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Pearson Edexcel
International
Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Chemistry

Advanced

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

Monday 9 June 2014 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

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 In aqueous solution, iodine reacts with propanone in the presence of a catalyst of dilute hydrochloric acid.

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

Which of the following methods would be suitable for investigating the rate of this reaction?

☒ **A** Measuring the increase in pH with a pH meter.

☒ **B** Measuring the change in rotation of plane-polarized light with a polarimeter.

☒ **C** Quenching with ice cold water, followed by titration with acid.

☒ **D** Quenching with sodium hydrogencarbonate solution, followed by titration with sodium thiosulfate solution.

(Total for Question 1 = 1 mark)

2 Hydrogen peroxide decomposes in a first order reaction.

The half-life for this reaction is 60 s.

In an experiment, the initial concentration of hydrogen peroxide is 0.100 mol dm^{-3}.

The concentration of hydrogen peroxide, in mol dm^{-3}, at 120 s is

☒ **A** 0.025

☒ **B** 0.050

☒ **C** 0.075

☒ **D** 0.100

(Total for Question 2 = 1 mark)

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

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3 To determine the activation energy, E_a, for a reaction, a graph was plotted of ln k against 1/T, where k is the rate constant.

The Arrhenius equation is

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

The gradient of the graph is equal to

☒ **A** E_a

☒ **B** $-E_a$

☒ **C** $\frac{E_a}{R}$

☒ **D** $-\frac{E_a}{R}$

(Total for Question 3 = 1 mark)

4 A bromoalkane was hydrolysed by an aqueous alkaline solution. The reaction was found to be first order with respect to the bromoalkane and zero order with respect to hydroxide ions.

A bromoalkane consistent with this information is

☒ **A** CH_3Br

☒ **B** CH_3CH_2Br

☒ **C** $CH_3CH_2CH_2Br$

☒ **D** $(CH_3)_3CBr$

(Total for Question 4 = 1 mark)

5 Which of the following is the correct order of increasing molar entropy under standard conditions?

	Lowest entropy	Medium entropy	Highest entropy
☒ **A**	oxygen	water	copper
☒ **B**	oxygen	copper	water
☒ **C**	copper	water	oxygen
☒ **D**	copper	oxygen	water

(Total for Question 5 = 1 mark)

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6

Enthalpy of solution of sodium chloride	+4 kJ mol^{-1}
Enthalpy of hydration of $Cl^-(g)$	−364 kJ mol^{-1}
Lattice energy of sodium chloride	−780 kJ mol^{-1}
Lattice energy of magnesium chloride	−2526 kJ mol^{-1}

(a) Use the data above to calculate the enthalpy of hydration of sodium ions, $Na^+(g)$.

The enthalpy of hydration of sodium ions, $Na^+(g)$ is

(1)

☒ **A** −412 kJ mol^{-1}

☒ **B** +412 kJ mol^{-1}

☒ **C** −420 kJ mol^{-1}

☒ **D** +420 kJ mol^{-1}

(b) Magnesium chloride has a more exothermic lattice energy than sodium chloride because

(1)

☒ **A** a magnesium ion has a higher charge and a larger radius than a sodium ion.

☒ **B** a magnesium ion has a higher charge and a smaller radius than a sodium ion.

☒ **C** a magnesium ion has the same charge and a larger radius than a sodium ion.

☒ **D** a magnesium ion has the same charge and a smaller radius than a sodium ion.

(Total for Question 6 = 2 marks)

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

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7 Nitrogen reacts with hydrogen to form ammonia.

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

(a) The units for the equilibrium constant, K_c, for this reaction are

(1)

☒ **A** mol dm^{-3}

☒ **B** mol^2 dm^{-6}

☒ **C** dm^3 mol^{-1}

☒ **D** dm^6 mol^{-2}

(b) The highest equilibrium yield of ammonia is produced at

(1)

☒ **A** high temperature and high pressure.

☒ **B** high temperature and low pressure.

☒ **C** low temperature and high pressure.

☒ **D** low temperature and low pressure.

