Write your name here

Surname	Other names

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)

Tuesday 31 October 2017 – Morning
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

Candidates must have: Data Booklet
Scientific calculator

Total Marks

Instructions

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

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- 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.
- Try to answer every question.
- Check your answers if you have time at the end.
- Show all your working in calculations and include units where appropriate.

Turn over ▶

P50788A

6/5/5/5/5/1/8/c2

P 5 0 7 8 8 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 The rate of the reaction between hydrogen and bromine is investigated.

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

(a) The progress of this reaction may be continuously monitored by measuring the change in

(1)

☐ **A** volume.

☐ **B** pressure.

☐ **C** pH.

☐ **D** colour.

(b) What can be deduced about the rate equation for this reaction from its chemical equation?

(1)

☐ **A** It is first order with respect to both hydrogen and bromine.

☐ **B** It is second order with respect to hydrogen bromide.

☐ **C** It is second order with respect to both hydrogen and bromine.

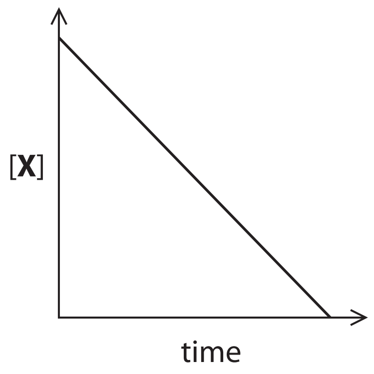
☐ **D** Nothing, because the chemical equation gives no information about the mechanism.

(Total for Question 1 = 2 marks)

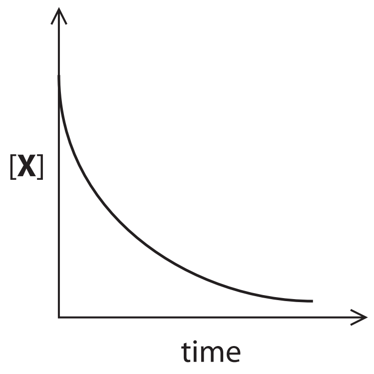
Use this space for any rough working. Anything you write in this space will gain no credit.

2 The decomposition of compound **X** is first order. The correct graph for this is

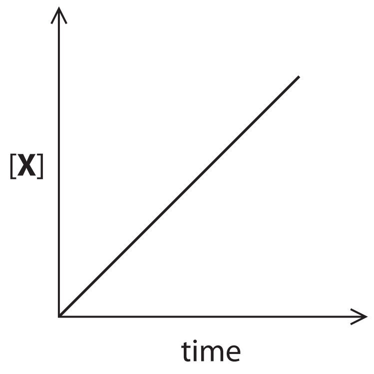
☒ **A**



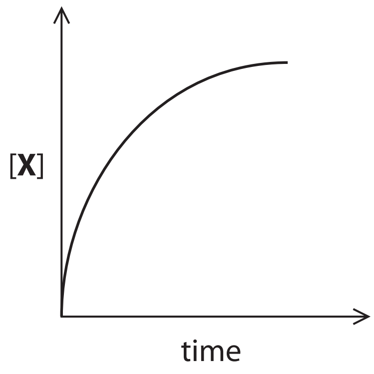
☒ **B**



☒ **C**



☒ **D**



(Total for Question 2 = 1 mark)

3 For a zero order reaction, the relationship between $[\mathbf{Y}]_0$ which is the concentration of **Y** at the start of any half-life, the rate constant, k, and the half-life, $t_{½}$, is

$$[\mathbf{Y}]_0 = 2kt_{½}$$

From this it can be deduced that for a zero order reaction the half-life

- ☒ **A** increases as the reaction proceeds.
- ☒ **B** decreases as the reaction proceeds.
- ☒ **C** remains constant when the temperature is constant.
- ☒ **D** remains constant under all conditions.

(Total for Question 3 = 1 mark)

4 If an endothermic reaction is thermodynamically feasible, it may be deduced that

- ☒ **A** the activation energy is low.
- ☒ **B** $\Delta S_{\text{surroundings}}$ is positive.
- ☒ **C** ΔS_{system} is positive.
- ☒ **D** ΔS_{total} is negative.

