Answer **all** questions in the spaces provided.

1 The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

1 (a) (i) Name ester **X**.

....
(1 mark)

1 (a) (ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

....
(1 mark)

1 (a) (iii) When the initial concentration of **X** was 0.024 $mol\,dm^{-3}$ and the initial concentration of hydroxide ions was 0.035 $mol\,dm^{-3}$, the initial rate of the reaction was 8.5×10^{-5} $mol\,dm^{-3}\,s^{-1}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation ....

....

....

....

Units ....

....
(3 marks)

1 (a) (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

....

....
(1 mark)

1 (a) (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part **1 (a) (iii)** and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

....

....
(1 mark)

1 (a) (vi) State the effect, if any, on the value of the rate constant *k* when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect ....

Explanation ....

....
(2 marks)

1 (b) Compound **A** reacts with compound **B** as shown by the overall equation

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

$$\text{rate} = k[A][B]^2$$

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step ....

Explanation ....

....
(2 marks)

11

Turn over ▶

2 This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

....

(1 mark)

2 (a) (ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

....

....

(1 mark)

2 (a) (iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

....

....

....

....

(2 marks)

2 (b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

....

....

....

....

....

....

(4 marks)

Question 2 continues on the next page

Turn over ▶

2 (c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

....

....

....

....

....

....

(2 marks)

2 (d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

2 (d) (i) Calculate the pH of this buffer solution.

....

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....

....

(4 marks)

2 (d) (ii) A 5.00 x 10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

....

....

....

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....

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....

....

....

(4 marks)

18

Turn over for the next question

3 Synthesis gas is a mixture of carbon monoxide and hydrogen. Methanol can be manufactured from synthesis gas in a reversible reaction as shown by the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H^\ominus = -91\ \text{kJ mol}^{-1}$$

3 (a) A sample of synthesis gas containing 0.240 mol of carbon monoxide and 0.380 mol of hydrogen was sealed together with a catalyst in a container of volume 1.50 dm^3. When equilibrium was established at temperature T_1 the equilibrium mixture contained 0.170 mol of carbon monoxide.

Calculate the amount, in moles, of methanol and the amount, in moles, of hydrogen in the equilibrium mixture.

Methanol ....

Hydrogen ....

(2 marks)

3 (b) A different sample of synthesis gas was allowed to reach equilibrium in a similar container of volume 1.50 dm^3 at temperature T_1

At equilibrium, the mixture contained 0.210 mol of carbon monoxide, 0.275 mol of hydrogen and 0.0820 mol of methanol.

3 (b) (i) Write an expression for the equilibrium constant K_c for this reaction.

....

....

(1 mark)

3 (b) (ii) Calculate a value for K_c for the reaction at temperature T_1 and state its units.

Calculation ....

....

....

....

....

Units ....

....

(4 marks)

3 (b) (iii) State the effect, if any, on the value of K_c of adding more hydrogen to the equilibrium mixture.

....

(1 mark)

3 (c) The temperature of the mixture in part **3 (b)** was changed to T_2 and the mixture was left to reach a new equilibrium position. At this new temperature the equilibrium concentration of methanol had increased.
Deduce which of T_1 or T_2 is the higher temperature and explain your answer.

Higher temperature ....

Explanation ....

....

....

(3 marks)

3 (d) The following reaction has been suggested as an alternative method for the production of methanol.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The hydrogen used in this method is obtained from the electrolysis of water.

Suggest **one** possible environmental disadvantage of the production of hydrogen by electrolysis.

....

....

(1 mark)

3 (e) One industrial use of methanol is in the production of biodiesel from vegetable oils such as

$CH_2OOCC_{17}H_{35}$
|
$CHOOCC_{17}H_{31}$
|
$CH_2OOCC_{17}H_{29}$

Give the formula of **one** compound in biodiesel that is formed by the reaction of methanol with the vegetable oil shown above.

....

(1 mark)

13

4 (a) Name compound **Y**, $HOCH_2CH_2COOH$

....
(1 mark)

4 (b) Under suitable conditions, molecules of **Y** can react with each other to form a polymer.

4 (b) (i) Draw a section of the polymer showing **two** repeating units.