(Total for Question 7 = 2 marks)

8 Calcium carbonate decomposes when heated.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant, K_c, for this reaction, is

$$K_c = [CO_2(g)]$$

The concentrations of calcium carbonate and calcium oxide are omitted from this expression because

☒ **A** they are constant.

☒ **B** they are equal.

☒ **C** they are very small compared with the concentration of carbon dioxide.

☒ **D** the concentration of calcium carbonate is much larger than the concentration of calcium oxide.

(Total for Question 8 = 1 mark)

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9 Which of the following shows the correct order of increasing boiling temperature?

	Lowest boiling temperature	Middle boiling temperature	Highest boiling temperature
☒ **A**	ethanol	ethanal	ethanoic acid
☒ **B**	ethanol	ethanoic acid	ethanal
☒ **C**	ethanal	ethanol	ethanoic acid
☒ **D**	ethanal	ethanoic acid	ethanol

(Total for Question 9 = 1 mark)

10 A carbonyl compound with molecular formula $C_5H_{10}O$ reacted with iodine in an alkaline solution to give a pale yellow precipitate with an antiseptic smell.

The carbonyl compound is

☒ **A** $CH_3CH_2CH_2CH_2CHO$

☒ **B** $CH_3CH_2CH_2COCH_3$

☒ **C** $CH_3CH_2CH(CH_3)CHO$

☒ **D** $CH_3CH_2COCH_2CH_3$

(Total for Question 10 = 1 mark)

11 Which of the following can form propanoic acid in a single step reaction?

☒ **A** 1-chloropropane

☒ **B** propanenitrile

☒ **C** propan-2-ol

☒ **D** propene

(Total for Question 11 = 1 mark)

12 The ester, ethyl propanoate, can be made in a single step from

☒ **A** CH_3CH_2OH and CH_3CH_2CHO

☒ **B** CH_3CH_2OH and CH_3CH_2COCl

☒ **C** $CH_3CH_2CH_2OH$ and CH_3COCl

☒ **D** $CH_3CH_2CH_2OH$ and CH_3CHO

(Total for Question 12 = 1 mark)

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13 The repeat unit of the polymer formed from $HOCH_2CH_2OH$ and $HOOCCH_2COOH$ is

☒ **A** —$OCH_2CH_2OOCCH_2CO$—

☒ **B** —$OCH_2CH_2COCH_2COO$—

☒ **C** —$OCH_2CH_2COOCH_2CO$—

☒ **D** —$OCH_2COOCH_2CH_2CO$—

(Total for Question 13 = 1 mark)

14 The compound bromochloroiodomethane, CHClBrI, has a chiral carbon atom and exists as a pair of enantiomers.

The enantiomers will have different

☒ **A** boiling temperatures.

☒ **B** effects on plane-polarized light.

☒ **C** chemical reactions.

☒ **D** colours.

(Total for Question 14 = 1 mark)

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

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15 An organic compound, **Y**, has the molecular formula $C_5H_{10}O$.

(a) The infrared spectrum of compound **Y** includes a strong absorbance at 1730 cm^{-1} but has no broad absorbance at 3750–3200 cm^{-1}.

Refer to pages 5 and 6 of the Data Booklet.

The compound could be

(1)

☒ **A** an alcohol, aldehyde or ketone.

☒ **B** a ketone but not an alcohol or aldehyde.

☒ **C** an aldehyde but not an alcohol or ketone.

☒ **D** an aldehyde or a ketone but not an alcohol.

(b) Compound **Z** is an isomer of **Y** and has the structure shown below

$$CH_3CH_2CH_2COCH_3$$

The high-resolution proton nmr spectrum for compound **Z** shows four peaks.

The splitting patterns in these peaks are likely to be

(1)

☒ **A** 1 singlet, 2 triplets and 1 sextuplet (split into six).

☒ **B** 1 singlet, 2 doublets and 1 sextuplet (split into six).

☒ **C** 1 singlet, 2 doublets and 1 triplet.

☒ **D** 2 doublets and 2 triplets.

(Total for Question 15 = 2 marks)

16 The pH of a sample of water is 7.

10 cm^3 of 1.0 mol dm^{-3} hydrochloric acid is added to 990 cm^3 of this water.