(Total for Question 4 = 1 mark)

5 Calcium carbonate is stable at room temperature but decomposes when heated strongly:

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

The best explanation for this is

- ☒ **A** $\Delta S_{\text{surroundings}}$ becomes less negative as temperature increases.
- ☒ **B** ΔS_{system} becomes more positive as temperature increases.
- ☒ **C** the entropy of gases is higher than that of solids.
- ☒ **D** the entropy of a substance increases with temperature.

(Total for Question 5 = 1 mark)

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

6 At 298 K, butane has a larger standard molar entropy than 2-methylpropane.
The explanation for this is that butane has

- ☒ **A** more ways of distributing energy quanta.
- ☒ **B** fewer ways of distributing energy quanta.
- ☒ **C** a less negative standard molar enthalpy change of formation.
- ☒ **D** a higher boiling temperature.

(Total for Question 6 = 1 mark)

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7 The cracking of alkanes is carried out at high temperature.
The equation for a typical reaction is

$$C_8H_{18}(g) \rightleftharpoons C_4H_{10}(g) + 2C_2H_4(g)$$

When the pressure is increased, the reaction shifts to the

- ☒ **A** right to re-establish the equilibrium.
- ☒ **B** left to re-establish the equilibrium.
- ☒ **C** right, and then moves to the left to re-establish the equilibrium.
- ☒ **D** left, and then moves to the right to re-establish the equilibrium.

(Total for Question 7 = 1 mark)

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

8 Water gas is a mixture of carbon monoxide and hydrogen produced by passing steam over white-hot carbon:

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$$

The equilibrium constant, K_p, for this reaction is given by the expression

☒ **A** $p(H_2) \times p(CO)$

☒ **B** $\dfrac{1}{p(H_2) \times p(CO)}$

☒ **C** $\dfrac{p(H_2) \times p(CO)}{p(H_2O)}$

☒ **D** $\dfrac{p(H_2O)}{p(H_2) \times p(CO)}$

(Total for Question 8 = 1 mark)

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9 In the Haber process, ammonia is produced on an industrial scale by an exothermic reaction.

(a) The equation for the Haber process can be written as

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \text{or} \quad \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

The units of the equilibrium constant, K_c, are

(1)

	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
☒ **A**	$dm^6\ mol^{-2}$	$dm^3\ mol^{-1}$
☒ **B**	$dm^6\ mol^{-2}$	$dm^6\ mol^{-2}$
☒ **C**	$mol^2\ dm^{-6}$	$mol\ dm^{-3}$
☒ **D**	$mol^2\ dm^{-6}$	$mol^2\ dm^{-6}$

(b) The Haber process is carried out at temperatures between 673 K and 773 K. What is the effect of increasing the temperature on the reaction?

(1)

	Rate	Equilibrium yield
☒ **A**	increased	increased
☒ **B**	increased	decreased
☒ **C**	decreased	increased
☒ **D**	decreased	decreased

(Total for Question 9 = 2 marks)

10 The equilibrium constant for a reaction always increases when there is an increase in

☒ **A** pressure

☒ **B** temperature

☒ **C** ΔS_{system}

☒ **D** ΔS_{total}

(Total for Question 10 = 1 mark)

11 When concentrated nitric and sulfuric acids are mixed, the reaction is

$$H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2NO_3^+$$

In this reaction, the Brønsted-Lowry acids are

☒ **A** H_2SO_4 and HNO_3

☒ **B** H_2SO_4 and $H_2NO_3^+$

☒ **C** HNO_3 and $H_2NO_3^+$

☒ **D** HNO_3 and HSO_4^-

(Total for Question 11 = 1 mark)

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

12 Hydrofluoric acid, HF, is a weak acid (pK_a = 3.2). What happens when a 1 mol dm^{-3} solution of hydrofluoric acid is diluted with an equal volume of water?

	Percentage of HF molecules dissociated	pH
☒ **A**	decreases	decreases
☒ **B**	decreases	increases
☒ **C**	increases	increases
☒ **D**	increases	decreases

(Total for Question 12 = 1 mark)

13 Two buffer solutions, **M** and **N**, were prepared by mixing 50 cm^3 of ethanoic acid and 50 cm^3 of sodium ethanoate solutions. In buffer **M**, both components were 2 mol dm^{-3} and in buffer **N**, both components were 1 mol dm^{-3}.

