORE sign	Atomic radii unless ionic radii also given Radius of cobalt chloride Polarising power decreases	**4**

Question Number	Acceptable Answers	Reject	Mark
21 (c)(ii) **QWC**	**First mark** Reference to enthalpy of hydration (may be in equation $\Delta H_{solution}$ = -LE + $\Delta H_{hydration}$) **(1)** **Second mark** Solubility depends on relative size of lattice energy and enthalpy of hydration **(1)** **Third mark** **EITHER** Solubility more likely if $\Delta H_{solution}$ is negative **OR** (If $\Delta H_{solution}$ is positive,) may / will dissolve if ΔS_{total} is positive *ACCEPT* solvation instead of hydration		**3**

Question Number	Acceptable Answers	Reject	Mark
21 (d) **QWC**	**First mark** **Third** ionization energy **high(er)** for Mg / Mg = 7733 kJ mol^{-1}, (third ionization energy for Co = 3232 kJ mol^{-1}) **(1)** **Second mark** (Third ionization energy for Mg is high) because the electron is being removed from an inner shell / full shell / 2p level / 2p orbital **(1)** **OR** Not compensated by higher lattice energy for Mg^{3+} (and so $\Delta H_{formation}$ of $MgCl_3$ would be highly endothermic) **(1)**		**2**

Write your name here

Surname	Other names

Centre Number	Candidate Number

Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 26 January 2011 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- 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 Methods for investigating reaction rates include

A colorimetry.

B measurement of change in volume.

C measurement of change of mass.

D quenching followed by titrating with acid.

Which method would be most suitable to investigate the rate of the following reactions?

(a) $HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $(CH_3)_2C{=}CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 1 = 3 marks)

2 $$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

This reaction is first order with respect to hydrogen and second order with respect to nitrogen(II) oxide.

By what factor will the initial rate increase if the concentration of hydrogen and nitrogen(II) oxide are both tripled?

☒ **A** 3

☒ **B** 9

☒ **C** 12

☒ **D** 27

(Total for Question 2 = 1 mark)

---

3 Which reaction has the most positive entropy change for the system, ΔS_{system}?

☒ **A** $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

☒ **B** $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

☒ **C** $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(l)$

☒ **D** $C_4H_{10}(g) \rightarrow C_2H_4(g) + C_2H_6(g)$

(Total for Question 3 = 1 mark)

---

4 Barium carbonate decomposes in an endothermic reaction when heated to 1500 K.

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

What are the signs of the entropy changes at 1500 K?

		ΔS_{system}	$\Delta S_{\text{surroundings}}$
☒	**A**	+	+
☒	**B**	+	–
☒	**C**	–	+
☒	**D**	–	–

(Total for Question 4 = 1 mark)

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

5 What are the units of K_c for the following equilibrium?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

☒ **A** atm

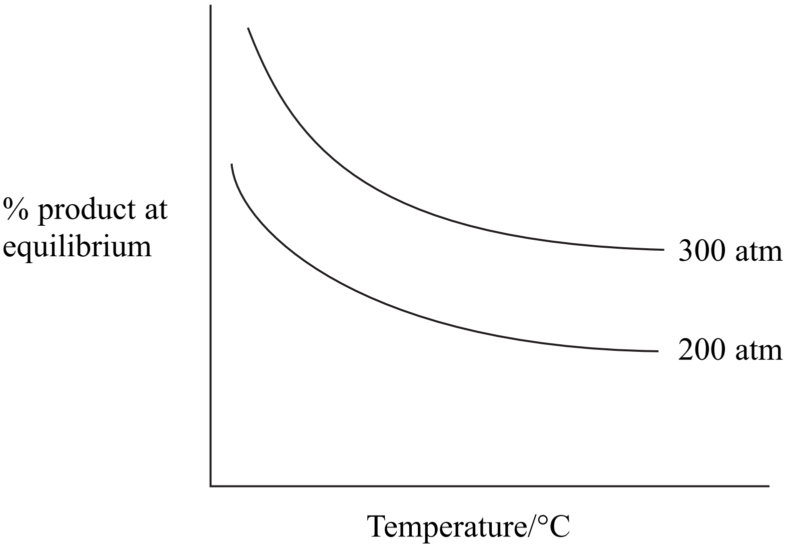
☒ **B** atm^{-1}

☒ **C** $dm^3\ mol^{-1}$

☒ **D** $mol\ dm^{-3}$

(Total for Question 5 = 1 mark)

6 The graph below shows the yield of product in a gaseous equilibrium at different temperatures and pressures.



The forward reaction in the equilibrium is

☒ **A** exothermic, and the number of moles of gas is increasing.

☒ **B** endothermic, and the number of moles of gas is increasing.

☒ **C** exothermic, and the number of moles of gas is decreasing.

☒ **D** endothermic, and the number of moles of gas is decreasing.

(Total for Question 6 = 1 mark)

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

7 Hydrogen cyanide, HCN, reacts with propanal, CH_3CH_2CHO, in the presence of potassium cyanide, KCN.

(a) The mechanism for this reaction is

(1)

☒ **A** nucleophilic addition.

☒ **B** nucleophilic substitution.

☒ **C** electrophilic addition.

☒ **D** electrophilic substitution.

(b) The first stage of the mechanism of this reaction is

(1)

☒ **A** the lone pair of electrons on carbon in CN^- attacking $C^{\delta+}$ of propanal.

☒ **B** the lone pair of electrons on nitrogen in CN^- attacking $C^{\delta+}$ of propanal.

☒ **C** the lone pair of electrons on oxygen in propanal attacking $C^{\delta+}$ of HCN.

☒ **D** the lone pair of electrons on oxygen in propanal attacking $H^{\delta+}$ in HCN.

(c) The product of the reaction is

(1)

☒ **A** 1-hydroxypropanenitrile.

☒ **B** 2-hydroxypropanenitrile.

☒ **C** 1-hydroxybutanenitrile.

☒ **D** 2-hydroxybutanenitrile.

(Total for Question 7 = 3 marks)

8 Which of the following does not have hydrogen bonding in a pure sample, but forms hydrogen bonds with water when it dissolves?

☒ **A** Propane

☒ **B** Propanal

☒ **C** Propanol

☒ **D** Propanoic acid

(Total for Question 8 = 1 mark)

9 Which of the following has both optical and E-Z isomers?

☒ **A** $ClCH_2CHClCH{=}CH_2$

☒ **B** $CH_2{=}CClCH_2CH_2Cl$

☒ **C** $ClCH_2CH{=}CHCH_2Cl$

☒ **D** $CHCl{=}CHCHClCH_3$

(Total for Question 9 = 1 mark)

10 One optically active isomer of 2-chlorobutane reacts with hydroxide ions to form butan-2-ol.

$$C_2H_5CHClCH_3 + OH^- \rightarrow C_2H_5CH(OH)CH_3 + Cl^-$$

The organic product is a **mixture** of enantiomers because

☒ **A** butan-2-ol contains a chiral carbon atom.

☒ **B** the reaction is a nucleophilic substitution.

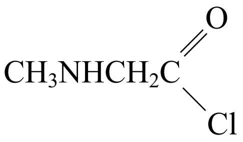
☒ **C** 2-chlorobutane forms a carbocation intermediate.

☒ **D** 2-chlorobutane forms a five-bonded transition state.

(Total for Question 10 = 1 mark)

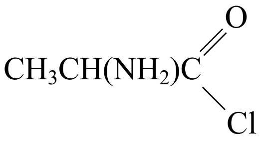
11 The organic product of the reaction between ethanoyl chloride and methylamine has the formula

☒ **A**



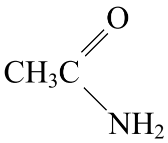
CH_3NHCH_2COCl

☒ **B**



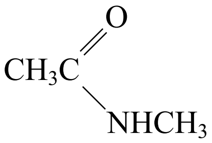
$CH_3CH(NH_2)COCl$

☒ **C**



CH_3CONH_2

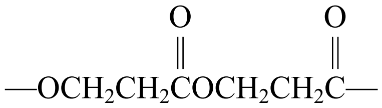
☒ **D**



$CH_3CONHCH_3$

(Total for Question 11 = 1 mark)

12 A section of a polymer is shown below. Which of the following monomers would form this polymer?



$$\text{—OCH}_2\text{CH}_2\overset{\overset{\large O}{\|}}{\text{C}}\text{OCH}_2\text{CH}_2\overset{\overset{\large O}{\|}}{\text{C}}\text{—}$$

☒ **A** $HOCH_2CH_2OH$ and $ClCOCH_2CH_2COCl$

☒ **B** $HOCH_2CH_2OH$ and $HOOCCH_2CH_2COOH$

☒ **C** $ClCH_2CH_2COCl$ alone

☒ **D** $HOCH_2CH_2COOH$ alone

(Total for Question 12 = 1 mark)

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13 Which of the following is **not** a reaction of a Brønsted-Lowry acid and base?

☒ **A** $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

☒ **B** $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

☒ **C** $H_2O + HSO_4^- \rightarrow H_2SO_4 + OH^-$

☒ **D** $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

(Total for Question 13 = 1 mark)

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14 A buffer solution is made from ammonia and ammonium chloride. When a small amount of acid is added to this buffer

☒ **A** hydrogen ions in the acid combine with chloride ions to make HCl.

☒ **B** hydrogen ions in the acid combine with NH_3 to make NH_4^+.

☒ **C** NH_4^+ ions dissociate to make more NH_3.

☒ **D** the hydrogen ions in the acid prevent dissociation of the NH_4Cl.

(Total for Question 14 = 1 mark)

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

15 Information about four samples of acid is shown below.

Sample 1: 1.0 mol dm^{-3} HCl

Sample 2: 1.0 mol dm^{-3} H_2SO_4

Sample 3: 0.1 mol dm^{-3} HCl

Sample 4: 0.1 mol dm^{-3} CH_3COOH

Which of the following lists shows the samples in order of increasing pH?

☒ **A** 1, 2, 3, 4

☒ **B** 4, 3, 2, 1

☒ **C** 2, 1, 3, 4

☒ **D** 4, 3, 1, 2

(Total for Question 15 = 1 mark)

16 Which reaction has an enthalpy change equal to the enthalpy of hydration of the sodium ion?

☒ **A** $Na^+(g) + \text{excess } H_2O(l) \rightarrow Na^+(aq)$

☒ **B** $Na^+(g) + 1 \text{ mol of } H_2O(l) \rightarrow Na^+(aq)$

☒ **C** $Na^+(s) + \text{excess } H_2O(l) \rightarrow Na^+(aq)$

☒ **D** $Na^+(s) + 1 \text{ mol of } H_2O(l) \rightarrow Na^+(aq)$

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 Hydrogen can be manufactured by reacting methane with steam, as shown in the equation below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus}_{298} = +206.1\,kJ\,mol^{-1}$$

Use these values:

the standard entropy of 1 mol of $H_2(g)$ is $(2 \times 65.3) = 130.6\ J\,mol^{-1}\,K^{-1}$
the standard entropy of 1 mol of $H_2O(g)$ is $188.7\ J\,mol^{-1}\,K^{-1}$

You will also need to refer to the data booklet in the calculations which follow.

(a) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction at 298 K.

(2)

(b) Calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(c) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

Explain why this value shows that the reaction is not spontaneous at this temperature.

(2)

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(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

	$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$			
Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer.

(6)

(ii) The total entropy change in J mol^{-1} K^{-1} is related to the equilibrium constant by the equation

$$\Delta S^{\ominus}_{\text{total}} = R\ln K_p \quad \text{or} \quad \Delta S^{\ominus}_{\text{total}} = 2.3R\log K_p$$

Calculate the total entropy change at the temperature of the reaction.

[R = 8.31 J mol^{-1} K^{-1}]

(1)

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S^{\ominus}_{\text{total}}$. Assume that ΔH is still +206.1 kJ mol^{-1} and that $\Delta S^{\ominus}_{\text{system}}$ = +225 J K^{-1} mol^{-1}. (This is not the same as the value for $\Delta S^{\ominus}_{\text{system}}$ calculated in (a) which is at 298 K.)

(2)

*(e) Use the magnitude and signs of the entropy changes to explain the effect of a temperature increase on the equilibrium constant of this endothermic reaction.

(2)

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(Total for Question 17 = 17 marks)

18 (a) Calculate the pH of 0.25 mol dm^{-3} hydrochloric acid.

(1)

(b) Propanoic acid, CH_3CH_2COOH, is a weak acid with $K_a = 1.3 \times 10^{-5}$ mol dm^{-3} at 25 °C.

(i) Write the expression for K_a for propanoic acid.

(1)

(ii) Calculate the pH of 0.25 mol dm^{-3} propanoic acid at 25 °C.

(2)

(c) During a titration, 10 cm^3 0.10 mol dm^{-3} sodium hydroxide was added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid.

(i) Write an equation for the reaction which occurs. State symbols are **not** required.

(1)

(ii) At this point the titration mixture contains 1.5×10^{-3} moles of propanoic acid and 1.0×10^{-3} moles of propanoate ion.

Use your expression for K_a for propanoic acid to calculate the pH of the mixture.

(2)

*(iii) When a further small amount of 0.10 mol dm^{-3} sodium hydroxide is added in the titration, the pH changes very little. Explain why the pH change is small.

(3)

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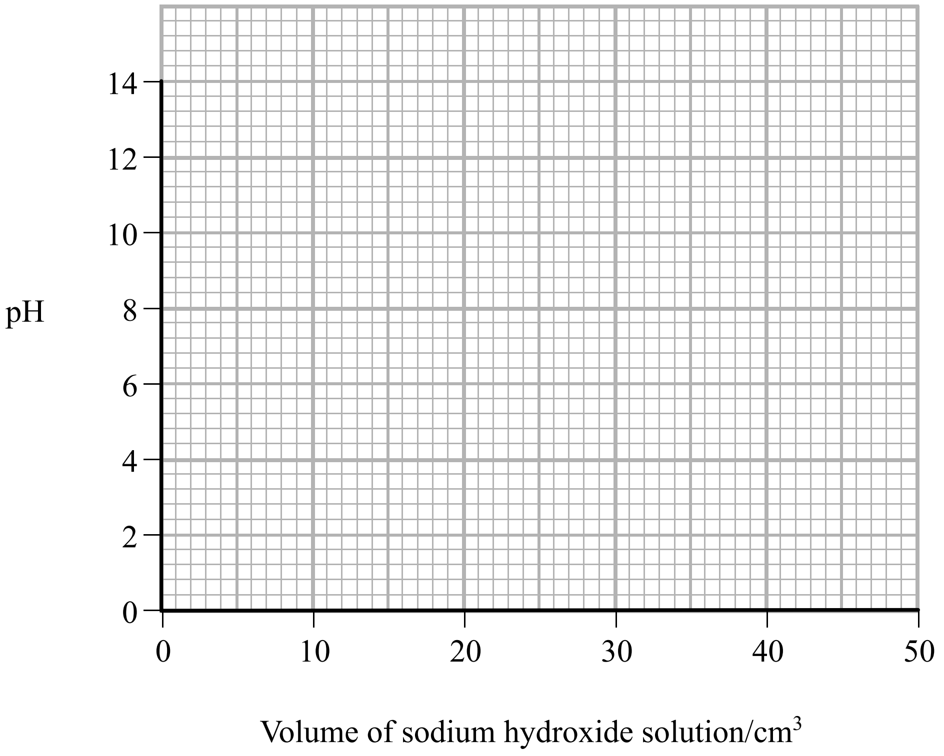
(iv) Draw the titration curve showing the change in pH when 0.10 mol dm^{-3} sodium hydroxide is added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid until present in excess. The equivalence point is 25 cm^3.

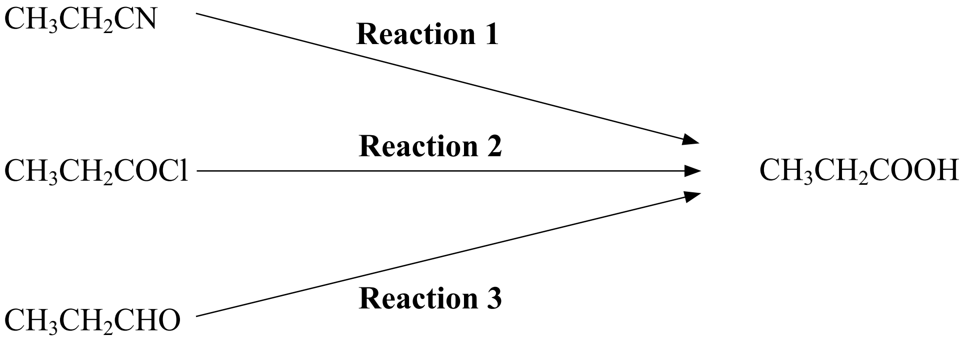
(3)



(v) Explain, referring to your data booklet, whether bromocresol green would be a suitable indicator for this titration.

(2)

(d) Propanoic acid is produced in the reactions shown below.



(i) Suggest a reagent which could be used to carry out **reaction 1**.

(1)

(ii) Write an equation for **reaction 2**. State symbols are **not** required.

(1)

(iii) What would be observed if **reaction 3** was carried out using potassium dichromate(VI) and sulfuric acid?

(1)

(e) What type of reagent would be used to convert propanoic acid to propan-1-ol? Identify a suitable reagent for this reaction.

(2)

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(Total for Question 18 = 20 marks)

19 A student investigated the reaction between iodine and propanone in acidic conditions.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

- 50 cm^3 of 0.020 mol dm^{-3} iodine solution was measured into a flask.
- 25 cm^3 of propanone and 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid were measured into a second flask.
- Several 10 cm^3 samples of 0.5 mol dm^{-3} sodium hydrogencarbonate solution were placed in separate conical flasks.
- The mixture of propanone and sulfuric acid was added to the iodine, and a clock started.
- At two minute intervals, 10 cm^3 of the reaction mixture was removed and added to one of the flasks containing sodium hydrogencarbonate solution.
- The contents of this flask were then titrated with 0.01 mol dm^{-3} sodium thiosulfate.

(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonate.

(2)

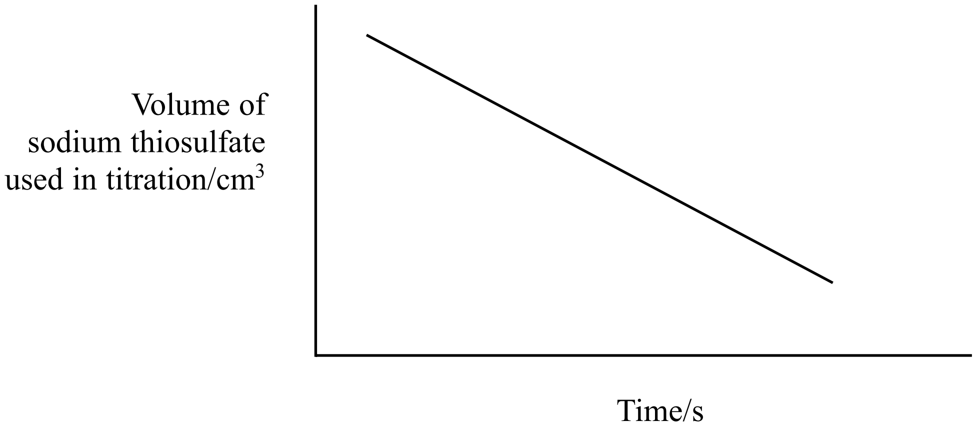
(b) What indicator should be used in the titration?

(1)

*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

(d) The shape of the graph obtained from the results of the experiment is shown below.



Use the graph to deduce the order of reaction with respect to iodine, explaining your reasoning.

(2)

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(e) The solutions used in this experiment could be measured using either measuring cylinders or pipettes.

Give **one** advantage of using a measuring cylinder and **one** advantage of using a pipette.

(2)

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(f) In a further investigation, different volumes of sulfuric acid, propanone, iodine and water were mixed. The time taken for the mixture to go colourless was measured.

The experiments were repeated and the results below show average values for the rate of the reaction.

Expt	2 mol dm^{-3} H_2SO_4 /cm^3	2 mol dm^{-3} propanone /cm^3	Water /cm^3	0.01 mol dm^{-3} iodine /cm^3	Rate /mol dm^{-3} s^{-1}
1	20.0	8.0	0	4.0	8×10^{-5}
2	10.0	8.0	10.0	4.0	4×10^{-5}
3	20.0	4.0	4.0	4.0	4×10^{-5}

(i) Explain why water is added in experiments 2 and 3.

(1)

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(ii) Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.

(3)

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(Total for Question 19 = 13 marks)

TOTAL FOR SECTION B = 50 MARKS

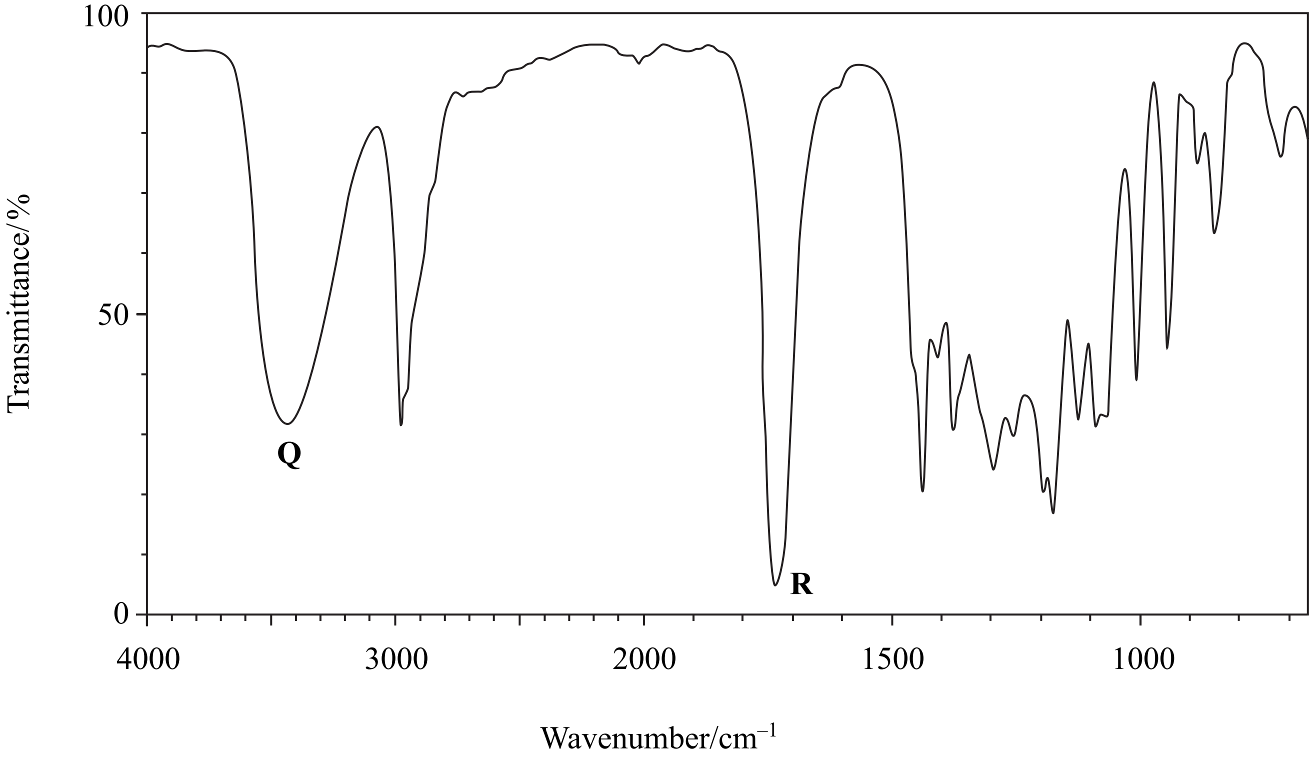
SECTION C

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

20 An organic compound **X** is an ester found in orange peel and has the molecular formula $C_5H_{10}O_3$.

(a) Identify the bonds responsible for the peaks labelled **Q** and **R** in the infrared spectrum of **X** shown below, referring to your data booklet.

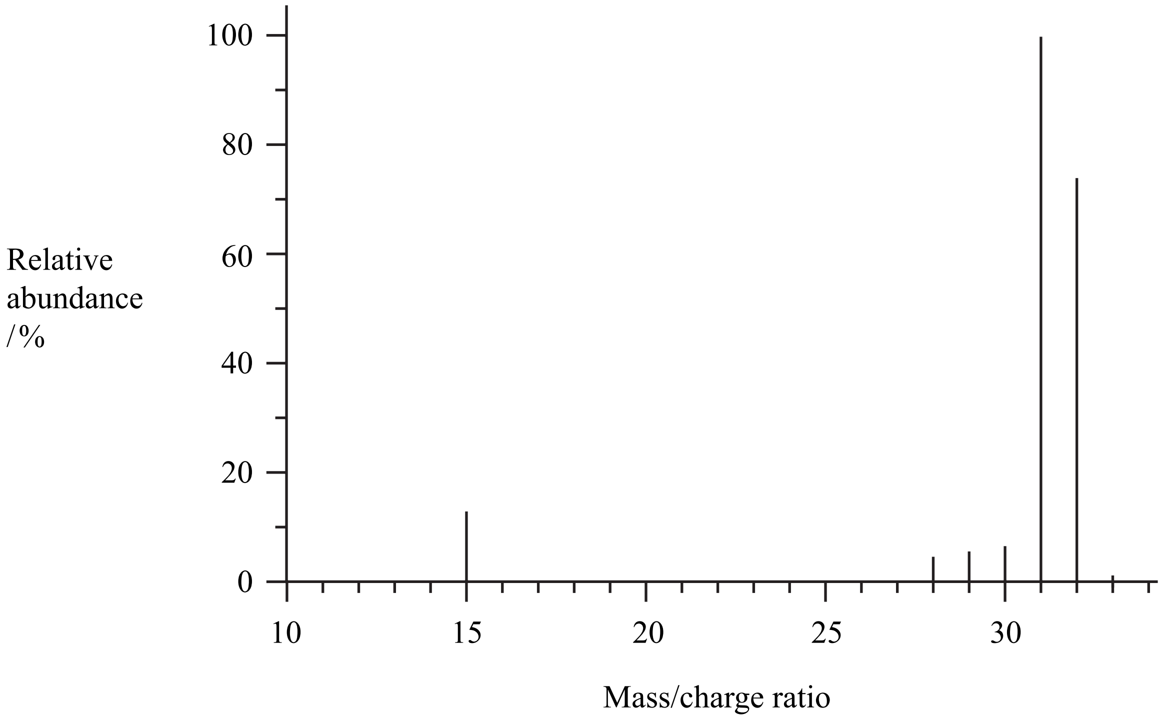
(2)



Q ....

R ....

(b) **X** was heated under reflux with dilute sulfuric acid. The resulting mixture was distilled and a liquid **Y** was collected. The mass spectrum of **Y** is shown below.



(i) Identify **Y**, by name or formula, using the information available. Use **two** pieces of data from the mass spectrum to support your answer.

(2)

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(ii) The identity of **Y** could be confirmed using nmr spectroscopy. Predict the number of peaks in the low resolution proton nmr spectrum of **Y**. Give the chemical shift range for each peak, referring to your data booklet.

(2)

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(c) A second product from the reaction of **X** with hydrochloric acid is **Z**, which has the molecular formula $C_4H_8O_3$.

What can you deduce about **Z** from the results of the following tests?

(i) One mole of **Z** reacts with two moles of phosphorus(V) chloride, PCl_5.

(1)

(ii) When sodium carbonate solution is added to **Z**, effervescence is seen.

(1)

(iii) **Z** is warmed gently with potassium dichromate(VI) and sulfuric acid. The organic product of the reaction gives a yellow precipitate with 2,4-dinitrophenylhydrazine (Brady's reagent) but does not react with Tollens' reagent.

(1)

(iv) **Z** reacts with a solution of iodine in sodium hydroxide to produce a yellow precipitate with an antiseptic smell.

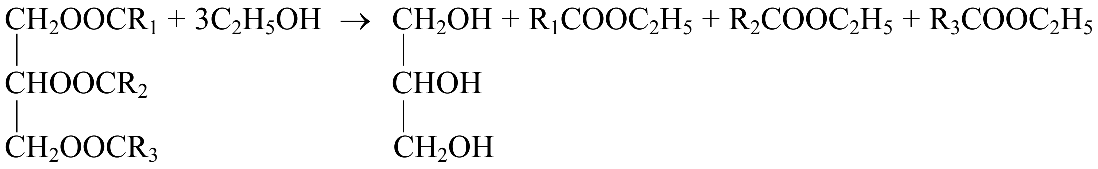
(1)

(d) Use the results of these tests to deduce the structural formula of **Z** and hence the structural formula of **X**.

(2)

(Total for Question 20 = 12 marks)

21 The equation below shows the type of reaction which can be used in the production of biodiesel from vegetable oils.



$$\begin{array}{l} \mathrm{CH_2OOCR_1} \\ | \\ \mathrm{CHOOCR_2} \\ | \\ \mathrm{CH_2OOCR_3} \end{array} + \mathrm{3C_2H_5OH} \rightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{R_1COOC_2H_5} + \mathrm{R_2COOC_2H_5} + \mathrm{R_3COOC_2H_5}$$

(a) (i) Name this type of reaction.

(1)

(ii) Suggest why water must not be present when this reaction with ethanol is carried out.

(1)

(b) Give **one** reason why biodiesel is considered a “greener” fuel than diesel produced from crude oil.

(1)

*(c) The products of the type of reaction shown with ethanol can be separated and identified using gas chromatography (GC).

In chromatography, compounds are separated because of the difference in distribution between a mobile phase and a stationary phase.

Explain why this difference in distribution occurs, and contrast the phases used in gas chromatography (GC) and high performance liquid chromatography (HPLC).

(5)

(Total for Question 21 = 8 marks)

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

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
																	(18)
(1)	(2)						1.0 **H** hydrogen 1					(13)	(14)	(15)	(16)	(17)	4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported
but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)
January 2011

GCE

GCE Chemistry (6CH04/01)

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Alternatively, you can speak directly to a subject specialist at Edexcel on our dedicated Science telephone line: 0844 576 0037

January 2011

Publications Code UA026200

Section A (multiple choice)

Question Number	Correct Answer	Mark
1 (a)	D	**1**

Question Number	Correct Answer	Mark
1 (b)	B	**1**

Question Number	Correct Answer	Mark
1 (c)	A	**1**

Question Number	Correct Answer	Mark
2	D	**1**

Question Number	Correct Answer	Mark
3	D	**1**

Question Number	Correct Answer	Mark
4	B	**1**

Question Number	Correct Answer	Mark
5	C	**1**

Question Number	Correct Answer	Mark
6	C	**1**

Question Number	Correct Answer	Mark
7 (a)	A	**1**

Question Number	Correct Answer	Mark
7 (b)	A	**1**

Question Number	Correct Answer	Mark
7 (c)	D	**1**

Question Number	Correct Answer	Mark
8	B	**1**

Question Number	Correct Answer	Mark
9	D	**1**

Question Number	Correct Answer	Mark
10	C	**1**

Question Number	Correct Answer	Mark
11	D	**1**

Question Number	Correct Answer	Mark
12	D	**1**

Question Number	Correct Answer	Mark
13	A	**1**

Question Number	Correct Answer	Mark
14	B	**1**

Question Number	Correct Answer	Mark
15	C	**1**

Question Number	Correct Answer	Mark
16	A	**1**

TOTAL FOR SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
17 (a)	ΔS_{system} = (3x2x65.3 +197.6) – (186.2 + 188.7) Correct data for CH_4 and CO (186.2 and 197.6) **(1)** = (+) **214.5 / 215** (J mol^{-1} K^{-1}) / (+) **0.2145 / 0.215 kJ** (mol^{-1} K^{-1}) **(1)** Units must be shown if data has been converted to kJ Full marks (2) for correct answer without working Ignore sf except 1 Answer of -214.5 scores (1) Answer of +18.6 if entropy of H not doubled scores (1) Answer of –46.7 if entropy of H_2 not tripled scores (1) ALLOW TE in second mark for minor error in data e.g. writing 63.5 instead of 65.3. No TE if data used is not entropy of compounds.	**214** **0.214**	**2**

Question Number	Acceptable Answers	Reject	Mark
17 (b)	($\Delta S_{surroundings}$) = $\frac{-\Delta H}{T}$ Expression or use of expression, $\frac{-206.1x(1000)}{298}$ **(1)** = **-691.6 J** (mol^{-1} K^{-1})/ **-0.6916 kJ** (mol^{-1} K^{-1}) **(1)** Ignore sf except 1		**2**

Question Number	Acceptable Answers	Reject	Mark
17 (c)	ΔS_{total} = (214.5+(-691.6)) = **-477.1** (J mol^{-1} K^{-1}) / - **0.4771** (kJ mol^{-1} K^{-1}) **(1)** ALLOW TE for answer to (a) plus answer to (b). If 214.5 is added to -0.69 no TE unless -0.69 is specified to be in joules. Ignore sf except 1 Negative / less than zero (so not spontaneous) / would be positive if spontaneous. **(1)** ALLOW "feasible" for spontaneous. If answer to calculation is positive, accept comment that it would be expected to be negative if not spontaneous	Addition of value in J to specified value in kJ Comments on kinetic stability	**2**

Question Number	Acceptable Answers	Reject	Mark
***17 (d) (i)**	$K_p = \frac{(pH_2)^3 x (pCO)}{(pCH_4)(pH_2O)}$ **(1)** 4 Correct partial pressures **(3)** | | CH_4 | H_2O | CO | H_2 | | pp | **0.25** | **0.25** | **0.375** | **1.125** | ALLOW partial pressures as fractions $K_p = \frac{(1.125)^3 \text{ x } (0.375)}{(0.25)(0.25)}$ = **8.54 atm^2** value of K_p **(1)** unit **(1)** (Stand alone mark) Correct calculation without working scores the 5 calculation marks. TE from K_p expression if inverted Ignore sf except 1 **If any partial pressures are incorrect:** Calculating total number of moles (6.4) **(1)** Calculating mole fractions (0.125, 0.125, 0.1875, 0.5625 if total number of moles is correct) **(1)** Multiplying mole fractions by total pressure (x 2 atm) **(1)** value of K_p **(1)** unit **(1)** (stand alone mark) ALLOW TE in value of K_p only from incorrect partial pressures, not using values in question as not using equilibrium moles If treated as a K_c calculation following K_p expression : K_p expression (1) units atm^2 (1) Max. mark (2)	Square brackets TE for K_p expression with addition, not multiplication	**6**

Question Number	Acceptable Answers	Reject	Mark
17 (d) (ii)	ΔS_{total} = (8.31 ln 8.54) = (+)**17.8** (J mol^{-1} K^{-1}) Accept any value that rounds to 17.8 TE from value in (i) K_p value of 87.48 (obtained by treating calculation in (i) as K_c) gives ΔS_{total} = **37.16 / 37.12**		**1**

Question Number	Acceptable Answers	Reject	Mark
17 (d) (iii)	$17.8 = 225 - \frac{206.1 \times 1000}{T}$ **(1)** $T = \frac{(206.1 \times 1000)}{207.2}$ = **995 / 990** (K) **(1)** Correct answer with no working shown scores 2 Correct method with wrong answer or missing 10^3 scores 1 TE from (ii) K_p value of 87.48 gives T = **1097** **OR** If ΔS_{total} is taken as zero $0 = 225 - \frac{206.1 \times 1000}{T}$ **(1)** T = **916**K **(1)** K_p value of 87.48 gives T = **916** Ignore sf except 1		**2**

Question Number	Acceptable Answers	Reject	Mark
***17 (e)**	$\Delta S_{\text{surroundings}}$ / $\frac{-\Delta H}{T}$ becomes less negative making ΔS_{total} more positive (as T increases) **OR** $\Delta S_{\text{surroundings}}$ / $\frac{-\Delta H}{T}$ becomes less negative making ΔS_{total} greater (as T increases) **OR** (magnitude of) $\Delta S_{\text{surroundings}}$ becomes less / lower making ΔS_{total} more positive / greater (as T increases) **(1)** Because ΔS_{total} increases equilibrium constant increases **(1)** **OR** value of ΔS_{total} at new temperature is more than at 298K (1) (must be clear that the two ΔS_{total} values at the different temperatures have been considered) Because ΔS_{total} increases equilibrium constant increases (1)	Le Chatelier statements without reference to entropy changes Just 'as temperature increases ΔS_{total} increases'	**2**

Question Number	Acceptable Answers	Reject	Mark
18 (a)	pH = (-log 0.25) = 0.602 / 0.60 / 0.6 Ignore significant figures		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b) (i)	$(K_a =) \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$ ALLOW $[H_3O^+]$ for $[H^+]$ ALLOW C_2H_5 for CH_3CH_2 ALLOW $\frac{[H^+][A^-]}{[HA]}$ if HA and A^- identified	Wrong / missing charge on $CH_3CH_2COO^-$ $K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]}$ unless full expression also given	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b) (ii)	$1.3 \times 10^{-5} = \frac{[H^+]^2}{0.25}$ / rearrangement of this expression **(1)** ($[H^+] = 1.8 \times 10^{-3}$) pH = **2.74** **(1)** Correct answer with no working scores (2) No TE for incorrect $[H^+]$ Ignore significant figures except 1 Minimum of 1 decimal place needed		**2**

Question Number	Acceptable Answers	Reject	Mark
18 (c) (i)	$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COO^{(-)}Na^{(+)} + H_2O$ OR $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O$ Accept $CH_3CH_2CO_2H$, C_2H_5COOH, $C_2H_5CO_2H$	Equations for ethanoic acid	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (c) (ii)	$1.3 \times 10^{-5} = \frac{[H^+][5 \times 10^{-2}]}{[7.5 \times 10^{-2}]}$ (concentration ratio) OR $1.3 \times 10^{-5} = \frac{[H^+](1 \times 10^{-3})}{(1.5 \times 10^{-3})}$ (ratio by moles) (ratio by moles allowed as volumes acid and salt equal) **(1)** ($[H^+]$ = **1.95×10^{-5}**) pH = **4.7** / 4.7099654 **(1)** Second mark dependent on first Correct answer with or without working **(2)** OR $\text{pH} = \text{p}K_a - \log \left(\frac{1.5 \times 10^{-3}}{1 \times 10^{-3}}\right)$ OR $\text{pH} = \text{p}K_a - \log \left(\frac{7.5 \times 10^{-2}}{5 \times 10^{-2}}\right)$ **(1)** pH = 4.7 **(1)** Correct answer with or without working **(2)** Accept any value which rounds to 4.7		**2**