(1 mark)

4 (b) (ii) Name the type of polymerisation involved.

....
(1 mark)

4 (c) When **Y** is heated, an elimination reaction occurs in which one molecule of **Y** loses one molecule of water. The organic product formed by this reaction has an absorption at 1637 cm^{-1} in its infrared spectrum.

4 (c) (i) Identify the bond that causes the absorption at 1637 cm^{-1} in its infrared spectrum.

....
(1 mark)

4 (c) (ii) Write the displayed formula for the organic product of this elimination reaction.

(1 mark)

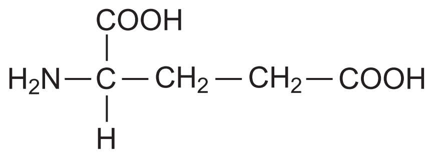
4 (c) (iii) The organic product from part **4 (c) (ii)** can also be polymerised.
Draw the repeating unit of the polymer formed from this organic product.

(1 mark)

4 (d) At room temperature, 2-aminobutanoic acid exists as a solid.
Draw the structure of the species present in the solid form.

(1 mark)

4 (e) The amino acid, glutamic acid, is shown below.



Draw the structure of the organic species formed when glutamic acid reacts with each of the following.

4 (e) (i) an excess of sodium hydroxide

(1 mark)

4 (e) (ii) an excess of methanol in the presence of concentrated sulfuric acid

(1 mark)

4 (e) (iii) ethanoyl chloride

(1 mark)

Question 4 continues on the next page

4 (f) A tripeptide was heated with hydrochloric acid and a mixture of amino acids was formed. This mixture was separated by column chromatography.
Outline briefly why chromatography is able to separate a mixture of compounds. Practical details are **not** required.

....

....

....

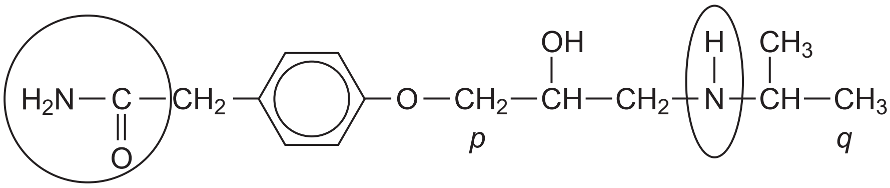
....

....

....
(3 marks)

13

5 Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



5 (a) Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** ....

Functional group labelled **K** ....

(2 marks)

5 (b) The [1]H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the [1]H n.m.r. spectrum is produced by the CH_2 group labelled *p* in the structure of atenolol.
Use **Table 2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values ....

Name of splitting pattern ....

(2 marks)

5 (c) N.m.r. spectra are recorded using samples in solution.
The [1]H n.m.r. spectrum was recorded using a solution of atenolol in $CDCl_3$

5 (c) (i) Suggest why $CDCl_3$ and **not** $CHCl_3$ was used as the solvent.

....

....

(1 mark)

5 (c) (ii) Suggest why $CDCl_3$ is a more effective solvent than CCl_4 for polar molecules such as atenolol.

....

....

(1 mark)

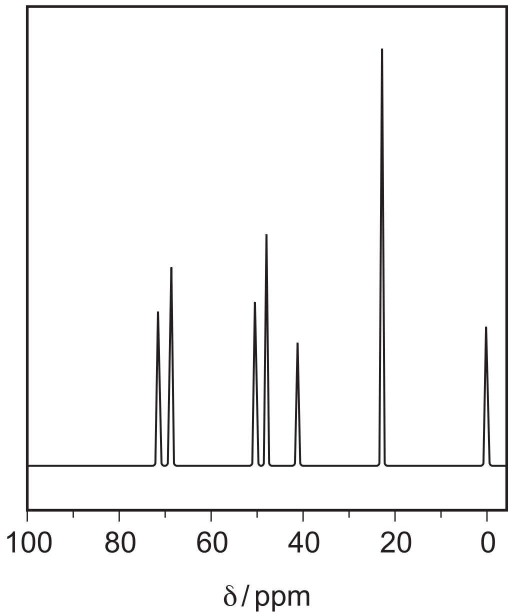
5 (d) The ^{13}C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the ^{13}C n.m.r. spectrum of atenolol.