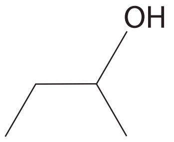
The pH values of **M** and **N** were compared initially and then 1 mol dm^{-3} hydrochloric acid was added to each until the first change in pH was observed.

	Initial pH	Effect of adding acid
☒ **A**	**M** higher pH	pH of **M** changed first
☒ **B**	**N** higher pH	pH of **N** changed first
☒ **C**	**M** and **N** same pH	pH of **M** changed first
☒ **D**	**M** and **N** same pH	pH of **N** changed first

(Total for Question 13 = 1 mark)

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

14 This question concerns four organic compounds:



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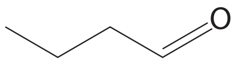

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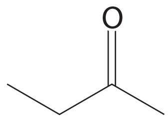

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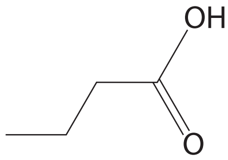

S

(a) The compound which will have the **fewest** peaks in its low resolution proton nmr spectrum is

(1)

☒ **A** **P**

☒ **B** **Q**

☒ **C** **R**

☒ **D** **S**

(b) The compound which is oxidised by acidified potassium dichromate(VI) **and** reduced by lithium tetrahydridoaluminate(III) is

(1)

☒ **A** **P**

☒ **B** **Q**

☒ **C** **R**

☒ **D** **S**

(c) Which two compounds react together to form a new organic compound?

(1)

☒ **A** **Q** and **S**

☒ **B** **R** and **S**

☒ **C** **P** and **S**

☒ **D** **Q** and **R**

(Total for Question 14 = 3 marks)

15 The most energy efficient method of heating a chemical reaction is using

- ☒ **A** microwave radiation.
- ☒ **B** infrared radiation.
- ☒ **C** a Bunsen burner.
- ☒ **D** a water bath.

(Total for Question 15 = 1 mark)

16 Magnetic Resonance Imaging (MRI) is widely used in hospitals and clinics for medical diagnosis. The technique uses

- ☒ **A** microwaves.
- ☒ **B** radio waves.
- ☒ **C** ultrasound.
- ☒ **D** X-rays.

(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 peroxide decomposes to form water and oxygen in a first order reaction.

$$H_2O_2(aq) \rightarrow H_2O(aq) + ½O_2(g)$$

The decomposition is slow under normal conditions but occurs rapidly in the presence of a catalyst such as manganese(IV) oxide.

(a) (i) Write the rate equation for the decomposition of hydrogen peroxide.

(1)

(ii) Draw a diagram of an apparatus that could be used to continuously monitor the progress of this reaction. State the measurements that would be made.

(3)

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P 5 0 7 8 8 A 0 1 1 2 8

(b) Data obtained in a suitable experiment were used to calculate some results.

$[H_2O_2(aq)]$ / mol dm^{-3}	Time / s
2.00	0.0
1.50	
1.00	
0.75	
0.50	560
0.25	

(i) Complete the table by inserting as many times as possible. If you think that it is not possible to give a time without using the value of the rate constant, put a cross (X) in the box.

(2)

(ii) Explain how the data in the completed table can be used to obtain the rate of the reaction at a particular concentration. No calculation is required.

(2)