Question Number	Acceptable Answers	Reject	Mark
***18 (c) (iii)**	Mixture is a buffer **(1)** EITHER OH^- combines with H^+ in solution **(1)** Propanoic acid dissociates to replace H^+ **(1)** *Correct equations could gain these marks* OR OH^- reacts with propanoic acid **(1)** *Correct equation could gain this mark* Significant quantities of weak acid and salt are both present /ratio of acid and salt does not change **(1)** ALLOW a reservoir of weak acid and salt are present: Allow conjugate base for salt	NaOH combines	**3**

Question Number	Acceptable Answers	Reject	Mark
18 (c) (iv)	S-shaped curve, vertical at 25 cm^3 (with kink at start) **(1)** Starting at pH 2-3 (TE from (b)(ii), finishing at pH 12 -13 **(1)** Vertical section between 3 and 6 units high centred round a pH of between 8 and 9 **(1)** Vertical section should not extend over more than $\pm 2.5 cm^3$ This section should start between 5.5 and 7.5 and finish between 9.5 and 11.5 but do not penalise for very small differences. Reverse curve maximum 2		**3**

Question Number	Acceptable Answers	Reject	Mark
18 (c) (v)	Either Need indicator changing in vertical region of curve / need indicator changing where pH changes sharply / bromocresol green changes before the vertical region **(1)** **Not** bromocresol green which changes at **3.8 – 5.4** **(1)** OR pK_{in} ±1 must be in vertical section / sharply changing section **(1)** **Not** bromocresol green because pK_{in} is **4.7** **(1)** TE from curve with vertical section including pH 3.7 – 5.7	Just “the equivalence point is outside the bromocresol green range”	**2**

Question Number	Acceptable Answers	Reject	Mark
18 (d) (i)	Dilute acid / dilute strong named acid or formula / NaOH(aq) followed by dilute acid /water plus dilute acid / water plus H^+	NaOH alone water any weak acid concentrated sulfuric acid HCN acid hydrolysis alone	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (d) (ii)	$CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$ / $C_2H_5COCl + H_2O \rightarrow C_2H_5COOH + HCl$ Accept displayed formula	Equations with NaOH or OH^-	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (d) (iii)	Colour change orange to green / blue		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (e)	Reducing agent /Reduction (of the acid) occurs **(1)** Li Al H_4 / lithium tetrahydridoaluminate / lithium aluminium hydride **(1)** Allow minor error in name if correct formula is given Ignore solvent ALLOW nucleophile AND H^- for 1 mark	Lithal without correct name or formula	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (a)	Quenches reaction / stops reaction / slows reaction / freezes reaction **(1)** EITHER by neutralizing the acid / removing the acid / neutralizing the catalyst / removing the catalyst **OR** So that the acid does not react with the thiosulfate **(1)**	By neutralizing HI Just "by diluting the reaction mixture" just "by neutralizing the reaction mixture"	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (b)	Starch (solution)		**1**

Question Number	Acceptable Answers	Reject	Mark
19 (c)	**First mark** So that [propanone] and [acid] are (virtually) constant **OR** so that the [propanone] and [H^+] do not affect the rate **OR** Propanone and acid are in excess so **changes in concentration** don't affect rate **(1)** **Second mark** And therefore rate changes would only depend on [iodine] **OR** so that the overall order is not determined ALLOW [Iodine] is the limiting factor **(1)** *NOTE* "so that only the [I_2] changes" scores **(2)** "so that only the I_2 concentration changes" scores **(2)** "so that only the I_2 changes" scores **(1)**	Propanone and acid are in excess, without reference to further comments	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (d)	Zero order **(1)** (Gradient =) **rate** is constant / I_2 (concentration) doesn't affect **rate** / **rate** of change of I_2 (concentration) doesn't change with time **(1)** **Mark independently**	Just 'straight line' Or just 'gradient is constant' [Thiosulfate] or volume of Thiosulfate is proportional to time without reference to iodine Reference to half life [I_2] is proportional to rate	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (e)	Measuring cylinder quicker / Measuring cylinder can measure a variety of volumes **(1)** ALLOW Measuring cylinder can be plastic so unbreakable Comment on lower cost of measuring cylinder if qualified with a reason Pipette more accurate / (graduated) pipette more precise / pipette can be used to extract samples from a reaction mixture (for titration) **(1)**	Just "Measuring cylinder easier to use" Easier to clean Measuring cylinder can be used for large volumes Pipette more reliable Ignore references to easier	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (f) (i)	To keep (total) volume constant / to make the (total) volume 32 cm^3 / to make concentrations proportional to volume of reactant	To keep concentrations constant	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (f) (ii)	First order wrt propanone with explanation **(1)** First order wrt hydrogen ions/ sulfuric acid, with explanation **(1)** Explanation can be in terms of experiments 1 and 3 (propanone) or 1 and 2 (acid) and can be in terms of concentration or volume **Rate** = **k**$[CH_3COCH_3][H^+]([I_2]^0)$ / **Rate** = **k**$[CH_3COCH_3][H_2SO_4]([I_2]^0)$ **(1)** ALLOW names of propanone and sulfuric acid in place of formulae Ignore case of k in rate equation Ignore order wrt iodine even if wrong Third mark is consequential if incorrect orders of propanone and acid given.	Expressions without rate or k Expressions with K_c R / r for rate	**3**

TOTAL FOR SECTION B = 50 MARKS

Section C

Question Number	Acceptable Answers	Reject	Mark
20 (a)	Q: O-H ALLOW OH – O – H **(1)** R: C=O ALLOW – C = O | – C = O **(1)** IGNORE names ACCEPT answers written on spectrum	Just 'alcohol' — OH Just 'carbonyl' - C O | C-O	**2**

Question Number	Acceptable Answers	Reject	Mark
20 (b) (i)	Y = methanol / CH_3OH **(1)** Any two of the following: Molecular ion / M^+ / M_r / CH_3OH^+ / methanol = 32 CH_3^+ = 15 CH_3O^+ / CH_2OH^+ = 31 $CHOH^+$/ CH_2O^+ =30 COH^+ = 29 CO^+ = 28 **(1)** Charges not required TE in second mark for two correct possible peaks from an incorrect compound.		**2**

Question Number	Acceptable Answers	Reject	Mark
20 (b) (ii)	Two **(1)** This mark may be scored if two shifts are given. Any two shifts correctly identified: -**OH** at 2.0-4.0 / any value in this range **H**-C-O at 3.0- 4.2 / any value in this range **H** in CH$_3$ OH at 3.39 (ppm) **(1)** Allow TE for ethanol with three peaks **(1)** and three correct shift values: -**OH** at 2.0-4.0 / any value in this range **H**-C-O at 3.0- 4.2 / any value in this range CH in an alkane at 0.1–1.9 **(1)**	CH in an alkane at 0.1–1.9 Just CH$_3$ OH at 3.39	**2**

Question Number	Acceptable Answers	Reject	Mark
20 (c) (i)	Z contains two –OH/ one alcohol + one acid ALLOW two alcohol groups / is a diol		**1**

Question Number	Acceptable Answers	Reject	Mark
20 (c) (ii)	Z is an acid / contains –COOH / contains –CO$_2$H/ contains a carboxylic acid group / contains H$^+$		**1**

Question Number	Acceptable Answers	Reject	Mark
20 (c) (iii)	Z is a secondary alcohol/ a ketone is **formed** from **Z** / | Z contains –C-OH **(1)** | H	**Z** is a ketone	**1**

Question Number	Acceptable Answers	Reject	Mark
20 (c) (iv)	(Iodoform produced) so **Z** contains CH$_3$ CH(OH)- TE if **Z** is identified as a ketone in (iii): **Z** contains CH$_3$ C=O / **Z** is a methyl ketone		**1**

Question Number	Acceptable Answers	Reject	Mark
20 (d)	Answers will be based on several pieces of information (molecular formula, products of ester hydrolysis, answers to (c)) which may be contradictory if errors have been made. ALLOW TE marks for formulae which are chemically possible (ie no 5 bonded carbons etc) and based on most of the deductions but **not necessarily all**. **Z** is $CH_3CH(OH)CH_2COOH$ **(1)** Stand alone mark ALLOW TE for an **acid** with OH in wrong position in **Z** if oxidation product identified as aldehyde TE for **Z** = CH_3COCH_2COOH if identified as ketone in (iii) **X** is $CH_3CH(OH)CH_2COOCH_3$ **(1)** Stand alone mark TE for a methyl ester of **Z**		**2**

Question Number	Acceptable Answers	Reject	Mark
21 (a) (i)	Transesterification Ethanol transesterification	Substituted esterification	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (a) (ii)	To prevent hydrolysis/ to stop fatty acids forming / to stop breakdown of esters / water reacts with esters/ water is a better nucleophile than ethanol	To dilute ethanol Ethanol would react with water A reaction would occur (unspecified)	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (b)	(Vegetable) Fats/ oils are renewable (crude oil is not) / biodiesel comes from a renewable source / doesn't use up fossil fuel resources/ carbon footprint is less / (closer to) carbon neutral / growing vegetables absorb CO_2 If more than one answer is given, and one is incorrect, no mark Ignore comments on biodegradability	Just "made from plants" Just "crude oil is not sustainable" Less polluting produces less greenhouse gases / less CO_2 Burns more cleanly Requires less energy for production	**1**

Question Number	Acceptable Answers	Reject	Mark
21 (c)	Substances to be separated have different (forces of) attraction to / affinity for / solubilities in / adsorption to one or both of the mobile and stationary phases OWTTE **(1)** ALLOW absorption GC: **mobile** phase a (inert / unreactive) **gas** OR GC: **mobile** phase nitrogen / helium / argon / other named inert gas **(1)** GC: **Stationary** phase a **liquid** (on an (inert) solid) / a solid **(1)** HPLC: **stationary** phase a **solid** / silica **(1)** HPLC: **mobile** phase a **liquid** **(1)**	Different retention times without a reason why Different volatilities Different masses Different reactivity Different reactions Different interactions	**5**

TOTAL FOR SECTION C = 20 MARKS

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Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 15 June 2011 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- 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 Which of the following methods would **not** be suitable for measuring the rate of the reaction between methanoic acid and bromine?

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

☒ **A** Colorimetry

☒ **B** Measuring change in electrical conductivity

☒ **C** Quenching samples and titrating with acid

☒ **D** Measuring change in pressure

(Total for Question 1 = 1 mark)

2 The equation below shows the hydrolysis of a bromoalkane.

$$RBr + OH^- \rightarrow ROH + Br^-$$

For a particular bromoalkane, the rate equation is

$$\text{rate} = k[RBr]$$

The bromoalkane, RBr, is most likely to be

☒ **A** CH_3Br

☒ **B** CH_3CH_2Br

☒ **C** $(CH_3)_3CCH_2Br$

☒ **D** $(CH_3)_3CBr$

(Total for Question 2 = 1 mark)

3 A decrease in the entropy of the system, ΔS_{system}, occurs when

☒ **A** water freezes.

☒ **B** water boils.

☒ **C** water reacts with sodium.

☒ **D** water reacts with ethanoyl chloride.

(Total for Question 3 = 1 mark)

4 Methanol is produced in the equilibrium reaction

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -18.3 \text{ kJ mol}^{-1}$$

Addition of more hydrogen to the equilibrium mixture at constant temperature

☒ **A** increases the equilibrium yield of methanol.

☒ **B** decreases the equilibrium yield of methanol.

☒ **C** increases the value of K_p.

☒ **D** decreases the value of K_p.

(Total for Question 4 = 1 mark)

---

5 The equation for the equilibrium between $NO_2(g)$ and $N_2O_4(g)$ can be written in two ways.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \text{Equilibrium constant} = K_c$$

or

$$NO_2(g) \rightleftharpoons \tfrac{1}{2}N_2O_4(g) \quad \text{Equilibrium constant} = K'_c$$

Which expression is correct?

☒ **A** $K_c = K'_c$

☒ **B** $K_c = (K'_c)^2$

☒ **C** $K_c = 2(K'_c)$

☒ **D** $K_c = \tfrac{1}{2}K'_c$

(Total for Question 5 = 1 mark)

---

6 4.0 mol of methanoic acid are reacted with 6.0 mol of ethanol.

$$HCOOH(l) + C_2H_5OH(l) \rightleftharpoons HCOOC_2H_5(l) + H_2O(l)$$

The equilibrium mixture contains 3.0 mol of $HCOOC_2H_5$.

The equilibrium constant, K_c, for the reaction is

☒ **A** 0.33

☒ **B** 1.0

☒ **C** 3.0

☒ **D** 4.0

(Total for Question 6 = 1 mark)

7 A solution of hydrochloric acid has pH 3.0. When it is made 10 times more dilute, the pH is

☒ **A** 0.3

☒ **B** 2.0

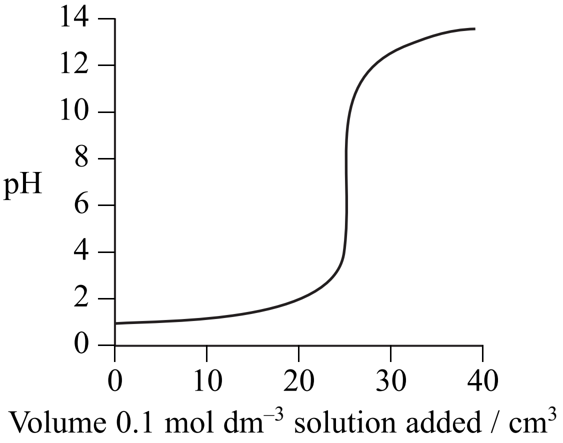
☒ **C** 4.0

☒ **D** 13.0

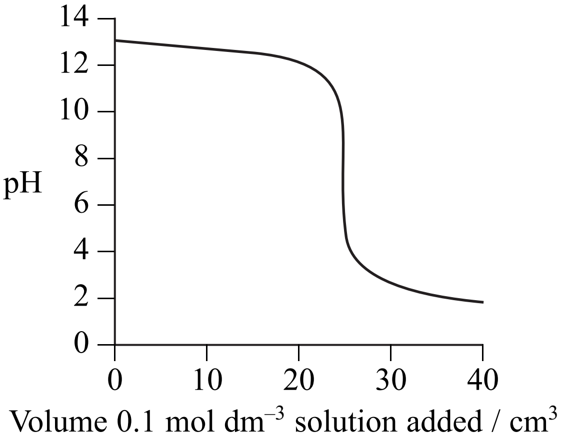
(Total for Question 7 = 1 mark)

8 The titration curves below were obtained using different acids and bases, each with concentration 0.1 mol dm^{-3}.

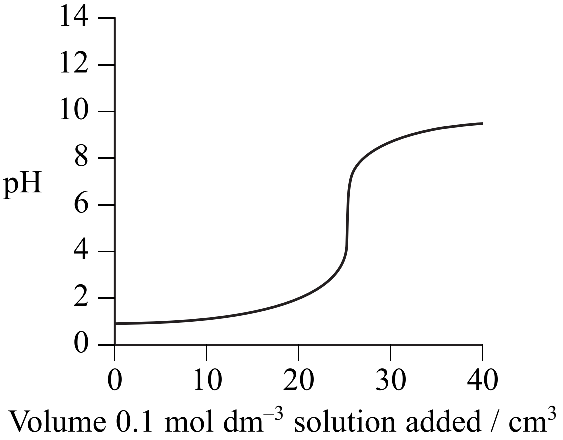
A



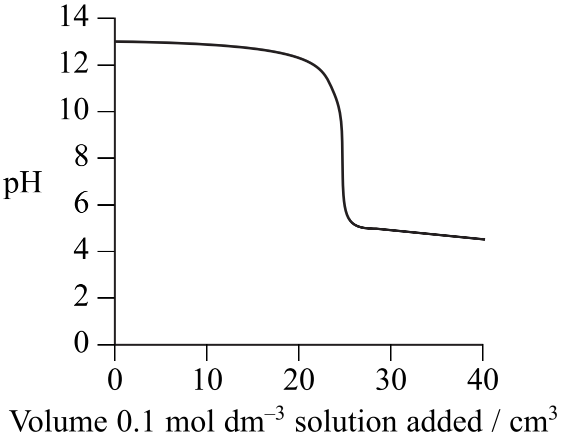
B



C



D



(a) Which curve is produced by adding ammonia to 25 cm^3 of hydrochloric acid?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which curve is produced by adding ethanoic acid to 25 cm^3 of sodium hydroxide?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) An indicator with pK_{In} 8.5 is suitable for the following titrations.

(1)

☒ **A** Titrations **A** and **B** only.

☒ **B** Titrations **A**, **B** and **D** only.

☒ **C** Titration **C** only.

☒ **D** Titrations **A**, **B**, **C** and **D**.

(Total for Question 8 = 3 marks)

---

9 Ethanoic acid is **not** a product in the reaction of

☒ **A** ethanal with lithium tetrahydridoaluminate.

☒ **B** ethanoyl chloride with water.

☒ **C** ethyl ethanoate with dilute sulfuric acid.

☒ **D** ethanol refluxed with potassium dichromate(VI) and sulfuric acid.

(Total for Question 9 = 1 mark)

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

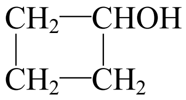
10 This question is about four compounds with molecular formula C_4H_8O.

A $CH_3COCH_2CH_3$

B $CH_3CH_2CH_2CHO$

C $CH_3CH{=}CHCH_2OH$

D



(a) The compounds which react when heated with a mixture of potassium dichromate(VI) and sulfuric acid are

(1)

☒ **A** compounds **A**, **B** and **C**.

☒ **B** compounds **A**, **B** and **D**.

☒ **C** compounds **A**, **C** and **D**.

☒ **D** compounds **B**, **C** and **D**.

(b) The compound which produces a yellow precipitate when heated with a mixture of iodine and sodium hydroxide is

(1)

☒ **A** compound **A**.

☒ **B** compound **B**.

☒ **C** compound **C**.

☒ **D** compound **D**.

(c) There would **not** be a significant peak at mass/charge ratio of 15 in the mass spectrum of

(1)

☒ **A** compound **A**.

☒ **B** compound **B**.

☒ **C** compound **C**.

☒ **D** compound **D**.

(Total for Question 10 = 3 marks)

11 The following tests can be carried out on organic compounds.

A Warm with 2,4-dinitrophenylhydrazine.

B Warm with Fehling's or Benedict's solution.

C Add solid sodium carbonate.

D Add phosphorus(V) chloride, PCl_5.

(a) Which test would give a positive result with propanoic acid but not with propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test would give a positive result with propanoic acid **and** with propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test would give a positive result with propanal but not with propanone?

(1)

☒ **A**

☒ **B**

☒ **C**

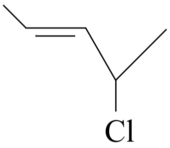
☒ **D**

(Total for Question 11 = 3 marks)

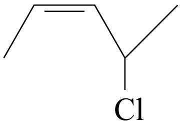
Use this space for any rough working. Anything you write in this space will gain no credit.

12 Which of the following compounds is a *Z* isomer **and** contains a chiral carbon atom?

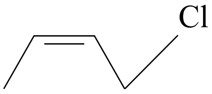
☒ **A**



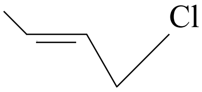
☒ **B**



☒ **C**



☒ **D**



(Total for Question 12 = 1 mark)

13 Which of the following statements about ethanoyl chloride is **not** correct?

☒ **A** It reacts with ammonia to make an amine.

☒ **B** It reacts with an amine to make an amide.

☒ **C** It reacts with an alcohol to make an ester.

☒ **D** It reacts with water to make an organic acid.

(Total for Question 13 = 1 mark)

14 In gas chromatography, mixtures are passed through a long tube containing a liquid as the stationary phase. The mixtures are separated into their components because the components differ in

☒ **A** relative molecular mass.

☒ **B** melting temperature.

☒ **C** volatility.

☒ **D** force of attraction to the liquid.

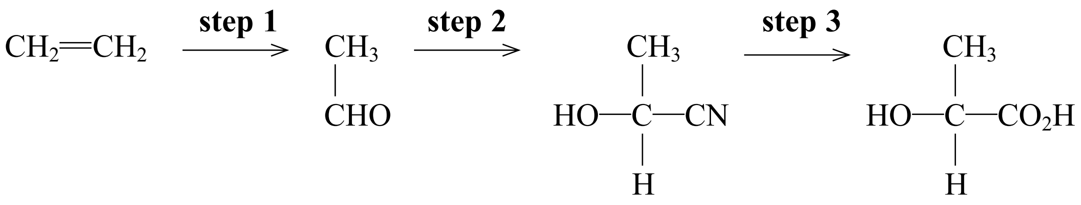
(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 A sequence of reactions for the production of lactic acid is shown below.



lactic acid

(a) (i) Name the type and mechanism of the reaction in **step 2**.

(2)

(ii) Which **two** substances need to be added to ethanal to carry out the reaction in **step 2**?

(2)

(iii) Give the mechanism for the reaction in **step 2**, using curly arrows to show movements of electron pairs.

(3)

*(iv) The product of **step 2** is not optically active even though it has a chiral carbon atom in its formula. Explain, by reference to the mechanism, the reason for the lack of optical activity.

(2)

....

....

....

....

....

(b) What reactant, or combination of reactants, is needed to carry out **step 3**?

(1)

....

(c) (i) What is the systematic name of lactic acid?

(1)

....

(ii) Lactic acid molecules can combine to form a biodegradable polymer, poly(lactic acid) or PLA. Draw a section of the polymer with **two** units of the polymer chain and showing all bonds.

(1)

(iii) Suggest why PLA is biodegradable.

(1)

....

....

(iv) Lactic acid can be prepared from ethene as shown in the scheme. Lactic acid also forms when milk turns sour.

Suggest **one** reason why it would be advantageous to make lactic acid from milk rather than from ethene.

(1)

....

....

....

....

(Total for Question 15 = 14 marks)

16 Nitrogen(IV) oxide, NO_2, is a brown gas which is a pollutant in air. It is produced in the reaction below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) The table below shows the results of a series of experiments to measure the rate of this reaction at 298 K.

Experiment number	Initial concentration / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	[O_2(g)]	[NO(g)]	
1	0.0050	0.0125	5.10×10^{-4}
2	0.0100	0.0125	10.2×10^{-4}
3	0.0100	0.0250	40.8×10^{-4}

(i) State, with reasons, the order of reaction with respect to oxygen and the order of reaction with respect to nitrogen(II) oxide, NO.

(2)

....

....

....

....

(ii) Write the rate equation for the reaction.

(1)

(iii) Calculate the value of the rate constant. Include units in your answer.

(2)

(b) Nitrogen(IV) oxide in air reacts with carbon monoxide in car exhausts. The following two-step reaction mechanism has been suggested.

Step 1: $2NO_2(g) \rightarrow NO(g) + NO_3(g)$ Slow

Step 2: $NO_3(g) + 2CO(g) \rightarrow NO(g) + 2CO_2(g)$ Fast

(i) Write the equation for the overall reaction which takes place.

(1)

(ii) The overall reaction is second order. Suggest a rate equation for this reaction, justifying your answer.

(2)

....

....

....

....

....

(Total for Question 16 = 8 marks)

17 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{\text{system}}$ for this reaction at 298 K. Give your answer in J mol^{-1} K^{-1} and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is 2 × 95.8 J mol^{-1} K^{-1}.]

(2)

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

(2)

....

....

....

....

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

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

(2)

(ii) Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, $\Delta S_{\text{total}} = -78.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Include a sign and units in your answer.

(1)

(iii) What does the value of ΔS_{total}, which is $-78.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?

(1)

....

....

....

(c) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 150 atm. The partial pressures of nitrogen and ammonia in the mixture are 21 atm and 36 atm respectively.

(i) Write an expression for the equilibrium constant, K_p, for the formation of ammonia, in terms of partial pressures for this reaction, and calculate its value at 700 K. Include units in your answer.

(4)

(ii) In the manufacture of ammonia, pressures of between 100 and 250 atm are used. State and explain **one** advantage, in terms of the yield of ammonia, of using a pressure above 100 atm.

(1)

*(iii) In the manufacture of ammonia, a temperature of about 700 K is used.

For this exothermic reaction how does $\Delta S_{\text{surroundings}}$ change as temperature increases?

Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.

Hence explain the disadvantage of using a temperature higher than 700 K.

(4)

(iv) Suggest **one** advantage of using a temperature higher than 700 K.

(1)

(Total for Question 17 = 18 marks)

18 Methanoic acid, ethanoic acid and iodic(I) acid, HIO, are all weak acids.

(a) The values of the acid dissociation constant, K_a, for methanoic and ethanoic acid at 298 K are given below. Iodic(I) acid has a pK_a of 10.64. Complete the table by calculating the value of K_a for iodic(I) acid.

(1)

Acid	K_a / mol dm^{-3}
methanoic acid	1.6×10^{-4}
ethanoic acid	1.7×10^{-5}
iodic(I) acid	

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm^{-3} at 298 K.

(3)

(iii) State **one** of the assumptions you have made when calculating the pH in (ii).

(1)

....

....

....

....

....

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids.

$$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$$

(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium.

(1)

....

....

(ii) Write an equation showing the products of the equilibrium which is set up when iodic(I) acid is mixed with ethanoic acid.

(1)

$HIO + CH_3COOH \rightleftharpoons$ .... + ...

(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.

(2)

(Total for Question 18 = 10 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

19 The chemical **X** is an ester with formula $CH_3COOC(CH_3)_3$ which occurs in raspberries and pears. It can be prepared in the laboratory by refluxing ethanoic acid with an alcohol in the presence of a catalyst.

(a) **Name** the alcohol and catalyst which would be used to make **X**.

(2)

Alcohol ....

Catalyst ....

(b) After refluxing, the resulting mixture is distilled to give an impure product containing **X**. The impure product is washed several times with sodium carbonate solution and then dried.

(i) Name the piece of equipment in which the impure product would be washed.

(1)

....

(ii) What is the purpose of washing the impure product with sodium carbonate solution?

(1)

....

(iii) Name a suitable drying agent.

(1)

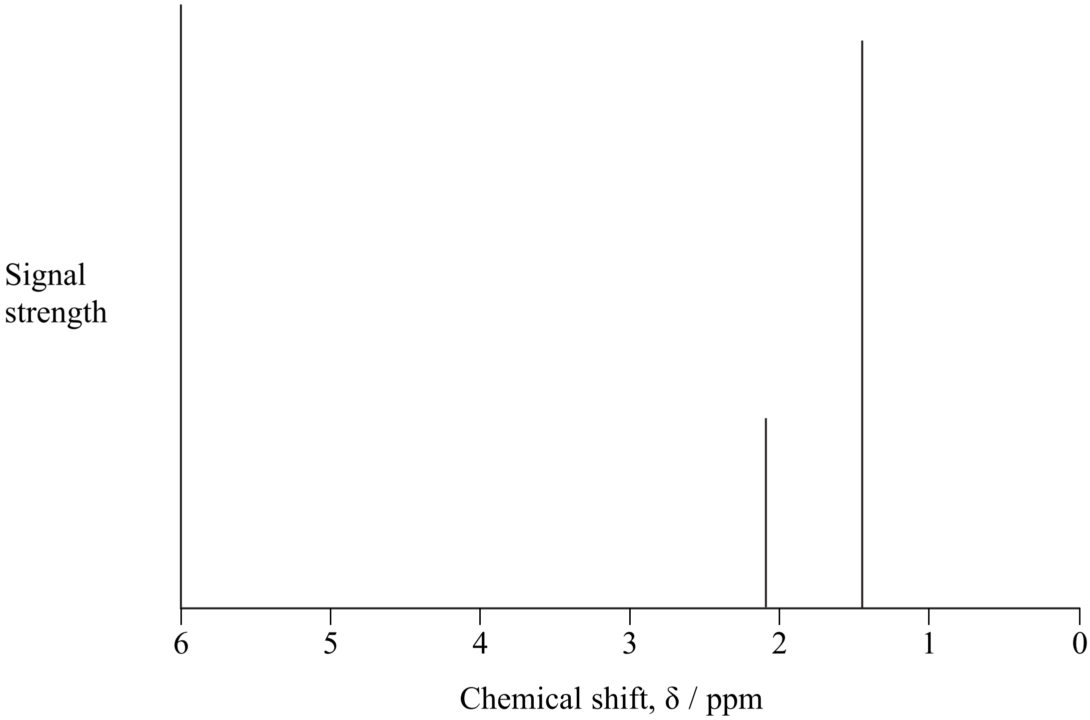
....

(iv) The impure product is then redistilled and **X**, which has a boiling temperature of 97 °C, is collected. Draw a labelled diagram of the apparatus you would use.

(3)

*(c) **Spectrum 1** is the high resolution proton nmr spectrum of **X**, $CH_3COOC(CH_3)_3$.

Spectrum 1



Explain how **spectrum 1** is consistent with the structure of **X**. You should refer to the number and height of the peaks, the atoms which produce them and their splitting patterns.

(4)

(d) **X** has an isomer, **Y**. **Y** is an ester which can be made from ethanoic acid and 2-methylpropan-1-ol.

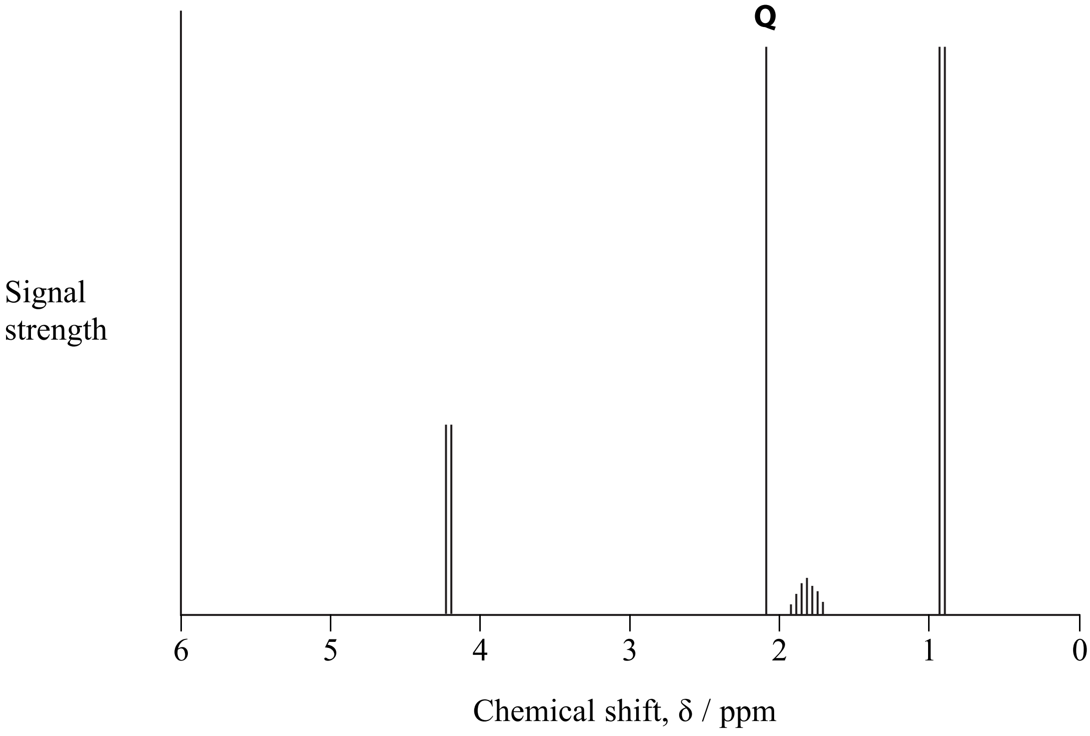
(i) Draw the structural formula of **Y**.

(1)

(ii) **Spectrum 2** is the high resolution proton nmr spectrum of **Y**. On your structural formula in (i), circle the atom or atoms causing the peak labelled **Q** on **spectrum 2**.

(1)

Spectrum 2



(e) **X** has several other structural isomers which have a broad peak at approximately 2960 cm^{-1} in their infrared spectra. Some of the isomers have a chiral carbon atom and all have a higher boiling temperature than **X**. None of them reacts with 2,4-dinitrophenylhydrazine.

*(i) Draw the structure of **one** of the isomers which is optically active, explaining how you use **all** the information in the question.

(5)

(ii) Could the compound you have drawn in (e)(i) be distinguished by infrared spectroscopy from its other isomers with the properties listed above? Explain your answer.

(1)

(Total for Question 19 = 20 marks)

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

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)

June 2011

GCE Chemistry (6CH04) Paper 01
General Principles of Chemistry

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June 2011
Publications Code UA027566

General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. Questions labelled with an **asterix (*)** are ones where the quality of your written communication will be assessed.