....

(1 mark)

5 (e) Part of the ^{13}C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



5 (e) (i) Give the formula of the compound that is used as a standard and produces the peak at δ = 0 ppm in the spectrum.

....

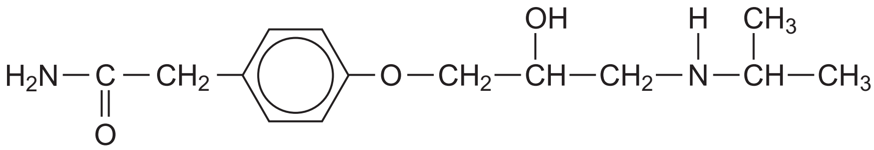
(1 mark)

5 (e) (ii) One of the peaks in the ^{13}C n.m.r. spectrum above is produced by the CH_3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

....

(1 mark)

5 (e) (iii) There are three CH_2 groups in the structure of atenolol. One of these CH_2 groups produces the peak at δ = 71 in the ^{13}C n.m.r. spectrum above.
Draw a circle around this CH_2 group in the structure of atenolol shown below.



(1 mark)

Question 5 continues on the next page

Turn over ▶

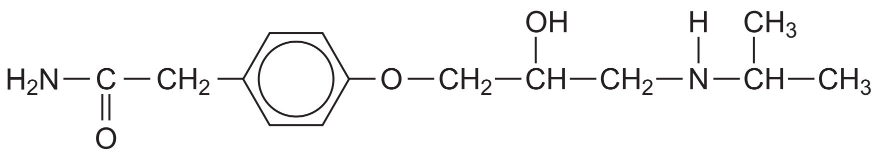
5 (f) Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

5 (f) (i) Suggest a reducing agent that could reduce a ketone to form atenolol.

....

(1 mark)

5 (f) (ii) Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



(1 mark)

5 (f) (iii) Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

....

....

....

....

(2 marks)

5 (f) (iv) Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage ....

....

Disadvantage ....

....

(2 marks)

16

Answer **all** questions in the spaces provided.

6 Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

6 (a) Consider the reaction of benzene with CH_3CH_2COCl

6 (a) (i) Write an equation for this reaction and name the organic product.
Identify the catalyst required in this reaction.
Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

....

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(5 marks)

(*Extra space)* ....

....

6 (a) (ii) Name and outline a mechanism for the reaction of benzene with this reactive intermediate.

....

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....

....

(4 marks)

(Extra space) ....

....

Question 6 continues on the next page

6 (b) Consider the reaction of propanal with HCN

6 (b) (i) Write an equation for the reaction of propanal with HCN and name the product.

....

....

....

(2 marks)

(*Extra space*) ....

....

6 (b) (ii) Name and outline a mechanism for the reaction of propanal with HCN

....

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....

....

....

....

(5 marks)

(Extra space) ....

....

6 (b) (iii) The rate-determining step in the mechanism in part **6 (b) (ii)** involves attack by the nucleophile.
Suggest how the rate of reaction of propanone with HCN would compare with the rate of reaction of propanal with HCN
Explain your answer.

....

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....

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....

....

(2 marks)

(Extra space) ....

....

18

Turn over for the next question

7 The compound $(CH_3CH_2)_2NH$ can be made from ethene in a three-step synthesis as shown below.

$$\text{ethene} \xrightarrow{\text{Step } \mathbf{1}} \mathbf{F} \xrightarrow{\text{Step } \mathbf{2}} \mathbf{G} \xrightarrow{\text{Step } \mathbf{3}} (CH_3CH_2)_2NH$$

7 (a) Name the compound $(CH_3CH_2)_2NH$

....

(1 mark)

7 (b) Identify compounds **F** and **G**.

Compound **F** ....

Compound **G** ....

(2 marks)

7 (c) For the reactions in Steps **1**, **2** and **3**,

- give a reagent or reagents
- name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

....

....

....

....

....

....

....

....

(6 marks)

(*Extra space*) ....

....

7 (d) Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

....

....

....

(2 marks)

(Extra space) ....

....