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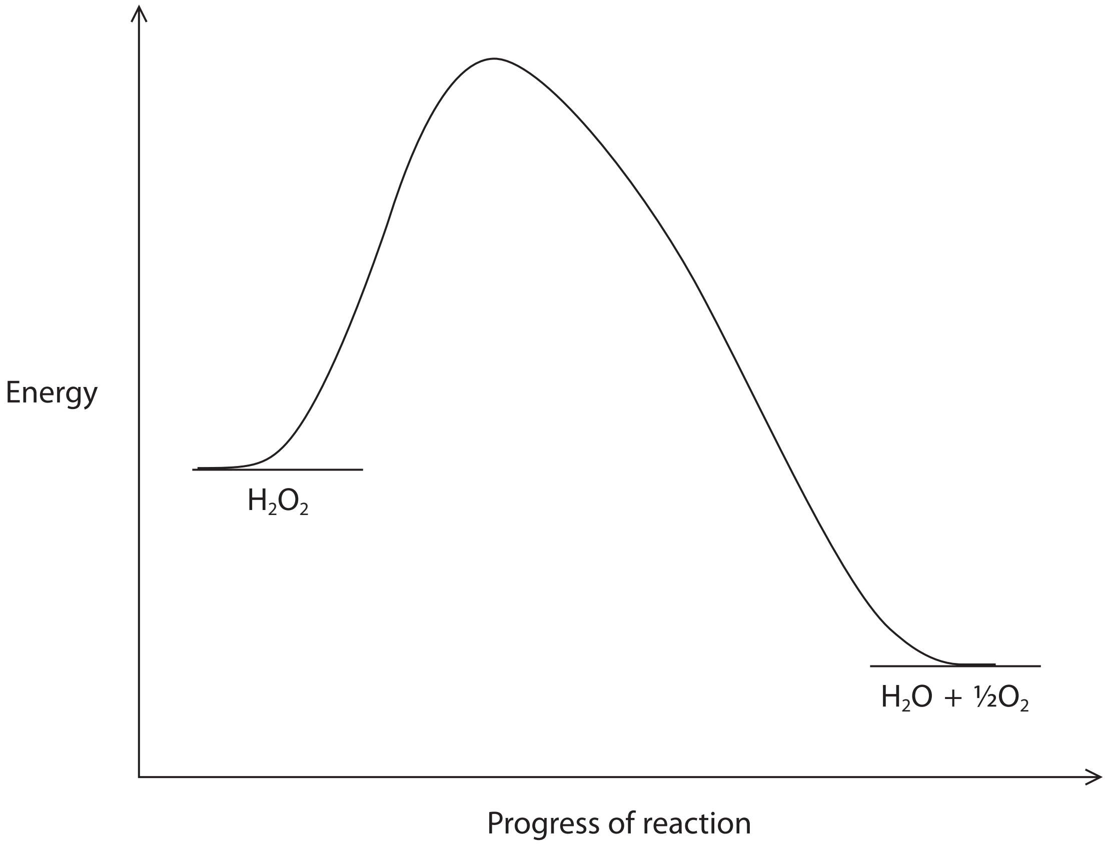
(iii) When the concentration of hydrogen peroxide was 0.75 mol dm^{-3}, the rate of reaction was 1.9×10^{-3} mol dm^{-3} s^{-1}.

Calculate the rate constant for the reaction. Include units with your answer.

(2)

(c) The diagram below shows the reaction profile for the decomposition of hydrogen peroxide without a catalyst. On the diagram draw the reaction profile for the catalysed reaction, which involves an intermediate.

(2)



(Total for Question 17 = 12 marks)

18 The contact process for the manufacture of sulfuric acid involves the oxidation of sulfur dioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\ominus}_{298} = -196 \text{ kJ mol}^{-1}$$

This reaction is usually carried out at 2 atm and 450°C.

(a) Give the expression for the equilibrium constant, K_p, for this equilibrium.

(1)

(b) A mixture containing 0.500 mol of sulfur dioxide, 0.100 mol of oxygen and 0.750 mol of sulfur trioxide is placed in a vessel at 2 atm and 500°C.
At this temperature $K_p = 2.50 \times 10^{10}$ atm^{-1}.

(i) Show by calculation that this system is **not** at equilibrium.

(3)

(ii) Explain, using your answer to (b)(i), the direction that the system would move to reach equilibrium.

(2)

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(iii) Explain, in terms of the entropy changes involved, why the equilibrium shifts to the right when the temperature is reduced from 500 °C to 450 °C.
No calculation is required.

(2)

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(c) Suggest **two** reasons why the contact process equilibrium is operated at just 2 atm although equilibrium yield increases at higher pressure.