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the <u>meaning</u> of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Mark
1	C	**1**

Question Number	Correct Answer	Mark
2	D	**1**

Question Number	Correct Answer	Mark
3	A	**1**

Question Number	Correct Answer	Mark
4	A	**1**

Question Number	Correct Answer	Mark
5	B	**1**

Question Number	Correct Answer	Mark
6	C	**1**

Question Number	Correct Answer	Mark
7	C	**1**

Question Number	Correct Answer	Mark
8 (a)	C	**1**

Question Number	Correct Answer	Mark
8 (b)	D	**1**

Question Number	Correct Answer	Mark
8 (c)	B	**1**

Question Number	Correct Answer	Mark
9	A	**1**

Question Number	Correct Answer	Mark
10 (a)	D	**1**

Question Number	Correct Answer	Mark
10 (b)	A	**1**

Question Number	Correct Answer	Mark
10 (c)	D	**1**

Question Number	Correct Answer	Mark
11 (a)	C	**1**

Question Number	Correct Answer	Mark
11 (b)	D	**1**

Question Number	Correct Answer	Mark
11 (c)	B	**1**

Question Number	Correct Answer	Mark
12	B	**1**

Question Number	Correct Answer	Mark
13	A	**1**

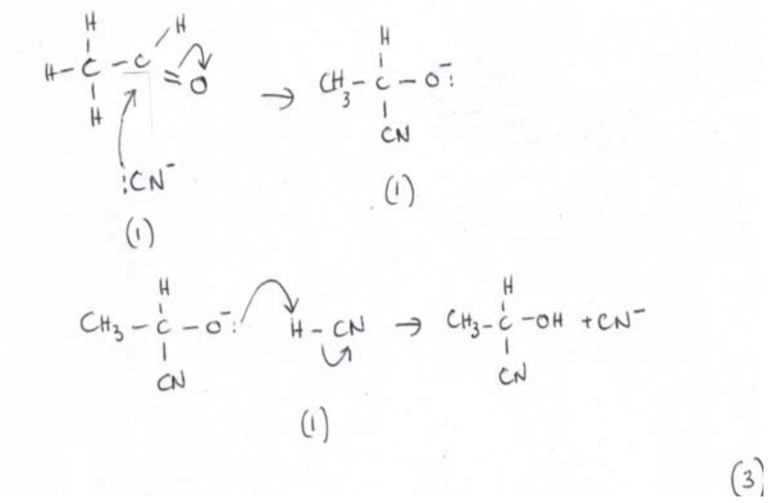
Question Number	Correct Answer	Mark
14	D	**1**

TOTAL FOR SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
15 (a)(i)	Addition **(1)** Nucleophilic **(1)** Either order	SN1 SN2	**2**

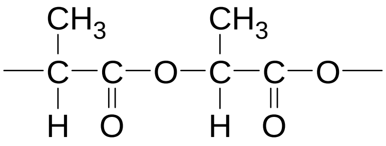
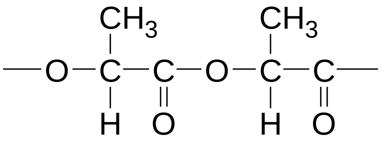
Question Number	Acceptable Answers	Reject	Mark
15 (a)(ii)	Hydrogen cyanide / HCN **(1)**		**2**
	Potassium cyanide / KCN/ sodium cyanide/ NaCN **(1)**	Just CN^-	
	OR		
	Potassium cyanide / KCN **(1)** With hydrochloric acid / sulfuric acid (to generate HCN) **(1)**	Just CN^- Just acid/ H^+ any weak acid	
	Ignore concentration of acids Mark for HCl etc is consequential on KCN		
	OR		
	Hydrogen cyanide / HCN **(1)** With sodium hydroxide / other base (to make cyanide ions) **(1)** Mark for NaOH etc is consequential on HCN	Just OH^-	

Question Number	Acceptable Answers	Reject	Mark
15 (a)(iii)	 Both arrows in first step of mechanism above correctly drawn **(1)** Correct intermediate with charge **(1)** Both arrows in second step with correct organic product (CN$^-$ is not required) **(1)** Use of HCN for first step max 2 marks Allow omission of lone pair on CN$^-$ and O$^-$ Allow curly arrow from negative charge or elsewhere on cyanide ion Allow arrow from O$^-$ in 2nd step to H$^+$ (no other product or only one product) or H_2O (with OH$^-$ formed)	C=O breaking before attack by CN$^-$ Arrows from atoms when they should be from bonds and vice versa	**3**

Question Number	Acceptable Answers	Reject	Mark
***15 (a)(iv)**	Attack (by nucleophile on the C) is from both sides (equally)/ above and below (at the planar reaction site in the aldehyde group) **(1)** So a mixture of two enantiomers/(optical)isomers **in equal proportions** forms OR racemic mixture forms **(1)** **First and second marks are independent**	Attack on **intermediate in reaction mechanism** is from both sides Attack from both ends/two angles Just "both enantiomers form"	**2**

Question Number	Acceptable Answers	Reject	Mark
15 (b)	Any named (aqueous) strong acid or its formula. Allow (aqueous) sodium hydroxide followed by named acid or formula Ignore references to concentration	Water H^+ Potassium dichromate + sulfuric acid Carboxylic acids	**1**

Question Number	Acceptable Answers	Reject	Mark
15 (c)(i)	2-hydroxypropanoic acid	2-hydroxylpropanoic acid 2-hydroxopropanoic acid 2-hydroxypropan-1-oic acid	**1**

Question Number	Acceptable Answers	Reject	Mark
15 (c)(ii)	 $-\overset{\overset{CH_3}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\underset{\underset{O}{\Vert}}{C}-O-\overset{\overset{CH_3}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\underset{\underset{O}{\Vert}}{C}-O-$ OR  $-O-\overset{\overset{CH_3}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\underset{\underset{O}{\Vert}}{C}-O-\overset{\overset{CH_3}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\underset{\underset{O}{\Vert}}{C}-$ All bonds in ester link must be shown More than 2 units may be shown but structure shown should be a repeat unit Ignore brackets/n	A dimer Missing H atoms Missing bonds at ends	**1**

Question Number	Acceptable Answers	Reject	Mark
15 (c)(iii)	**Ester** (link/bond) in PLA can be hydrolysed/broken down (by enzymes) **OR Ester** (link/bond) in PLA can be broken down	Just "it can be hydrolysed"	**1**

Question Number	Acceptable Answers	Reject	Mark
15 (c)(iv)	Ethene is (from crude oil so) non-renewable/ milk is from a renewable source/ energy required to make ethene is **high**/ high temperatures needed to make ethene/ energy requirements for process from sour milk **less**/ process from milk doesn't use toxic chemicals / process from milk doesn't use cyanide	Milk is more readily available Greater atom economy No other chemicals needed in process from milk	**1**
	Allow process from ethene requires many steps **so** expensive/**so** loss of material occurs at each step /**so** more reagents needed	Just "process from ethene requires many steps"	
	Ignore references to cost, unless answer gives a reason for lower cost.	Just "cheaper"	

Question Number	Acceptable Answers	Reject	Mark
16 (a)(i)	**O_2** : first order as increasing $[O_2]$ x 2 increases rate x 2 / as rate is (directly) proportional to oxygen concentration **(1)** (Experiments 1 and 2 or [NO] constant) **NO:** second order as increasing [NO] x 2 increases rate x 4/ by 2^2 **(1)** (Experiments 2 and 3 or $[O_2]$ constant) Two correct orders with no explanation **(1)** only	Two correct orders based on stoichiometry	**2**

Question Number	Acceptable Answers	Reject	Mark
16 (a)(ii)	Rate = k $[O_2][NO]^2$ Rate equation must be consistent with answer in (a)(i)	Just k $[O_2][NO]^2$ i.e. no rate/R Non square brackets	**1**

Question Number	Acceptable Answers	Reject	Mark
16 (a)(iii)	Rate = $k[O_2][NO]^2$ TE from (i) $k=((5.10 \times 10^{-4})/(0.005)(0.0125)^2) = 652.8$ / 653/650 OR $k=((10.2 \times 10^{-4})/(0.0100)(0.0125)^2) = 652.8$ / 653/650 OR $k=((40.8 \times 10^{-4})/(0.0100)(0.025)^2) = 652.8$ / 653/650 **(1)** TE for value of k from rate equation given $dm^6\ mol^{-2}\ s^{-1}$ (allow any order) **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
16 (b)(i)	$NO_2 + CO \rightarrow NO + CO_2$ Allow multiples	Equation not cancelled down eg NO_3 on both sides.	**1**

Question Number	Acceptable Answers	Reject	Mark
16 (b)(ii)	Rate = $k[NO_2]^2$ OR Rate = $k[NO_2]^2[CO]^0$ OR Rate = $k[NO_2]^2[CO]^0 [NO_3]^0$ **(1)** Only molecules/reactant in slow step are (2)NO_2 OR CO appears after the rate determining/slow step (and $2NO_2$ molecules in slow step) OR CO is not involved in rate determining / slow step OR Only the molecules in the slow step are in the rate equation OR Step 1 is slowest so determines rate equation **(1)** **Second mark:** **No TE on rate equation containing incorrect species. Only allow TE if k missing in correct rate equation**	Equations involving CO to power other than zero	**2**

Question Number	Acceptable Answers	Reject	Mark
17 (a)(i)	$\Delta S_{\text{system},}$ = ((2 x 192.3) –(2 x 95.8) – (2x3x65.3)) **(1)** = **-198.8 / -199** (J mol^{-1} K^{-1}) Allow – 200 (2 SF) If units are not those in which data is given, must be correct. **(1)** *Note check working* Correct answer without working **(2)** Correct choice of multiples and data but wrong answer scores first mark **(1)** Correct value with wrong sign based on entropy of reactants – entropy of products (giving +199) **(1)** TE for second mark if multiples for hydrogen, nitrogen and ammonia are missed/ incorrect, but correct data used. or multiples correct and one error in data.	198	**2**

Question Number	Acceptable Answers	Reject	Mark
17 (a)(ii)	**If answer to (a)(i) is negative:** Disorder decreases / order increases (as reaction goes forward) **(1)** Reference to order or disorder required for the mark. As number of (gas)molecules/moles/particles decreases **(1)** OR 4 moles of gas produces 2 moles Ignore comments on number of different types of molecule in equilibrium mixture **If answer to (a)(i) is positive:** Must say this is unexpected with correct reasons to score 2 marks No marks if the positive answer is expected	Just "entropy decreases"	**2**

Question Number	Acceptable Answers	Reject	Mark
17 (b)(i)	ΔS_{surr} = -(-110.2 x 1000)/ 700 **(1)** (+157.4285) **=** (+) **157.4 / 157** (J mol^{-1} K^{-1}) OR (+) 0.1574 / 0.157 **kJ mol^{-1} K^{-1} (1)** Ignore sf except 1 Correct answer without working **(2)** Correct value with negative sign **(1)** Use of ΔS_{surr} = $-\Delta H/T$ but wrong answer **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
17 (b)(ii)	($\Delta S_{system} = \Delta S_{total} - \Delta S_{surr}$) =(-78.7-157.4)) = **-236.1/ -236** (J mol^{-1} K^{-1}) OR -0.2361 / -0.236 (kJ mol^{-1} K^{-1}) Allow -235.7 if 157 used and -238.7 if 160 used Ignore units unless value in kJ given as J or vice versa TE from (b)(i)	values in kJ added to values in J	**1**

Question Number	Acceptable Answers	Reject	Mark
17 (b)(iii)	Reactants predominate / more nitrogen and hydrogen (than ammonia)	Just “Equilibrium lies to the left” Just “no ammonia is present”. The gases are present in ratio 1:3:2	**1**

Question Number	Acceptable Answers	Reject	Mark
17 (c)(i)	K_p = $(pNH_3)^2$/ $(pN_2)(pH_2)^3$ **(1)** Can be written in other formats eg p^2NH_3 etc pH_2 = (150 –21 –36) = **93** (atm) **(1)** $K_\mathbf{p}$ =$((36)^2$/ $(21)(93)^3)$ = (7.6724994 x 10^{-5}) =**7.67 x 10^{-5} (1)** Ignore sf except 1 TE on incorrect pH_2 atm^{-2} **(1)** TE for units on incorrect $\boldsymbol{K}_\mathbf{p}$ expression Correct answer including units without quoting **K_p expression scores 3**	Square brackets in first mark No TE for value on incorrect $\boldsymbol{K}_\mathbf{p}$ Expression Units other than atm	**4**

Question Number	Acceptable Answers	Reject	Mark
17 (c)(ii)	(Yield of ammonia is increased) because there are fewer moles / molecules (of gas) on the right OR System tries to reduce the pressure by going to the side with fewer moles/ molecules (of gas) Ignore comments about value of $\boldsymbol{K}_\mathbf{p}$ changing Ignore comments about more collisions occurring/more molecules having energy greater than or equal to activation energy	Just 'equilibrium moves right'	**1**

Question Number	Acceptable Answers	Reject	Mark
***17 (c)(iii)**	**First mark** At higher temperature ΔS_{surr} is less positive/ decrease/more negative **(1)** **Second mark** making ΔS_{total} more negative / less positive/decreases No TE for 2nd mark if ΔS_{surr} is said to increase. **(1)** **Third mark** (so) K_p decreases **(1)** **Third mark depends on second mark being correct/neutral answer** **Fourth mark** so equilibrium position further left /in endothermic direction/ in reverse direction OR lower yield of ammonia / reaction is less feasible **(1)** **Fourth mark is a stand alone mark**		**4**

Question Number	Acceptable Answers	Reject	Mark
17 (c)(iv)	Rate (of reaching equilibrium)is higher / faster Ignore comments about increasing numbers of successful collisions at higher temperature		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (a)	K_a = ($10^{-10.64}$) = **2.3×10^{-11}** / 2.2909×10^{-11} (mol dm^{-3}) Ignore sf except 1		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b)(i)	$K_a = \dfrac{[HCOO^-][H^+]}{[HCOOH]}$ OR written as HCO_2^- and HCO_2H OR with H_3O^+ instead of H^+ Allow $K_a = \dfrac{[A^-][H^+]}{[HA]}$ if formula of HA and A^- given as HCOOH and $HCOO^-$	$K_a = \dfrac{[H^+]^2}{[HCOOH]}$ without also giving full expression	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (b)(ii)	$1.6 \times 10^{-4} = \dfrac{[H^+]^2}{0.50}$ **(1)** $[H^+] = \sqrt{1.6 \times 10^{-4} x 0.5}$ **(1)** ($= \sqrt{8x10^{-5}} = 8.94 \times 10^{-3}$) pH = (2.048455) **= 2.05 / 2.0 (1)** Correct answer with no working **(3)** TE for third mark if $[H^+]$ calculated incorrectly No TE from incorrect K_a expression Ignore sf except 1	pH =2 pH =2.1	**3**

Question Number	Acceptable Answers	Reject	Mark
18 (b)(iii)	All H^+ comes from acid / none from water / $[H^+] = [HCOO^-]$ OR $[H^+] = [A^-]$ OR Dissociation of acid is negligible / very small OR $[HA]_{initial} = [HA]_{equilibrium}$	K_a is measured at 298K Just “dissociation of acid is partial”	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (c)(i)	HCOOH $CH_3COOH_2^+$ both correct **(1)**		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (c)(ii)	(HIO + CH_3COOH ⇌) H_2IO^+ + CH_3 COO^- / (HIO + CH_3COOH ⇌) $HIOH^+$ + CH_3 COO^- Ignore position of positive charges		**1**

Question Number	Acceptable Answers	Reject	Mark
18 (d)	(pH = 4.9) so $[H^+]$ = (1.2589254 x 10^{-5}) =**1.259 x 10^{-5} (1)** ($\frac{K_a}{[H^+]} = \frac{[HCOO^-]}{[HCOOH]}$ = $\frac{1.6 \times 10^{-4}}{1.259 \times 10^{-5}}$) **= 12.7 (:1) / 13(:1) ($HCOO^-$ per HCOOH or base:acid)** (12.709252 from unrounded $[H^+]$ 12.708499 from $[H^+]$ rounded to 1.259 x10^{-5} 12.3 from $[H^+]$ rounded to 1.3 x10^{-5}) TE from error in **$[H^+]$** **Allow 800:63** **(1)** **Correct answer scores 2** Accept (0.0786828) = **0.079 HCOOH per $HCOO^-$ for acid:base ratio** (0.0786874) = 0.079 from rounded pH **OR** $pK_a = -\log K_a = 3.79$ $3.79 = 4.9 - \log \frac{[base]}{[acid]}$ (1) $\log \frac{[base]}{[acid]} = 1.11$ $\frac{[base]}{[acid]}$ = (12.882496) = **12.9 (:1)** **(1)** **Correct answer scores 2** Accept **0.0776/ 0.078 HCOOH per $HCOO^-$ for acid:base ratio** (0.0776247) TE from error in pK_a Ignore sf except 1		**2**

TOTAL FOR SECTION B = 50 MARKS

Section C

Question Number	Acceptable Answers	Reject	Mark
19 (a)	Alcohol; (2)-methylpropan-2-ol **(1)** Catalyst: sulfuric acid OR any named strong acid Ignore concentration of acid **(1)** Accept formula for acid	Formula of alcohol Just acid/H^+ for catalyst	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(i)	Tap funnel / separating funnel	Buchner funnel Filter funnel	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(ii)	To neutralize / remove/ react with (excess) acid Allow To neutralize / remove / react with (excess) H^+ To remove acidic impurities To remove ethanoic acid To remove the acid (used as a) catalyst Ignore additional comments on quenching or reaction stopping	To purify it To remove excess acid **and** alcohol Just "to quench acid catalyst/stop reaction"	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(iii)	Add (anhydrous) calcium chloride/ sodium sulfate/ magnesium sulfate/ Allow silica gel Allow formulae of drying agents	Conc. sulfuric acid Anhydrous copper sulphate Just "silica"	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (b)(iv)	Round bottomed or pear-shaped flask + still head with stopper or thermometer + heat source **(1)** This mark cannot be given if apparatus is completely sealed /large gaps between components Downwards sloping condenser (with correct water flow) **+** collection vessel **(1)** Thermometer in correct position with bulb opposite condenser opening **(1)** Ignore fractionating column if included between flask and condenser	Conical flask Flat bottomed flask	**3**

Question Number	Acceptable Answers	Reject	Mark
***19 (c)**	**First mark** (Two signals so) two hydrogen environments **(1)** This mark may be gained by a description of the only two environments, but reference to hydrogen must be made. **Second mark** (Numbers of hydrogen in each environment are/ are predicted to be) in ratio 3:9 or 1:3 OR Peak due to $(CH_3)_3$ is 3x higher than peak due to CH_3 **(1)** **Third mark** Environments are CH_3COO and $(CH_3)_3$ (H may have been specified in first marking point) These may be shown on a diagram of the formula of the molecule OR H-C-C=O (peak at 2.1) and H-C-C (peak at 1.3) **(1)** **Fourth mark** Singlets/ no splitting as no H on adjacent C OR Singlets as the hydrogen environments are not adjacent to other H environments Allow "only one peak" for no splitting **(1)**	Just "the peaks are due to $(CH_3)_3$ and CH_3	**4**

Question Number	Acceptable Answers	Reject	Mark
19 (d)(i)	$CH_3COOCH_2CH(CH_3)_2$ Or correctly displayed Allow $CH_3COOCH_2CH(CH_3)$ CH_3		**1**

Question Number	Acceptable Answers	Reject	Mark
19 (d)(ii)	The H on the CH_3COO Accept circle round all of first methyl group Accept a hydrogen in this environment if rest of molecule is incorrect	Circle round C of first methyl group	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (e)(i)	Any acid with 6C (5C + COOH) which is chiral, so will have a branched chain $C_3 H_7 CH(CH_3) COOH$ OR $C_2H_5 CH(CH_3) CH_2 COOH$ OR $(CH_3)_2 CHCH(CH_3) COOH$ **(1)** Infrared indicates (O-H present in a) carboxylic acid **(1)** High boiling temperature due to hydrogen bonding (between atoms in OH groups so not an ester.) Hydrogen bonds must be possible for structure shown Allow acids can form dimers. Allow TE from formula of straight chain molecule with explanation that London forces are higher in a linear molecule **(1)** (Optically active so) contains chiral C/ C bonded to four different groups The formula suggested must contain a chiral carbon to score this mark This may be shown by a chiral carbon being labelled in the formula **(1)** Carbonyl compound/ Carbonyl group/ Aldehyde **and** ketone absent (as no reaction with 2,4-dinitrophenylhydrazine)/ Allow carboxylic acids do not react with 2,4-dinitrophenylhydrazine/ **(1)**	Infrared indicates O-H Infrared indicates alkyl group Just "does not contain C=O (group)"	**5**

Question Number	Acceptable Answers	Reject	Mark
19 (e)(ii)	No because the isomers (which are carboxylic acids) contain same bonds / groups (C=O, C-O, C-H etc) **(1)** OR Yes because could be distinguished by infrared fingerprint **(1)**	Yes because spectrum is unique	**1**

TOTAL FOR SECTION C = 20 MARKS

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Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Thursday 26 January 2012 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

7/7/5/3/3/3/

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 The reaction between carbon monoxide and hydrogen reaches a dynamic equilibrium.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

(a) Which of these statements about a dynamic equilibrium is **not** true?

(1)

☒ **A** The forward rate of reaction is equal to the backward rate of reaction.

☒ **B** The concentrations of the products and reactants do not change.

☒ **C** The concentrations of the products and reactants are equal.

☒ **D** The equilibrium can be approached from either direction.

(b) The K_c expression for the above reaction is

(1)

☒ **A** $K_c = \frac{[CH_3OH]}{[CO] \times [H_2]^2}$

☒ **B** $K_c = \frac{[CO] \times 2[H_2]}{[CH_3OH]}$

☒ **C** $K_c = \frac{[CO] \times [H_2]^2}{[CH_3OH]}$

☒ **D** $K_c = \frac{[CH_3OH]}{[CO] \times 2[H_2]}$

(Total for Question 1 = 2 marks)

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

2 Hydrogen and iodine, both with an initial concentration of 0.010 mol dm^{-3}, were allowed to react. At equilibrium, the concentration of hydrogen iodide was 0.0030 mol dm^{-3}.

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

K_c is calculated using the values

		$H_2(g)$ / mol dm^{-3}	$I_2(g)$ / mol dm^{-3}	$HI(g)$ / mol dm^{-3}
☒	**A**	0.0070	0.0070	0.0030
☒	**B**	0.0040	0.0040	0.0030
☒	**C**	0.0040	0.0040	0.0060
☒	**D**	0.0085	0.0085	0.0030

(Total for Question 2 = 1 mark)

3 The reaction below reached a dynamic equilibrium from an initial mixture of all four substances P, Q, R and S in aqueous solution.

$$P + Q \rightleftharpoons R + S$$

The following data were obtained.

Substance	Concentration at equilibrium / mol dm^{-3}
P	0.050
Q	0.040
R	0.020
S	0.010

K_c for the equilibrium is

☒ **A** 0.10

☒ **B** 0.33

☒ **C** 3.00

☒ **D** 10.0

(Total for Question 3 = 1 mark)

4 The Haber process is used to make ammonia from nitrogen and hydrogen at 450 °C.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.0 \text{ kJ mol}^{-1}$$

(a) If the partial pressures of these gases were measured in atm, the units of the equilibrium constant K_p will be

(1)

☒ **A** atm

☒ **B** atm^2

☒ **C** atm^{-2}

☒ **D** atm^{-1}

(b) When the temperature of the system is increased

(1)

☒ **A** K_p decreases.

☒ **B** K_p increases.

☒ **C** K_p stays the same.

☒ **D** K_p first decreases and then increases.

(Total for Question 4 = 2 marks)

5 In high performance liquid chromatography, HPLC, which of these factors does **not** affect the time taken for a component to pass through the column?

☒ **A** Type of detector

☒ **B** Material of stationary phase

☒ **C** Particle size of stationary phase

☒ **D** Temperature of column

(Total for Question 5 = 1 mark)

6 When equimolar amounts of the solutions below are mixed, which forms a buffer solution with a pH less than 7?

☒ **A** Hydrochloric acid and sodium chloride

☒ **B** Ethanoic acid and sodium ethanoate

☒ **C** Sodium hydroxide and sodium chloride

☒ **D** Ammonia and ammonium chloride

(Total for Question 6 = 1 mark)

7 The pH of a 1.5 mol dm^{-3} solution of hydrochloric acid, HCl(aq), is

☒ **A** −1.50

☒ **B** −0.18

☒ **C** 0.18

☒ **D** 1.50

(Total for Question 7 = 1 mark)

---

8 Which of these solid substances is likely to have the greatest standard entropy? Use of the data booklet is not required.

☒ **A** SnO

☒ **B** SnO_2

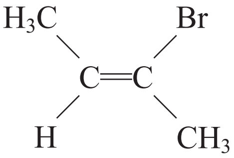
☒ **C** $SnBr_2$

☒ **D** $SnBr_4$

(Total for Question 8 = 1 mark)

---

9 What is the correct name for the molecule shown below?



☒ **A** *Z*-2-bromobut-2-ene

☒ **B** *E*-2-bromobut-2-ene

☒ **C** *E*-3-bromobut-2-ene

☒ **D** *Z*-3-bromobut-2-ene

(Total for Question 9 = 1 mark)

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

10 Ketones react with hydrogen cyanide, HCN, in the presence of cyanide ions, CN^-.

(a) Which of these ketones does **not** form a racemic mixture in this reaction?

(1)

☒ **A** $CH_3CH_2CH_2COCH_3$

☒ **B** $CH_3CH_2COCH_2CH_3$

☒ **C** $CH_3CH_2CH_2CH_2COCH_3$

☒ **D** $CH_3CH_2CH_2COCH_2CH_3$

(b) This type of reaction is classified as

(1)

☒ **A** nucleophilic substitution.

☒ **B** nucleophilic addition.

☒ **C** electrophilic addition.

☒ **D** electrophilic substitution.

(Total for Question 10 = 2 marks)

11 Which of these is **not** observed when ethanoyl chloride reacts with water?

☒ **A** Misty fumes given off.

☒ **B** The gas given off turns damp blue litmus paper red.

☒ **C** The mixture gets hot.

☒ **D** A white precipitate forms.

(Total for Question 11 = 1 mark)

12 UV light is useful in initiating some reactions because it

☒ **A** lowers the activation energy of the reaction.

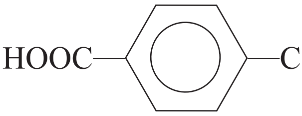
☒ **B** causes bonds in molecules to stretch and bend.

☒ **C** causes molecules to form ions.

☒ **D** causes molecules to form free radicals.

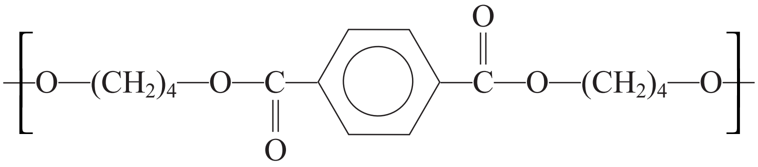
(Total for Question 12 = 1 mark)

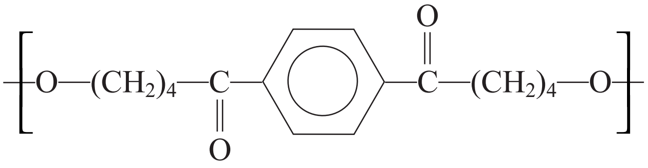
13 Butane-1,4-diol, $HO(CH_2)_4OH$, and benzene-1,4-dicarboxylic acid,

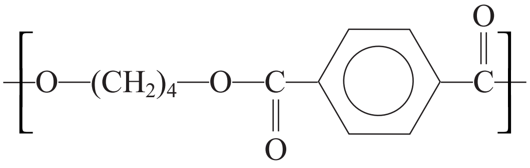
, react to form a polyester.

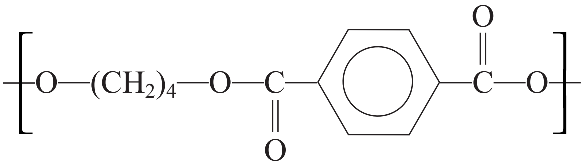
(a) The repeat unit of the polyester is

(1)

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(b) The type of reaction is

(1)

☒ **A** hydrolysis.

☒ **B** addition.

☒ **C** substitution.

☒ **D** condensation.

(Total for Question 13 = 2 marks)

14 The equation for the enthalpy of hydration for a magnesium ion is

☒ **A** $Mg^{2+}(s) + aq \rightarrow Mg^{2+}(aq)$

☒ **B** $Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$

☒ **C** $Mg^{2+}(aq) \rightarrow Mg^{2+}(g) + aq$

☒ **D** $Mg^{2+}(aq) \rightarrow Mg^{2+}(s) + aq$

(Total for Question 14 = 1 mark)

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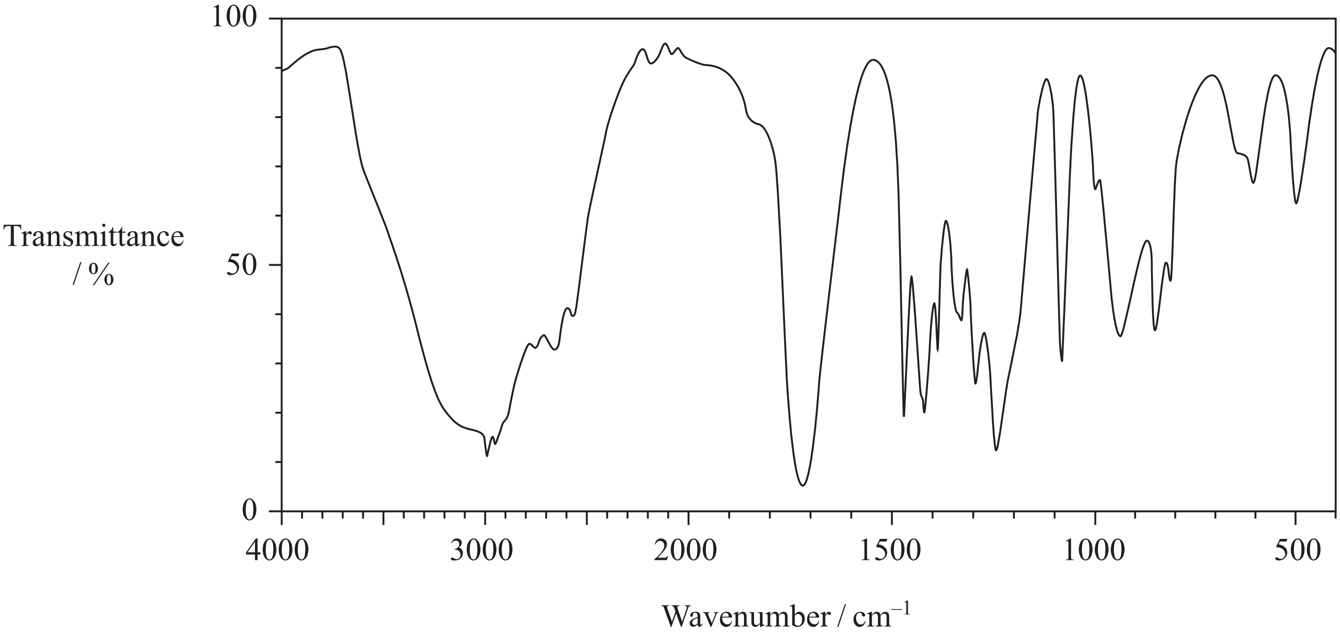
15 The IR spectrum of a substance is shown below.



Which of the following substances has this spectrum?

You may use the information on page 6 of the data booklet.

☒ **A** Propan-1-ol

☒ **B** Propanal

☒ **C** Propanone

☒ **D** Propanoic acid

(Total for Question 15 = 1 mark)

16 Two ketones, $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$, both have M_r = 86. Which peak due to fragmentation into singly charged ions would you expect to be present in the mass spectrum of one but not the other?

☒ **A** 71

☒ **B** 57

☒ **C** 43

☒ **D** 29

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 Two organic compounds, **X** and **Y**, both with the molecular formula C_4H_8O, contain a carbonyl group.

(a) Describe what you would see when 2,4-dinitrophenylhydrazine is added to either of these compounds.

(1)

....

(b) It is suspected that **X** is a ketone and **Y** is an aldehyde. Outline a chemical test you could carry out to confirm this, describing the results in each case.

(3)

....

....

....

....

....

....

(c) (i) Give the structural formulae of the two possible isomers of **Y** which are aldehydes.

(1)

(ii) Name the technique you would use to purify the product of the test with 2,4-dinitrophenylhydrazine.

(1)

....

(iii) Other than by spectroscopic techniques, how would you use the purified product to identify compound **Y**? [Practical details are not required.]

(2)

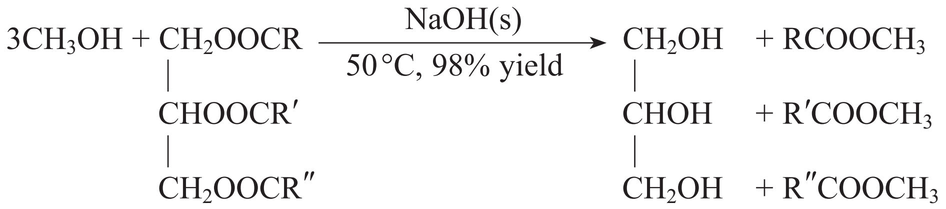
....

....

....

(Total for Question 17 = 8 marks)

18 Kits for manufacturing biodiesel from vegetable oils and methanol are sold for home use. The reaction which takes place may be represented by the following equation.



$$\begin{array}{lllll} 3CH_3OH + & CH_2OOCR & \xrightarrow[50\,^\circ C,\ 98\%\ \text{yield}]{NaOH(s)} & CH_2OH & + RCOOCH_3 \\ & | & & | & \\ & CHOOCR' & & CHOH & + R'COOCH_3 \\ & | & & | & \\ & CH_2OOCR'' & & CH_2OH & + R''COOCH_3 \end{array}$$

*(a) Describe any two of the main hazards when carrying out this reaction. What precaution would you take to minimise the risk in each case?

(4)

Hazard

Precaution

Hazard

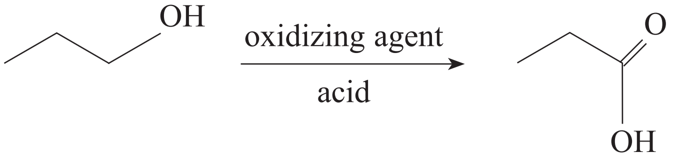
Precaution

(b) Suggest **two** environmental benefits of using these kits, despite the associated risks.

(2)

(Total for Question 18 = 6 marks)

19 The carboxylic acid, propanoic acid, can be prepared by oxidation of the alcohol, propan-1-ol.



propan-1-ol propanoic acid

(a) (i) Identify a suitable oxidizing agent you could use in this reaction.

(1)

....

(ii) If you carried out this preparation in the laboratory, describe **two** measures you would take to ensure the maximum possible yield of propanoic acid is obtained.

(2)

....

....

....

....

(iii) Propanoic acid can be made by the hydrolysis of a nitrile. Give the structural formula of the nitrile and write an equation for this reaction.

(3)

Structural formula ....

Equation

*(b) Propanoic acid reacts with methanol, CH_3OH, to form the ester, methyl propanoate.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

Even with the use of a catalyst, this reaction is quite slow and incomplete. Suggest a reagent, to replace the propanoic acid, which would form the ester at a faster rate. Suggest **two** reasons why your chosen reagent reacts faster.

(3)

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....

(c) The structure of methyl propanoate can be investigated by using high resolution ^1H nuclear magnetic resonance (nmr) spectroscopy.

(i) What type of radiation interacts with ^1H nuclei in nmr spectroscopy?

(1)

....

(ii) Describe what happens to ^1H nuclei when they absorb this radiation.

(2)

....

....

....

(iii) Complete the table to show values for the chemical shift of the different ^1H nuclei in methyl propanoate and their splitting pattern. Page 7 of the data booklet gives information about chemical shifts.

(2)

^1H environment	Chemical shift, δ / ppm	Splitting pattern
CH_3O–	3.7	Singlet
–CH_2–	2.3	
–CH_3		Triplet

(Total for Question 19 = 14 marks)

20 The exothermic reaction between carbon monoxide and hydrogen can be used industrially to make methanol. The process is carried out at 250 °C and between 50 and 100 atm.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

(a) Explain why increasing the pressure increases the yield of methanol. Give **one** disadvantage of increasing the pressure.

(2)

....

....

....

....

(b) The reaction gives a greater equilibrium yield at 100 °C than at 250 °C.

(i) Explain, in terms of the entropy change of the surroundings and the total entropy change of the reaction, why this is so.

A calculation is **not** required.

(2)

....

....

....

....

(ii) Explain why the reaction is, nevertheless, carried out at 250 °C.

(1)

....

....

(c) Given that the reaction is an equilibrium, suggest **two** ways in which the atom economy of this process could be maximised without changing the temperature or pressure.

(2)

....

....

(Total for Question 20 = 7 marks)

21 This question is about the kinetics of the reaction between bromoethane and aqueous hydroxide ions.

(a) The results of an experiment to find the initial rate of the reaction are shown in the table below.

$[CH_3CH_2Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
0.100	0.150	1.54×10^{-6}

The rate equation for the reaction is

$$\text{rate} = k[CH_3CH_2Br][OH^-]$$

(i) Calculate the value of k. Give your answer to three significant figures and include units.

(3)

(ii) Calculate the initial rate if the concentrations of both reactants were changed to 0.020 mol dm^{-3}.

(1)

(b) (i) State the order of the reaction.

(1)

....

(ii) The mechanism for this reaction can be inferred from the rate equation. Draw the transition state formed in the reaction between bromoethane and hydroxide ions.

(2)

(c) The rate constant for the reaction between bromoethane and hydroxide ions was determined at five different temperatures. The results are shown in the table below.

Temperature (T) / K	1/Temperature (1/T) / K^{-1}	Rate constant, *k*	ln *k*
293	3.41×10^{-3}	5.83×10^{-5}	−9.75
303	3.30×10^{-3}	1.67×10^{-4}	−8.70
313	3.19×10^{-3}	5.26×10^{-4}	−7.55
323	3.10×10^{-3}	1.36×10^{-3}	−6.60
333		3.77×10^{-3}	

(i) Complete the missing values in the table.

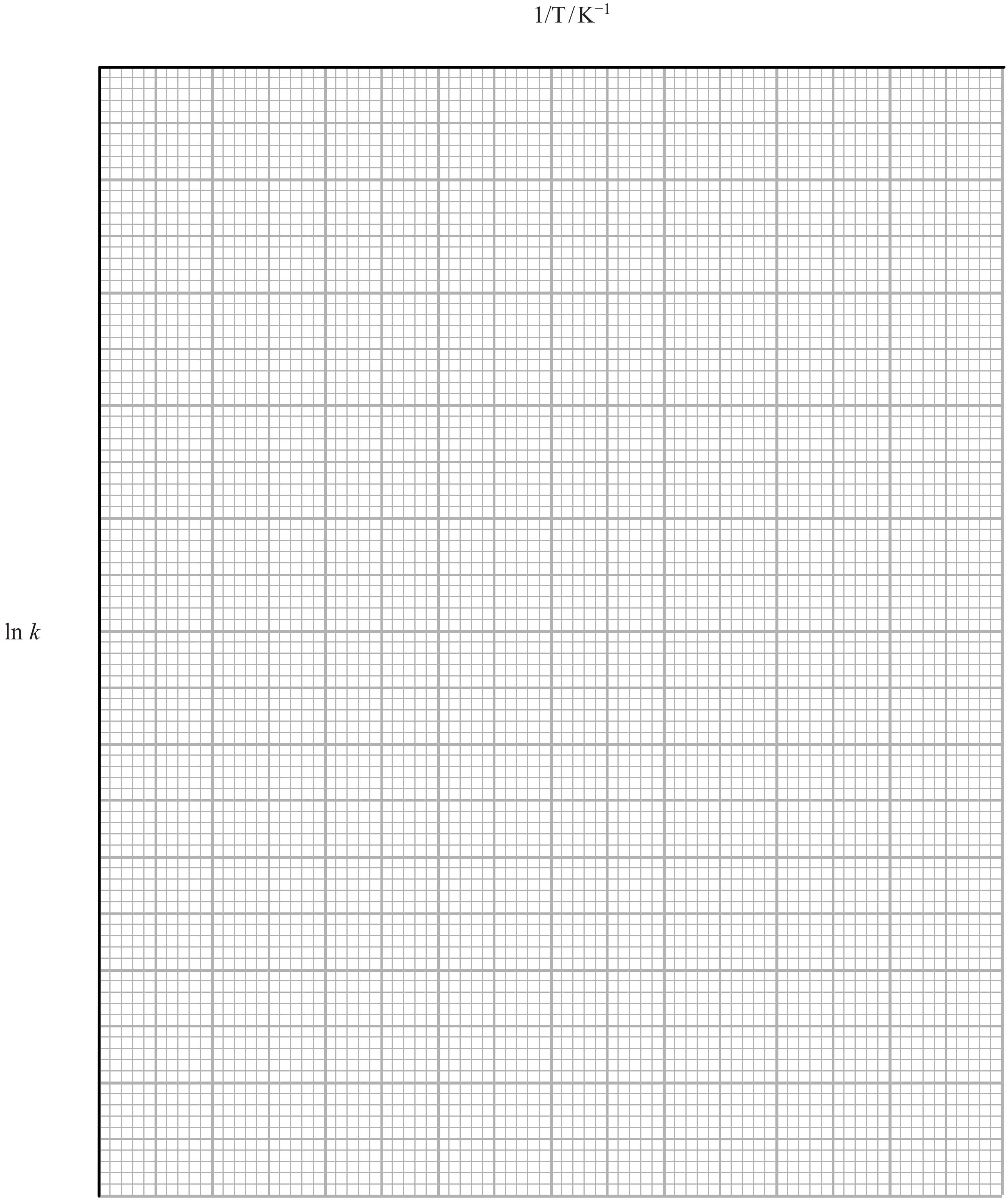
(2)

(ii) Plot a graph of ln *k* against 1/T. Calculate the gradient of your graph and use this to calculate the activation energy, E_A. The Arrhenius equation can be expressed as

$$\ln k = \frac{-E_A}{R} \times \left(\frac{1}{T}\right) + \text{a constant}$$

[Gas constant, R = 8.31 J K^{-1} mol^{-1}]

(5)



(Total for Question 21 = 14 marks)

TOTAL FOR SECTION B = 49 MARKS

SECTION C

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

22 The hydrocarbon butane can be cracked to form propene and methane by passing it over a heated aluminium oxide catalyst at a temperature of 700 K. The equation for the reaction is

$$C_4H_{10}(g) \rightarrow C_3H_6(g) + CH_4(g) \qquad \Delta H = +71.9 \text{ kJ mol}^{-1}$$

(a) (i) Use page 20 of the data booklet to complete the table below.

(1)

Hydrocarbon	$S^{\ominus}$/ J mol^{-1} K^{-1}
$C_4H_{10}(g)$	+310.1
$C_3H_6(g)$	+266.9
$CH_4(g)$	

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction. Include a sign in your answer.

(2)

(iii) Was the sign for your answer as you expected? Fully justify your answer.

(2)

....

....

....

....

(iv) Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, at 700 K.

Include a sign and units in your answer.

Use this value and your answer to (ii) to explain why butane cracks into propene and methane at this temperature.

(3)

....

....

....

....

(v) Calculate the minimum temperature needed for this reaction to be thermodynamically feasible.

(3)

(b) The aluminium oxide behaves as a heterogeneous catalyst. Explain both what is meant by the term **heterogeneous** and how, in terms of activation energy, the catalyst is able to speed up the reaction.