What is the pH of the solution formed?

☒ **A** 0

☒ **B** 1

☒ **C** 2

☒ **D** 3

(Total for Question 16 = 1 mark)

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17 A buffer solution is made by mixing ethanoic acid with sodium ethanoate solution in a 3 to 1 mole ratio.

K_a for ethanoic acid = 1.7×10^{-5} mol dm^{-3}

The pH of the buffer solution is

☒ **A** 2.4

☒ **B** 4.3

☒ **C** 4.8

☒ **D** 5.2

(Total for Question 17 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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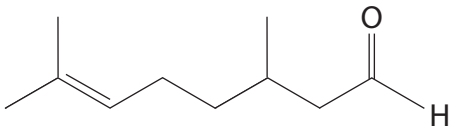
SECTION B

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

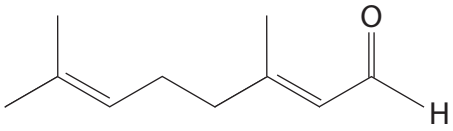
18 Citronella oil is obtained from lemongrass.

It is a source of chemicals for the perfume industry.

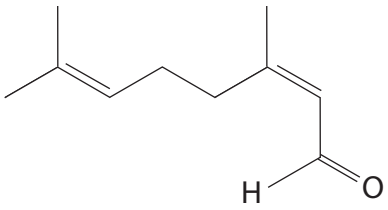
Three of the aldehydes found in citronella oil are shown below.



citronellal



geranial



neral

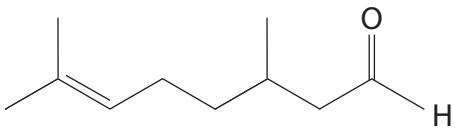
(a) Give the molecular formula for citronellal.

(1)

.....

(b) Citronellal has one chiral carbon atom.
Draw a circle around the chiral carbon atom on the structure of citronellal below.

(1)



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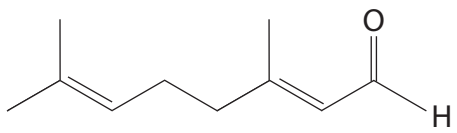
(c) Geranial and neral are a pair of *E-Z* isomers.

(i) Explain how this type of isomerism arises.

(2)

(ii) Draw a circle around any part of the geranial structure below that causes its *E-Z* isomerism.

(1)

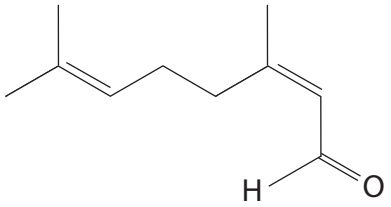


(d) Describe a simple test tube reaction to show that these three carbonyl compounds are aldehydes and not ketones. State the observation you would make.

(2)

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(e) The skeletal formula of neral is shown below.



Draw the **skeletal** formula for the organic product of the reaction of neral with

(i) excess hydrogen in the presence of a nickel catalyst.

(1)

(ii) lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether.

(1)

(Total for Question 18 = 9 marks)

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19 (a) A student investigated the kinetics of the reaction in which an acidified, aqueous solution of hydrogen peroxide oxidizes iodide ions to iodine.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

(i) The results of three experiments are shown in the table below.

Experiment number	$[H_2O_2(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.5	1.0	0.5	7.0×10^{-6}
2	1.0	1.0	0.5	1.4×10^{-5}
3	0.5	2.0	0.5	7.0×10^{-6}

Determine the order with respect to hydrogen peroxide and $H^+(aq)$ ions.

Explain your reasoning.

(3)

Order with respect to $H_2O_2(aq)$

.....

.....

.....

Order with respect to $H^+(aq)$

.....