(2)

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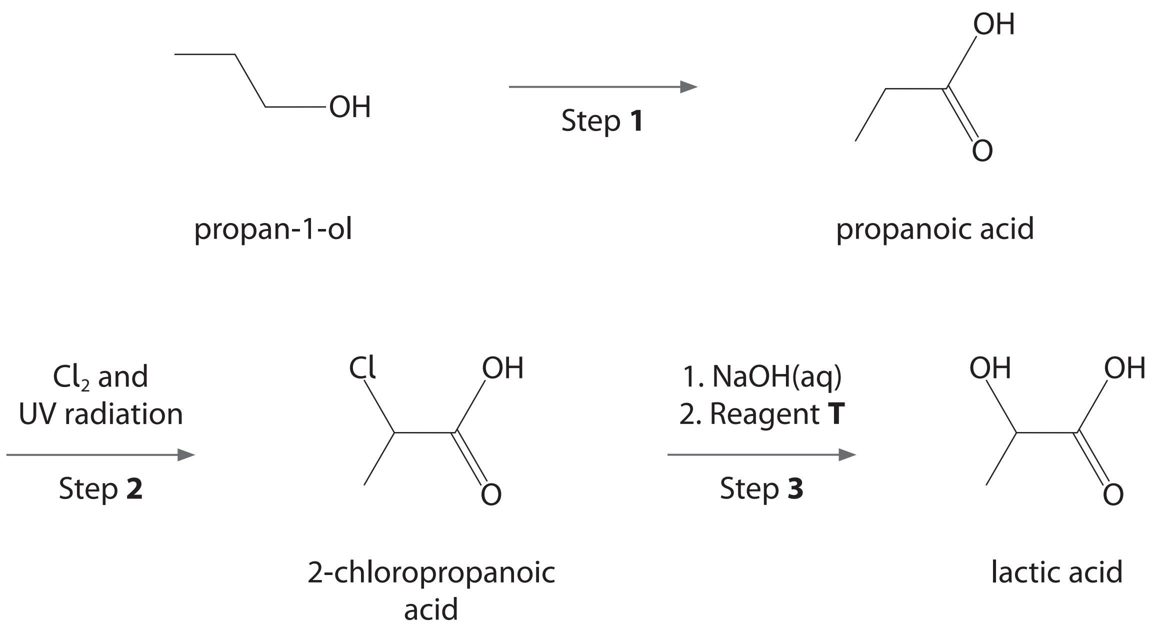
(Total for Question 18 = 10 marks)

19 Lactic acid (2-hydroxypropanoic acid) can be synthesised from propan-1-ol in the following sequence.



(a) (i) **Name** the reagents and state the conditions required for Step **1**.

(2)

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(ii) Suggest the type and mechanism of the reaction in Step **2**.

(2)

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(iii) Suggest why Step **2** is likely to give a low yield of 2-chloropropanoic acid.

(1)

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(iv) Identify reagent **T** in Step **3** and explain why it is needed.

(2)

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(b) The reaction of 2-chloropropanoic acid with NaOH(aq) in Step **3** is a nucleophilic substitution which occurs by a mixture of S_N1 and S_N2 mechanisms.

(i) Give the S_N2 mechanism for this reaction, showing the relevant curly arrows and lone pairs.

(4)

(ii) Some halogenoalkanes react with alkali entirely by an S_N1 mechanism while others react entirely by an S_N2 mechanism.
Give the rate equations for these two mechanisms, using RCl for the halogenoalkanes.
Explain why the rate equations are different.
You are not required to draw any further mechanisms.
(3)

(c) 2-chloropropanoic acid and lactic acid both exist as optical isomers.

(i) State the property associated with optical isomerism.
(1)

(ii) State the structural relationship between a pair of optical isomers, and use a labelled diagram to identify the structural feature that results in optical isomerism in **one** of these compounds.
(2)

*(iii) A single optical isomer of 2-chloropropanoic acid reacts with sodium hydroxide in an S_N2 reaction. State and explain, in terms of this mechanism, the stereoisomerism of the lactic acid formed.

(3)

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(d) Describe how the infrared spectra of propan-1-ol and lactic acid will be similar and how they will differ. Quote values from your Data Booklet.

(2)

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(Total for Question 19 = 22 marks)

20 An aliphatic compound **Z** with five carbon atoms, gave an orange precipitate with 2,4-dinitrophenylhydrazine but **no reaction** when warmed with ammoniacal silver nitrate. In the mass spectrum of **Z** the molecular ion peak was at $m/e = 86$.

Draw the three possible structures of **Z**. Explain your reasoning.