11

END OF QUESTIONS

GCE Chemistry Data Sheet

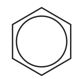
Table 1
Infrared absorption data

Bond	Wavenumber /cm^{-1}
N—H (amines)	3300–3500
O—H (alcohols)	3230–3550
C—H	2850–3300
O—H (acids)	2500–3000
C≡N	2220–2260
C=O	1680–1750
C=C	1620–1680
C—O	1000–1300
C—C	750–1100

Table 2
^{1}H n.m.r. chemical shift data

Type of proton	δ/ppm
RO**H**	0.5–5.0
RC**H**$_3$	0.7–1.2
RN**H**$_2$	1.0–4.5
R$_2$C**H**$_2$	1.2–1.4
R$_3$C**H**	1.4–1.6
R—C(=O)—C(—**H**)—	2.1–2.6
R—O—C(—**H**)—	3.1–3.9
RC**H**$_2$Cl or Br	3.1–4.2
R—C(=O)—O—C(—**H**)—	3.7–4.1
R(—)C=C(—)**H**	4.5–6.0
R—C(=O)—**H**	9.0–10.0
R—C(=O)—O—**H**	10.0–12.0

Table 3
^{13}C n.m.r. chemical shift data

Type of carbon		δ/ppm
—**C**—**C**—		5–40
R—**C**—Cl or Br		10–70
R—C(=O)—**C**—		20–50
R—**C**—N<		25–60
—**C**—O—	alcohols, ethers or esters	50–90
>**C**=**C**<		90–150
R—**C**≡N		110–125
		110–160
R—**C**(=O)—	esters or acids	160–185
R—**C**(=O)—	aldehydes or ketones	190–220

The Periodic Table of the Elements

Key

relative atomic mass
symbol
name
atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (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	96.0 **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	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

* **58 – 71** Lanthanides	140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71
† **90 – 103** Actinides	232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

Answer **all** questions in the spaces provided.

1 A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation.

Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.

$$2CH_3CHO \longrightarrow \underset{\mathbf{X}}{CH_3CH(OH)CH_2CHO}$$

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k[CH_3CHO][OH^-]$$

1 (a) Give the IUPAC name of compound **X**.

....

(1 mark)

1 (b) The initial rate of the reaction at 298 K was found to be 2.2×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was 0.020 mol dm^{-3}.
Calculate a value for the rate constant at this temperature and give its units.

Calculation ....

....

....

Units ....

(3 marks)

1 (c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

....

....

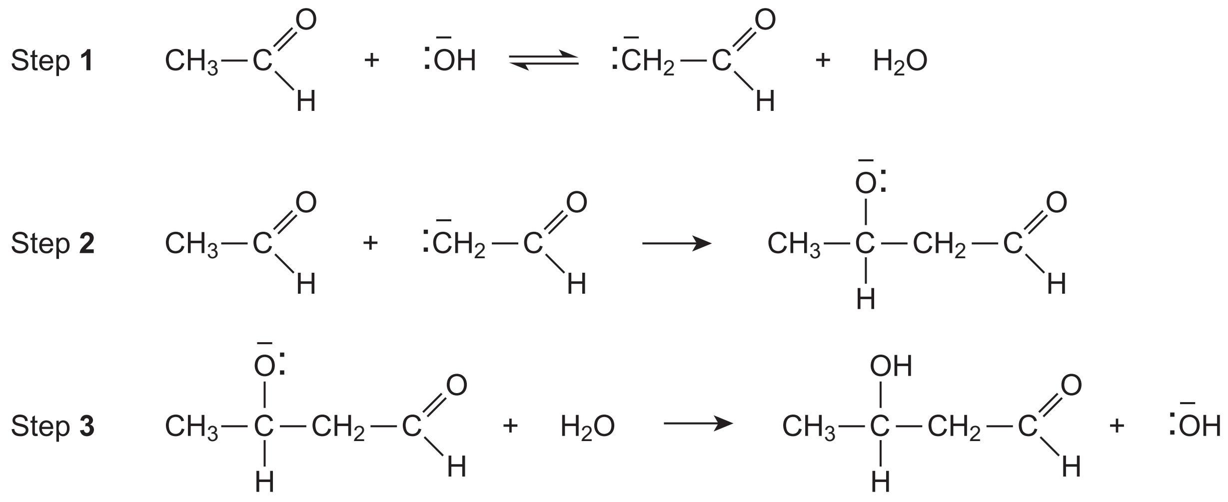
....