(3)

(Total for Question 22 = 14 marks)

23 The bubble bath ‘Colour Change Matey’ has amongst its ingredients the weak acid benzoic acid, as well as the indicator bromocresol green. When it is added to bath water, its colour changes from yellow to blue.

(a) (i) Write the K_a expression for the dissociation of benzoic acid, C_6H_5COOH.

(1)

(ii) Use the data on page 18 of the data booklet to calculate the pH of a solution of benzoic acid, C_6H_5COOH, of concentration 0.0025 mol dm^{-3}.

(2)

*(b) Use the data on page 19 of the data booklet, and your answer to (a)(ii), to suggest why the bubble bath changes colour when it is diluted by being added to the bath water.

(4)

(Total for Question 23 = 7 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
							1.0 **H** hydrogen 1										(18) 4.0 **He** helium 2
(1)	(2)											(13)	(14)	(15)	(16)	(17)	
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)
January 2012

GCE Chemistry (6CH04) Paper 01

General Principles of Chemistry I Rates Equilibria and Further Organic Chemistry

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January 2012
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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. Questions labelled with an **asterix (*)** are ones where the quality of your written communication will be assessed.

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the <u>meaning</u> of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication
Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1(a)	C		1

Question Number	Correct Answer	Reject	Mark
1(b)	A		1

Question Number	Correct Answer	Reject	Mark
2	D		1

Question Number	Correct Answer	Reject	Mark
3	A		1

Question Number	Correct Answer	Reject	Mark
4(a)	C		1

Question Number	Correct Answer	Reject	Mark
4(b)	A		1

Question Number	Correct Answer	Reject	Mark
5	A		1

Question Number	Correct Answer	Reject	Mark
6	B		1

Question Number	Correct Answer	Reject	Mark
7	B		1

Question Number	Correct Answer	Reject	Mark
8	D		1

Question Number	Correct Answer	Reject	Mark
9	A		1

Question Number	Correct Answer	Reject	Mark
10 (a)	B		1

Question Number	Correct Answer	Reject	Mark
10 (b)	B		1

Question Number	Correct Answer	Reject	Mark
11	D		1

Question Number	Correct Answer	Reject	Mark
12	D		1

Question Number	Correct Answer	Reject	Mark
13 (a)	C		1

Question Number	Correct Answer	Reject	Mark
13 (b)	D		1

Question Number	Correct Answer	Reject	Mark
14	B		1

Question Number	Correct Answer	Reject	Mark
15	D		1

Question Number	Correct Answer	Reject	Mark
16	C		1

TOTAL FOR SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
17(a)	Orange/yellow **and** precipitate/ppt or solid or crystals ALLOW orange-red or red-orange for colour	Any other colour alone or in combination, e.g.red	**1**

Question Number	Acceptable Answers	Reject	Mark
17(b)	(Heat with) Benedict's/Fehling's (solution) **(1)**		**3**
	Ketone/X would remain blue/no change/no reaction **(1)**		
	Aldehyde/Y would form red/brown **and** ppt/Cu_2O **(1)**	Just orange	
	ALLOW combinations of red or brown with orange		
	OR		
	(Heat with) Tollens' Reagent/ammoniacal silver nitrate **(1)**		
	Ketone/X remains colourless/no change/no reaction **(1)**		
	Aldehyde/Y forms a silver mirror or black/grey precipitate/Ag/silver **(1)**		
	OR		
	(Heat with) acidified dichromate((VI)) (ions) **(1)**		
	Ketone/X remains orange/no change/no reaction **(1)**		
	Aldehyde/Y goes green/blue **(1)** ALLOW *answer with acidified or alkaline $KMnO_4$*	Ppt	
	Ketone/X remains purple/pink/no change/no reaction **(1)**		
	Aldehyde/Y goes colourless (with acid)/goes green (with alkali) **(1)**	Just clear	
	Near miss on reagent (e.g. silver nitrate not ammoniacal silver nitrate) observations can score 2		
	ALLOW iodoform test with ketone identified (since X can only be butanone) (Aqueous) sodium hydroxide and iodine **(1)**		
	Ketone/X forms yellow precipitate/solid/crystals **(1)**		
	Aldehyde/Y no change/no reaction **(1)**		

Question Number	Acceptable Answers	Reject	Mark
17(c)(i)	**Both** $CH_3CH_2CH_2CHO$ And $(CH_3)_2CHCHO$ ACCEPT displayed or skeletal formulae if structural formulae not given	COH unless shown correctly in a displayed or skeletal formula	**1**

Question Number	Acceptable Answers	Reject	Mark
17(c)(ii)	Recrystallization IGNORE solvent	Just crystallization	**1**

Question Number	Acceptable Answers	Reject	Mark
17(c)(iii)	Measure melting temperature / point **(1)** Compare with literature/database / known value **(1)** Second mark can only be awarded if first mark scored	Just boiling temperature	**2**

Question Number	Acceptable Answers	Reject	Mark
18(a)	Hazard – **methanol/alcohol** is flammable **(1)** IGNORE flammability of vegetable/diesel oils Precaution – use electrical heating source/water bath /avoid naked flames **(1)** OR Hazard – **methanol/alcohol** is toxic **(1)** Precaution – Use in well-ventilated area/fume cupboard/store away from children/wear gloves **(1)** OR Hazard – **NaOH/reaction mixture** is corrosive /burns (the skin)/damages the eyes **(1)** IGNORE references to (strong) alkali(ne) Precaution – wear gloves/goggles ALLOW any 2 hazards but the precaution must be associated with the appropriate hazard If the Hazard is not clearly identified but the precaution is appropriate then allow one mark, e.g. "Use of flammable substances so avoid naked flames" = **(1)** mark	Just volatile Just dangerous /harmful Just irritant	4

Question Number	Acceptable Answers	Reject	Mark
18(b)	**Any two from:** Reuses/reduces waste (vegetable) oil/ lessens need to dispose of (vegetable) oil **(1)** Could lessen use of (non-renewable/non-sustainable) crude oil/fossil fuels OR vegetable oil/biodiesel/reactants renewable/ sustainable **(1)** Plants grown for vegetable oil could offset some CO_2 emissions **(1)** IGNORE references to transport/temperature/ energy savings cost/profit/high yield/ biodegradability/greenhouse gases	Just methanol is renewable Just carbon neutral/just reduces carbon footprint	**2**

Question Number	Acceptable Answers	Reject	Mark
19(a)(i)	Sodium/potassium dichromate((VI))/potassium manganate ((VII))/$Na_2Cr_2O_7$/$K_2Cr_2O_7$/$KMnO_4$ IGNORE references to acid	Just $Cr_2O_7^{2-}$ /MnO_4^-	**1**

Question Number	Acceptable Answers	Reject	Mark
19(a)(ii)	(Heat under) reflux **(1)** Use excess/sufficient oxidizing agent/reagent named in (a)(i), even if incorrect **(1)** IGNORE references to (excess) acid Stand alone marks		**2**

Question Number	Acceptable Answers	Reject	Mark
19(a)(iii)	CH_3CH_2CN/C_2H_5CN **(1)** ACCEPT displayed or skeletal formulae $CH_3CH_2CN + H^+ + 2H_2O \rightarrow CH_3CH_2COOH + NH_4^+$ OR $CH_3CH_2CN + HCl + 2H_2O \rightarrow CH_3CH_2COOH + NH_4Cl$ **(2)** If equation is incorrect then presence of H^+ or acid in equation/or above arrow **and** water on LHS scores (1) Mark cq on formula of nitrile ALLOW one mark for the following equation without H^+. $CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2COOH + NH_3$ ALLOW two marks for either of the following with H^+ above the arrow $CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2COOH + NH_3$ $CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2COOH + NH_4^+$ ALLOW answers for alkaline hydrolysis **followed by** acidification $CH_3CH_2CN + OH^- + H_2O \rightarrow CH_3CH_2COO^- + NH_3$ **(1)** Then $CH_3CH_2COO^- + H^+ \rightarrow CH_3CH_2COOH$ **(1)** If propanamide, $CH_3CH_2CONH_2$ is given initially then ALLOW the two equation marks for the hydrolysis $CH_3CH_2\ CONH_2 + H^+ + H_2O \rightarrow CH_3CH_2COOH + NH_4^+$ If no acid is used then only one mark $CH_3CH_2\ CONH_2 + H_2O \rightarrow CH_3CH_2COOH + NH_3$	Hydroxynitriles	**3**

Question Number	Acceptable Answers	Reject	Mark
19(b)	Reagent - Propanoyl chloride/CH_3CH_2COCl **(1)** **Any two from:** C-Cl bond is weaker (than C- 0) **(1)** Cl^-/chloride (ion) is a better leaving group **(1)** Carbonyl carbon is more positive/more $\delta+$/more attractive to nucleophiles **(1)** OR Reagent - Propanoic anhydride/$(CH_3CH_2CO)_2O$ **(1)** CH_3COO^-/propanoate (ion) is a better leaving group **(1)** Carbonyl carbon is more positive/more $\delta+$/more attractive to nucleophiles **(1)** IGNORE references to eversible/equilibrium/ catalysts IGNORE bond polarity	Propyl chloride Just Cl is more electronegative	**3**

Question Number	Acceptable Answers	Reject	Mark
19(c)(i)	Radio waves/radio frequency	Just radio	**1**

Question Number	Acceptable Answers	Reject	Mark
19(c)(ii)	**Any two from:** Protons/nuclei/they have a property called spin/ have a magnetic moment/ have a magnetic field/ are aligned with the external magnetic field **(1)** **which** flips/changes **(1)** align against the external magnetic field (when radiation is absorbed) **(1)**	starts to spin just dipole moment polarity flips any reference to electrons or molecules scores zero	**2**

Question Number	Acceptable Answers	Reject	Mark
19(c)(iii)	Quartet **(1)** ALLOW quadruplet/indication of four (peaks) Value from 0.1 to 1.9 (ppm) inclusive **(1)** ACCEPT any range within the above range		**2**

Question Number	Acceptable Answers	Reject	Mark
20(a)	(Greater yield) as fewer moles/molecules (of gas) on RHS OR 3 moles/molecules on left but only 1 on right **(1)** ALLOW arguments in terms of K_p remaining constant Disadvantage: Extra cost of (building) equipment (to withstand higher pressure)/ thicker pipes/compressor/maintaining equipment **(1)** OR Higher cost **of energy** needed for compression **(1)** IGNORE references to explosion	Just (higher) cost	**2**

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	(Reaction is exothermic) so the value of $\Delta S_{\text{surroundings}}$ becomes more positive/larger (at 100 °C) **(1)** Therefore ΔS_{total} becomes more positive/larger/less negative(at 100 °C) **(1)** Second mark consequential on first		**2**

Question Number	Acceptable Answers	Reject	Mark
20(b)(ii)	(Higher temperature gives a) faster rate of reaction /more particles have $E \geq E_a$ (ALLOW more successful collisions (per second) IGNORE references to yield		**1**

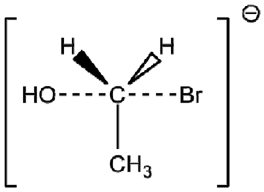
Question Number	Acceptable Answers	Reject	Mark
20(c)	Remove methanol/the product (as it is formed) **(1)** Recycle/reuse **unreacted** reactants **(1)** IGNORE references to catalyst and increasing amounts of reactants		**2**

Question Number	Acceptable Answers	Reject	Mark
21(a)(i)	*k* = $(1.54 \times 10^{-6}) \div (0.1 \times 0.15)$ **(1)** (= 1.0267×10^{-4}) = 1.03×10^{-4} **(1)** must be to 3 SF $dm^3\ mol^{-1}\ s^{-1}$ **(1)** Unit mark is stand alone and units can be in any order Correct answer with units but no working **(3)** marks	1.02×10^{-4}	**3**

Question Number	Acceptable Answers	Reject	Mark

21(a)(ii)	If correct unrounded answer to (a) (i) stored in calculator then
	$4.1067 \times 10^{-8} = 4.1 \times 10^{-8}$ (mol $dm^{-3}\ s^{-1}$)
	OR
	If 1.0267×10^{-4} used then
	$4.1068 \times 10^{-8} = 4.1 \times 10^{-8}$ (mol $dm^{-3}\ s^{-1}$)
	OR
	If 1.03×10^{-4} used then
	$4.12 \times 10^{-8} = 4.1 \times 10^{-8}$ (mol $dm^{-3}\ s^{-1}$)
	IGNORE sf except 1sf
	IGNORE units even if incorrect
	TE from (a)(i)
			1

Question Number	Acceptable Answers	Reject	Mark
21(b)(i)	2(nd)/second/two/(1 + 1) = 2 (order)		**1**

Question Number	Acceptable Answers	Reject	Mark
21(b)(ii)	 Structure **(1)** ALLOW structure without wedged bonds Dotted bonds must be shown and OH and Br must be on opposite sides with a C-C or C-H bond between them Charge **(1)** Charge mark can be awarded for a near miss with a single error in the structure (e.g. one hydrogen atom missing) ALLOW –ve charge shown as δ− on both OH and Br Brackets not essential ALLOW –ve charge to be anywhere on the structure IGNORE δ+ on carbon atom		**2**

Question Number	Acceptable Answers	Reject	Mark
21(c)(i)	3.00×10^{-3} **(1)** IGNORE sf for 1/T −5.58 **(1)** IGNORE sf except 1sf	 -5.60	**2**

Question Number	Acceptable Answers	Reject	Mark
21(c)(ii)	Appropriate scale **(1)** Plotted points **must** cover at least half of the graph paper on each axis. Points plotted correctly **and** straight line drawn through all points **(1)** Gradient = —10230 ± 500 **(1)** Example E_a = 10230 x 8.31**(1)** allow TE from incorrect gradient E_a = (+) 85.0 kJ(mol^{-1})/(+) 85 000 J (mol^{-1}) **(1)** 3 sf E_a range from 80.9 to 89.2 kJ mol^{-1} ALLOW TE from incorrect gradient IGNORE SF except 1	K^{-1}	**5**

TOTAL FOR SECTION B = 49 MARKS

Section C

Question Number	Acceptable Answers	Reject	Mark
22 (a)(i)	(+)186.2 (J mol^{-1} K^{-1})		**1**

Question Number	Acceptable Answers	Reject	Mark
22(a)(ii)	(266.9 + 186.2) – 310.1 **(1)** **=** + 143 (J mol^{-1} K^{-1}) **(1)** − 143 scores (1) Correct answer with sign and no working scores (2) marks ALLOW TE from (i)		**2**

Question Number	Acceptable Answers	Reject	Mark
22(a)(iii)	Yes, as reaction produces 2 molecules/moles from one/more molecules/moles **(1)** (and) all products are gases **(1)** IGNORE references to volumes More moles/molecules of **gas produced** scores (2) OR Yes, (as the reaction is endothermic) $\Delta S_{surroundings}$ is negative **(1)** Since the reaction takes place/goes (spontaneously) ΔS_{total} is positive and therefore ΔS_{system} is positive **(1)** ALLOW TE from (a)(ii) i.e. 'No, as….'		**2**

Question Number	Acceptable Answers	Reject	Mark
22(a)(iv)	$\Delta S_{surr} = -\Delta H/T$ **(1)** $= -71900/700$ $= -102.7$ **J** K^{-1} mol^{-1}/$-$ 0.1027 **kJ** K^{-1} mol^{-1} **(1)** Correct answer and sign with no working scores (2) — 0.103 **J** K^{-1} mol^{-1} scores (1) **Third mark** So ΔS_{total} is positive (so reaction is feasible) **(1)** OR ΔS_{total} = **+**40.3 J K^{-1} mol^{-1} (so reaction is feasible) **(1)** ALLOW TE from (a)(ii)	1 or 2 sf	**3**

Question Number	Acceptable Answers	Reject	Mark
22(a)(v)	$\Delta S_{total} = 0$ OR $\Delta S_{surroundings} = —143$ **(1)** $T = \Delta H \div \Delta S_{surroundings}$ OR T = (—) 71900 ÷ (—)143 **(1)** = 502.8 (K) **(1)** IGNORE sf except 1sf Correct answer with no working scores (3) ALLOW 0.5028 (K) for (2) marks ALLOW — 502.8 (K) for (2) marks ALLOW — 0.5028 (K) for (1) mark ALLOW TE from (a)(ii) If the calculation is not based on $\Delta S_{total} = 0$ then a maximum of (2) marks can be awarded if done correctly		**3**

Question Number	Acceptable Answers	Reject	Mark
22(b)	The catalyst is in a different state/phase to the reactants **(1)** IGNORE references to products **Any two from** It provides an alternative (reaction) route/mechanism/gases adsorbed on catalyst surface **(1)** Of lower activation energy/weakens bonds in reactants **(1)** Greater proportion of molecules have E ≥ Ea **(1)**		**3**

Question Number	Acceptable Answers	Reject	Mark
23 (a)(i)	(Ka =) $[H^+][C_6H_5COO^-]/[C_6H_5COOH]$ Penalise missing charges ALLOW $[H_3O^+]$ in place of $[H^+]$ IGNORE state symbols and units even if incorrect	$Ka = [H^+]^2/[C_6H_5COOH]$	**1**

Question Number	Acceptable Answers	Reject	Mark
23(a)(ii)	$[H^+] = \sqrt{(6.3 \times 10^{-5} \times 0.0025)}$ (1) pH = $-\log\sqrt{(6.3 \times 10^{-5} \times 0.0025)}$ = 3.4 **(1)** Answer without working scores (2) marks 6.8 scores (1) IGNORE sf except 1	answer if units given	**2**

Question Number	Acceptable Answers	Reject	Mark
23(b)	(pH) range (of indicator) 3.8 to 5.4 OR pK_{in} = 4.7 **(1)** Bubble bath is (initially yellow since) pH less than 3.8 / is 3.4 **(1)** Adding of water/dilution (of acid) causes pH to rise/ means $[H^+]$ decreases **(1)** Hence pH rises to ≥ 5.4 so blue/changes colour **(1)** If a(ii) pH>3.8 and <5.4 then loses second marking point but can score other marking points. If a(ii) pH>5.4 then can score first and third marking points only	Water neutralizes acid	**4**

TOTAL FOR SECTION C = 21 MARKS

TOTAL FOR PAPER = 90 MARKS

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Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 13 June 2012 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

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 of the following interacts with the nuclei of hydrogen atoms in a nuclear magnetic resonance spectrometer?

☒ **A** Gamma rays

☒ **B** X-rays

☒ **C** Microwaves

☒ **D** Radio waves

(Total for Question 1 = 1 mark)

2 HPLC stands for

☒ **A** high pressure liquid column.

☒ **B** high performance liquid chromatography.

☒ **C** heterogeneous phase liquid chromatography.

☒ **D** homogenous phase liquid column.

(Total for Question 2 = 1 mark)

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

3 Consider the equilibrium below.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

(a) An increase in pressure by a factor of 2 will

(1)

☒ **A** quadruple K_p.

☒ **B** double K_p.

☒ **C** have no effect on K_p.

☒ **D** halve K_p.

(b) The units of K_p are

(1)

☒ **A** atm^{-2}

☒ **B** atm^{-1}

☒ **C** atm

☒ **D** atm^{2}

(Total for Question 3 = 2 marks)

---

4 Which of these will **not** improve the **overall** yield of the Haber process?

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

☒ **A** Increasing the pressure.

☒ **B** Liquefying then removing the ammonia from the reaction.

☒ **C** Increasing the temperature.

☒ **D** Recycling unreacted nitrogen and hydrogen.

(Total for Question 4 = 1 mark)

---

5 The equation for the reaction between ethanoic acid and phosphorus(V) chloride is

☒ **A** $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

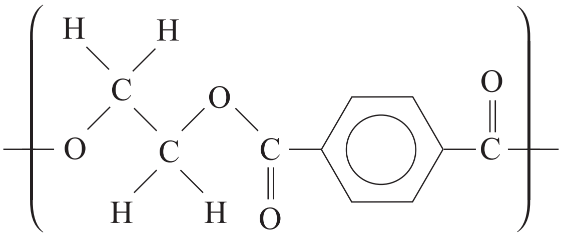
☒ **B** $CH_3COOH + PCl_5 \rightarrow CH_3COOCl + PCl_3 + HCl$

☒ **C** $CH_3COOH + PCl_5 \rightarrow CH_3COCl + PCl_3 + HOCl$

☒ **D** $2CH_3COOH + PCl_5 \rightarrow (CH_3CO)_2O + PCl_3 + H_2O + Cl_2$

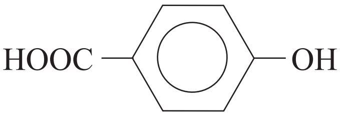
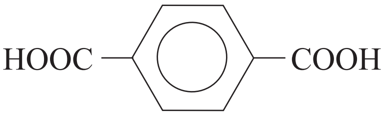
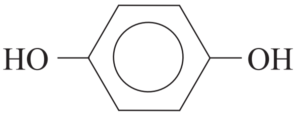
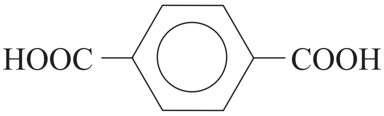
(Total for Question 5 = 1 mark)

6 An example of a polyester is



(a) The two monomers needed to form this polymer are

(1)

	Monomer One	Monomer Two
☒ **A**		$HO(CH_2)_2OH$
☒ **B**		$HO(CH_2)_2OH$
☒ **C**		$HOOC(CH_2)_2COOH$
☒ **D**		$HOOC(CH_2)_2COOH$

(b) The type of reaction to form this polymer is

(1)

☒ **A** addition.

☒ **B** substitution.

☒ **C** condensation.

☒ **D** hydrolysis.

(Total for Question 6 = 2 marks)

7 In which of these reactions is the hydrogensulfate ion, HSO_4^-, behaving as a Brønsted-Lowry base?

☒ **A** $HSO_4^- + H_3O^+ \rightarrow H_2SO_4 + H_2O$

☒ **B** $HSO_4^- + Ba^{2+} \rightarrow BaSO_4 + H^+$

☒ **C** $HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$

☒ **D** $HSO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + HCO_3^-$

(Total for Question 7 = 1 mark)

8 The reaction below is carried out at 25 °C. Use the equation and the data to answer the questions that follow.

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O(g) \qquad \Delta H = -107.4 \text{ kJ mol}^{-1}$$

Substance	Standard molar entropy, $S^{\ominus}$ / J mol^{-1} K^{-1}
$SO_2(g)$	248
$H_2S(g)$	206
$H_2O(g)$	189
$S(s)$	32

(a) The standard entropy change of the system, in J mol^{-1} K^{-1}, is

(1)

☒ **A** −186

☒ **B** +186

☒ **C** −233

☒ **D** +233

(b) The standard entropy change of the surroundings, in J mol^{-1} K^{-1}, is

(1)

☒ **A** 107.4 × 1000 / 25

☒ **B** −107.4 × 1000 / 25

☒ **C** 107.4 × 1000 / 298

☒ **D** −107.4 × 1000 / 298

(Total for Question 8 = 2 marks)

9 A halogenoalkane, RX, reacts with hydroxide ions, OH^-, to form an alcohol.

$$RX + OH^- \rightarrow ROH + X^-$$

The rate equation for the reaction is rate = k[RX]. Which of these statements is **incorrect**?

☒ **A** Rate ∝ [RX].

☒ **B** RX is a primary halogenoalkane.

☒ **C** The reaction mechanism is S_N1.

☒ **D** A carbocation intermediate forms in the reaction.

(Total for Question 9 = 1 mark)

10 The rate equation for the reaction between hydrogen gas and nitrogen monoxide gas is

$$\text{rate} = k[NO]^2[H_2]$$

If the concentration of both reactants is doubled, the rate will increase by a factor of

☒ **A** 3

☒ **B** 4

☒ **C** 6

☒ **D** 8

(Total for Question 10 = 1 mark)

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

11 A reaction has the rate equation rate = $k[X][Y]^2[Z]$. The concentrations of each reactant are shown in the table below.

Reactant	Concentration / mol dm^{-3}
X	0.040
Y	0.20
Z	0.12

(a) If the rate of reaction under these conditions has a value of 0.24 mol dm^{-3} s^{-1}, then the numerical value of k is

(1)

☒ **A** 0.00080

☒ **B** 0.533

☒ **C** 1.875

☒ **D** 1250

(b) The units for the rate constant, k, are

(1)

☒ **A** mol^{-3} dm^{9} s^{-1}

☒ **B** mol^{3} dm^{9} s^{-1}

☒ **C** mol^{-3} dm^{-9} s^{-1}

☒ **D** mol^{3} dm^{-9} s^{-1}

(Total for Question 11 = 2 marks)

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

12 This question is about the four organic substances shown below.

A $CH_3CH_2CH_2CH_2CHO$

B $CH_3CH_2CH_2CH_2COOH$

C $CH_3COCH_2CH_2CH_3$

D $CH_3CH_2CH_2CH_2COCl$

Which substance will

(a) give a positive result with both Brady's and Tollens' reagents?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) be formed by the oxidation of a secondary alcohol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) form the most acidic solution when equal amounts are each mixed with 100 cm^3 of water?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) form steamy fumes in the reaction with PCl_5?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 12 = 4 marks)

13 In order to make $CH_3CH_2CONHCH_3$, you could use

☒ **A** $CH_3CH_2COOCH_3 + NH_3$

☒ **B** $CH_3CH_2COCl + CH_3NH_2$

☒ **C** $CH_3CH_2COO^-Na^+ + CH_3NH_2$

☒ **D** $CH_3CH_2CONH_2 + CH_3NH_2$

(Total for Question 13 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

14 In a pH titration, 30 cm^3 of sodium hydroxide solution was added, in 1 cm^3 portions, to 20 cm^3 of ethanoic acid solution, $CH_3COOH(aq)$. The concentration of both solutions was 0.50 mol dm^{-3}. After the addition of each 1 cm^3, the pH was recorded using a pH meter.

(a) (i) Write the K_a expression for ethanoic acid.

(1)

(ii) Using your answer to (i), calculate the pH of the 0.50 mol dm^{-3} ethanoic acid solution before the titration starts. Refer to page 18 of the data booklet.

(2)

(iii) Deduce the volume of sodium hydroxide solution required to reach the end point.

(1)

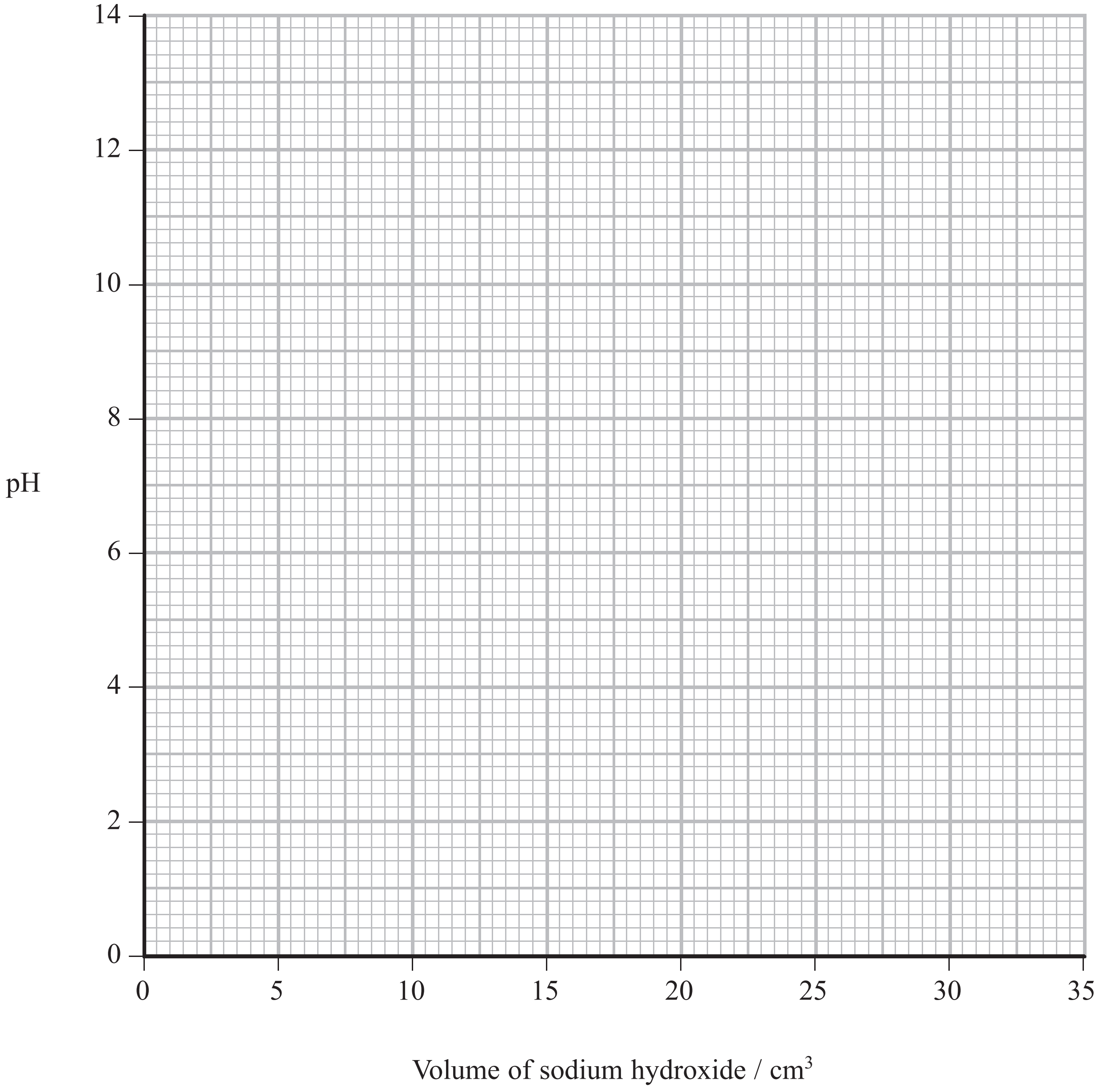
....

(iv) Calculate the pH of the solution after all of the sodium hydroxide is added.

(4)

(v) On the axes below sketch a graph to show how the pH changes during the titration.

(3)



(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

(i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol^{-1}) that would be added to 500 cm^3 of ethanoic acid, concentration 1.0 mol dm^{-3}, in order to make a buffer solution of pH = 4.70.

(4)

*(ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added.

(3)

....

....

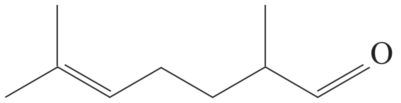
....

....

....

....

(Total for Question 14 = 18 marks)

15 The molecule  is sometimes known as melonal as it smells similar to watermelon.

(a) Give the systematic name for melonal.

(2)

....

(b) (i) Melonal can be prepared by the oxidation of a compound, **X**. Suggest the formula of compound **X** and the names or formulae of the reagents needed to oxidize **X**.

(3)

Compound **X**

Reagents needed for oxidation ....

....

(ii) Briefly suggest a practical measure to maximise the yield of melonal in (b)(i). Justify your answer.

(2)

....

....

....

....

(c) Infrared spectra can be used to confirm the presence of functional groups in a molecule. Use page 5 of the data booklet to suggest the position of two absorptions and the identity of the bonds responsible which can confirm the presence of the two functional groups in melonal.

(2)

Wavenumber range / cm^{-1}	Bond	Functional group present in melonal

(d) The mass spectrum of melonal shows small peaks at *m/e* = 57 and *m/e* = 83.

Give the formula of each of the fragments most likely to have caused these peaks.

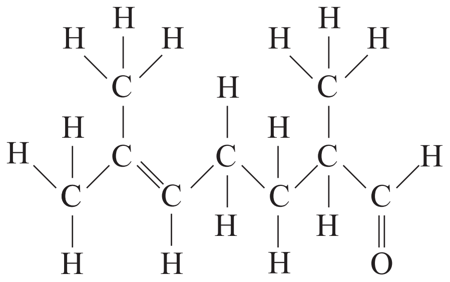
(2)

m/e = 57..

m/e = 83..

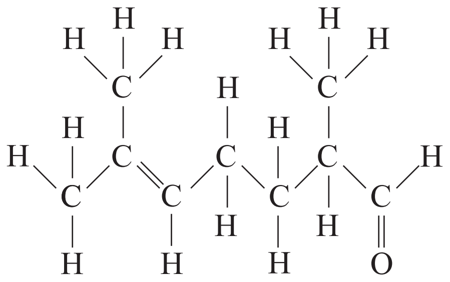
(e) (i) On the displayed formula below, circle the hydrogen atom that has a triplet peak in the proton nmr spectrum of melonal.

(1)



(ii) On the displayed formula below, circle the atom that gives rise to a peak at a chemical shift of δ = 9.65 ppm in the proton nmr spectrum of melonal. Refer to page 7 of the data booklet.

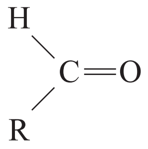
(1)



(f) Aldehydes react with HCN in the presence of CN^- ions.

(i) Give the mechanism for this reaction, using the simplified displayed formula below.

(3)



(ii) The product of this reaction has a chiral centre. Would you expect the reaction to produce a solution that rotates the plane of plane-polarized light? Explain your answer.

(3)

(Total for Question 15 = 19 marks)

16 Iodine reacts with propanone in the presence of an acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

An experiment was carried out to investigate the kinetics of this reaction by monitoring the concentration of iodine. The progress of the reaction was followed by mixing together the reagents, removing samples of the mixture every five minutes, quenching the reaction and then titrating to find the concentration of iodine at a given time.

(a) (i) Suggest a suitable reagent with which you could titrate the iodine.

(1)

....

(ii) State and explain how you would quench the reaction.

(2)

....

....

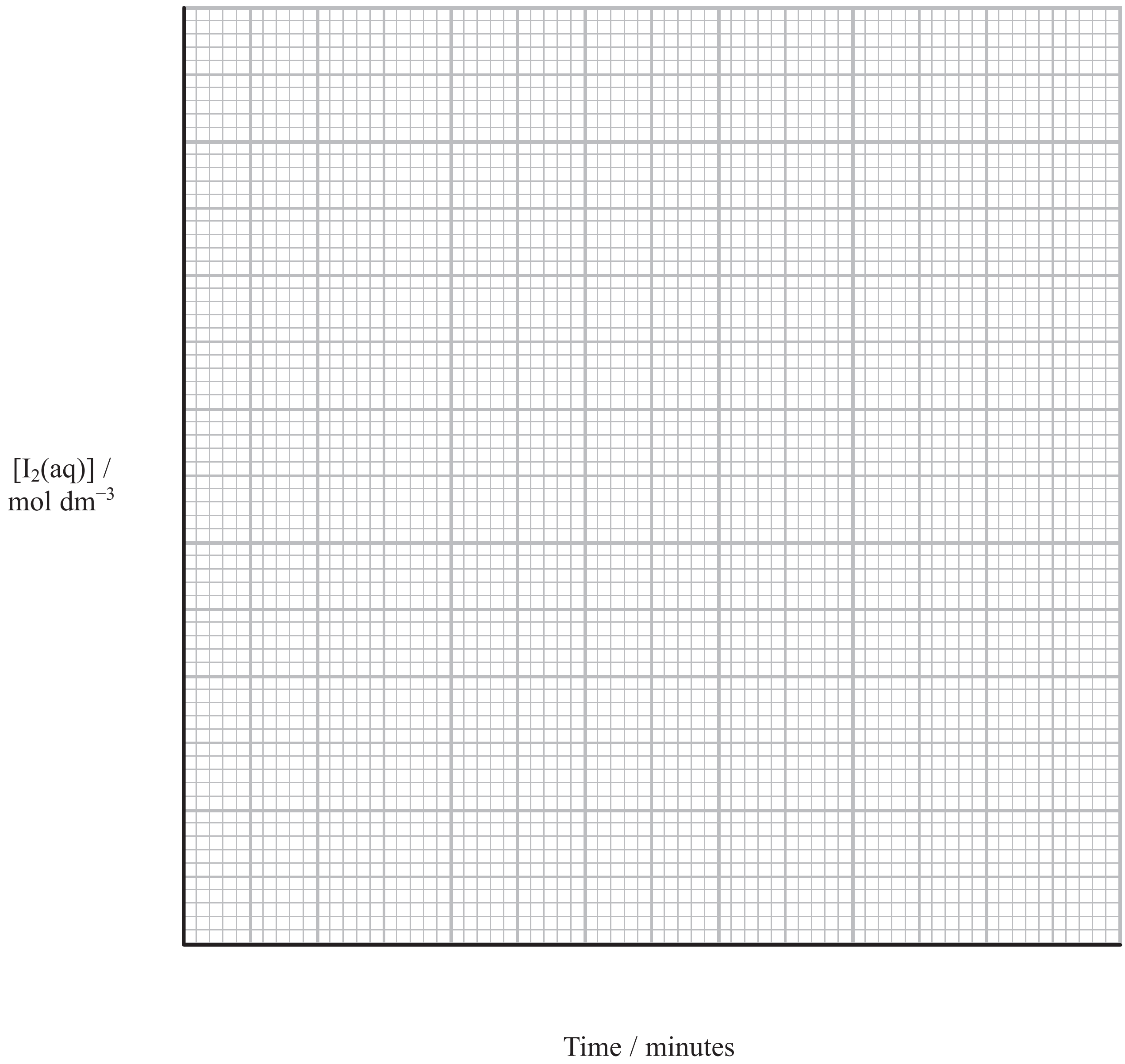
....

....

(b) (i) Data obtained from the experiment are shown in the table below. Use the data to plot a suitable graph to determine the order of the reaction with respect to iodine and state this order.

(3)

Time / mins	$[I_2(aq)]$ / mol dm^{-3}
5	9.74×10^{-4}
10	9.50×10^{-4}
15	9.25×10^{-4}
20	9.03×10^{-4}
25	8.80×10^{-4}
30	8.55×10^{-4}



Order with respect to iodine ....

(ii) Explain how you determined the order using your graph.

(2)

....

....

....

....

(c) State an alternative practical procedure that could be used to monitor the concentration of iodine.

(1)

....

(Total for Question 16 = 9 marks)

17 The ester $CH_3CH_2COOCH_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

(a) (i) Name the ester.

(1)

....

(ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)

....

....

....

....

(b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c, for the reaction.