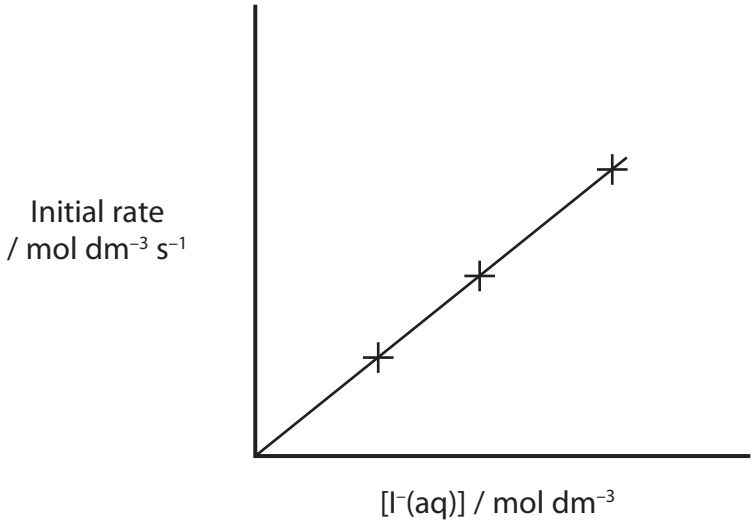
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(ii) The student carried out three more experiments in which the initial concentrations of hydrogen peroxide and $H^+(aq)$ ions were kept constant and the initial concentration of iodide ions was changed.

A graph of the results is shown below.



State the order with respect to $I^-(aq)$ and explain your reasoning.

(2)

.....

.....

.....

(iii) Use your answers to (a)(i) and (a)(ii) to write the rate equation for the reaction.

(1)

(iv) Use the data from the table and your answer to (a)(iii) to calculate the value for the rate constant. Include units in your answer.

(2)

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(b) Nitrogen dioxide reacts with carbon monoxide.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The reaction is second order with respect to nitrogen dioxide, and zero order with respect to carbon monoxide.

(i) Suggest a possible two-step mechanism for this reaction.

Write the rate determining step first.

(2)

Rate determining step

.....

Step 2

.....

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the reaction between nitrogen dioxide and carbon monoxide at 298 K. Include a sign and units in your answer.

You will need to use the standard molar entropies on pages 20 and 27 of the Data Booklet.

(2)

(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction between nitrogen dioxide and carbon monoxide at 298 K is –226 kJ mol^{-1}, 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)

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

State what the sign of $\Delta S^{\ominus}_{total}$ indicates about this reaction at 298 K.

(2)

.....

.....

(Total for Question 19 = 16 marks)

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20 Propanal, CH_3CH_2CHO, is used in the chemical industry in the manufacture of plastics, and as a disinfectant and preservative.

(a) (i) Give the mechanism for the reaction between propanal and hydrogen cyanide in the presence of potassium cyanide.

Include the dipole on the carbonyl group.

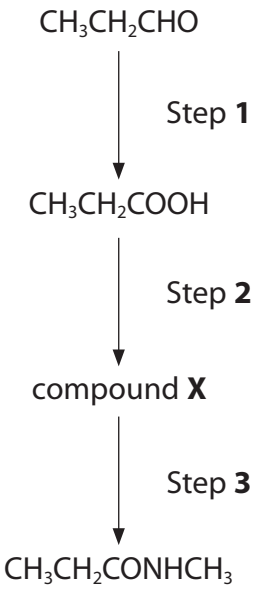
(4)

(ii) Classify the type and mechanism of the reaction between propanal and hydrogen cyanide.

(2)

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(b) Propanal can be converted into *N*-methyl propanamide, $CH_3CH_2CONHCH_3$, in three steps.



(i) The reagent used in Step **2** is phosphorus(V) chloride, PCl_5.

Identify, by name or formula, compound **X**.

(1)

(ii) Identify, by name or formula, the reagent needed for Step **3**.

(1)

(iii) State the number of peaks you would expect in the **low** resolution proton nmr spectrum of *N*-methyl propanamide.