(6)

(Total for Question 20 = 6 marks)

TOTAL FOR SECTION B = 50 MARKS

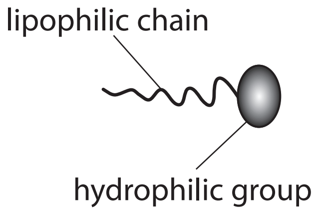
SECTION C

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

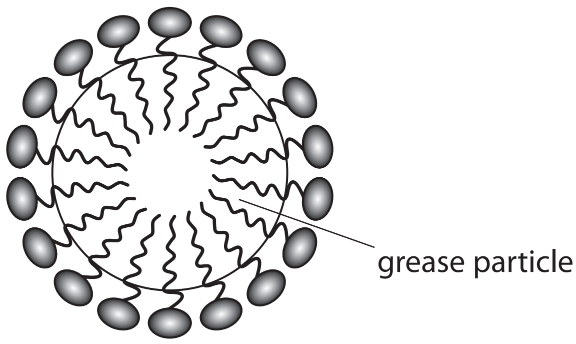
21 Soaps and Detergents

Soaps and detergents are cleaning agents. Soaps are usually the sodium salt of a carboxylic acid with a very long carbon chain; they are made by treating naturally occurring fats and oils with sodium hydroxide. Sodium stearate, $C_{17}H_{35}COO^-Na^+$, is a typical soap. The use of soaps was first recorded 4500 years ago, but detergents were developed in Germany around 1916 when there was a shortage of the raw materials required for manufacturing soap. Modern detergents are manufactured from petrochemicals. The alkylbenzene sulfonate $C_{18}H_{29}SO_3^-Na^+$ is a typical modern detergent.

Soaps and detergents clean because the long hydrocarbon chain is lipophilic ('fat-attracting') and the ionic end of the structure is hydrophilic ('water-attracting'). A fat or grease particle, which contains a long chain of carbon atoms, binds to the hydrocarbon chains of soap or detergent forming a tiny sphere, the surface of which is covered with hydrophilic groups making it water soluble. These spheres are called micelles.



soap or detergent



micelle

*(a) Name and describe the forces that bind the lipophilic part of a soap or detergent to a grease particle.

(3)

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(b) Identify the interaction between the hydrophilic part of the stearate ion and water. Draw a diagram to illustrate your answer.

(2)

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(c) Chemically, stearic acid is a typical carboxylic acid, but it is only slightly soluble in water.

Data: $pK_a = 4.89$; solubility in water $= 0.34$ g dm^{-3} at 25 °C

(i) Explain why stearic acid is only slightly soluble in water whereas ethanoic acid is fully miscible in water. A detailed description of the forces involved is **not** required.

(2)

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(ii) Write the equation for the dissociation of stearic acid, $C_{17}H_{35}COOH$, in aqueous solution. Include state symbols.

(1)

(iii) Write the expression for K_a for stearic acid.