(3)

	CH_3CH_2COOH	CH_3OH	$CH_3CH_2COOCH_3$	H_2O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol			0.21	

(Total for Question 17 = 6 marks)

TOTAL FOR SECTION B = 52 MARKS

SECTION C

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

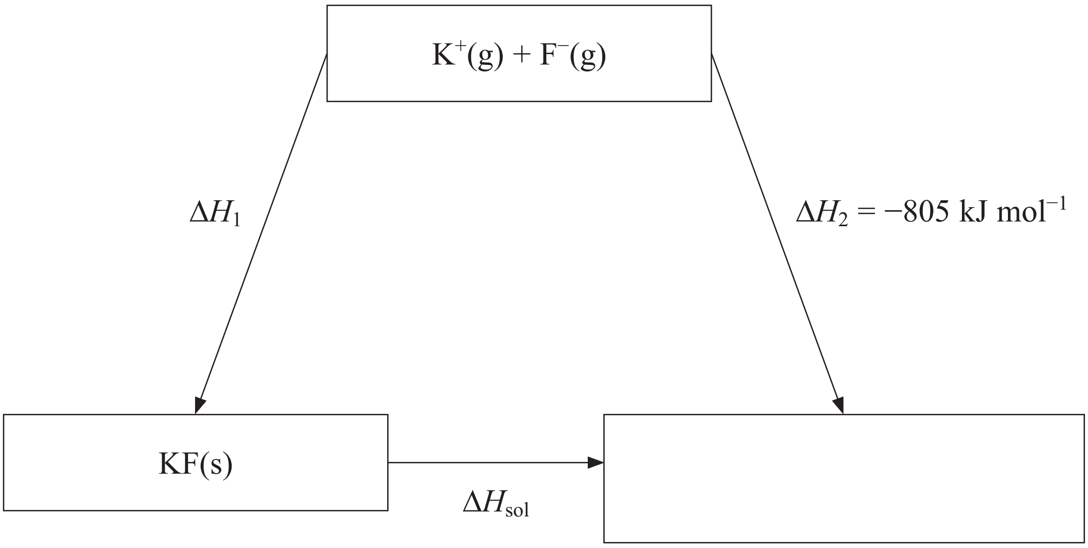
18 This question is about the solubility of some Group 1 halides.

(a) Potassium fluoride is a soluble, white, crystalline solid used in etching glass. A Hess cycle can be used to calculate its enthalpy of solution, using data including enthalpies of hydration of ions.

Define the term **enthalpy of hydration** of an ion.

(2)

(b) Consider the Hess cycle below.



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

(1)

(ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 .

(1)

ΔH_{sol} =

(iii) Give the name of the energy change ΔH_1.

(1)

....

(iv) Referring to page 12 of the data booklet and your answer to (ii), calculate the standard enthalpy of solution of potassium fluoride.

(2)

(c) The standard enthalpy of solution of sodium chloride is + 3 kJ mol^{-1}.

(i) 1 g of sodium chloride was added to 250 cm^3 of water in a beaker and stirred with a thermometer graduated in intervals of 1 °C. Describe and explain what would happen to the reading on the thermometer as the sodium chloride dissolves. No calculation is required.

(3)

....

....

....

....

....

*(ii) Explain, in terms of entropy changes, why sodium chloride dissolves in water under standard conditions. No calculation is required.

(4)

*(d) Lithium iodide is generally much more soluble in organic solvents than lithium chloride. Explain this observation using values of lattice energies from your data booklet and your knowledge of the trend in ionic radii down Group 7.

(4)

(Total for Question 18 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
							1.0 **H** hydrogen 1										*(18)*
(1)	*(2)*											*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)

Summer 2012

GCE Chemistry (6CH04) Paper 01

General Principles of Chemistry I Rates, Equilibria and Further Organic Chemistry (Including synoptic assessment)

Summer 2012
Publications Code UA031863

General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. Questions labelled with an **asterix (*)** are ones where the quality of your written communication will be assessed.

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1	D		**1**
2	B		**1**
3 a	C		**1**
3 b	B		**1**
4	C		**1**
5	A		**1**
6 a	B		**1**
6 b	C		**1**
7	A		**1**
8 a	A		**1**
8 b	C		**1**
9	B		**1**
10	D		**1**
11 a	D		**1**
11 b	A		**1**
12 a	A		**1**
12 b	C		**1**
12 c	D		**1**
12 d	B		**1**
13	B		**1**
		Total for Section A	**20 marks**

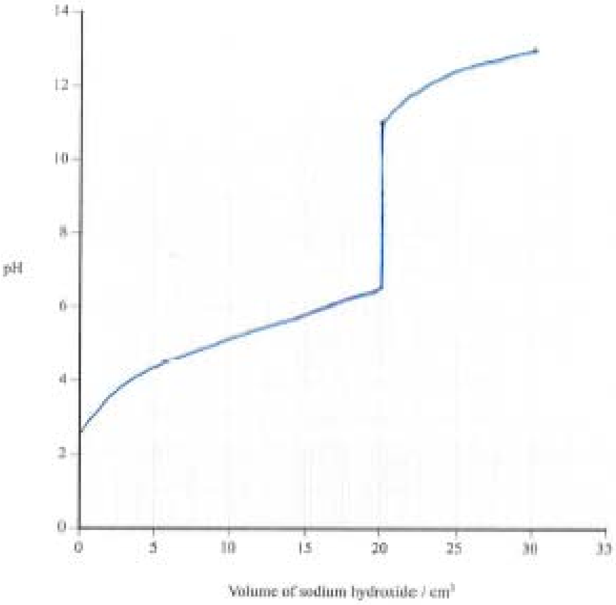
Section B

Question Number	Acceptable Answers	Reject	Mark
14 (a)(i)	$Ka = [CH_3CO_2^-] [H^+]/[CH_3CO_2H]$ OR $Ka = [CH_3CO_2^-] [H_3O^+]/[CH_3CO_2H]$ OR Use of $[CH_3COO^-]$ instead of $[CH_3CO_2^-]$ and $[CH_3COOH]$ instead of $[CH_3CO_2H]$ IGNORE state symbols even if wrong	Numerator as $[H^+]^2$ Expressions in terms of HA alone Round/curved brackets '()' Any other carboxylic acid	**1**

Question Number	Acceptable Answers	Reject	Mark
14(a)(ii)	$1.7 \times 10^{-5} = [H^+]^2 / 0.5$ $[H^+] = \sqrt{1.7 \times 10^{-5} \times 0.5} / 2.915(476) \times 10^{-3}$ **(1)** $pH = (-\log[H^+]) = 2.53529$ OR = 2.54 OR = 2.5 **(1)** ALLOW TE for second mark from any hydrogen ion concentration as long as pH less than 7 Correct answer alone scores **(2)** ALLOW pH = 2.53 if $[H^+]$ is rounded to 2.92×10^{-3} IGNORE sf except 1	4.77 or 4.8 from using pH = -log Ka loses both marks	**2**

Question Number	Acceptable Answers	Reject	Mark
14(a)(iii)	20 (cm^3) IGNORE units OR 0.02 dm^3		**1**

Question Number	Acceptable Answers	Reject	Mark
14(a)(iv)	Moles of excess NaOH = 10/1000 x 0.50 = 5 x 10^{-3} **(1)** So [NaOH/OH^-] = 5 x 10^{-3} x 1000/50 = 0.10 mol dm^{-3} **(1)** EITHER Kw route: [H^+] x 0.1 = 1 x 10^{-14} **(1)** So pH = - log 1 x 10^{-14} / 0.1 = 13 **(1)** OR pOH route: pOH = 1 **(1)** So pH = (14 – 1) = 13 **(1)** ALLOW TE throughout Correct final answer scores **(4)**		**4**

Question Number	Acceptable Answers	Reject	Mark
14(a)(v)	Starting at pH 2-3 AND finishing at pH between 12 and 13.7 inclusive **(1)** Vertical section at 20 cm^3 **(1)** S-shaped curve, with gradual rise and vertical section within the pH range 5.5 and 11.5 and of 3 to 5 units in length **(1)** These are stand alone marks 		**3**

Question Number	Acceptable Answers	Reject	Mark
14(b)(i)	EITHER [base] = Ka [acid]/[H^+] Or [H+] = ($10^{-pH4.70}$) = 1.995 x 10^{-5} **(1)** [base] = 1.7 x 10^{-5} x 1/(1.995 x 10^{-5}) = 0.852 **(1)** moles base = 0.852 x 0.5 = 0.426 (mol) **(1)** mass base = 0.426 x 82 = 34.9 g **(1)** IGNORE sf except 1 Correct answer, with or without working **(4)** OR pH = p*K*a – log[acid]/[base] 4.70 = 4.8 – log [1/[base]] Log[1/[base]] = 0.1 **(1)** [base] = 0.794(328) (mol dm^{-3}) **(1)** So in 500 cm^3 Moles = 0.794 x 0.5 = 0.397 mol **(1)** Mass = 0.397 x 82 = 32.554/32.6 g **(1)** (ALLOW using p*K*a = 4.77)		**4**

Question Number	Acceptable Answers	Reject	Mark
14(b)(ii)	**First mark** Buffer has large amount/ excess/ reservoir of CH_3COOH (and CH_3COO^-) **(1)** **Second mark** OH^- ions added react with CH_3COOH OR $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ OR $OH^- + H^+ \rightarrow H_2O$ **and** $CH_3COOH \rightarrow CH_3COO^- + H^+$ OR Equations described in words **(1)** **Third mark** Ratio / values of $[CH_3COOH]$ to $[CH_3COO^-]$ remains (almost) unchanged **(1)** IGNORE concentration of hydrogen ions remains constant ALLOW answers in terms of HA and A^-		**3**

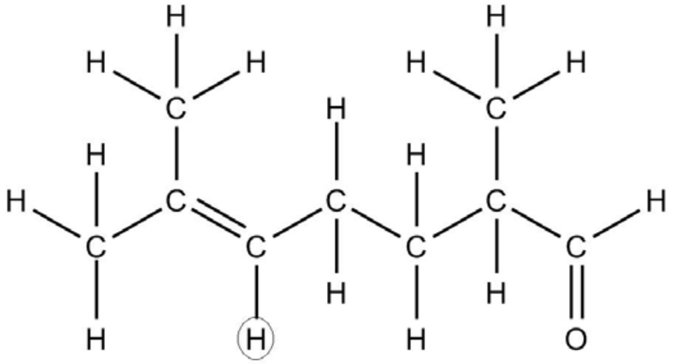
Question Number	Acceptable Answers	Reject	Mark
15(a)	2,6-dimethylhept-5-enal **(2)** Either part scores **(1)** e.g. 2,6-dimethyl **(1)** hept-5-enal **(1)** IGNORE missing/misplaced/misused hyphens or commas ALLOW ene for en ALLOW methy or methly for methyl		**2**

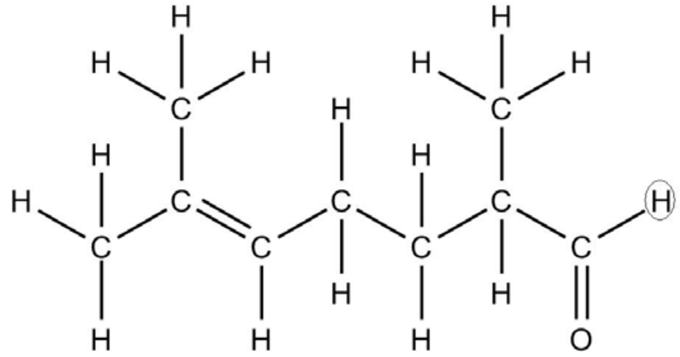
Question Number	Acceptable Answers	Reject	Mark
15(b)(i)	$CH_3C(CH_3)=CHCH_2CH_2CH(CH_3)CH_2OH$ **(1)** OR $CH_3C(CH_3)CHCH_2CH_2CH(CH_3)CH_2OH$ OR $CH_3C(CH_3)=CHCH_2CH_2C\ (CH_3)\ HCH_2OH$ ALLOW displayed or skeletal formulae $K_2Cr_2O_7$/$Na_2Cr_2O_7$/name (oxidation state must be correct if given (VI)) **(1)** This is a stand alone mark H_2SO_4/name (ignore any references to concentration) **(1)** ALLOW H^+ and $Cr_2O_7^{2-}$ **(2)** 'Acidified dichromate' **(1)**	$C_9H_{18}O$ $KMnO_4$ (0) for last 2 marks HCl (0) for 3rd mark	**3**

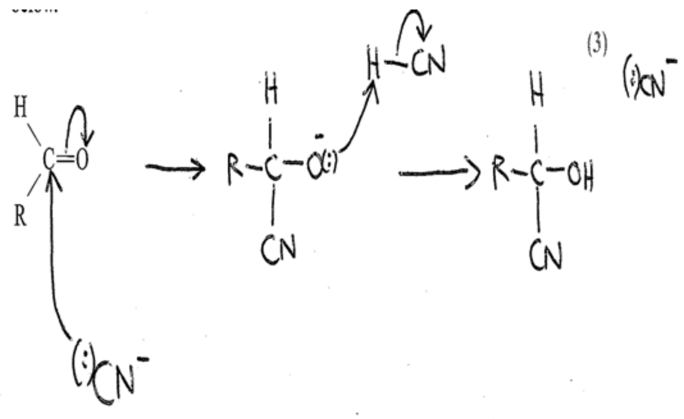
Question Number	Acceptable Answers	Reject	Mark
15(b)(ii)	(Steam) **distil** off melonal (as it forms) Allow add a limited amount of oxidizing agent/excess alcohol/excess X **(1)** To prevent further oxidation/To prevent carboxylic acid forming **(1)** Stand alone marks		**2**

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>15(c)</td><td>
<table>
<tr><th>Wavenumber range / cm^{-1}</th><th>Bond</th><th>Functional group present in melonal</th><th></th></tr>
<tr><td>1740 – 1720
OR
2900 – 2820
/
2775 – 2700</td><td>C=O
C-H</td><td>(saturated) Aldehyde/CHO</td><td>(1)</td></tr>
<tr><td>1669 – 1645
OR
3095 - 3010</td><td>C=C
C-H</td><td>Alkene
ALLOW ‘carbon to carbon double bond’</td><td>(1)</td></tr>
</table>
ALLOW any single value or range within the ranges above
ALLOW one mark if both wavenumber ranges and bond columns are correct but neither bond identified</td><td>Just carbonyl
Just C=C in 3rd column</td><td>2</td></tr>
</table>

Question Number	Acceptable Answers	Reject	Mark
15(d)	$C_3H_5O^+$/CH_3CHCHO^+ **(1)** $C_6H_{11}^+$ **(1)** [ALLOW Structural, skeletal or displayed formulae] Penalise omission of + charge once only ALLOW any order of atoms if correct totals.	$C_4H_9^+$ $C_5H_7O^+$	**2**

Question Number	Acceptable Answers	Reject	Mark
15(e)(i)		Circle around any other additional atoms	**1**

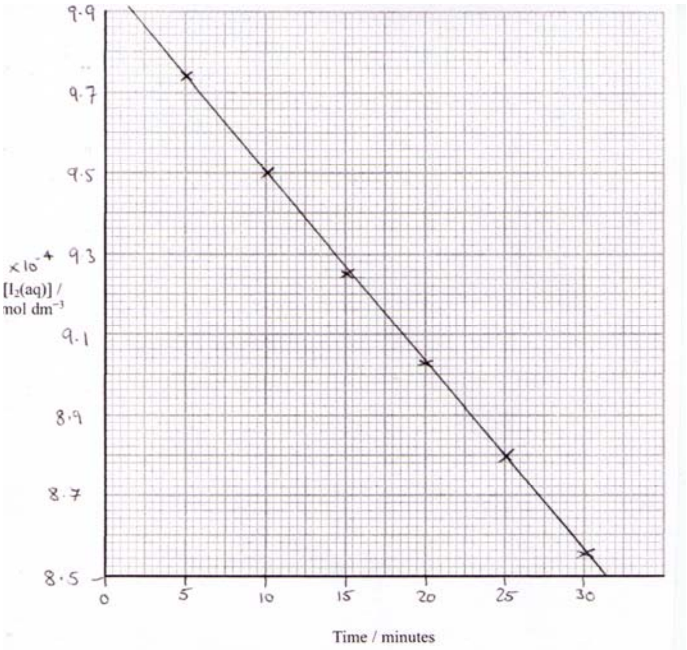
Question Number	Acceptable Answers	Reject	Mark
15(e)(ii)		Circle around any other additional atoms	**1**

Question Number	Acceptable Answers	Reject	Mark
15(f)(i)	 Arrow from anywhere on the cyanide ion to the carbon of the carbonyl. Arrow to the O must come from the carbonyl bond **(1)** Formula of intermediate **(1)** Arrow from oxygen to H and from H-CN bond to CN **(1)** ALLOW arrow from O^- to H^+ or to H_2O	Starting from HCN/ $CN^{\partial-}$ Single headed arrows	**3**

Question Number	Acceptable Answers	Reject	Mark
15(f)(ii)	**These marks are stand alone** **EITHER** No **First mark:** Reaction site/carbonyl/aldehyde/molecule is planar **(1)** **Second mark:** Attack (equally likely) from both sides OR Attack (equally likely) from above and below **(1)** **Third mark:** (gives) racemic mixture/(gives) equal amounts of each isomer/(gives) equal amounts of each enantiomer **(1)** OR Yes Melonal has a chiral carbon atom **(1)** Correct identification of chiral centre **(1)** This chiral centre unaffected by reaction **(1)**	attack on a (planar) carbocation OR attack on a (planar) intermediate OR S_N1 OR S_N2 OR "planar product" Any/either direction or any/either angle	**3**

Question Number	Correct Answer	Reject	Mark
16 (a)(i)	Sodium thiosulfate/$Na_2S_2O_3$ ALLOW $S_2O_3^{2-}$ or thiosulfate ions	Just thiosulfate	**1**

Question Number	Acceptable Answers	Reject	Mark
16(a)(ii)	Add (excess) sodium hydrogencarbonate/ $NaHCO_3$ **(1)** To neutralize/remove/react with acid (catalyst) **(1)** Cool in ice (water) with no reference to neutralization – allow 1 mark but ignore if either of first two marks awarded	NaOH/ sodium hydroxide/ alkali just cold water	**2**

Question Number	Acceptable Answers	Reject	Mark
16(b)(i)	Suitable graph and scale **(1)** Points plotted and line of best fit **(1)** 0 order (with respect to iodine) **(1)** 		**3**

Question Number	Acceptable Answers	Reject	Mark
16(b)(ii)	Graph is a straight line/Gradient is constant **(1)** Rate stays constant (as iodine used up)/ Concentration has no effect on rate **(1)** Stand alone marks	Half life is constant	**2**

Question Number	Acceptable Answers	Reject	Mark
16(c)	Colorimetry/use of pH meter/conductivity/titrate with $AgNO_3$/titrate with alkali (to monitor change in $[H^+]$)	C**a**lorimetry Use of starch/ Iodine clock reaction	**1**

Question Number	Correct Answer	Reject	Mark
17 (a)(i)	Methyl propanoate ALLOW methy or methly for methyl		**1**

Question Number	Acceptable Answers	Reject	Mark
17(a)(ii)	Toxic (steamy/misty) fumes/ toxic HCl(gas)/corrosive HCl(gas)/toxic propanoyl chloride/lachrymatory propanoyl chloride **(1)** So use in a fume cupboard **(1)** OR Corrosive Propanoyl chloride is **(1)** So wear gloves when handling **(1)**	HCl(aq)/ hydrochloric acid Just harmful/irritant Just harmful/irritant	**2**

Question Number	Acceptable Answers	Reject	Mark
17(b)	Table 0.31, 0.16, 1.41 all 3 scores 2, 2 out of 3 scores 1, 1 or 0 out of 3 scores 0 **(2)** $K_c = \frac{(0.21/V) \times (1.41/V)}{(0.16/V) \times (0.31/V)}$ $K_c = 5.969758$ $K_c = 5.97$ **(1)** IGNORE sf except 1 IGNORE any units ALLOW TE from incorrect values in table.		**3**

TOTAL FOR SECTION B = 52 MARKS

Question Number	Correct Answer	Reject	Mark
18(a)	**First mark** Enthalpy change when 1 mol of **gaseous** ions **(1)** ALLOW energy change/heat change/energy evolved/released/ given out/exothermic **Second mark** Is dissolved/hydrated/solvated such that further dilution causes no further heat change OR Is dissolved to produce an infinitely dilute solution/in excess water **(1)** ALLOW Is dissolved to produce a solution of 1.0 mol dm^{-3}	Energy required or energy taken in Atoms or molecules (0) 1 mol of water	**2**

Question Number	Acceptable Answers	Reject	Mark
18(b)(i)	$K^+(aq)$ (+) $F^-(aq)$	K^+ $F^-(aq)$	**1**

Question Number	Acceptable Answers	Reject	Mark
18(b)(ii)	$\Delta H_{sol} = -\Delta H_1 + \Delta H_2$ OR $\Delta H_{sol} = \Delta H_2 - \Delta H_1$		**1**

Question Number	Acceptable Answers	Reject	Mark
18(b)(iii)	(Standard) Lattice(enthalpy/energy/ΔH)	LE/Lat **-** Lattice	**1**

Question Number	Acceptable Answers	Reject	Mark
18(b)(iv)	**First mark** Selection of (-)817 rather than (-)807 **(1)** **Second mark** ΔH_{sol} = 817 – 805 = (+)12 (kJ mol^{-1}) **(1)** Just (+)12 (kJ mol^{-1}) **(2)** ALLOW TE for second mark e.g. for 807 gives (+) 2 (kJ mol^{-1}) ALLOW TE from incorrect b(ii)	-12 (max 1)	**2**

Question Number	Acceptable Answers	Reject	Mark
18(c)(i)	EITHER No change/no measurable change in temperature OR (Very small) decrease in temperature **(1)** Thermometer not sensitive/precise enough/precision of thermometer is + or - 0.5 ^{o}C/graduations too large **(1)** Amount of energy taken in is small /ΔH_{sol} is small/mass of sodium chloride is small/slightly endothermic **(1)**	Any reference to temp increase /exothermic Just accuracy +/- 1 ^{o}C	**3**

Question Number	Acceptable Answers	Reject	Mark
***18(c)(ii)**	(The reaction is endothermic so) Entropy(change) of surroundings decreases OR ΔS_{sur} is negative OR -$\Delta H/T$ is negative **(1)** But entropy (change)of system increases (as there is an increase in disorder) OR ΔS_{sys} is positive **(1)** Increase in entropy of system outweighs/greater than decrease in entropy of surroundings / value for entropy change of system is greater than entropy change of surroundings **(1)** Total entropy (change) is positive **(1)** All marks are stand alone	S_{sur} is negative S_{sys} is positive	**4**

Question Number	Acceptable Answers	Reject	Mark
***18(d)**	Any four from: The difference between Born Haber and theoretical LE is greater for LiI than for LiCl **(1)** (845 and 848 =) 3 for LiCl whereas (738 and 759 =) 21 for LiI **(1)** Iodide ion is larger than chloride ion/lower charge density on iodide ion **(1)** The iodide ion is more likely (than the chloride ion) to be polarized (by lithium ion) **(1)** LiI likely to have more covalent character than LiCl **(1)**	Reject values with + Iodine/Chlorine atoms or molecules Iodine/Chlorine atoms or molecules	**4**

TOTAL FOR SECTION C = 18 MARKS

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Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Monday 14 January 2013 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

P41214A

7/6/5/5/4/

P 4 1 2 1 4 A 0 1 2 8

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 Methods for investigating reaction rates include

A colorimetry

B collecting and measuring the volume of a gas

C quenching, followed by titration with acid

D quenching, followed by titration with iodine solution.

Which method would be most suitable to investigate the rate of the following reactions?

(a) $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $C_4H_9Br(l) + OH^-(aq) \rightarrow C_4H_9OH(l) + Br^-(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 1 = 2 marks)

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

2 For a given initial reactant pressure, the half-life for a first order gaseous reaction was found to be 30 minutes.

If the experiment were repeated at half the initial reactant pressure, the half-life would be

☒ **A** 15 minutes.

☒ **B** 30 minutes.

☒ **C** 45 minutes.

☒ **D** 60 minutes.

(Total for Question 2 = 1 mark)

---

3 To determine the activation energy (E_a) for a reaction, the variation of reaction rate with temperature is investigated.

The rate constant, *k*, for the reaction is related to the absolute temperature, T, by the expression

$$\ln k = -\frac{E_a}{R} \times \left(\frac{1}{\mathrm{T}}\right) + \text{constant}$$

where *R* is the gas constant.

The activation energy for the reaction could be obtained by plotting a graph of

		vertical axis	**horizontal axis**
☒	**A**	k	T
☒	**B**	k	$\frac{1}{\mathrm{T}}$
☒	**C**	$\ln k$	T
☒	**D**	$\ln k$	$\frac{1}{\mathrm{T}}$

(Total for Question 3 = 1 mark)

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

4 Energy is evolved when one mole of gaseous calcium ions is hydrated.

$$Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq)$$

This reaction is more exothermic than the corresponding value for barium ions, Ba^{2+}, because the

☒ **A** ionization energy of calcium is greater than that of barium.

☒ **B** lattice energy of calcium oxide is more exothermic than that of barium oxide.

☒ **C** solubility of calcium hydroxide in water is less than that of barium hydroxide.

☒ **D** ionic radius of Ca^{2+} is less than that of Ba^{2+}.

(Total for Question 4 = 1 mark)

5 The following cycle represents the enthalpy changes **w**, **x**, **y** and **z**, occurring when an ionic solute, $AX_2(s)$, dissolves in water.

$$\begin{tikzcd} & A^{2+}(g) + 2X^{-}(g) \arrow[d, "\mathbf{x} + \mathbf{y}"] \\ AX_2(s) \arrow[ur, "\mathbf{w}"] \arrow[r, "\mathbf{z}"'] & A^{2+}(aq) + 2X^{-}(aq) \end{tikzcd}$$

Which of the changes is the lattice energy of $AX_2(s)$?

☒ **A** ½ **w**

☒ **B** − **w**

☒ **C** **z**

☒ **D** **z** − **x** − **y**

(Total for Question 5 = 1 mark)

6 The equation for the synthesis of methanol is

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, when the temperature is 340 K, the total pressure is 20 atm. The moles of each component present at equilibrium are shown in the table below.

Formula	Equilibrium moles / mol	Mole fraction
CO	0.15	0.23
H_2	0.32	
CH_3OH	0.18	0.28

(a) The mole fraction of hydrogen in the equilibrium mixture is

(1)

☒ **A** 0.23

☒ **B** 0.46

☒ **C** 0.49

☒ **D** 0.92

(b) The numerical value for the equilibrium partial pressure of the carbon monoxide, in atmospheres, is

(1)

☒ **A** 3.0

☒ **B** 4.6

☒ **C** 5.0

☒ **D** 9.2

(c) Units for the equilibrium constant, K_p, for this reaction are

(1)

☒ **A** no units

☒ **B** atm

☒ **C** atm^{-1}

☒ **D** atm^{-2}

(Total for Question 6 = 3 marks)

7 An aqueous solution of ammonium chloride, NH_4Cl, has a pH of less than 7 because

☒ **A** the ammonium ions donate protons to water molecules giving rise to oxonium ions, $H_3O^+(aq)$.

☒ **B** the chloride ions combine with hydrogen ions from water to form hydrochloric acid, HCl(aq).

☒ **C** an aqueous solution of ammonium chloride is unstable and evolves ammonia gas, $NH_3(g)$, leaving dilute hydrochloric acid.

☒ **D** the ammonium chloride reacts with carbon dioxide from the atmosphere giving ammonium carbonate, $(NH_4)_2CO_3(aq)$, and hydrochloric acid, HCl(aq).

(Total for Question 7 = 1 mark)

8 Which one of the following indicators is most suitable for titrating ethanoic acid with 0.1 mol dm^{-3} sodium hydroxide?

(Refer to page 19 of your data booklet.)

☒ **A** Thymol blue (acid)

☒ **B** Bromothymol blue

☒ **C** Thymol blue (base)

☒ **D** Alizarin yellow R

(Total for Question 8 = 1 mark)

9 What is the conjugate base of the acid, HCO_3^-?

☒ **A** H_2CO_3

☒ **B** CO_3^{2-}

☒ **C** OH^-

☒ **D** CO_2

(Total for Question 9 = 1 mark)

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

10 What is the approximate pH of a buffer solution containing 0.20 mol of a weak acid, HA, ($pK_a = 4.8$) and 0.20 mol of the sodium salt of the acid, NaA, in a total volume of 1 dm^3 of solution?

☒ **A** 7.0

☒ **B** 5.8

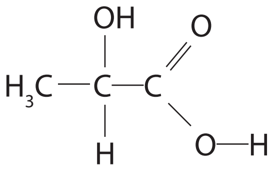
☒ **C** 4.8

☒ **D** 3.8

(Total for Question 10 = 1 mark)

---

11 Ethanal, CH_3CHO, can be converted by a two-step synthesis into 2-hydroxypropanoic acid.



2-hydroxypropanoic acid

The reagents and conditions are

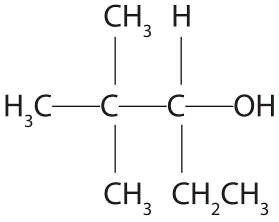
	1st step	**2nd step**
☒ **A**	$Na_2Cr_2O_7$ and dilute H_2SO_4, heat under reflux	NaOH(aq), heat under reflux
☒ **B**	Cl_2, UV light	NaOH(aq), heat under reflux
☒ **C**	$LiAlH_4$ in dry ether	CO_2, room temperature
☒ **D**	HCN, in presence of KCN(aq)	dilute HCl(aq), heat under reflux

(Total for Question 11 = 1 mark)

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

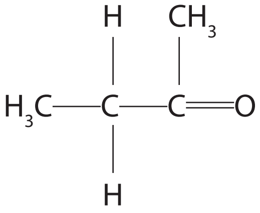
12 Questions (a) to (d) concern the following organic compounds.

Compound A



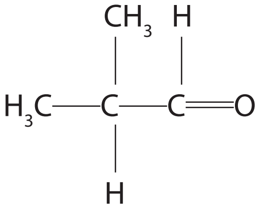
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_2CH_3}{C}}-OH$

Compound B



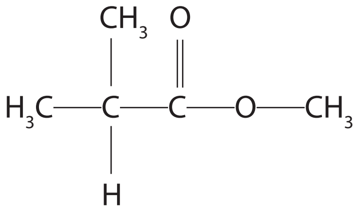
$H_3C-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=O$

Compound C



$H_3C-\overset{CH_3}{\underset{H}{C}}-\overset{H}{C}=O$

Compound D



$H_3C-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_3$

Select from **A** to **D** the compound that

(a) forms iodoform with iodine in the presence of alkali.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) is chiral.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) reacts with Tollens' reagent.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) can be oxidized to form a ketone.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 12 = 4 marks)

13 Ethanoic acid, CH_3COOH, can be converted into ethanoyl chloride, CH_3COCl, by the action of

☒ **A** phosphorus(V) chloride.

☒ **B** chlorine.

☒ **C** dilute hydrochloric acid.

☒ **D** concentrated hydrochloric acid.

(Total for Question 13 = 1 mark)

14 A compound, **Q**, gives an orange precipitate with 2,4-dinitrophenylhydrazine.
Compound **Q** is resistant to oxidation.
On reduction, **Q** gives a product made up of a pair of optical isomers.

Which of the following compounds could be compound **Q**?

☒ **A** $CH_3CH_2CH_2COCH_3$

☒ **B** $CH_3CH{=}CHCH(OH)CH_3$

☒ **C** $CH_3CH_2CH_2CH_2CHO$

☒ **D** $CH_3CH_2COCH_2CH_3$

(Total for Question 14 = 1 mark)

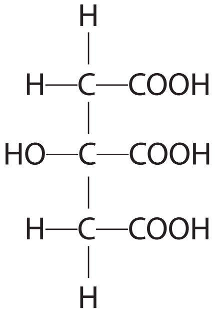
TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 Citric acid is found in lemon juice.

The structure and formula of citric acid are shown below.



$\mathbf{C_6H_8O_7}$

(a) In the presence of a small amount of moisture, citric acid reacts with sodium hydrogencarbonate as shown in the equation below.

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

Use the structural formula of citric acid to explain why one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

(1)

(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

....

....

....

....

(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, for this reaction at 298 K.

(1)

(v) What does the sign of $\Delta S^{\ominus}_{\text{total}}$ suggest about this reaction at 298 K?

(1)

....

....

(Total for Question 15 = 9 marks)

16 Methanoic acid, HCOOH, is present in ant stings.

A scientist analyzed 25.0 cm^3 of an aqueous solution of methanoic acid, solution **Z**, by titrating it with dilute sodium hydroxide, NaOH(aq).

- 20.0 cm^3 of sodium hydroxide was required to neutralize the methanoic acid
- The equation for the neutralization of methanoic acid is

$$\text{HCOOH(aq)} + \text{NaOH(aq)} \rightarrow \text{HCOONa(aq)} + \text{H}_2\text{O(l)}$$

(a) (i) Give the expression for K_w, the ionic product of water.

(1)

(ii) The concentration of the sodium hydroxide, NaOH(aq), used in the titration was 0.00750 mol dm^{-3}.

Calculate the pH of the sodium hydroxide solution.

[K_w = 1.00 x 10^{-14} mol^2 dm^{-6}]

(2)

(b) Use the equation for the reaction and the data from the titration to show that the concentration of the methanoic acid in solution **Z** was 6.00 × 10^{-3} mol dm^{-3}.

(2)

(c) Methanoic acid is a weak acid.

(i) Explain the term **weak acid**.

(2)

Weak ....

....

Acid..

....

(ii) The equation for the dissociation of methanoic acid in aqueous solution is shown below.

$$HCOOH(aq) \rightleftharpoons HCOO^{-}(aq) + H^{+}(aq)$$

Write the expression for the acid dissociation constant, K_a, for methanoic acid.

(1)

*(iii) At 298 K, the acid in ant stings has a concentration of 6.00×10^{-3} mol dm^{-3} and a pH of 3.01.

Calculate the value of K_a for methanoic acid at 298 K.

State clearly any assumptions that you have made.

(4)

Calculation:

Assumption(s):

....

....

....

....

(Total for Question 16 = 12 marks)

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20			

(iii) Explain why K_c for this reaction has no units.

(1)

....

....

(iv) Calculate the numerical value of K_c.

(1)

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:

Bonds made:

(ii) Explain why ΔH for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, K, of a reaction.

(1)

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

(e) An alternative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

(i) Give the equation for the reaction.

(1)

(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)

(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 \ + \ NaOH \ \rightarrow$

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

(Total for Question 17 = 19 marks)

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18 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

....

....

....

$Br^-(aq)$

....

....

....

....

(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

(Total for Question 18 = 12 marks)

TOTAL FOR SECTION B = 52 MARKS

SECTION C

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

19 An organic compound, **X**, was analyzed in a laboratory.

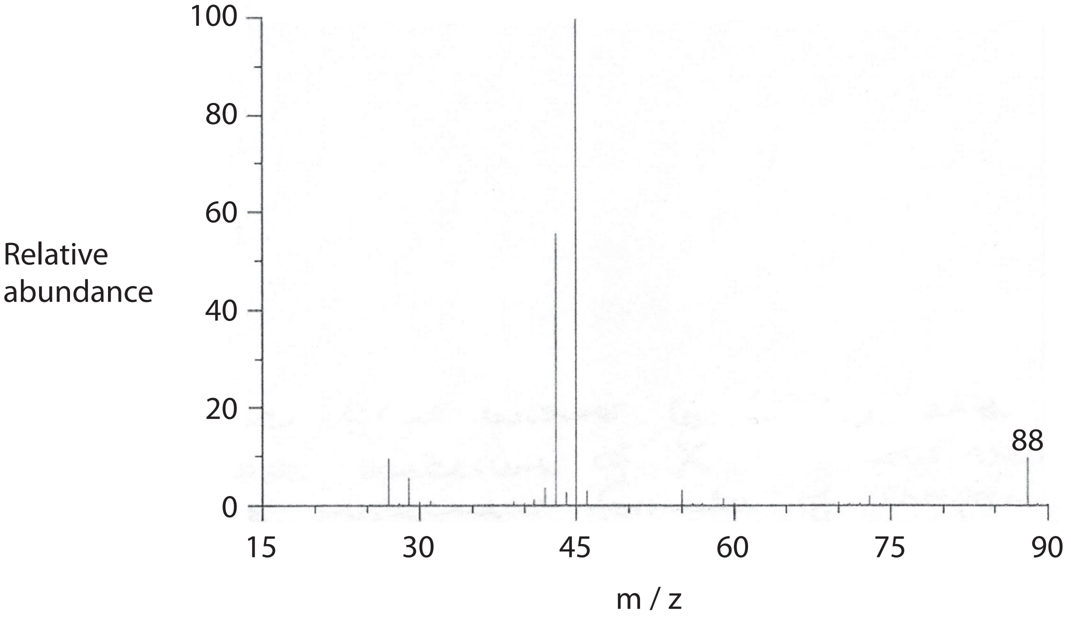
(a) Compound **X** was found to have the following percentage composition by mass:

carbon, C = 54.5%
hydrogen, H = 9.1%
oxygen, O = 36.4%

(i) Use these data to calculate the empirical formula of compound **X**, showing your working.

(2)

(ii) The mass spectrum of **X** is shown below.



Use your answer to (a)(i), and the mass spectrum of **X**, to show that the molecular formula of compound **X** is $C_4H_8O_2$.

(2)

(b) The infrared spectrum of **X** has a broad peak at approximately 3500 cm^{-1} and a sharp peak at approximately 1700 cm^{-1}. Identify the **bond** responsible for the peak at

(2)

3500 cm^{-1}

1700 cm^{-1}

(c) (i) Some chemical information about compound **X** is given below.

- **X** is a neutral organic compound.
- **X** has no effect on Tollens' reagent.
- **X** turns hot acidified potassium dichromate(VI) solution from orange to green.

What does each of these three pieces of information suggest about the nature of **X**?

(4)

....

....

....

....

....