(2 marks)

Question 1 continues on the next page

Turn over ▶

1 (d) A three-step mechanism has been proposed for this reaction according to the following equations.



1 (d) (i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step ....

Explanation ....

....

(2 marks)

1 (d) (ii) Deduce the role of ethanal in Step **1**.

....

(1 mark)

1 (d) (iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step **2**.

....

(1 mark)

1 (d) (iv) In the space below draw out the mechanism of Step **2** showing the relevant curly arrows.

(2 marks)

1 (e) In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

Deduce the structure of this trimer.

(1 mark)

13

Turn over ▶

2 The reaction of methane with steam produces hydrogen for use in many industrial processes. Under certain conditions the following reaction occurs.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad \Delta H^{\ominus} = +165\ kJ\,mol^{-1}$$

2 (a) Initially, 1.0 mol of methane and 2.0 mol of steam were placed in a flask and heated with a catalyst until equilibrium was established. The equilibrium mixture contained 0.25 mol of carbon dioxide.

2 (a) (i) Calculate the amounts, in moles, of methane, steam and hydrogen in the equilibrium mixture.

Moles of methane ....

Moles of steam ....

Moles of hydrogen ....

(3 marks)

2 (a) (ii) The volume of the flask was 5.0 dm^3. Calculate the concentration, in $mol\,dm^{-3}$, of methane in the equilibrium mixture.

....

....

(1 mark)

2 (b) The table below shows the equilibrium concentration of each gas in a different equilibrium mixture in the same flask and at temperature *T*.

gas	$CH_4(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
concentration / $mol\ dm^{-3}$	0.10	0.48	0.15	0.25

2 (b) (i) Write an expression for the equilibrium constant, K_c, for this reaction.

....

....

....

(1 mark)

2 (b) (ii) Calculate a value for K_c at temperature T and give its units.

Calculation ....

....

....

....

Units of K_c ....

(3 marks)

2 (c) The mixture in part (b) was placed in a flask of volume greater than 5.0 dm^3 and allowed to reach equilibrium at temperature T.
State and explain the effect on the amount of hydrogen.

Effect on amount of hydrogen ....

Explanation ....

....

....

....

(3 marks)

2 (d) Explain why the amount of hydrogen decreases when the mixture in part **(b)** reaches equilibrium at a lower temperature.

....

....

....

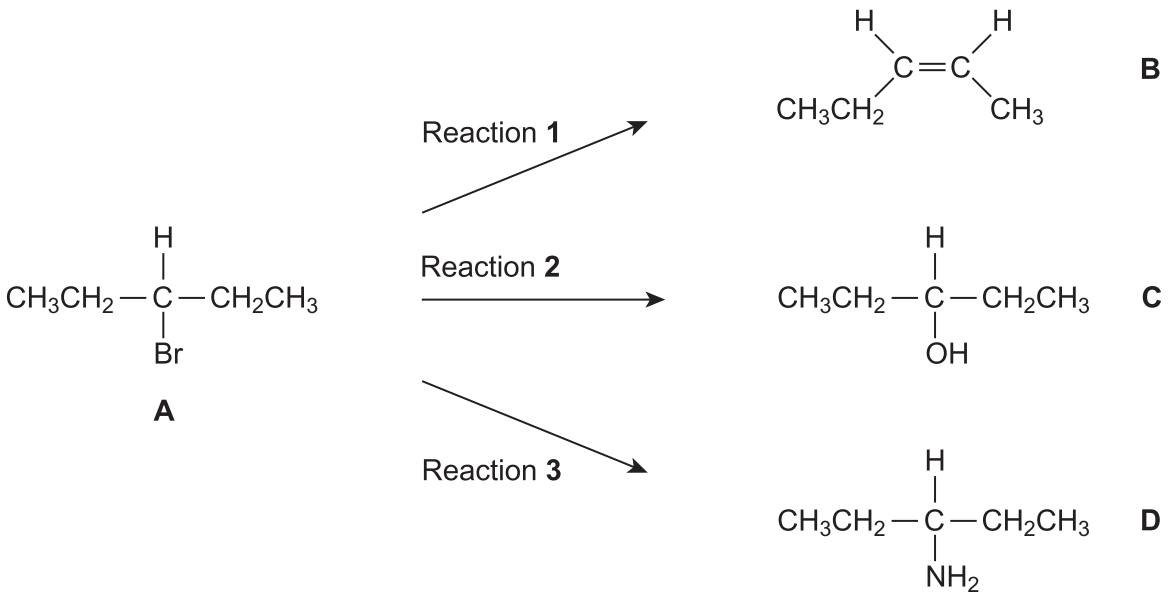
....