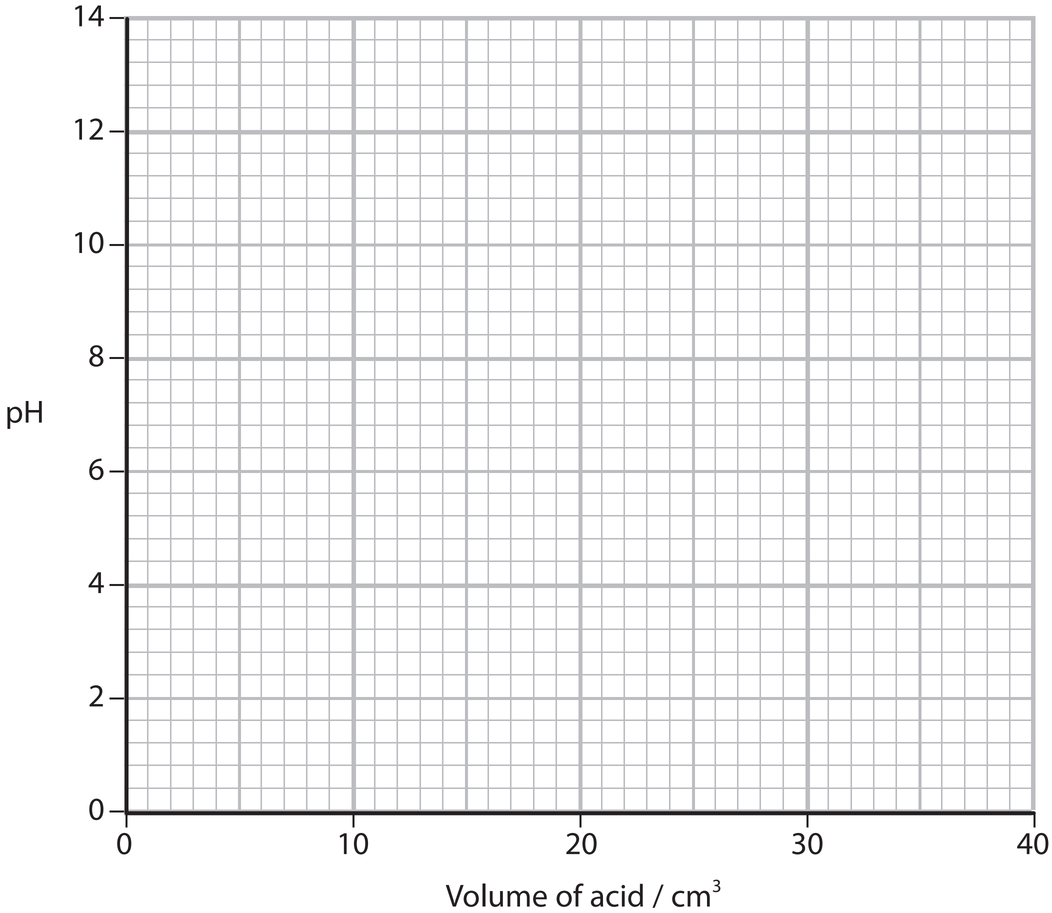
(1)

(iv) Calculate the concentration of a saturated solution of stearic acid at 25 °C and hence calculate its pH.

(4)

(v) On the axes below, sketch the curve that you would expect when a saturated solution of stearic acid is added to $25\,cm^3$ of sodium hydroxide of the **same** molar concentration. Use $K_w = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$ to calculate the pH of the sodium hydroxide solution.

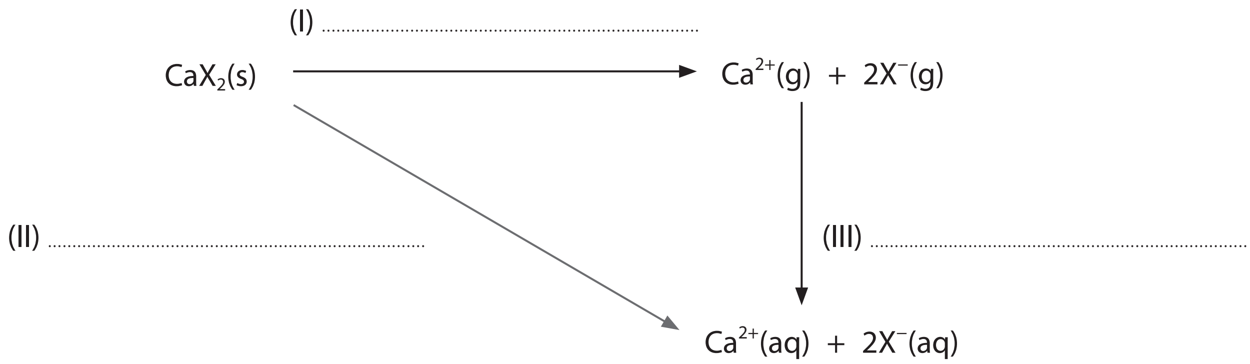
(3)



*(d) One of the main advantages of detergents over soaps is that the calcium salts of alkylbenzene sulfonates are much more soluble in water than calcium stearate. When soaps are used in 'hard' water, which contains calcium ions, calcium stearate precipitates out as an insoluble 'scum'.

Complete the energy cycle below by inserting the names or symbols of the three energy changes, and then use the cycle to explain why calcium stearate is much less soluble than the calcium salt of an alkylbenzene sulfonate. No calculation is required.

(4)



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(Total for Question 21 = 20 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)
(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