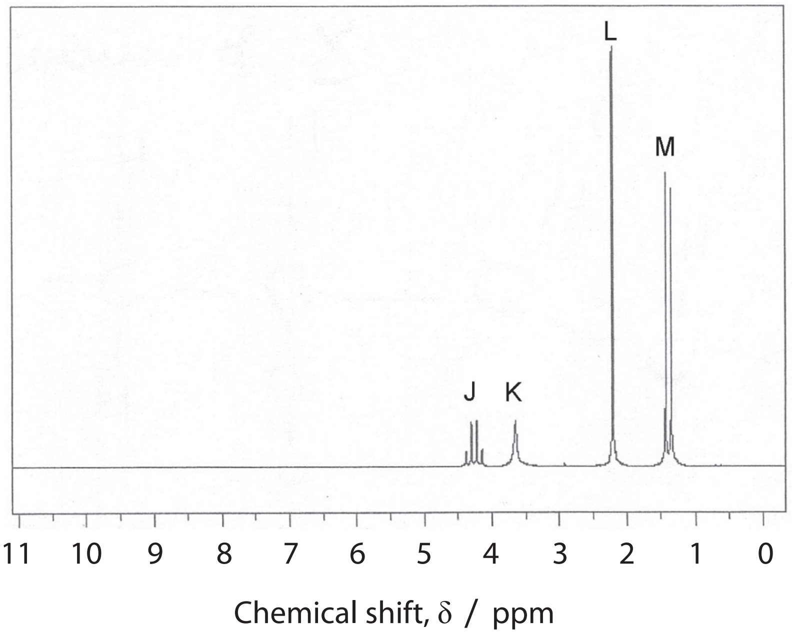
....

(ii) Use your answers to parts (b) and (c)(i) to name the two functional groups present in **X**.

(1)

....

*(d) The high resolution proton nmr spectrum of **X** is shown below.



The relative number of protons causing the peaks shown are: J = 1, K = 1, L = 3 and M = 3.

Use the information above to determine the structural formula of **X**.

In your answer, you should refer to the number of peaks, their relative sizes and their splitting patterns.

(7)

(Total for Question 19 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	*(18)*
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)

January 2013

GCE Chemistry (6CH04) Paper 01

General Principles of Chemistry I Rates, Equilibria and Further Organic Chemistry

January 2013
Publications Code US034336

General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. The strands are as follows:

  i) ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
  ii) select and use a form and style of writing appropriate to purpose and to complex subject matter
  iii) organise information clearly and coherently, using specialist vocabulary when appropriate

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication
Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A

Question Number	Correct Answer	Mark
1(a)	A	**1**

Question Number	Correct Answer	Mark
1(b)	C	**1**

Question Number	Correct Answer	Mark
2	B	**1**

Question Number	Correct Answer	Mark
3	D	**1**

Question Number	Correct Answer	Mark
4	D	**1**

Question Number	Correct Answer	Mark
5	B	**1**

Question Number	Correct Answer	Mark
6(a)	C	**1**

Question Number	Correct Answer	Mark
6(b)	B	**1**

Question Number	Correct Answer	Mark
6(c)	D	**1**

Question Number	Correct Answer	Mark
7	A	**1**

Question Number	Correct Answer	Mark
8	C	**1**

Question Number	Correct Answer	Mark
9	B	**1**

Question Number	Correct Answer	Mark
10	C	**1**

Question Number	Correct Answer	Mark
11	D	**1**

Question Number	Correct Answer	Mark
12(a)	B	**1**

Question Number	Correct Answer	Mark
12(b)	A	**1**

Question Number	Correct Answer	Mark
12(c)	C	**1**

Question Number	Correct Answer	Mark
12(d)	A	**1**

Question Number	Correct Answer	Mark
13	A	**1**

Question Number	Correct Answer	Mark
14	A	**1**

Section B

Question Number	Acceptable Answers	Reject	Mark
15(a)	(It has) three (moles of) COOH groups / three (moles of) carboxylic acid groups / three (moles of) protons /three (moles of) H^+ /it is tribasic / three acid groups/ three (moles of) replaceable hydrogens/triprotic ALLOW Three acid groups	'carbonyl'/'carboxylate'	**1**

Question Number	Acceptable Answers	Reject	Mark
15(b)(i)	**FIRST, CHECK THE FINAL ANSWER** **IF** answer = **+**546 (J mol^{-1} K^{-1}) award **2** marks "546" (J mol^{-1} K^{-1}) scores **(1)** as sign omitted) ($\Delta S^{\ominus}_{system}$ =)[200.5 + (3 x 213.6) + (3 x 69.9)] − [199.9 + (3 x 101.7)] **(1)** = [+1051] − [+ 505] = **+**546 (J mol^{-1} K^{-1}) **(1)** Allow **+** 0.546 **kJ mol^{-1} K^{-1}** 2nd mark is CQ on entropy values used for example EITHER Omission of factor of x3 for some or all substances in the equation OR The use of one incorrect entropy value(s) from the data book OR One missing value Note If two or more of the above three errors are made together, (0) awarded. **IGNORE** sf except 1 sf	**Incorrect** units (no 2nd mark)	**2**

Question Number	Acceptable Answers	Reject	Mark
15(b)(ii)	**First mark** Gas formed (from solid) OR Liquid formed (from solid) OR Gas and liquid formed (from solid) **(1)** **Second mark** EITHER More moles of product than reactants / more moles formed OR 4 mol (of reactants) to 7 mol (of products) OR 4 'molecules' to 7 'molecules' NOTE: If specific numbers are stated, these must be correct (ie 4→7) OR Increase in disorder / increase in ways of arranging particles **(1)** IGNORE 'entropy increases' **NOTE:** Both points may be made in the same sentence	**Just** 'more product' / 'more particles formed' 2 substances going to 3 substances	**2**

Question Number	Acceptable Answers	Reject	Mark
15(b)(iii)	($\Delta S^{\ominus}_{\text{surroundings}}$ =) $\frac{-\Delta H}{T}$ OR $\frac{-70000}{298}$ **(1)** = −234.8993289 = **−235 J mol^{-1} K^{-1}** **(1)** OR ($\Delta S^{\ominus}_{\text{surroundings}}$ =) $\frac{-\Delta H}{T}$ OR $\frac{-70}{298}$ **(1)** = **− 0.235 kJ mol^{-1} K^{-1}** **(1)** **IGNORE** sf except 1 sf **NOTE***:* Correct units are required for the award of the second mark +235 with units scores **(1)**	Incorrect rounding (e.g. −234 / −234.89) no 2nd mark +235 with no units **(0)** overall	**2**

Question Number	Acceptable Answers	Reject	Mark
15(b)(iv)	($\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}}$) $= (+546) + (-235)$ $= (+)311$ (J mol^{-1} K^{-1}) OR $= (+)0.311$ **kJ mol^{-1} K^{-1}** CQ on (i) and (iii) **IGNORE** sf except 1 sf	Incorrect units	**1**

Question Number	Acceptable Answers	Reject	Mark
15(b)(v)	Positive so feasible / spontaneous / will occur / reaction goes / reacts (at 298 K) **NOTE:** **LOOK BACK** at answer to (b)(iv) **IF** answer to (b)(iv) has a positive sign (the + sign can be **stated** or **implied**) **THEN ALLOW JUST** feasible / spontaneous / will occur / reaction goes / reacts (at 298 K) **Mark CQ on sign of answer to (iv)**		**1**

(Total 9 marks)

Question Number	Acceptable Answers	Reject	Mark
16(a)(i)	$K_w = [H^+] \times [OH^-]$ OR $K_w = [H_3O^+] \times [OH^-]$ State symbols are not required IGNORE any incorrect state symbols	Inclusion of $[H_2O]$	**1**

Question Number	Acceptable Answers	Reject	Mark
16(a)(ii)	**FIRST, CHECK THE FINAL ANSWER** **IF** answer pH = 11.875 / 11.88 / 11.9 /12 award **2** marks **IGNORE** sf except 1 sf $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.00750}$ $= 1.3333 \times 10^{-12}$ $= 1.33 \times 10^{-12}$ **(1)** (mol dm^{-3}) **ALLOW** first mark for just $[H^+] = \frac{K_w}{[OH^-]}$ $\text{pH} = -\log_{10}[H^+] = 11.875$ $= 11.88 / 11.9$ **(1)** OR $\text{pOH} = -\log_{10}[OH^-] = 2.12$ **(1)** $\text{pH} = \text{p}K_w - \text{pOH}$ $\text{pH} = 11.88 / 11.9$ **(1)** Second mark only awarded CQ if pH between 8 and 14		**2**

Question Number	Acceptable Answers	Reject	Mark
16(b)	**First mark** Moles NaOH = $\frac{0.00750 \text{ x } 20.0}{1000}$ = $1.50 \text{ x } 10^{-4}$ (mol) **(1)** (Since HCOOH : NaOH ratio is 1:1) **Second mark** [HCOOH(aq)] = $\frac{1.50 \text{ x } 10^{-4}}{0.0250}$ **OR** = $1.50 \text{ x } 10^{-4} \text{ x } \frac{1000}{25.0}$ **(1)** (= $6.00 \text{ x } 10^{-3}$ mol dm^{-3}) **ALTERNATIVE APPROACH:** Use of an expression such as 0.00750 x 20.0 = 25 x **y** **(1)** **y** = $\frac{0.00750 \text{ x } 20.0}{25}$ **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
16(c)(i)	**(Weak)** dissociates / ionizes to a small extent **OR** dissociate / ionizes partially **OR** dissociates / ionizes incompletely **OR** does not fully dissociate / ionize **OR** forms an equilibrium when reacted with water **(1)** **(Acid)** proton donor ALLOW 'proton donator' **OR** produces / releases H^+ ions **OR** produces / releases H_3O^+ ions **(1)** Ignore reference to typical acid reactions	'not easily dissociated'	**2**

Question Number	Acceptable Answers	Reject	Mark
16(c)(ii)	(K_a =) $\frac{[HCOO^-]\,[H^+]}{[HCOOH]}$ State symbols are NOT required IGNORE any incorrect state symbols	(K_a =) $\frac{[H^+]^2}{[HCOOH]}$ Inclusion of $[H_2O]$	**1**

Question Number	Acceptable Answers	Reject	Mark
16(c)(iii)	**IGNORE** sf except 1 sf THROUGHOUT **FIRST, CHECK THE FINAL ANSWER** **IF** answer $K_a = 1.59 \times 10^{-4}$ (mol dm^{-3}) award the first two **2** marks $[H^+]$ (= 10^{-pH} = $10^{-3.01}$) = 9.77×10^{-4} (mol dm^{-3}) **(1)** $K_a = \frac{[H^+]^2}{[HCOOH]}$ $K_a = \frac{(9.77 \times 10^{-4})^2}{6.00 \times 10^{-3}}$ = 1.59×10^{-4} (mol dm^{-3}) **(1)** **Assumption 1** $[H^+] = [HCOO^-]$ **OR** no H^+ from the (ionization of) water **OR** H^+ only from the acid **(1)** **Assumption 2** Ionization of the (weak) acid is negligible / very small / insignificant **OR** $[HCOOH]_{initial} - x = [HCOOH]_{eqm}$ **OR** $[HCOOH]_{eqm} = [HCOOH]_{initial}$ **OR** $[HCOOH]_{eqm} = 6.00 \times 10^{-3}$ (mol dm^{-3}) **OR** $[H^+] << [HA]$ **(1)** **Assumptions can be in either order**	If incorrect units max 1 **Just** 'partial' / 'incomplete' **Or** ' no dissociation'	**4**

16(c)(iii) cont'd	**OR** $[H^+]$ (= 10^{-pH} = $10^{-3.01}$) = 9.77×10^{-4} (mol dm^{-3}) **(1)** $K_a = \frac{[H^+]^2}{[HCOOH]}$ $K_a = \frac{(9.77 \times 10^{-4})^2}{(6.00 \times 10^{-3} - 9.77 \times 10^{-4})}$ **(1)** = 1.90×10^{-4} (mol dm^{-3}) **(1)** **Assumption** $[H^+] = [HCOO^-]$ **OR** no $[H^+]$ from the (ionization of) water **OR** H^+ only from the acid **(1)** Ignore references to constant temperature		

(Total 12 marks)

Question Number	Acceptable Answers	Reject	Mark
17(a)(i)	(K_C =) $\frac{[CH_3COOCH_2CH_3]\ [H_2O]}{[CH_3COOH]\ [CH_3CH_2OH]}$ ALLOW C_2H_5 for CH_3CH_2 State symbols are not required IGNORE any incorrect state symbols		**1**

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>17(a)(ii)</td><td colspan="2">
<table>
<tr><td>Component</td><td>$CH_3COOH(l)$</td><td>$CH_3CH_2OH(l)$</td><td>$CH_3COOCH_2CH_3(l)$</td><td>$H_2O(l)$</td></tr>
<tr><td>Equilibrium amount / mol</td><td>(0.20)</td><td>0.10</td><td>0.20</td><td>0.35</td></tr>
</table>
BOTH 0.10 AND 0.20 (1) 0.35 (1)
0.10 and 0.20 scores first mark
Allow 0.1 and 0.2
0.35 scores second mark</td><td>2</td></tr>
</table>

Question Number	Acceptable Answers	Reject	Mark
17(a)(iii)	Units cancel **OR** same number of **moles**/same number of **molecules** on each side **OR** volume / V cancels Ignore statements such as 'concentrations cancel' 'products and reactants cancel' 'same number of products as reactants'	Concentrations are the same	**1**

Question Number	Acceptable Answers	Reject	Mark
17(a)(iv)	$K_C = \frac{(0.20)/V \text{ x } (0.35)/V}{(0.20)/V \text{ x } (0.10)/V}$ = 3.5 / 3.50 Correct answer with or without working scores 1 Ignore omission of V TE from values in (ii) table	K_C = 4	**1**

Question Number	Acceptable Answers	Reject	Mark
17(b)	• No effect on (position of) equilibrium **(1)** • Rate (of attainment of equilibrium) is faster / equilibrium reached sooner **(1)**		**2**

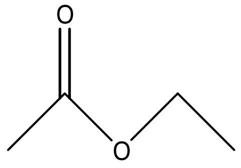
Question Number	Acceptable Answers	Reject	Mark
17(c)(i)	**Bonds Broken** C—O **and** O—H **(1)** Ignore where these bonds are broken in the acid and alcohol molecules. **ALLOW** C—OH for C—O CO−H for O—H **Bonds Made** C—O **and** O—H **(1)** Ignore where these bonds are made in the ester and water molecules. **ALLOW** C—OC for C—O H—OH for O−H Marks can be awarded by annotating displayed or structural formulae. Comment: Max **1** if any other bonds mentioned	**Two** O—H bonds formed in H_2O molecule **ONLY** C—O bond broken and made scores **(0)** overall	**2**

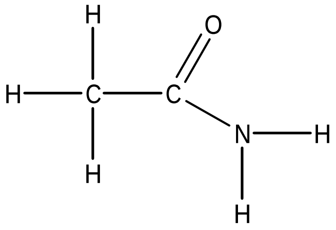
Question Number	Acceptable Answers	Reject	Mark
17(c)(ii)	(C−O and O−H) bond enthalpies differ in: different environments /different molecules /different compounds OR Bond enthalpies/bond energies are average values **ALLOW** Bonds being broken and made are attached to different atoms	'Heat loss'	**1**

Question Number	Acceptable Answers	Reject	Mark
17(d)(i)	$\Delta S_{\text{total}} = R \ln K$ Allow ΔS_{total} is proportional to **<u>ln</u>**K ALLOW K_c or K_p instead of K	log instead of ln ΔS_{total} is proportional to K / ΔS_{total} increases as K increases	**1**

Question Number	Acceptable Answers	Reject	Mark
***17(d)(ii)**	**First mark:** (ΔH = 0 so) $\Delta S_{\text{surroundings}} = 0$ OR $-\dfrac{\Delta H}{T} = 0$ **(1)** IGNORE "$\Delta S_{\text{surroundings}}$ stays the same". **Second mark:** (so) ΔS_{total} does not change OR (so) $\Delta S_{\text{total}} = \Delta S_{\text{system}}$ **(1)** **Third mark:** (As $\Delta S_{\text{total}} = R \ln K$) ***K*** does not alter **(1)** **ALLOW** "it does not alter" to assume *K* does not alter. ALLOW use of K_c or K_p instead of *K* **Each point is stand alone** **IGNORE** justifications in terms of Le Chatelier's Principle **NOTE:** **Can award max (1) (i.e. the third scoring point) if the effect on *K* stated follows on CQ from a change to ΔS_{total}**	If only mentions 'no effect on position of equilibrium' rather than the equilibrium constant	**3**

Question Number	Acceptable Answers	Reject	Mark
17(e)(i)	$CH_3COCl + CH_3CH_2OH \rightarrow$ $CH_3COOCH_2CH_3 +$ HCl Allow C_2H_5 for CH_3CH_2 Allow $CH_3CO_2CH_2CH_3$ for $CH_3COOCH_2CH_3$ IGNORE missing or incorrect state symbols	CH_3CClO/ CH_2CH_3OH	**1**

Question Number	Acceptable Answers	Reject	Mark
17(e)(ii)	 **IGNORE** Bond angles and length of the lines.		**1**

Question Number	Acceptable Answers	Reject	Mark
17(e)(iii)	 **IGNORE** Other products of the reaction if the above structure has been correctly drawn.	NH_2 or CH_3	**1**

Question Number	Acceptable Answers	Reject	Mark
17(f)(i)	($CH_3COOCH_2CH_3$ + NaOH →) $CH_3COONa + CH_3CH_2OH$ /C_2H_5OH Allow ionic representations of the sodium salt $CH_3COO^-Na^+$ IGNORE missing or incorrect state symbols	CH_2CH_3OH for ethanol	**1**

Question Number	Acceptable Answers	Reject	Mark
17(f)(ii)	(Reaction with sodium hydroxide is) **not** an equilibrium / **not** reversible / goes to completion OR Reverse argument for acid hydrolysis		**1**

(Total 19 marks)

Question Number	Acceptable Answers	Reject	Mark
18(a)(i)	• In experiments 1 and 2, $[H^+]$ doubles (whilst keeping other concentrations constant) **and** the rate quadruples / rate increases x 4 **(1)** • Second order (with respect to H^+) **(1)** • In experiments 1 and 3, $[Br^-]$ doubles **and** $[BrO_3^-]$ triples (with $[H^+]$ constant) **(1)** • Rate increases by 3 x 2 / rate increases x 6 / rate increases to 5.04×10^{-5} (then to 1.01×10^{-4} stated or implied) **(1)** • First order with respect to Br^- **(1)** **OR** • In experiments 2 and 3,$[Br^-]$ doubles **and** $[BrO_3^-]$ triples **and** $[H^+]$ halves **(1)** • Rate increases by 3 x 0.25 x 2 / rate increases x 1.5 **(1)** • First order with respect to Br^- **(1)** **Penalise OMISSION of Experiment Numbers once only** **Mark each point independently**		**5**

Question Number	Acceptable Answers	Reject	Mark
18(a)(ii)	Rate = $k\ [BrO^-{}_3]\ [Br^-]\ [H^+]^2$ Mark CQ on (a)(i) Allow "r" or "R" for "rate" in the rate equation. **IGNORE** If *k* appears to be in upper case.		**1**

Question Number	Acceptable Answers	Reject	Mark
18(a)(iii)	**IGNORE** sf except 1 sf THROUGHOUT **FIRST, CHECK THE FINAL ANSWER** **IF** answer $k = 1.49 \text{ x } 10^{-2}$ **$dm^9\ mol^{-3}\ s^{-1}$** award **(3)** marks $k = \frac{\text{rate}}{[BrO^-{}_3]\ [Br^-]\ [H^+]^2}$ $= \frac{1.68 \text{ x } 10^{-5}}{0.05 \text{ x } 0.25 \text{ x } (0.30)^2}$ **(1)** $= 0.014933333$ $= 0.0149$ **(1)** **$dm^9\ mol^{-3}\ s^{-1}$ / $mol^{-3}\ dm^9\ s^{-1}$** **(1)** **IGNORE** sf except 1 sf Mark CQ from (a)(ii) or, if no rate equation in (a)(ii), then any rate equation stated in (a)(iii) **NOTE:** **IF** the rate equation in (a)(ii) is given as Rate = $k\ [BrO^-{}_3]\ [H^+]^2$ CQ $k = 3.73 \text{ x } 10^{-3}\ dm^6\ mol^{-2}\ s^{-1}$ scores **(3)** **IF** $[H^+]$ is not squared in the correct rate equation: $k = 4.48 \text{ x} 10^{-3}\ dm^9\ mol^{-3}\ s^{-1}$ OR $k = 4.48 \text{ x} 10^{-3}\ dm^6\ mol^{-2}\ s^{-1}$ scores **(2)** **ALLOW** Correct answers derived from the data in the table for Experiment 2 or Experiment 3		**3**

Question Number	Acceptable Answers	Reject	Mark
18(b)	The number(s) (of particles) in the rate equation / rate-determining step do not match those in the equation for the reaction **OR** The chance of (simultaneous) collision of 12 particles is unlikely **OR** The chance of (simultaneous) collision of 4 particles is unlikely **OR** The chance of (simultaneous) collision of 3 reactants is unlikely **ALLOW** 'molecules' / 'substances' for 'particles' ***NOTE*** **ALLOW AS A CQ from (a)(ii)** Br^- ions not in rate equation / Br^- ions not in rate-determining step / Zero order with respect to Br^- / (Only) two reactants in the rate-determining step / (only) two reactants in the rate-equation/ particles are in the equation (for the reaction) that are not in the rate equation		**1**

Question Number	Acceptable Answers	Reject	Mark
18(c)	**REMEMBER TO SCROLL DOWN BELOW THE SPACE LEFT FOR A SKETCH-GRAPH TO SEE WHAT CANDIDATE HAS WRITTEN ON THE DOTTED LINES** • (Calculate) gradient (of tangent) **(1)** **ALLOW** 'slope' for 'gradient' • At t = 0 / at the start / at the beginning / when reaction is at its fastest / at the origin **(1)** **Each mark is stand-alone** **NOTE:** Answer may be annotated on a suitable sketch-graph **IGNORE** any sketch-graph that shows an increase in concentration with time **MAX (1)** if sketch-graph shows a **decrease** in the concentration of a reactant / Br_2	Answers relating to half-life score **(0)** overall If sketch-graph or comments suggest that gradient is measured at other than t = 0 or at several values of t then **max (1)**	**2**

(Total 12 marks)

SECTION C

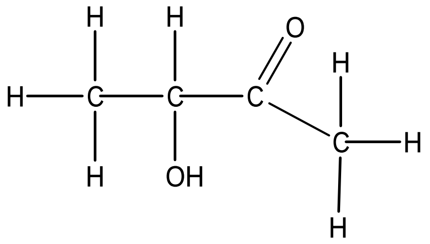
Question Number	Acceptable Answers	Reject	Mark
19(a)(i)	C : H : O Mole ratio / mol $\frac{54.5}{12}$: $\frac{9.1}{1}$: $\frac{36.4}{16}$ **(1)** = 4.5417 : 9.1 : 2.275 = 1.996 : 4 : 1 = 2 : 4 : 1 C_2H_4O **(1)** Correct empirical formula of C_2H_4O, with or without working, scores **(2)**		**2**

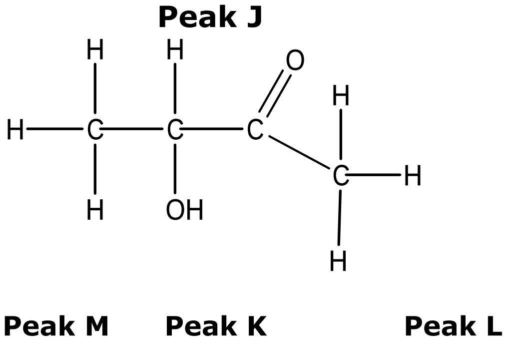
Question Number	Acceptable Answers	Reject	Mark
19(a)(ii)	**First mark:** Any mention of **44** or of doubling C_2H_4O **(1)** **Second mark:** Any mention of **88 in the context of the mass spectrum** eg mentions 'molecular ion' / M^+ / heaviest peak / peak furthest to the right / annotation at 88 on the mass spectrum itself / highest $\frac{m}{z}$ value **(1)**	**88** obtained **just** by adding up the relative atomic masses in $C_4H_8O_2$ scores **(0)** for 2nd scoring point	**2**

Question Number	Acceptable Answers	Reject	Mark
19(b)	(Peak at 3500 cm^{-1}) **O—H** **(1)** Allow OH (Peak at 1700 cm^{-1}) **C=O** **(1)** **Penalise extra extension bond on an otherwise correct answer once only** (eg —O—H **and** —C=O scores (1)) **IGNORE** any names for the bonds suggested even if incorrect	—O—H / —OH C—O / —C=O / CO	**2**

Question Number	Acceptable Answers	Reject	Mark
19(c)(i)	**First mark:** (**X** is neutral) so not a (carboxylic) acid **(1)** **IGNORE** **"X** doesn't have a charge as it is neutral" / "**X** is not an alkali" / "**X** is not a base" **Second mark:** **(X** does not react with Tollens') so is **not** an aldehyde / is a ketone **(1)** **Third mark:** (**X** reacts with H^+ / $Cr_2O_7^{2-}$ so) is an alcohol /contains an OH (group) / contains R—OH / contains hydroxyl (group) **(1)** **IGNORE** 'not an acid' if this is deduced **solely** from the H^+ / $Cr_2O_7^{2-}$ information **Fourth mark:** a primary or a secondary (alcohol) **both needed** **OR** (**X** is) not tertiary (alcohol) **(1)** **Mark each point separately** **NOTE:** **'X** is a primary or a secondary alcohol' scores both the third and fourth marks **ALLOW** Correct formulae for the functional groups, instead of their names	**X** is an aldehyde scores **(0)** for this scoring point / **X** is not a ketone scores **(0)** for this scoring point	**4**

Question Number	Acceptable Answers	Reject	Mark
19(c)(ii)	(primary or secondary) alcohol **and** ketone **NOTE** **BOTH names** are required here	Just ‘hydroxyl for ‘alcohol’ and/or ‘C=O /carbonyl’ for ketone/	**1**

Question Number	Acceptable Answers	Reject	Mark
19(d)	**MARKING ADVICE** Check answer for the suggested structure of X. If the correct structure is shown  Mark answer according to the following. However if no structure for **X** is shown or an incorrect structure for **X** is proposed, mark answer according to “COMMENTS” scheme below **MARKS CAN BE AWARDED FROM SUITABLY ANNOTATED FORMULAE FOR X.**		**7**
	<u>**First mark:**</u> Four different H / hydrogen / proton environments **(1)**	**Just** ‘four different **chemical** environments’	
	<u>**Any five from following seven points**</u>: **Either** Application of the (n+1) rule to peak **J** (which is a quartet / splits into **four**) **or** application of the (n+1) rule peak **M** (which is a doublet / splits into **two**) **(1)** Any mention to explain **no** splitting for peak **L** as there is no H is attached to the adjacent carbon **(1)** Peak **L** $(C\mathbf{H}_3)$ next to C=O **(1)** Peak **M** $(C\mathbf{H}_3)$ next to CH **(1)** Peak **K** O**H** **(1)** Peak **J** (C**H**) next to CH_3 **(1)**		
	Any **one** correct δ value quoted within ± 0.2 of the following chemical shifts: 1.4(**M**) or 2.2 (**L**) or 3.7(**K**) or 4.2 (**J**) (ppm) **(1)**	If any incorrect chemical shift **OR A RANGE** of chemical shifts is quoted, this scoring point is not available	

	<u>Final mark</u> (Compound **X** is) $CH_3CH(OH)COCH_3$ **NO** other compound allowed. **ACCEPT** any unambiguous formula, e.g. displayed formula  **ACCEPT** 3-hydroxybutan-2-one **(1)**		

(Total 18 marks)

Total marks 90

COMMENT

Strategy for marking answers with an incorrect structure for X or where no structure is suggested for X.
The maximum mark in such cases is FOUR OUT OF SEVEN or TWO OUT OF SEVEN IF NO STRUCTURE DRAWN (as second and fourth marks are not available)

Scoring points:
First mark:

States four different H / hydrogen / proton environments

Second mark:

Structure drawn for **X** has exactly 4 hydrogen environments

Third mark:

Peak **K** is due to OH

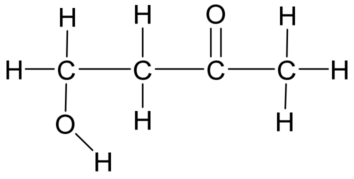
Fourth Mark:

Providing the structure drawn for X would produce ONE of these splits.

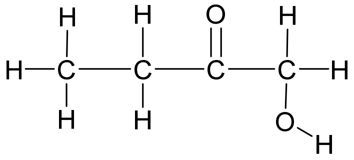
Any ONE of

Application of the (n+1) rule to peak to explain a peak which is a quartet splits into **four**
or
Application of the (n+1) rule to peak to explain a peak which is a doublet / splits into **two**
or
Application of the (n+1) rule to peak to explain a peak which is a singlet due to a CH_3 next to C=O

SEE NEXT PAGE FOR MAXIMUM MARKS AVAILABLE FOR SOME LIKELY INCORRECT STRUCTURES FOR **X**



Max 4



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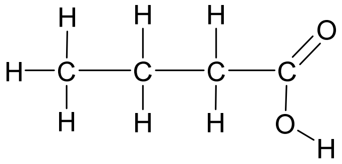

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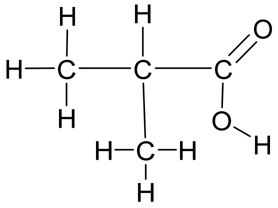

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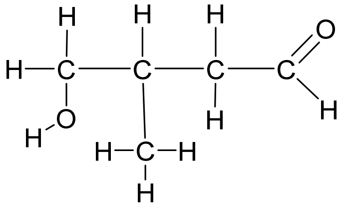

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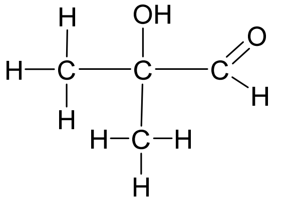
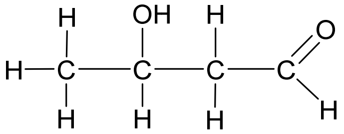
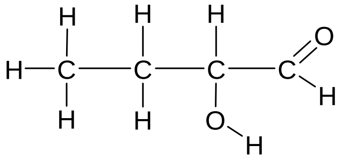


Max 2



Max 3



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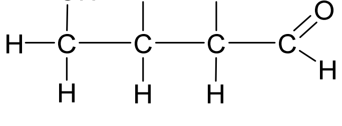

Max 2

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Surname	Other names

Centre Number	Candidate Number

Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 12 June 2013 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

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6/5/7/7/7/7/

P 4 1 5 7 2 A 0 1 2 4

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 The overall equation for a reaction between two chemicals, M and N, is

$$M + 2N \rightarrow P + Q$$

(a) This reaction occurs spontaneously at room temperature. Which of the following **must** be true?

(1)

☒ **A** $\Delta H^{\ominus}_{\text{reaction}}$ is positive.

☒ **B** $\Delta H^{\ominus}_{\text{reaction}}$ is negative.

☒ **C** $\Delta S^{\ominus}_{\text{total}}$ is positive.

☒ **D** $\Delta S^{\ominus}_{\text{total}}$ is negative.

(b) The reaction above occurs in two stages via an intermediate, T.

$$M + N \rightarrow T \qquad \text{slow}$$

$$N + T \rightarrow P + Q \qquad \text{fast}$$

From this it can be deduced that the rate equation for the reaction between M and N is

(1)

☒ **A** rate = k[M][N]

☒ **B** rate = k[M][N]^2

☒ **C** rate = k[M][T]

☒ **D** rate = k[N][T]

(Total for Question 1 = 2 marks)

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

2 Calcium carbonate decomposes at high temperature to form calcium oxide and carbon dioxide:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Calcium carbonate is **thermodynamically** stable at room temperature because for this reaction

☒ **A** the activation energy is high.

☒ **B** the enthalpy change, ΔH, is positive.

☒ **C** entropy change of the system (ΔS_{system}) is positive.

☒ **D** entropy change of the system (ΔS_{system}) is negative.

(Total for Question 2 = 1 mark)

3 2-methylpropane has a smaller standard molar entropy at 298 K than butane. The best explanation for this is that 2-methylpropane has

☒ **A** a lower boiling temperature.

☒ **B** a higher standard molar enthalpy change of formation.

☒ **C** fewer ways of distributing energy quanta.

☒ **D** more ways of distributing energy quanta.

(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) For the equilibrium reaction between hydrogen and iodine

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

increasing the pressure of the system

(1)

☒ **A** has no effect on the rate or the position of equilibrium.

☒ **B** increases the rate but does not affect the position of equilibrium.

☒ **C** increases the rate and shifts the equilibrium to the right.

☒ **D** increases the rate and shifts the equilibrium to the left.

(b) The equation for the equilibrium reaction between hydrogen and iodine may also be written as

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

This change to the equation, compared to that in part (a),

(1)

☒ **A** has no effect on the value of the equilibrium constant.

☒ **B** halves the value of the equilibrium constant.

☒ **C** doubles the value of the equilibrium constant.

☒ **D** square roots the value of the equilibrium constant.

(Total for Question 4 = 2 marks)

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

5 The first stage in the manufacture of nitric acid is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \quad \Delta H = -906 \text{ kJ mol}^{-1}$$

(a) In modern industrial plants this reaction is carried out at a pressure of around 3 atm. Which of the following statements is **incorrect**? The raised pressure

(1)

☒ **A** helps push the reactants through the reactor.

☒ **B** shifts the position of equilibrium to the right.

☒ **C** increases the cost of the reactor.

☒ **D** increases the energy cost of this part of the process.

(b) A platinum-rhodium alloy catalyst is used in this reaction. Which of the following statements is **incorrect**? The catalyst

(1)

☒ **A** lowers the activation energy of the reaction.

☒ **B** has no effect on the equilibrium constant for the reaction.

☒ **C** alters the enthalpy change of the reaction.

☒ **D** reduces the energy cost of this part of the process.

(c) The operating temperature of this reaction is about 900 °C. The use of a high temperature

(1)

☒ **A** increases the rate of the reaction and the equilibrium yield.

☒ **B** increases the rate of the reaction and decreases the equilibrium yield.

☒ **C** decreases the rate of the reaction and the equilibrium yield.

☒ **D** decreases the rate of the reaction and increases the equilibrium yield.

(Total for Question 5 = 3 marks)

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

6 Ammonium chloride decomposes on heating:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The equilibrium constant, K_p, for this reaction equals

☒ **A** $P_{NH_3} \times P_{HCl}$

☒ **B** $\dfrac{1}{P_{NH_3} \times P_{HCl}}$

☒ **C** $\dfrac{P_{NH_3} \times P_{HCl}}{P_{NH_4Cl}}$

☒ **D** $\dfrac{P_{NH_4Cl}}{P_{NH_3} \times P_{HCl}}$

(Total for Question 6 = 1 mark)

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7 The dissociation constant of water, K_w, increases with increasing temperature. When the temperature increases, water

☒ **A** remains neutral.

☒ **B** dissociates less.

☒ **C** becomes acidic.

☒ **D** becomes alkaline.

(Total for Question 7 = 1 mark)

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8 The reaction between concentrated sulfuric acid and pure ethanoic acid is

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$$

The Brønsted-Lowry acids in this equilibrium are

☒ **A** CH_3COOH and H_2SO_4

☒ **B** $CH_3COOH_2^+$ and HSO_4^-

☒ **C** H_2SO_4 and $CH_3COOH_2^+$

☒ **D** CH_3COOH and HSO_4^-

(Total for Question 8 = 1 mark)

9 An aqueous solution of ethanoic acid is gradually diluted. Which of the following statements is **incorrect**?

☒ **A** The pH decreases.

☒ **B** The value of K_a is unchanged.

☒ **C** The concentration of ethanoic acid molecules decreases.

☒ **D** The proportion of ethanoic acid molecules which dissociates increases.

(Total for Question 9 = 1 mark)

10 Methyl orange and phenolphthalein are both acid-base indicators. In the titration of a strong acid against a weak alkali

☒ **A** methyl orange is a suitable indicator but phenolphthalein is not.

☒ **B** phenolphthalein is a suitable indicator but methyl orange is not.

☒ **C** both phenolphthalein and methyl orange are suitable indicators.

☒ **D** neither phenolphthalein nor methyl orange is a suitable indicator.

(Total for Question 10 = 1 mark)

11 Select the word that best describes the effect of a chiral molecule on the plane of plane-polarized light. The plane of polarization of light is

☒ **A** reflected.

☒ **B** refracted.

☒ **C** resolved.

☒ **D** rotated.

(Total for Question 11 = 1 mark)

12 An organic compound reacts with **both** acidified potassium dichromate(VI) **and** lithium tetrahydridoaluminate (lithium aluminium hydride). The organic compound could be

☒ **A** a primary alcohol.

☒ **B** an aldehyde.

☒ **C** a ketone.

☒ **D** a carboxylic acid.

(Total for Question 12 = 1 mark)

13 Ketones react with

☒ **A** both 2,4-dinitrophenylhydrazine solution and Tollens' reagent.

☒ **B** 2,4-dinitrophenylhydrazine solution but not with Tollens' reagent.

☒ **C** Tollens' reagent but not with 2,4-dinitrophenylhydrazine solution.

☒ **D** neither Tollens' reagent nor 2,4-dinitrophenylhydrazine solution.

(Total for Question 13 = 1 mark)

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14 Ethanoic acid, CH_3COOH, may be prepared from ethanenitrile, CH_3CN. This reaction is best described as

☒ **A** reduction.

☒ **B** oxidation.

☒ **C** hydrolysis.

☒ **D** condensation.