(1)

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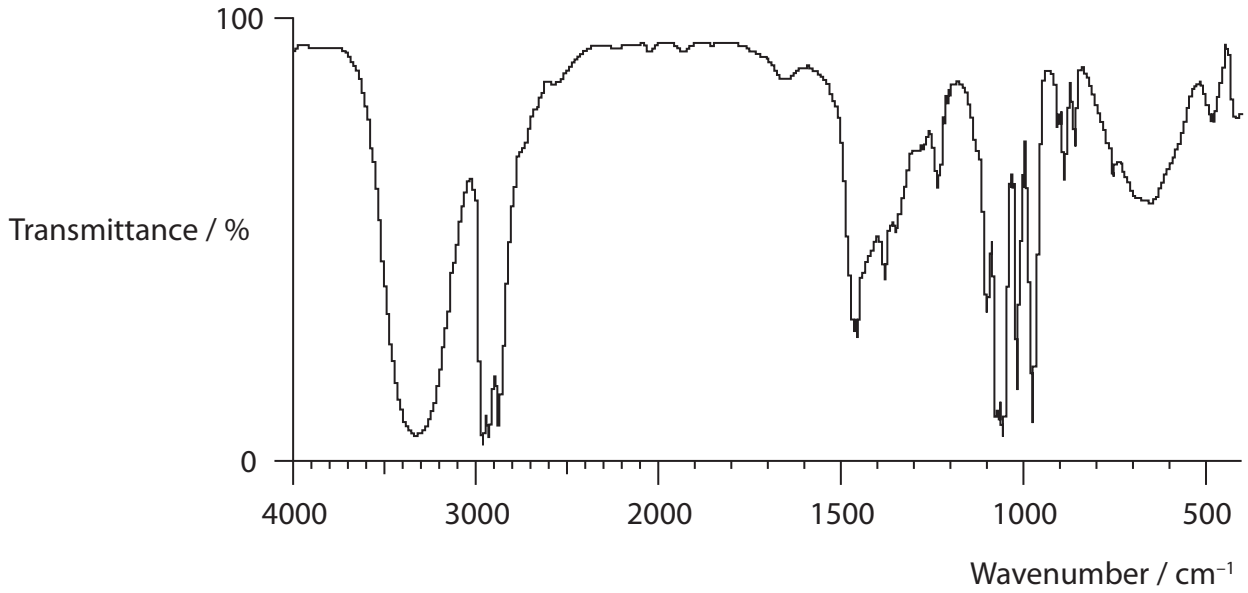
(c) Write the equation for the reaction between propanoic acid and propan-2-ol, in the presence of an acid catalyst, showing the structure of the organic product.

State symbols are not required.

(2)

(d) A sample of propanoic acid was reduced to form compound **Q**.

The infrared spectrum of compound **Q** is shown below.



Use the infrared spectrum to identify compound **Q**.

Explain your reasoning, quoting suitable data.

(2)

(Total for Question 20 = 13 marks)

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21 This question concerns the reaction of hydrogen with iodine to form hydrogen iodide at 700 K.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -10 \text{ kJ mol}^{-1}$$

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

(1)

*(ii) 1 mol of hydrogen was mixed with 1 mol of iodine in a sealed container and left to reach equilibrium at 700 K.

The total pressure was 5 atm.

At equilibrium, the amount of iodine remaining was 0.21 mol.

Calculate the partial pressure of each gas at equilibrium.

Use the partial pressures to calculate the value of K_p, stating its units, if any.

(5)

K_p = ... units .....

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(b) State the effect of increasing the pressure on the equilibrium position. Justify your answer by using the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -10 \text{ kJ mol}^{-1}$$

(1)

(c) (i) Explain how increasing the temperature affects the value of ΔS_{total} of this reaction. Assume that ΔS_{system} does not change when the temperature increases.

(2)

*(ii) Use your answer to (c)(i) to explain the effect of an increase in temperature on the value of K_p and the equilibrium yield of hydrogen iodide.

(2)

(Total for Question 21 = 11 marks)

TOTAL FOR SECTION B = 49 MARKS

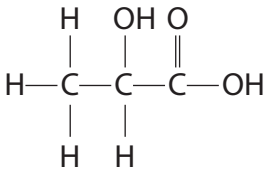
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SECTION C

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

22 Lactic acid, 2-hydroxypropanoic acid, is found in sour milk.

The structure of lactic acid, $CH_3CH(OH)COOH$, is shown below.