(Total for Question 14 = 1 mark)

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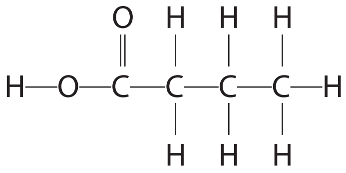
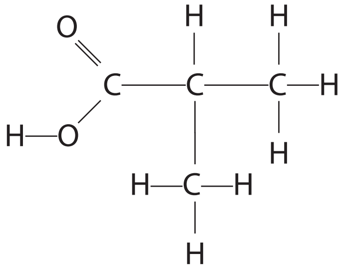
15 Propanoic acid reacts with methanol to form an ester. The structure of the ester is

☒ **A**

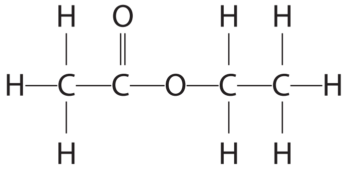


$$\begin{array}{ccccccccccccc} & & & & \text{O} & & \text{H} & & \text{H} & & \text{H} & & \\ & & & & \| & & | & & | & & | & & \\ \text{H} & - & \text{O} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & | & & | & & | & & \\ & & & & & & \text{H} & & \text{H} & & \text{H} & & \end{array}$$

☒ **B**



☒ **C**



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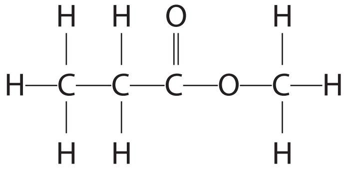
☒ **D**



$$\begin{array}{ccccccccccccc} & & \text{H} & & \text{H} & & \text{O} & & & & \text{H} & & \\ & & | & & | & & \| & & & & | & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{O} & - & \text{C} & - & \text{H} \\ & & | & & | & & & & & & | & & \\ & & \text{H} & & \text{H} & & & & & & \text{H} & & \end{array}$$

(Total for Question 15 = 1 mark)

16 The boiling temperature of ethanoic acid is very much higher than that of butane although these molecules have similar numbers of electrons. This is because ethanoic acid has

☒ **A** stronger covalent bonds.

☒ **B** stronger ionic bonds.

☒ **C** greater London forces.

☒ **D** hydrogen bonding.

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 The equation for the combustion of hydrogen is

$$H_2(g) \quad + \quad ½O_2(g) \quad \rightarrow \quad H_2O(l)$$

(a) Use the standard molar entropies on page 2 and page 25 of the data booklet to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{\text{system}}$) for this reaction.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of oxygen, $S^{\ominus}[½O_2(g)] = +102.5\ J\ mol^{-1}\ K^{-1}$.

(3)

(b) The standard enthalpy change for the combustion of hydrogen is –285.8 kJ mol^{-1}. Use this value to calculate the entropy change of the surroundings for the combustion of hydrogen at 298 K. Give your answer to **3** significant figures and include a sign and units.

(3)

(c) Use your answers to (a) and (b) to calculate the total entropy change ($\Delta S^{\ominus}_{\text{total}}$) for the combustion of 1 mol of hydrogen. Include a sign and units in your answer.

(2)

*(d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

(2)

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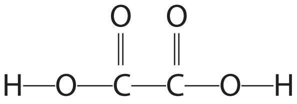
(Total for Question 17 = 10 marks)

18 Ethanedioic acid, $H_2C_2O_4$, is a dicarboxylic acid which occurs in many plants, for example in rhubarb leaves, and is used as a rust remover and strong descaler. The structure of ethanedioic acid is shown below.



$$\mathrm{H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H}$$

Ethanedioic acid is a much stronger acid than carboxylic acids such as ethanoic acid, having a pK_a of 1.38. The hydrogenethanedioate ion, $HC_2O_4^-$, is a weaker acid than ethanedioic acid, having a pK_a of 4.28, although slightly stronger than ethanoic acid.

(a) (i) Write an equation for the reaction of the hydrogenethanedioate ion with water to form an acidic solution. Include state symbols in your equation.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, of the weak acid, $HC_2O_4^-$.

(1)

(iii) A solution containing hydrogenethanedioate ions behaves as a typical weak acid. Use your answer to (a)(ii) and the pK_a of the hydrogenethanedioate ion to calculate the pH of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate, $NaHC_2O_4$.

(3)

(b) (i) State **two** approximations used in the calculation of pH in (a)(iii).

(2)

1. ....

....

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2. ....

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*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

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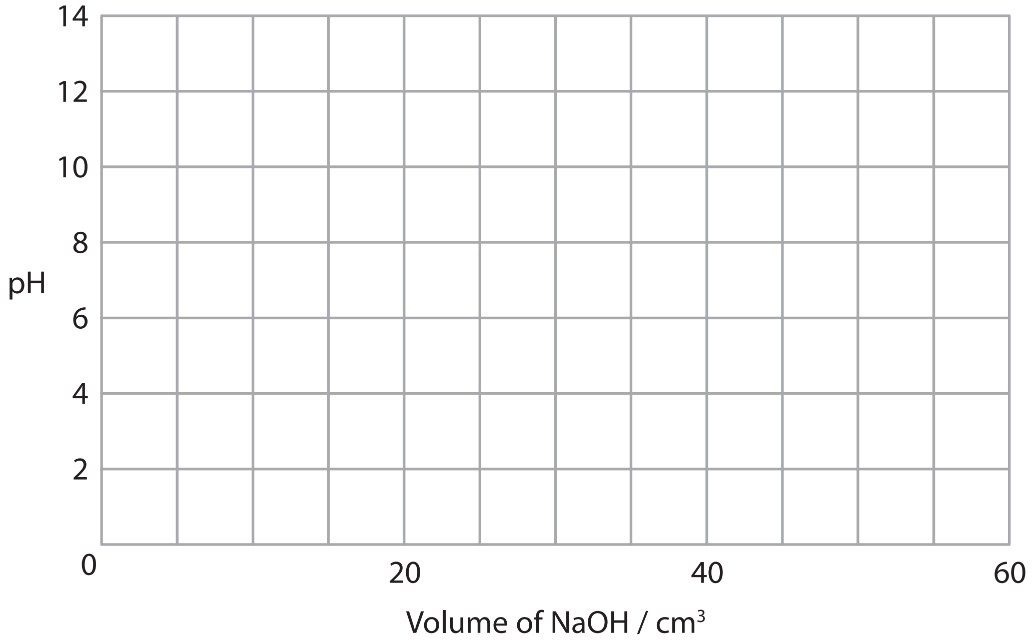
(c) 25 cm^3 of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



*(ii) When 25 cm^3 of a 0.050 mol dm^{-3} solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm^3.

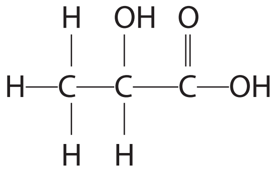
When methyl yellow indicator is used, the colour changes at around 25 cm^3.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

(Total for Question 18 = 15 marks)

19 2-hydroxypropanoic acid, lactic acid, is a chiral molecule which is found in muscles and in sour milk. The 2-hydroxypropanoic acid formed in muscles is optically active but that in sour milk is not.



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

2-hydroxypropanoic acid

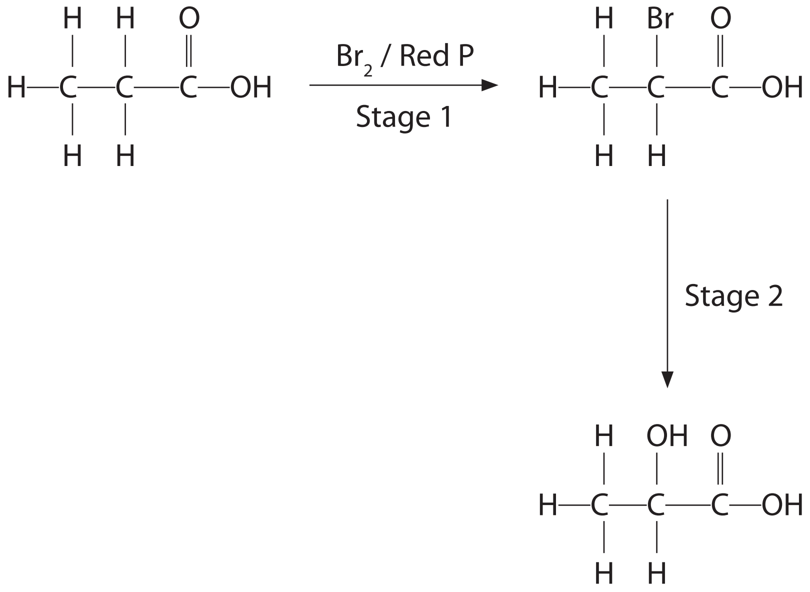
(a) (i) Explain the term **chiral**, stating the feature of 2-hydroxypropanoic acid that makes it chiral. Label this feature on the formula above.

(3)

(ii) What is the difference between the 2-hydroxypropanoic acid formed in muscles and that found in sour milk which gives rise to the difference in optical activity?

(2)

(b) 2-hydroxypropanoic acid may be prepared in the laboratory from propanoic acid in a two-stage sequence in which 2-bromopropanoic acid is formed as an intermediate:



(i) Stage 2 of this sequence was carried out in two steps. Identify the reagent required for each step in Stage 2.

(2)

First step ....

Second step ....

(ii) When an optically active isomer of 2-bromopropanoic acid is used in Stage 2, the resulting 2-hydroxypropanoic acid is also optically active. State and explain what this indicates about the mechanism of the first reaction in Stage 2.

(3)

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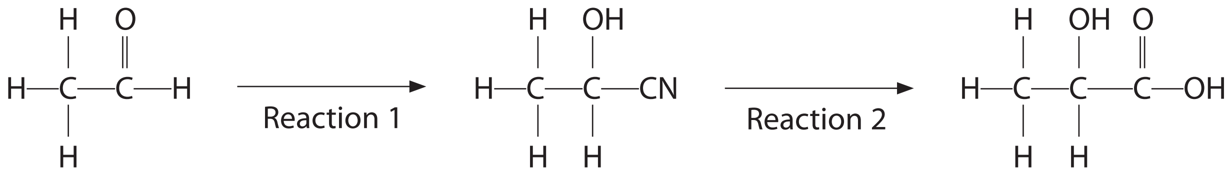
(c) 2-hydroxypropanoic acid may also be prepared from ethanal in the following sequence:



(i) Name the mechanism and type of reaction occurring in Reaction 1.

(2)

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(ii) Identify the attacking species in Reaction 1.

(1)

....

(iii) Give the first step of the mechanism of Reaction 1, showing the formation of the intermediate.

(2)

*(iv) Explain, by referring to the mechanism in (c)(iii), why the 2-hydroxypropanoic acid formed from ethanal shows no optical activity.

(3)

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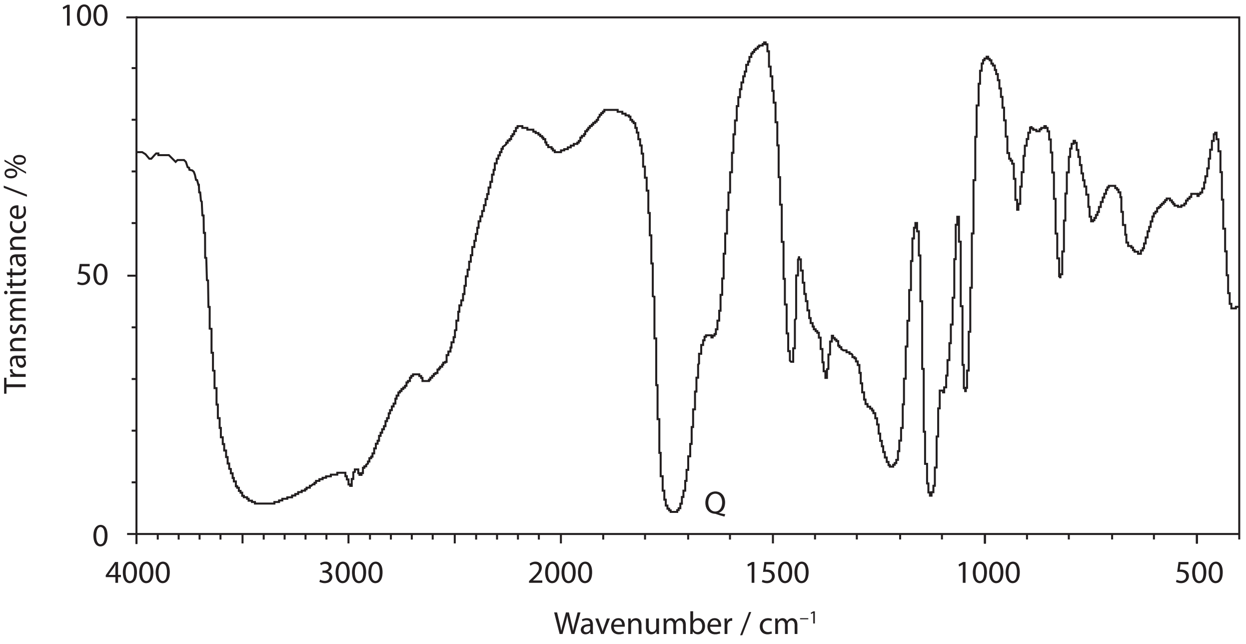
(d) The infrared spectrum of 2-hydroxypropanoic acid is shown below.



(i) Give the wavenumber of the peak that is present in the infrared spectrum of 2-hydroxypropanoic acid but will not be present in the infrared spectrum of ethanal, identifying the group most likely to be responsible for this peak. Use the data on pages 5 and 6 of the data booklet.

(1)

*(ii) Identify the bond responsible for absorption peak Q in the spectrum. By considering the wavenumber of this peak, and the data on pages 5 and 6 of the data booklet, explain whether this peak **alone** can be used to distinguish between ethanal and 2-hydroxypropanoic acid.

(3)

(e) Ethanal and 2-hydroxypropanoic acid can be distinguished by the use of chemical tests. Give two suitable tests **not** involving indicators. For each test, state the observation associated with a positive result.

(4)

Test which is positive for ethanal but not for 2-hydroxypropanoic acid.

Test which is positive for 2-hydroxypropanoic acid but not for ethanal.

(Total for Question 19 = 26 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

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

20 The ionic equation for the reaction of ammonium peroxodisulfate (persulfate), $(NH_4)_2S_2O_8$, with potassium iodide, KI, is

$$S_2O_8^{2-}(aq) \quad + \quad 2I^-(aq) \quad \rightarrow \quad 2SO_4^{2-}(aq) \quad + \quad I_2(aq)$$

(a) In a series of experiments to determine the rate equation for this reaction, 10 cm^3 of 0.0050 mol dm^{-3} sodium thiosulfate was mixed with 20 cm^3 of $(NH_4)_2S_2O_8$ solution and 5 drops of starch solution. 20 cm^3 of KI solution was added with mixing and the time taken for the solution to darken was noted. The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions and the times for the mixture to darken are shown below.

Experiment Number	Initial concentration / mol dm^{-3}		Time for solution to darken / s
	$S_2O_8^{2-}$	I^-	
1	0.10	0.20	35
2	0.05	0.20	69
3	0.10	0.10	70

(i) Explain the purpose of the sodium thiosulfate solution.

(2)

....

....

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(ii) Use the data in the table to deduce the rate equation for the reaction between $S_2O_8^{2-}$ and I^- ions. Explain, by referring to the data, how you arrived at your answer.

(3)

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(b) A further experiment was carried out to confirm the order of the reaction with respect to iodide ions. $(NH_4)_2S_2O_8$ was mixed with KI to form a solution in which the initial concentration of $(NH_4)_2S_2O_8$ was 2.0 mol dm^{-3} and that of KI was 0.025 mol dm^{-3}. The concentration of iodine was measured at various times until the reaction was complete.

(i) Outline a method, **not** involving sampling the mixture, which would be suitable for measuring the iodine concentrations in this experiment. Experimental details are not required but you should state how you would use your measurements to obtain iodine concentrations.

(3)

(ii) Explain why the initial concentration of $(NH_4)_2S_2O_8$ is much higher than that of KI.

(1)

(iii) State how the initial rate of reaction may be obtained from the results of this type of experiment.

(2)

(iv) In such an experiment a student calculated the initial rate of reaction to be 8.75×10^{-5} mol dm^{-3} s^{-1}. Use this value, the initial concentrations in (b) and the rate equation that you obtained in (a)(ii), to calculate the rate constant for this reaction. Include units in your answer.

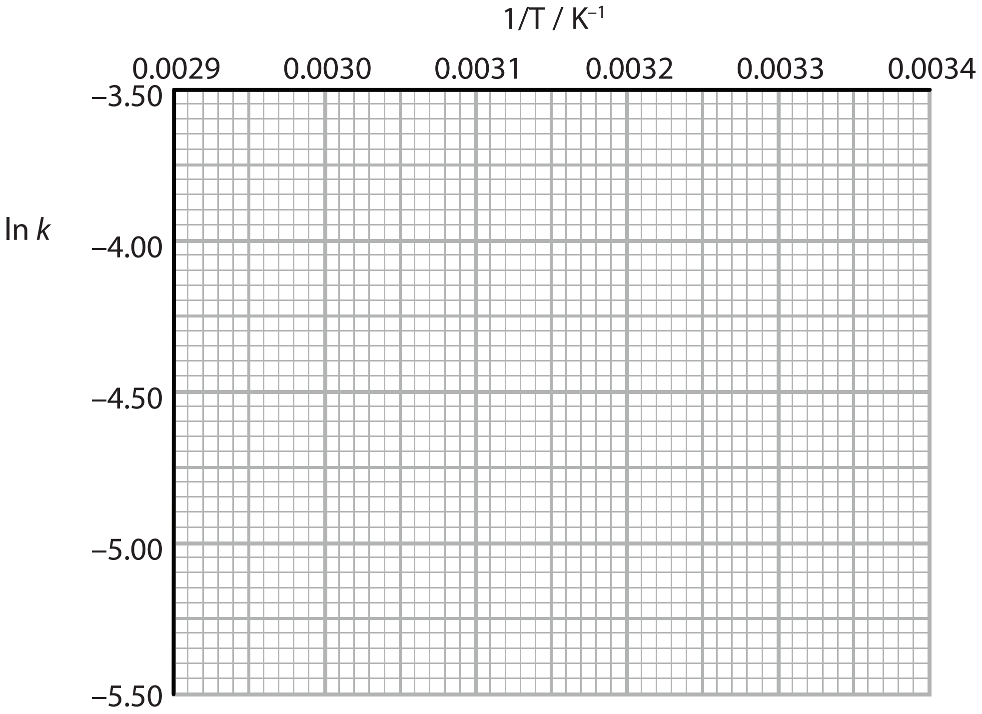
(2)

(c) Using the method outlined in (b), the rate constant for this reaction was determined at various temperatures. The data from these experiments are shown in the table below. Note that none of the temperatures corresponds to that used in (b) and that the rate constant is given in appropriate units.

Temperature T / K	Rate constant *k*	ln *k*	1/T / K^{-1}
300	0.00513	–5.27	0.00333
310	0.00833	–4.79	0.00323
320	0.0128	–4.36	0.00313
330	0.0201	–3.91	0.00303
340	0.0301	–3.50	0.00294

(i) Use the data in the table to plot a graph of ln *k* (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points.

(2)



(ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a, of the reaction, stating the units.

(4)

The rate constant of a reaction, *k*, is related to the temperature, T, by the expression

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

(Total for Question 20 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
							1.0 **H** hydrogen 1										*(18)* 4.0 **He** helium 2
(1)	*(2)*											*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)

Summer 2013

GCE Chemistry 6CH04/01
General Principles of Chemistry I

Summer 2013

Publications Code UA035570

General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. The strands are as follows:

  i) ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
  ii) select and use a form and style of writing appropriate to purpose and to complex subject matter
  iii) organise information clearly and coherently, using specialist vocabulary when appropriate

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.

Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication
Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1(a)	C		**1**
(b)	A		**1**

Question Number	Correct Answer	Reject	Mark
2	B		**1**

Question Number	Correct Answer	Reject	Mark
3	C		**1**

Question Number	Correct Answer	Reject	Mark
4(a)	B		**1**
(b)	D		**1**

Question Number	Correct Answer	Reject	Mark
5(a)	B		**1**
(b)	C		**1**
(c)	B		**1**

Question Number	Correct Answer	Reject	Mark
6	A		**1**

Question Number	Correct Answer	Reject	Mark
7	A		**1**

Question Number	Correct Answer	Reject	Mark
8	C		**1**

Question Number	Correct Answer	Reject	Mark
9	A		**1**

Question Number	Correct Answer	Reject	Mark
10	A		**1**

Question Number	Correct Answer	Reject	Mark
11	D		**1**

Question Number	Correct Answer	Reject	Mark
12	B		**1**

Question Number	Correct Answer	Reject	Mark
13	B		**1**

Question Number	Correct Answer	Reject	Mark
14	C		**1**

Question Number	Correct Answer	Reject	Mark
15	D		**1**

Question Number	Correct Answer	Reject	Mark
16	D		**1**

Total for Section A = 20 Marks

Section B

Question Number	Acceptable Answers	Reject	Mark
17(a)	Units are not required in (a) or (c) but if used should be correct. Penalise incorrect units in (a), (b) & (c) once only IGNORE case of J and K order of units **First mark:** 65.3/ 130.6 **and** 69.9 (J mol^{-1} K^{-1}) **(1)** **Second mark:** ΔS = 69.9 − (130.6 +102.5) **(1)** **Third mark:** ΔS = −163.2 = −163 (J mol^{-1} K^{-1}) **(1)** Correct answer with no working scores 3 Ignore SF except 1 SF TE at each stage If 65.3 used instead of 130.6 penalize once (answer is then ΔS = −97.9 (J mol^{-1} K^{-1})	+163 or any positive answer	**3**

Question Number	Acceptable Answers	Reject	Mark
17(b)	$\Delta S_{\text{surroundings}} = -\Delta H / T$ or just numbers **(1)** = +285800/298 = +959.06 = +959 J mol^{-1} K^{-1} / +0.959 kJ mol^{-1} K^{-1} Correct value to 3SF **(1)** Correct units and positive sign **(1)** Correct answer with no working scores 3	answer with no sign	**3**

Question Number	Acceptable Answers	Reject	Mark
17(c)	$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ **(1)** Allow $\Delta S_{reaction}$ for ΔS_{system} ΔS_{total} = answer (a) + answer (b) $= -163.2 + 959$ $= (+)795.8 = (+)796$ (J mol^{-1} K^{-1}) If $\Delta S_{surroundings}$=+959.06 then ΔS_{total} = +795.9 **(1)** Correct answer with no working scores 2 Ignore SF except 1 SF TE on values in (a) & (b) no TE on incorrect equation If answer to (a) = -97.9 (J mol^{-1} K^{-1}) ΔS_{total} = (+)861.1 (J mol^{-1} K^{-1})		**2**

Question Number	Acceptable Answers	Reject	Mark
17(d)	A mixture of hydrogen and oxygen is **thermodynamically** unstable **because** ΔS_{total} is positive OR Reaction between hydrogen and oxygen is **thermodynamically** feasible **because** ΔS_{total} is positive ALLOW ΔS for ΔS_{total} **(1)** No TE on negative ΔS_{total} from (c) The mixture is kinetically inert /stable or reaction is (very) slow **because** the activation energy is (very) high **(1)** Mixture / reaction is **kinetically** inert / stable but **thermodynamically** unstable / feasible scores 1 mark IGNORE References to spark / flame providing the (activation) energy for reaction	Reference to the stability of individual elements	**2**

Total for Question 17 = 10 Marks

Question Number	Acceptable Answers	Reject	Mark
18(a)(i)	$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$ (or →) ALLOW $H_2O(aq)$ Equation **(1)** states **(1)** ALLOW for 1 mark $HC_2O_4^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + H^+(aq)$ States mark is not stand alone but can be awarded if the equation has a minor error e.g. an incorrect charge		**2**

Question Number	Acceptable Answers	Reject	Mark
18(a)(ii)	$K_a = [C_2O_4^{2-}][H_3O^+] / [HC_2O_4^-]$ OR $K_a = [C_2O_4^{2-}][H^+] / [HC_2O_4^-]$ No TE on incorrect equation in (a)(i) Penalise incorrect charges in (i) and (ii) once only	$K_a =$ $[H^+]^2 / [HC_2O_4^-]$ $[H^+][A^-]/[HA]$	**1**

Question Number	Acceptable Answers	Reject	Mark
18 (a) (iii)	No TE on (a)(ii) $K_a = 10^{-4.28}$ OR 5.24807×10^{-5} (mol dm^{-3}) **(1)** $K_a = [H^+]^2 / [HC_2O_4^-]$ $K_a = [H^+]^2 / 0.050$ $[H^+] = \sqrt{(0.05 \times 10^{-4.28})} = 1.61988 \times 10^{-3}$ (mol dm^{-3}) **(1)** TE on incorrect K_a value pH = $-\log 1.61988 \times 10^{-3} = 2.7905 = 2.8$ **(1)** For final mark TE on algebraic / arithmetical errors providing pH ≥ 1.3 Correct answer with no working scores 3 Ignore SF except 1 SF		**3**

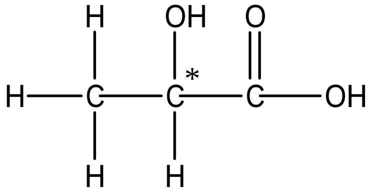
Question Number	Acceptable Answers	Reject	Mark
18(b)(i)	IGNORE explanations **First mark:** $HC_2O_4^-$/hydrogenethanedioate ion ionization negligible ALLOW Acid for $HC_2O_4^-$ Slight / partial / incomplete / does not dissociate for negligible OR $[HC_2O_4^-]_{equilibrium} = [HC_2O_4^-]_{initial}$ / 0.050 (mol dm^{-3}) **(1)** **Second mark:** $[H^+]$ due to ionization of water negligible OR auto ionization of water negligible OR $[H^+]$ only due to ionization of $HC_2O_4^-$/acid OR $[C_2O_4^{2-}] = [H^+]$ **(1)** IGNORE references to temperature and to HA and A^- Penalize omission of [] in discussion once only	Use of $NaHC_2O_4$ for $HC_2O_4^-$ OR sodium hydrogen-ethanedioate for hydrogen-ethanedioate ion throughout this item	**2**

Question Number	Acceptable Answers	Reject	Mark
18(b)(ii)	Ethanedioic acid is a (much) stronger acid (than hydrogenethanedioate ion / sodium hydrogenethanedioate) OR Ethanedioic acid has a (much) smaller pK_a (than hydrogenethanedioate) OR Ionization / dissociation of ethanedioic acid is (much) greater (than hydrogenethanedioate) OR Reverse arguments **(1)** IGNORE $NaHC_2O_4$ ionization negligible Approximation of negligible ionization invalid / incorrect OR $[H_2C_2O_4]_{equilibrium}$ not equal to $[H_2C_2O_4]_{initial}$ **(1)** No TE on 18(a)(iii) IGNORE Second ionization occurs	Ethanedioic acid is a strong acid / fully dissociated Just 'approximation invalid'	**2**

Question Number	Acceptable Answers	Reject	Mark
18(c)(i)	Start pH at 2.8 ALLOW 2—4 **(1)** Vertical section at 25 cm^3 within pH range 6-11 and 2.5-4 units long **(1)** end pH (approaching) value in range 12-13 (asymptotically) **(1)**	deviation from vertical maximum before final pH	**3**

Question Number	Acceptable Answers	Reject	Mark
18(c)(ii)	**First mark:** Methyl yellow range = 2.9—4 and the phenolphthalein range = 8.2—10 ALLOW pK_{in} (methyl yellow) = 3.5 and pK_{in} (phenolphthalein) = 9.3 **(1)** **Second mark:** (The volumes are different) because ethanedioic acid is dibasic / diprotic / has two **replaceable/acidic** hydrogen atoms ALLOW dicarboxylic (acid) (therefore there are two stages to the neutralization) OR Methyl yellow range coincides with neutralization of first proton and phenolphthalein range coincides with neutralization of second proton **(1)**		**2**

Total for Question 18 = 15 Marks

Question Number	Acceptable Answers	Reject	Mark
19(a)(i)	A chiral molecule is non-superimposable on its mirror image / 3D molecule with no plane of symmetry **(1)** 2-hydroxypropanoic acid has a carbon atom which is asymmetric / has **four** different groups attached **(1)** **Middle** carbon labelled in any clear way **(1)** e.g.  $H-C(H)(H)-\overset{*}{C}(OH)(H)-C(=O)-OH$ ALLOW asymmetric C described but not labelled IGNORE references to rotation of plane polarized light	just 'non-superimposable' just 'no plane of symmetry' Molecules for groups	**3**

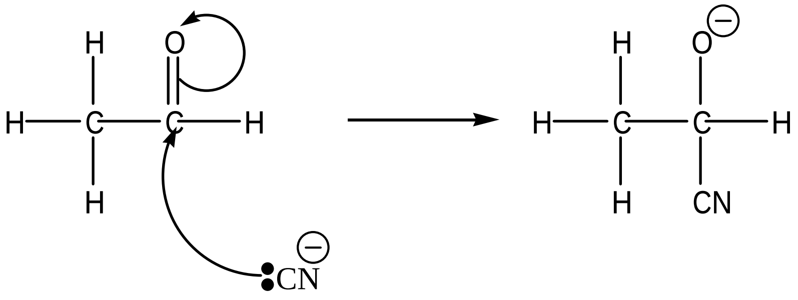
Question Number	Acceptable Answers	Reject	Mark
19(a)(ii)	2-hydroxypropanoic acid formed in muscles is a single (allow pure) enantiomer /(optical) isomer ALLOW Unequal mixture of enantiomers /(optical) isomers **(1)** 2-hydroxypropanoic acid formed in milk is a racemic mixture / equimolar mixture of the two enantiomers / racemate **(1)** If milk and muscles are reversed but the rest is correct, one mark is awarded	Just "not a racemic mixture" Just 'a mixture of enantiomers'	**2**

Question Number	Acceptable Answers	Reject	Mark
19(b)(i)	**First step** NaOH(aq) / KOH(aq) or names **(1)** Second mark dependent on first being correct **Second step** HCl(aq) / hydrochloric acid / H_2SO_4(aq) / sulfuric acid ALLOW HNO_3 / nitric acid /dil HCl /(dil) H_2SO4 /(dil) HNO_3 or any strong acid (name or formula) including HBr((aq)) and HI((aq)) **(1)** IGNORE Omission of (aq) and references to temperature Ethanolic /alcoholic solutions ALLOW One mark for correct two reagents in the wrong order One mark for ‘alkali / OH^- followed by acid / H^+ /H_3O^+’	OH^- / alkali H^+ / H_3O^+ /acid	**2**

Question Number	Acceptable Answers	Reject	Mark
19(b)(ii)	**First mark** (Stand alone) A racemic mixture is not formed OR More of one enantiomer /(optical) isomer is formed OR Only one enantiomer /(optical) isomer is formed **(1)** **Second mark** (Stand alone) (Some of the) reaction is S_N2 **(1)** **Third mark** (Stand alone) Nucleophile / OH^- only attacks from one side of the molecule / from the opposite side to leaving group **(1)** ALLOW Use of ‘intermediate’ for ‘transition state’ in description of S_N2 Reverse argument based on S_N1 forming a racemic mixture	Carbocation (for molecule)	**3**

Question Number	Acceptable Answers	Reject	Mark
19(c)(i)	Nucleophilic **(1)** Addition **(1)**	S_N1/S_N2	**2**

Question Number	Acceptable Answers	Reject	Mark
19(c)(ii)	Cyanide (ion) / CN^- / $C\equiv N^-$ / $:C\equiv N^-$ / ^-CN	HCN/ $C\equiv N$	**1**

Question Number	Acceptable Answers	Reject	Mark
19 (c) (iii)	 Both curly arrows **(1)** Intermediate **(1)** ALLOW Omission of lone pair Curly arrow from anywhere on nucleophile including from charge or nitrogen Formation of charged canonical form followed by attack of cyanide ion IGNORE δ+/δ- even if unbalanced	Omission of charges (penalise once only) Full charges on ethanal —C—NC in intermediate	**2**

Question Number	Acceptable Answers	Reject	Mark
19 (c) (iv)	Racemic mixture / equal amounts of the two enantiomers / racemate formed **(1)** Stand alone mark CHO / aldehyde group is (trigonal) planar **(1)** ALLOW ethanal / molecule is (trigonal) planar Cyanide (ion) / CN^- /nucleophile attacks (equally) from above or below / either side (of the molecule) **(1)** Penalise use of intermediate / ion for aldehyde group **once** only Third mark cannot be awarded if the reaction is described as a nucleophilic substitution	Intermediate / carbonyl group /C_O is planar two positions Intermediate	**3**

Question Number	Acceptable Answers	Reject	Mark
19(d)(i)	Any value /range within the range 3750—2500 cm^{-1} due to O—H / OH / —OH IGNORE COOH / CO_2H / carboxylic acid	Wavenumbers alone OH in alcohol	**1**

Question Number	Acceptable Answers	Reject	Mark
19(d)(ii)	These three marks are stand alone Q is due to C═O **(1)** The (C═O) aldehyde range is 1740—1720 cm^{-1} **and** (C═O) carboxylic acid range is 1725—1700 cm^{-1} **(1)** So the peaks / absorptions cannot be used to distinguish these two compounds because they overlap. OR The (broad) absorption Q covers both the aldehyde and the carboxylic acid ranges **(1)** ALLOW 'too close'/'quite similar' for 'overlap'	Carboxylic acid / COOH group Just 'cannot be used to distinguish the compounds'	**3**

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr>
<td>**19(e)**</td>
<td>
If reagent incorrect, observation mark can only be awarded for a near miss

Test positive for ethanal
<table>
<tr><th>Reagent (1)</th><th>Observation (1)</th></tr>
<tr><td>Tollens’</td><td>Silver mirror / black / grey **ppt**</td></tr>
<tr><td>Fehling’s / Benedict’s</td><td>Red-brown **ppt**</td></tr>
<tr><td>2,4-DNP(H) / Brady’s reagent</td><td>Orange / red / yellow **ppt**
ALLOW brick-red **ppt**</td></tr>
</table>

Test positive for 2-hydroxypropanoic acid
<table>
<tr><th>Reagent (1)</th><th>Observation (1)</th></tr>
<tr><td>PCl_5 / Phosphorus (V)chloride / phosphorus pentachloride</td><td>Steamy fumes*
ALLOW gas evolved turns (blue) litmus / UI red</td></tr>
<tr><td>Named metal carbonate (solution)</td><td>Effervescence
ALLOW **gas / CO_2** evolved turns lime water cloudy</td></tr>
<tr><td>Sodium hydrogencarbonate (solution)</td><td>Effervescence
ALLOW **gas / CO_2** evolved turns lime water cloudy</td></tr>
<tr><td>Magnesium (& water)</td><td>Effervescence</td></tr>
<tr><td>Ethanol & H_2SO_4/named strong acid</td><td>Sweet / fruity / pear drops / glue smell</td></tr>
<tr><td>Ethanoic acid & H_2SO_4/named strong acid</td><td>Sweet / fruity / pear drops / glue smell</td></tr>
</table>

ALLOW
Na and effervescence / gas evolved pops with a lighted splint for2-hydroxypropanoic acid
(2)

ALLOW
fizzing / bubbling for effervescence

IGNORE
names of product

IF two tests given for one substance both must be correct for full marks

*misty fumes / white fumes / gas for fumes
</td>
<td>Iodine in alkali / iodoform test
Acidified potassium dichromate

Smoke
Just ‘fumes’

Any indicator as sole test

incorrect formulae of reagents</td>
<td>**4**</td>
</tr>
</table>

Total for Question 19 = 26 Marks

Total for Section B = 51 Marks

Section C

Question Number	Acceptable Answers	Reject	Mark
20(a)(i)	(Sodium thiosulfate) (rapidly) reacts with / reduces the iodine (as it is formed) **(1)** So prevents the starch-iodine colour appearing until a fixed amount of reaction has occurred ALLOW (for second mark) So prevents the starch-iodine colour appearing until all the thiosulfate has reacted OR Moles of iodine reacted / thiosulfate ÷ time is (approximately) proportional to the (initial) rate of reaction **(1)** ALLOW Use of 'thio' for thiosulfate	iodide / I^-	**2**

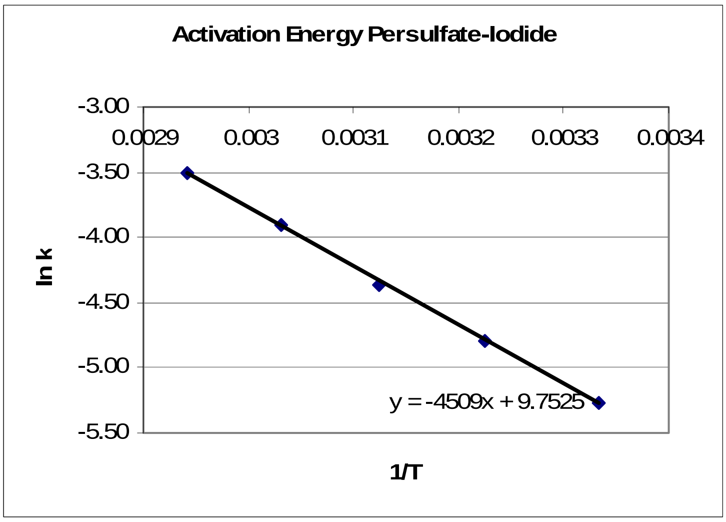
Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	(From 2 to 1) **$[S_2O_8^{2-}]$** doubles ($[I^-]$ unchanged) and rate doubles / time halves so order wrt **$S_2O_8^{2-}$** = 1 **(1)** (From 3 to 1) **$[I^-]$** doubles ($[$**$S_2O_8^{2-}$**$]$ unchanged) and rate doubles / time halves so order **wrt I^-** = 1 OR (if first mark awarded) (From 3 to 2) **$[I^-]$** doubles ($[$**$S_2O_8^{2-}$**$]$ halved) and rate unchanged so order **wrt I^-** = 1 **(1)** Penalise omission of concentration/square brackets once only Rate = $k[S_2O_8^{2-}][I^-]$ **(1)** Third mark stand alone if no working & TE on incorrect orders IGNORE case of k	Rate equation =	**3**

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	**First mark** Colorimetry /Use a colorimeter **(1)** **Second mark** Measure transmittance / absorbance (at various times) **(1)** **Third mark** (Use a calibration curve to) convert transmittance / absorbance into concentration. OR transmittance / absorbance proportional to concentration ALLOW Colorimetry may be used because iodine (solution) is coloured (and other reagents are colourless) / to measure intensity of the iodine colour **(1)** ALLOW (for the same three marks) Electrical conductivity Measured at various times / (use a calibration curve to) convert conductivity into concentration. Conductivity reduces as reaction proceeds because 3 mol ions converted to 2 mol ions / fewer ions on right hand side	Sampling methods calorimeter pH meter Just conductivity changes	**3**

Question Number	Acceptable Answers	Reject	Mark
20(b)(ii)	[$(NH_4)_2S_2O_8$] / [$S_2O_8^{2-}$] / [peroxodisulfate] / [persulfate] remains (approximately) unchanged during the reaction. OR [KI] / [I^-] is the only variable	$(NH_4)_2S_2O_8$ in excess. [$(NH_4)_2S_2O_8$] etc does not affect the rate Only [KI] / [I^-] affects the rate	**1**

Question Number	Acceptable Answers	Reject	Mark
20(b)(iii)	Plot a graph of concentration (of iodine/I_2) (on the y axis) against time **(1)** Measure the initial gradient / gradient at t=0 **(1)** 'Plot a graph and measure the initial gradient / gradient at t=0' alone scores second mark		**2**

Question Number	Acceptable Answers	Reject	Mark
20(b)(iv)	TE on 20(a)(ii) on numerical answer and appropriate units 8.75 x 10^{-5} = k x 2.0 x 0.025 k = 8.75 x 10^{-5} / (2.0 x 0.025) = 1.75 x 10^{-3} **(1)** dm^3 mol^{-1} s^{-1} **(1)** ALLOW units in any order Correct answer including units with no working scores 2	1 SF	**2**

Question Number	Acceptable Answers	Reject	Mark
20(c)(i)	 Use the overlay to mark the graph At least 4 points within the circles on the overlay **(1)** Best fit line on points given **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
20(c)(ii)	Gradient = −(−3.50 − −5.27) / (0.00333 − 0.00294) = (−)4538 = (−)4500 ALLOW values from (−)4300 to (−)4700 **(1)** gradient value negative **(1)** E_a = −gradient x R = −−4538 x 8.31 = (+)37700 J mol^{-1} (= (+)38 kJ mol^{-1}) **(1)** TE on value of gradient even if it is positive −4300 gives 35.7; −4700 gives 39.1 Correct units **(1)** Correct answer from the gradient calculation with units scores final 2 marks **BUT** correct answer with units but no gradient calculation scores units mark only		**4**

Total for Section C = 19 Marks

Total for Paper = 90 Marks

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Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Wednesday 12 June 2013 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH04/01R

You must have: Data Booklet

Candidates may use a calculator.

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.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

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 An important step in the production of sulfuric acid is the oxidation of sulfur dioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -196 \text{ kJ mol}^{-1}$$

Which of the conditions below is best suited to produce a high yield of sulfur trioxide, SO_3?

☒ **A** 1 atm pressure and 800 °C.

☒ **B** 2 atm pressure and 800 °C.

☒ **C** 1 atm pressure and 400 °C.

☒ **D** 2 atm pressure and 400 °C.

(Total for Question 1 = 1 mark)

2 Which of the following statements is true about **all** substances that form acidic solutions in water?

☒ **A** They are corrosive.

☒ **B** They are liquids.

☒ **C** They contain hydrogen atoms.

☒ **D** They form $H^+(aq)$ ions.

(Total for Question 2 = 1 mark)

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

3 Select the correct pH for each of the following solutions.

(a) Nitric acid, HNO_3, of concentration 2 mol dm^{-3}, assuming it is fully dissociated.

(1)

☒ **A** –0.3

☒ **B** 0.0

☒ **C** 0.3

☒ **D** 2.0

(b) Sodium hydroxide, NaOH, of concentration 2 mol dm^{-3}, using $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

(1)

☒ **A** –13.7

☒ **B** 13.7

☒ **C** 14.0

☒ **D** 14.3

(c) Ethanoic acid, CH_3COOH, of concentration 2 mol dm^{-3}, making the usual assumptions.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$$

(1)

☒ **A** 2.2

☒ **B** 2.4

☒ **C** 4.5

☒ **D** 4.8

(d) The mixture formed when 25 cm^3 of 2 mol dm^{-3} sodium hydroxide solution is added to 50 cm^3 of 2 mol dm^{-3} ethanoic acid, for which $K_a = 1.7 \times 10^{-5}$ mol dm^{-3}.

(1)

☒ **A** 2.2

☒ **B** 2.5

☒ **C** 4.5

☒ **D** 4.8

(Total for Question 3 = 4 marks)

4 A solution of 2,4-dinitrophenylhydrazine (Brady's reagent) is used as a test for organic functional groups.

(a) The positive result of the test is the formation of

(1)

☒ **A** a yellow solution.

☒ **B** an orange precipitate.

☒ **C** a red solution.

☒ **D** a green precipitate.

(b) Which of the following gives a positive result with a solution of 2,4-dinitrophenylhydrazine?

(1)

☒ **A** Only aldehydes

☒ **B** Only ketones

☒ **C** Only aldehydes and ketones

☒ **D** Any compound containing the C=O group

(c) The initial attack by 2,4-dinitrophenylhydrazine, when it reacts, is by

(1)

☒ **A** a free radical.

☒ **B** an electrophile.

☒ **C** a nucleophile.

☒ **D** a negative ion.

(d) The product of a positive test, a 2,4-dinitrophenylhydrazone, contains which of the following bonds?

(1)

☒ **A** N=N

☒ **B** C=N

☒ **C** C=C

☒ **D** C=O

(Total for Question 4 = 4 marks)

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Turn over for Question 5

5 This question is about the following isomeric compounds with the molecular formula C_4H_8O and molar mass 72 g mol^{-1}.

A $CH_3CH_2CH_2CHO$

B $(CH_3)_2CHCHO$

C $CH_3CH_2COCH_3$

D $CH_3CH{=}CHCH_2OH$

(a) Which compound would you expect to give a peak at *m/e* = 41 in its mass spectrum?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which compound would NOT react with an acidified solution of potassium dichromate(VI)?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which compound would give a pale yellow precipitate when reacted with iodine in alkaline solution?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) Which compound can be reduced to give a chiral product?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(e) Which compound would NOT react with hydrogen cyanide under suitable conditions to form a hydroxynitrile?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 5 = 5 marks)

---

6 Transesterification involves the conversion of

☒ **A** esters into different esters.

☒ **B** esters into carboxylic acids.

☒ **C** *cis* carbon-carbon double bonds to the *trans* arrangement.

☒ **D** *trans* carbon-carbon double bonds to the *cis* arrangement.

(Total for Question 6 = 1 mark)

---

7 Biodiesel is formed by transesterification. It is used as a fuel in preference to untreated vegetable oils because

☒ **A** on combustion, biodiesel produces less carbon dioxide than vegetable oils.

☒ **B** on combustion, biodiesel produces more energy than vegetable oils.

☒ **C** biodiesel vaporises more easily than vegetable oils.

☒ **D** biodiesel is less volatile than vegetable oils.

(Total for Question 7 = 1 mark)

---

8 The main reason for hardening vegetable oils when producing low-fat spreads is to

☒ **A** prevent oxidation.

☒ **B** make the oil less viscous.

☒ **C** increase the melting temperature.

☒ **D** decrease the cholesterol content.

(Total for Question 8 = 1 mark)

9 Which atoms are not detected by X-rays but are detected by nuclear magnetic resonance imaging which also shows their environments?

☒ **A** Carbon

☒ **B** Hydrogen

☒ **C** Nitrogen

☒ **D** Oxygen

(Total for Question 9 = 1 mark)

10 In one type of high-performance liquid chromatography (HPLC), the stationary phase is non-polar and a polar solvent is used as the eluent. Which of the following would travel through the chromatography column most quickly?

☒ **A** Tetrachloromethane

☒ **B** Chloromethane

☒ **C** Iodomethane

☒ **D** Hexane

(Total for Question 10 = 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.

11 This question is about the equilibrium reaction below.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

The equilibrium is reached slowly.

*(a) Describe the changes you would see if aqueous solutions of iron(II) sulfate and silver nitrate were mixed and allowed to stand for a few hours.

(2)

(b) The concentration of silver ions in the equilibrium mixture can be found by titration with potassium thiocyanate. Silver thiocyanate precipitates.

$$Ag^{+}(aq) + CNS^{-}(aq) \rightleftharpoons AgCNS(s)$$

When all the silver ions have reacted, a deep red complex ion of iron(III) thiocyanate forms.

In an experiment, 25.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution was added to 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) sulfate solution, mixed thoroughly, and allowed to stand overnight in an air-tight container.

10.0 cm^3 samples of the reaction mixture were then titrated with 0.0200 mol dm^{-3} potassium thiocyanate solution. The average titre was 5.60 cm^3.

(i) The initial concentrations of silver ions and iron(II) ions **in the reaction mixture** are the same.

Calculate this initial concentration in mol dm^{-3}.

(1)

(ii) Calculate the number of moles of silver ions in the 10.0 cm^3 sample at equilibrium and hence calculate the equilibrium concentration of silver ions in the mixture.

(2)

(iii) Deduce the equilibrium concentration of iron(II) ions.

(1)

(iv) Hence calculate the equilibrium concentration of iron(III) ions.

(1)

(v) Write the expression for the equilibrium constant, K_c, for the reaction

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Calculate its value and give your answer, with appropriate units, to **three** significant figures.

(4)

(c) (i) The relationship between the total entropy change for a reaction and the equilibrium constant is

$$\Delta S^{\ominus}_{\text{total}} = R \ln K$$

Calculate the total entropy change for this reaction, giving a sign and appropriate units.

[$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]

(2)

(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

$\Delta S^{\ominus}_{\text{system}}$ for this reaction is $-208.3 \text{ J mol}^{-1} \text{ K}^{-1}$

Use ideas about entropy to explain why this value is negative.

(2)

....

....

....

....

(iii) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$.

(1)

(iv) Use your answer to (c)(iii) to calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction at 298 K.

Hence state and explain the effect of increasing temperature on the value of ΔS_{total}.

(3)

*(d) After the samples from the original mixture for the titration are taken, the remainder was filtered and then allowed to stand overnight, in an air-tight container at the same temperature. Another 10.0 cm^3 sample was taken and titrated. How, if at all, would you expect the titre to change?

Justify your answer. A calculation is not required.

(2)

(Total for Question 11 = 21 marks)

12 This question is about the reactions of butanoic acid, $CH_3CH_2CH_2COOH$. It has a foul smell and behaves like a typical carboxylic acid.

(a) (i) The addition of sodium carbonate solution is often used as a chemical test to distinguish carboxylic acids, like butanoic acid, from other compounds, such as aldehydes.

Explain why old stocks of aldehydes often react with sodium carbonate solution.

(1)

(ii) How would the result of this test distinguish between a carboxylic acid and an old stock of an aldehyde?

(1)

(iii) Write the balanced chemical equation, including state symbols, for the reaction of sodium carbonate solution with butanoic acid.

(2)

*(iv) Infrared spectroscopy is a good physical method to distinguish carboxylic acids from other organic compounds. Give the wavenumbers of **two** characteristic absorptions for a carboxylic acid. Indicate the bond responsible for each absorption. Suggest why one of the absorptions is broad.

(3)

(v) High resolution nuclear magnetic resonance spectroscopy is a suitable physical method to use alongside infrared spectroscopy to identify butanoic acid. State the total number of peaks and suggest the splitting pattern for each peak that you would expect for butanoic acid, $CH_3CH_2CH_2COOH$.

(3)

....

....

....

....

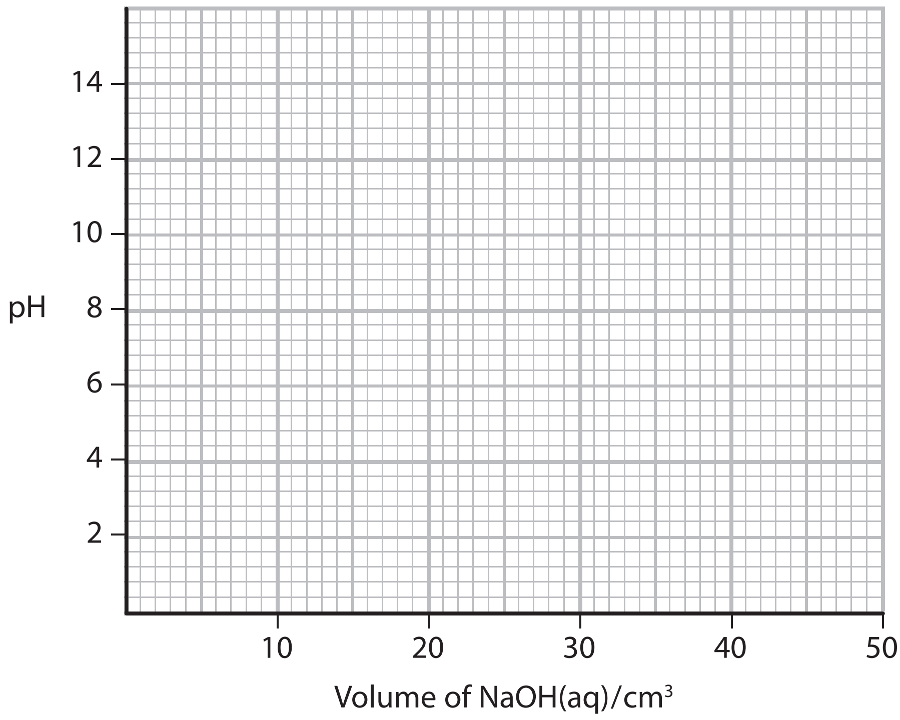
....

....

....

(b) Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

(4)



(c) (i) What would you see when phosphorus pentachloride, PCl_5, reacts with butanoic acid?

(1)

....

....

(ii) Give the structural formula and name of the organic product of this reaction.

(2)

Structural formula

Name ....

(d) (i) Give the name or formula of the organic product of the reaction between butanoic acid and lithium tetrahydridoaluminate (lithium aluminium hydride).

(1)

....

(ii) Water cannot be used as the solvent in this reaction because it reacts with lithium tetrahydridoaluminate. Suggest a suitable solvent.

(1)

....

(iii) State the type of reaction that takes place between butanoic acid and lithium tetrahydridoaluminate. Justify your classification.

(2)

Type ....

Justification ....

....

....

(e) (i) Butanoic acid can be reacted with methanol to make methyl butanoate. State **two** conditions that help to speed up this reaction.

(2)

....

....

(ii) Draw the **displayed** formula of methyl butanoate.

(1)

(iii) Identify another chemical, by name or formula, which could be added to methanol to make methyl butanoate.

(1)

....

*(iv) Give **two** advantages and **one** disadvantage of using the reaction occurring in (e)(iii), compared to the reaction in (e)(i), when making methyl butanoate.

(3)

Advantages ....

....

....

....

Disadvantage ....

....

(Total for Question 12 = 28 marks)

TOTAL FOR SECTION B = 49 MARKS)

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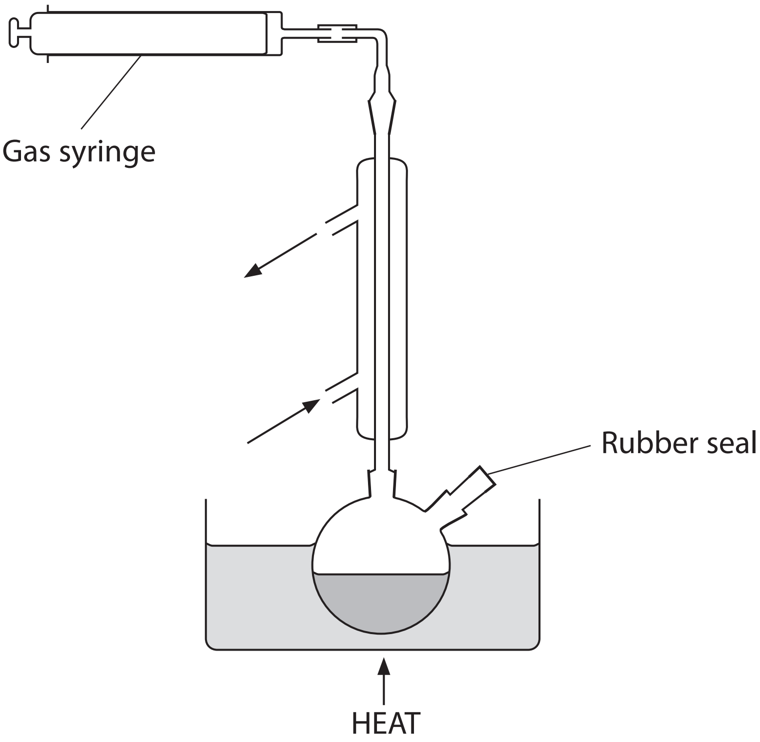
SECTION C

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

13 This question is about the elimination of hydrogen bromide from bromoalkanes by reaction with alcoholic potassium hydroxide.

$$C_4H_9Br + KOH \rightarrow C_4H_8 + KBr + H_2O$$

To investigate the kinetics of this reaction the following apparatus was used:



A solution of concentrated potassium hydroxide in ethanol was refluxed and the gas syringe connected as shown.

0.6 cm^3 of 1-bromobutane was added to the solution with a hypodermic syringe through a rubber seal.

A stop clock was started and the volume of gas, V_t, measured at 2 minute intervals, for 12 minutes. When there was no further evolution of gas the volume of gas, V_{final}, was 76.5 cm^3.

(a) (i) Calculate the number of moles of 1-bromobutane used. You will need the values of the density and molar mass of 1-bromobutane from your Data booklet.

(2)

(ii) Calculate the maximum volume of gaseous but-1-ene, in cm^3, that could form.

[Molar volume of a gas 24 000 cm^3 under reaction conditions]

Suggest **two** reasons why this volume is unlikely to form.

(3)

....

....

....

....

(b) The results obtained are shown in the table below.

Time t/min	Volume of but-1-ene V_t/cm^3	($V_{final} - V_t$)/cm^3
0	0	76.5
2	31.5	45.0
4	51.0	25.5
6	62.5	14.0
8	68.5	8.0
10	72.0	4.5
12	74.0	2.5

(i) Explain why a large excess of potassium hydroxide is used in this experiment.

(1)

....

....

....

....

(ii) Plot a graph of $(V_{final} - V_t)/cm^3$ against t/min.

(3)

(iii) Suggest why the value of $(V_{final} - V_t)$ was plotted on your graph.

(1)

(iv) Measure two successive half lives from your graph.

(2)

First half life .... min

Second half life .... min

(v) Deduce the order of reaction with respect to 1-bromobutane.

Justify your answer.

(2)

....

....

....

....

(c) In another experiment, an excess of 1-bromobutane is reacted with varying concentrations of hydroxide ions. The results for the initial rate of the reaction are shown in the table below.

Experiment Number	$[C_4H_9Br]$ $/10^{-2}$ mol dm^{-3}	$[OH^-]$ $/10^{-3}$ mol dm^{-3}	Initial rate $/10^{-5}$ mol dm^{-3} min^{-1}
1	2.50	2.50	5.00
2	2.50	1.25	2.50
3	2.50	0.50	1.00

(i) Deduce the order of reaction with respect to hydroxide ions. Justify your answer using the data in the table.

(2)

....

....

....

....

(ii) Write the rate equation for the reaction using your answers to parts (b)(v) and (c)(i).

(1)

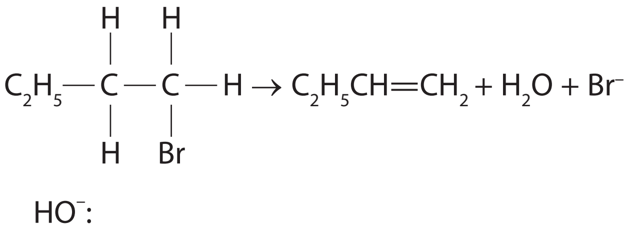
(iii) Give the units of the rate constant.

(1)

*(iv) It is suggested that the reaction begins with the slow attack by a hydroxide ion on a hydrogen atom in the 1-bromobutane, as shown below.

Complete the electron pair movement for this reaction using curly arrows and explain why this step is consistent with the rate equation for the reaction you have given in (c)(ii).

(3)



$$C_2H_5-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H \rightarrow C_2H_5CH{=}CH_2 + H_2O + Br^-$$

HO^-:

(Total for Question 13 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103

Mark Scheme (Results)

Summer 2013

GCE Chemistry 6CH04/01R
General Principles of Chemistry I

Summer 2013
Publications Code UA035568

General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. The strands are as follows:

  i) ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
  ii) select and use a form and style of writing appropriate to purpose and to complex subject matter
  iii) organise information clearly and coherently, using specialist vocabulary when appropriate

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear

- select and use a form and style of writing appropriate to purpose and to complex subject matter

- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1	D		**1**

Question Number	Correct Answer	Reject	Mark
2	D		**1**

Question Number	Correct Answer	Reject	Mark
3 (a)	A		**1**

Question Number	Correct Answer	Reject	Mark
(b)	D		**1**

Question Number	Correct Answer	Reject	Mark
(c)	A		**1**

Question Number	Correct Answer	Reject	Mark
(d)	D		**1**

Question Number	Correct Answer	Reject	Mark
4(a)	B		**1**

Question Number	Correct Answer	Reject	Mark
(b)	C		**1**

Question Number	Correct Answer	Reject	Mark
(c)	C		**1**

Question Number	Correct Answer	Reject	Mark
(d)	B		**1**

Question Number	Correct Answer	Reject	Mark
5(a)	D		**1**

Question Number	Correct Answer	Reject	Mark
(b)	C		**1**

Question Number	Correct Answer	Reject	Mark
(c)	C		**1**

Question Number	Correct Answer	Reject	Mark
(d)	C		**1**

Question Number	Correct Answer	Reject	Mark
(e)	D		**1**

Question Number	Correct Answer	Reject	Mark
6	A		**1**

Question Number	Correct Answer	Reject	Mark
7	C		**1**

Question Number	Correct Answer	Reject	Mark
8	C		**1**

Question Number	Correct Answer	Reject	Mark
9	B		**1**

Question Number	Correct Answer	Reject	Mark
10	B		**1**

SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
*11(a)	(A green solution) forms a yellow / orange / brown (solution) ALLOW reddish-brown **(1)** A grey / black precipitate ALLOW silver ppt ALLOW solid / crystals for precipitate **(1)**	Red 'Green(ish)' with any other colour Silver mirror silver compound	**2**

Question Number	Acceptable Answers	Reject	Mark
11(b)(i)	0.05(00) (mol dm^{-3})		**1**

Question Number	Acceptable Answers	Reject	Mark
11(b)(ii)	Amount of silver ion in 10 cm^3 = amount of thiocyanate = $\frac{5.6 \times 0.0200}{1000}$ = 0.000112/1.12×10^{-4} (mol) **(1)** So concentration of silver ion = $0.000112 \times \frac{1000}{10}$ = 0.0112/1.12×10^{-2} (mol dm^{-3}) **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
11(b)(iii)	0.0112/1.12×10^{-2} (mol dm^{-3}) Accept TE = answer to (ii)		**1**

Question Number	Acceptable Answers	Reject	Mark
11(b)(iv)	0.0500 – 0.0112 = 0.0388/3.88×10^{-2} (mol dm^{-3}) Accept TE = 0.05 - answer to (iii) Accept answer to (i) – answer to (iii)		**1**

Question Number	Acceptable Answers	Reject	Mark
11(b)(v)	$K_c = \dfrac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]\,[Ag^{+}(aq)]}$ ALLOW $K_c = \dfrac{[Fe^{3+}]}{[Fe^{2+}]\,[Ag^{+}]}$ **(1)** $= \dfrac{0.0388}{0.0112^2}$ $= 309.311 = 309\ dm^3\ mol^{-1}$ Value **(1)** Unit (any order) **(1)** Three SF **(1)** Accept TE from (iii) and (iv): (use of 0.1 from (i) gives 708 $dm^3\ mol^{-1}$) If [Ag] is included in the numerator and taken as =[Fe^{3+}(aq)], then allow unit and SF marks ONLY, but must either state 'no units' or show working	[Ag] in numerator	**4**

Question Number	Acceptable Answers	Reject	Mark
11(c)(i)	$\Delta S^{\ominus}_{total}$ = 8.31 x ln 309 = + 47.6(4) / +47.6(5)J $mol^{-1}\ K^{-1}$ OR = 8.31 x ln 309.311 = +47.6(5) J $mol^{-1}\ K^{-1}$ Accept TE : 8.31 x ln(answer from b(v)) Value **(1)** Sign **and** Unit (any order) **(1)** IGNORE sf except 1		**2**

Question Number	Acceptable Answers	Reject	Mark
11(c)(ii)	First Mark: One of the products is a solid OR Two moles going to two moles but one of them is a solid OR Two moles of solution react to form one mole of solution / liquid and one mole of solid **(1)** **Second Mark** (Hence) RHS more ordered / LHS less ordered **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
11(c)(iii)	$\Delta S^{\ominus}_{\text{surroundings}} = \Delta S^{\ominus}_{\text{total}} - \Delta S^{\ominus}_{\text{system}}$ = +47.6 – (-208.3) = (+)255.9 (J mol^{-1} K^{-1}) Accept TE on c(i) IGNORE sf except 1		**1**

Question Number	Acceptable Answers	Reject	Mark
11(c)(iv)	Because $\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H^{\ominus}}{T}$ **(1)** ΔH= -298 x 255.9 = -76258 (J mol^{-1}) = -76.258 (kJ mol^{-1}) **(1)** Units if given must be correct Correct answer with or without working scores 2 marks IGNORE SF except 1 As T increases $\Delta S^{\ominus}_{\text{surroundings}}$ becomes less positive / decreases **therefore** ΔS_{total} becomes less positive / decreases ALLOW more negative for less positive **(1)**	$\Delta S^{\ominus}_{\text{total}} = \frac{-\Delta H^{\ominus}}{T}$	**3**

Question Number	Acceptable Answers	Reject	Mark
11*(d)	No change in the titre ALLOW No significant change Stand alone mark **(1)** (though silver solid was removed the equilibrium constant remains the same so) the equilibrium **concentration(s)** would remain the same **(1)** Second mark dependent on first IGNORE references to temperature		**2**

Total for Question 11 = 21 Marks

Question Number	Acceptable Answers	Reject	Mark
12(a)(i)	Aldehydes often contain (carboxylic) **acid** formed by oxidation (by the oxygen in air)		**1**

Question Number	Acceptable Answers	Reject	Mark
12(a)(ii)	A larger volume of sodium carbonate solution is neutralized / a larger volume of carbon dioxide forms / faster reaction / more effervescence / more vigorous ALLOW reverse argument for impure aldehyde	(The old stock of) aldehyde does not react	**1**

Question Number	Acceptable Answers	Reject	Mark
12(a)(iii)	$Na_2CO_3(aq)$ + $2C_3H_7COOH(aq)$ → $2C_3H_7COO^{(-)}Na^{(+)}(aq)$ + $CO_2(g)$ + $H_2O(l)$ Correct balanced equation **(1)** Correct state symbols on correct species **(1)** ALLOW $H_2O(aq)$ $C_3H_7COO^{(-)}Na^{(+)}(s)$ $C_3H_7COOH(l)$	$NaCO_3$	**2**

Question Number	Acceptable Answers	Reject	Mark
12(a)*(iv)	3300 -2500 (cm^{-1}) AND O-H (stretching) **(1)**	COOH (group)	**3**
	1725 – 1700 (cm^{-1}) AND C=O (stretching) **(1)** ALLOW single numbers or ranges within these ranges ALLOW 1300-1250 (cm^{-1}) AND C-O in COOH	COOH (group)	
	Very broad (O-H) due to hydrogen bonding **(1)**	Hydrogen Bonding in C=O	

Question Number	Acceptable Answers	Reject	Mark
12(a)(v)	**First mark** (stand alone) 4 peaks OR 4 hydrogen environments ALLOW 4 chemical shifts **(1)** **Second and Third Marks** Splitting pattern:		**3**
	($CH_3CH_2CH_2COO\underline{\mathbf{H}}$) singlet /1 line	1 split	
	($CH_3CH_2C\underline{\mathbf{H_2}}COOH$) triplet / three lines	3 splits	
	($CH_3C\underline{\mathbf{H_2}}CH_2COOH$) sextuplet / sextet / six lines	6 splits	
	($C\underline{\mathbf{H_3}}CH_2CH_2COOH$) triplet / three lines	3 splits	
	All four correct **(2)** any three **(1)** ALLOW No splits, 2 splits, five splits, 2 splits scores 2 1,3,6,3 'splits' scores 1 mark		

Question Number	Acceptable Answers	Reject	Mark
12(b)	Start pH at 2.9 ALLOW 2—4 **(1)**		**4**
	Initial sharp rise to buffer region then vertical section at 25 cm^3 ALLOW Gradual rise to vertical section at 25 cm^3 **(1)**	Horizontal from start	
	Vertical within pH range 6-11 **and** 2.5-4 units long **(1)**	deviation from vertical	
	End pH value in range 12-13 **(1)**	maximum before final pH Graph ending before 50cm^3	

Question Number	Acceptable Answers	Reject	Mark
12(c)(i)	White / steamy / misty fumes ALLOW 'gas' for fumes IGNORE correct indicator test on product	White smoke Effervescence Just 'fumes' Just 'gas'	**1**

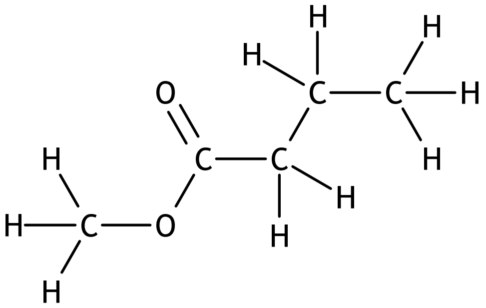
Question Number	Acceptable Answers	Reject	Mark
12(c)(ii)	$CH_3CH_2CH_2COCl$ **(1)** ALLOW displayed formula butanoyl chloride **(1)** ALLOW Butanyl chloride No TE on incorrect structure	C_3H_7COCL Butyl Chloride Buthyl Chloride	**2**

Question Number	Acceptable Answers	Reject	Mark
12(d)(i)	Butan-1-ol OR $CH_3CH_2CH_2CH_2OH$ If 2 answers are given both must be correct	Butanol Butanal C_4H_9OH	**1**

Question Number	Acceptable Answers	Reject	Mark
12(d)(ii)	(Dry) Ethoxyethane / diethylether / Ether OR $C_2H_5OC_2H_5$ / $CH_3CH_2OCH_2CH_3$ If 2 answers are given they must both be correct		**1**

Question Number	Acceptable Answers	Reject	Mark
12(d)(iii)	The responses are in pairs: a type (1) and an **associated** justification (1) Reduction (of butanoic acid) **(1)** By addition of hydrogen / loss of oxygen **(1)** **OR** Oxidation of lithium tetrahydroidaluminate / aluminium hydride / $LiAlH_4$ **(1)** By addition of oxygen **(1)** **OR** (Nucleophilic) addition **(1)** of hydride / H^- **(1)** **OR** Redox **(1)** Because butanoic acid has been reduced AND $LiAlH_4$ has been oxidised **(1)**	Any substitution Electrophilic addition	**2**

Question Number	Acceptable Answers	Reject	Mark
12(e)(i)	(Concentrated / dilute) sulfuric / hydrochloric acid ALLOW any **strong** acid ALLOW 'acid (catalyst)' **(1)** (heat or boil under) reflux ALLOW Heat / warm **(1)** Elevated temp≤65^0C	Just 'catalyst' Just H^+ Just 'boil' Just 'distil' High temperature Increased concentration	**2**

Question Number	Acceptable Answers	Reject	Mark
12(e)(ii)	 All bonds must be shown except ALLOW CH_3 at either end of molecule.	Omitted Hydrogen / sticks	**1**

Question Number	Acceptable Answers	Reject	Mark
12(e)(iii)	Butanoyl chloride / $CH_3CH_2CH_2COCl$ ALLOW Butanyl chloride OR Butanoic anhydride / ($CH_3CH_2CH_2CO)_2O$ OR Specified alkyl butanoate (not methyl butanoate) If name and structure are both given they must both be correct	Butyl Chloride Buthyl Chloride	**1**

Question Number	Acceptable Answers	Reject	Mark
12(e)(iv)	**Advantage** marks are dependent on correct reagent (or near miss e.g. propanoyl chloride) in (iii). No TE on random answer to (iii) eg H_2SO_4 Advantages – any **two** from: Higher yield / goes to completion/ not an equilibrium reaction / not reversible No heat / no refluxing / less energy needed No catalyst needed / faster By-product is a gas (so easier to separate) **(2)** Disadvantage (marked independently of (e)(iii)) any **one** of: (Acyl chloride is) more expensive / corrosive IGNORE Acyl chloride is toxic / hazardous / harmful / difficult to store OR toxic /corrosive **and** HCl /gas / fumes evolved IGNORE harmful/ hazardous/ dangerous OR has lower atom economy **(1)**	Good yield	**3**

Total for Question 12 = 28 Marks

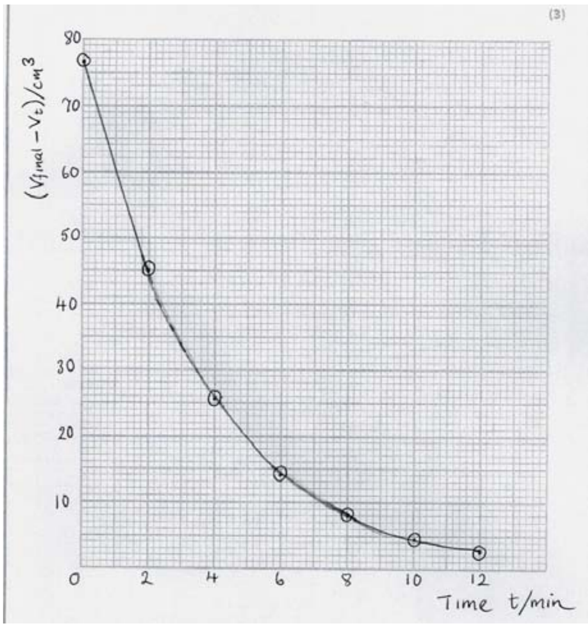
Total for Section B = 49 Marks

Section C

Question Number	Acceptable Answers	Reject	Mark
13(a)(i)	Mass of bromobutane = 0.6 x 1.276 (=0.7656 (g)) **(1)** Amount of bromobutane = $\frac{0.6 \times 1.276}{137.0}$ = 5.5883 x 10^{-3} = 5.59 x 10^{-3} / 0.00559 (mol) OR Amount of bromobutane = $\frac{0.6 \times 1.276}{136.9}$ = 5.5924 x 10^{-3} = 5.59 x 10^{-3} / 0.00559 (mol) TE on incorrect mass ALLOW 6 x 10^{-3} (mol) **(1)** Correct answer with no working scores 2 marks		**2**

Question Number	Acceptable Answers	Reject	Mark
13(a)(ii)	5.5883 x 10^{-3} x 24 000 = 134.12 (134.22 from 136.9)=134 cm^3 **(1)** ALLOW answer from (i) x 24000 IGNORE SF except 1 Any two from: Formation of butan-1-ol / other / side reactions Incomplete reaction Some but-1-ene may remain in solution **(2)** IGNORE Reaches equilibrium / reaction reversible But-1-ene reacts with ethanol/ solvent	Transfer losses Gas escapes Gas reacts with water But-1-ene condenses	**3**

Question Number	Acceptable Answers	Reject	Mark
13(b)(i)	So [OH$^-$] remains (effectively) constant OR [1-bromobutane] is the only variable IGNORE So [OH$^-$] is not the limiting factor	Ensure that all C_4H_9Br reacts [OH$^-$] is in excess [OH$^-$] does not affect the rate Just 'Only [1-bromobutane] affects the rate'	**1**

Question Number	Acceptable Answer	Reject	Mark
13 (b)(ii)	 Axes correct with sensible scales to use at least half of graph paper on both axes **(1)** Labels ((V_{final} - V_t) and t) fully correct with units **(1)** All 7 points correctly plotted and smooth curve drawn **(1)**	Axes plotted wrong way round 'Volume'	**3**

Question Number	Acceptable Answers	Reject	Mark
13(b)(iii)	(V_{final} - V_t) is proportional to the concentration of 1-bromobutane		**1**

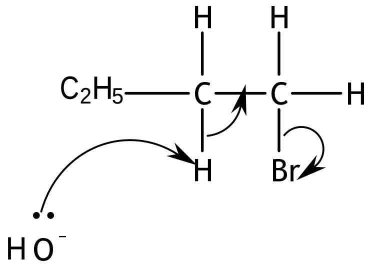
Question Number	Acceptable Answers	Reject	Mark
13(b)(iv)	Two values 2.5 ± 0.3 (min) (each scores one mark) **(2)**		**2**

Question Number	Acceptable Answers	Reject	Mark
13(b)(v)	Answer must be consistent with values in (iv) Because half lives are constant / similar **(1)** The reaction is first order... **(1)** If values in (iv) are 2.5 and 5, then: Reaction is 2nd order because half lives are increasing scores both marks. Reaction is 1st order because half lives are constant scores 1 mark		**2**

Question Number	Acceptable Answers	Reject	Mark
13(c)(i)	Order one **(1)** Any one of: (Exp 1 and 2) $[OH^-]$ halves and rate halves. (Exp 1 and 3) $[OH^-]$ 1/5 and rate 1/5 (Exp 2 and 3) $[OH^-]$ 2/5 and rate 2/5 ALLOW reverse logic **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
13(c)(ii)	Rate = $k[C_4H_9Br][OH^-]$ IGNORE case of K/k TE on b(v) and c(i)		**1**

Question Number	Acceptable Answers	Reject	Mark
13(c)(iii)	$dm^3 mol^{-1} min^{-1}$ ALLOW $dm^3 mol^{-1} s^{-1}$ any sequence of units TE on (ii)		**1**

Question Number	Acceptable Answers	Reject	Mark
13(c)*(iv)	 Arrows from OH-to H and from C-H bond to make additional bond between carbons **(1)** Third arrow from bond between carbon and bromine to bromine **(1)** (Because) both 1–bromobutane and hydroxide ion appear in the RDS ALLOW Attack of OH- on H is slow, therefore this is the RDS (Because) both 1–bromobutane and hydroxide ion appear in the slow step **(1)** IGNORE mention of rate equation	Both are involved in the reaction Mechanism described as S_N2	**3**

Total for Section C = 21 Marks

Total for Paper = 90 Marks

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