(a) (i) State what is meant by a Brønsted-Lowry acid.

(1)

.....

.....

(ii) Write the equation for the reaction of lactic acid with water to form an acidic solution. State symbols are not required.

(1)

(iii) Write the expression for the acid dissociation constant, K_a, for lactic acid.

(1)

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(iv) Calculate the pH of a solution of lactic acid of concentration 0.15 mol dm^{-3} at 298 K.

The pK_a of lactic acid is 3.86 at 298 K.

State clearly any assumptions you have made.

(5)

Calculation:

Assumptions:

.....

.....

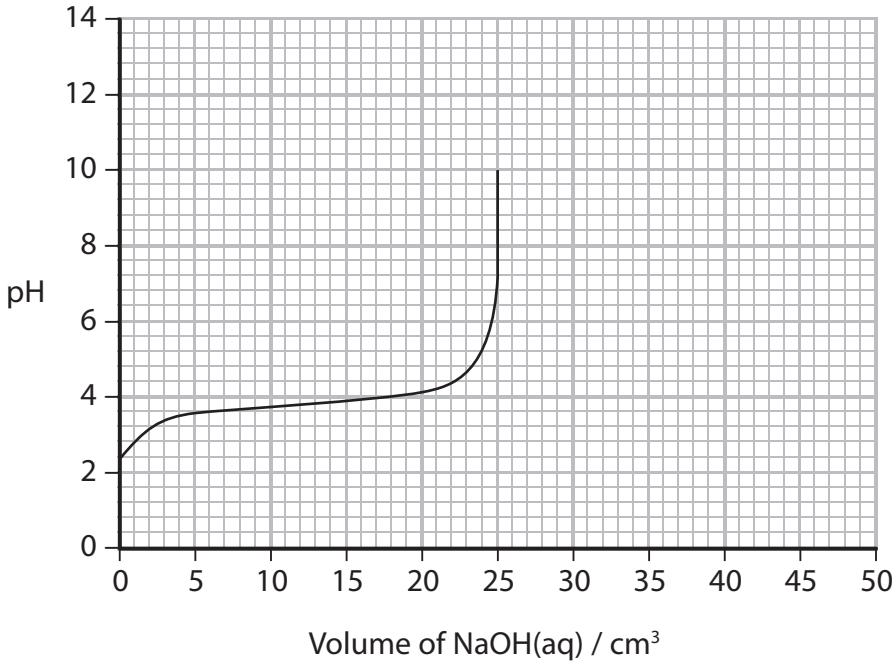
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(b) 25 cm^3 of a 0.15 mol dm^{-3} solution of lactic acid was titrated with 50 cm^3 of sodium hydroxide solution of the same concentration.

Part of the titration curve is shown below.



(i) Calculate the pH of 0.15 mol dm^{-3} sodium hydroxide solution. Give your answer to one decimal place.

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

(2)

(ii) Complete the titration curve on the diagram above to show the change in pH until 50.0 cm^3 of the sodium hydroxide solution has been added to the solution of lactic acid.

(1)

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(iii) Use the information given in your Data Booklet to select a suitable indicator for this titration, giving the colour change you would expect to see.

Justify your selection.

(3)

(iv) The equation for the neutralization in the titration is

$$CH_3CH(OH)COOH(aq) + NaOH(aq) \rightarrow CH_3CH(OH)COONa(aq) + H_2O(l)$$

Use the titration curve to suggest the pH of a 0.075 mol dm^{-3} solution of sodium lactate. Justify your answer.

(2)

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*(v) Explain, using ionic equations, how a solution containing lactic acid and sodium lactate can act as a buffer solution.

(4)

(c) Ethanoic acid, CH_3COOH, has a pK_a of 4.8 at 298 K.

Complete the equation to show the conjugate acid-base pairs that could be produced when pure samples of lactic acid and ethanoic acid are mixed.

(1)

$CH_3CH(OH)COOH + CH_3COOH \rightarrow$ ..... + ...

(Total for Question 22 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass **atomic symbol** name atomic (proton) number									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

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
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

* Lanthanide series

* Actinide series

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