(2 marks)

13

Turn over for the next question

3 Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



3 (a) (i) Draw a **branched-chain** isomer of **A** that exists as optical isomers.

(1 mark)

3 (a) (ii) Name the type of mechanism in Reaction **1**.

....

(1 mark)

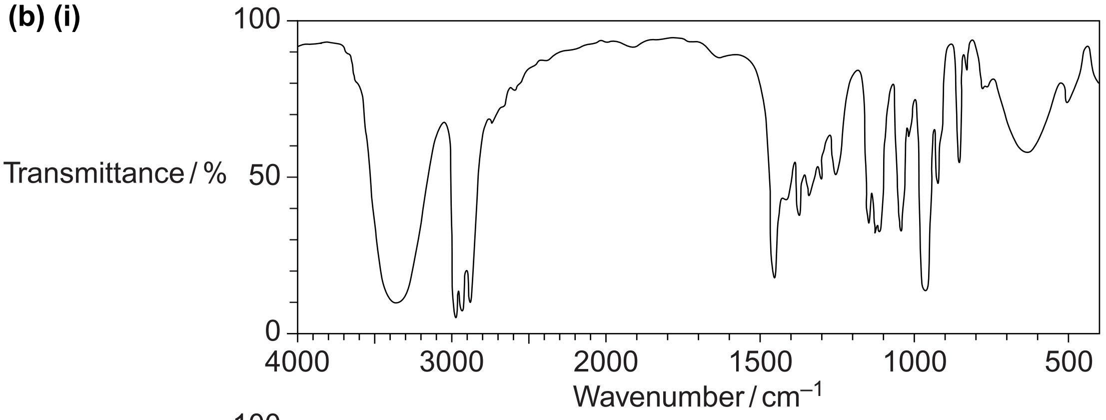
3 (a) (iii) Give the full IUPAC name of compound **B**.

....

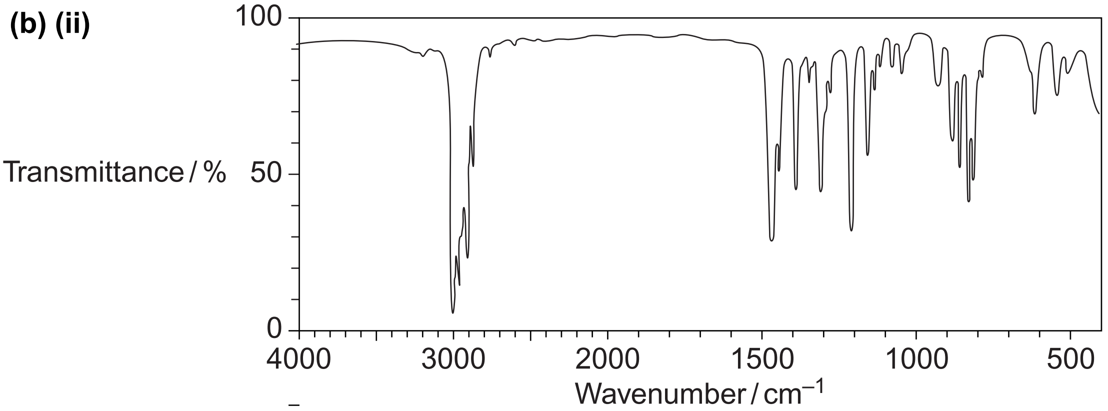
(1 mark)

3 (b) The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**. Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

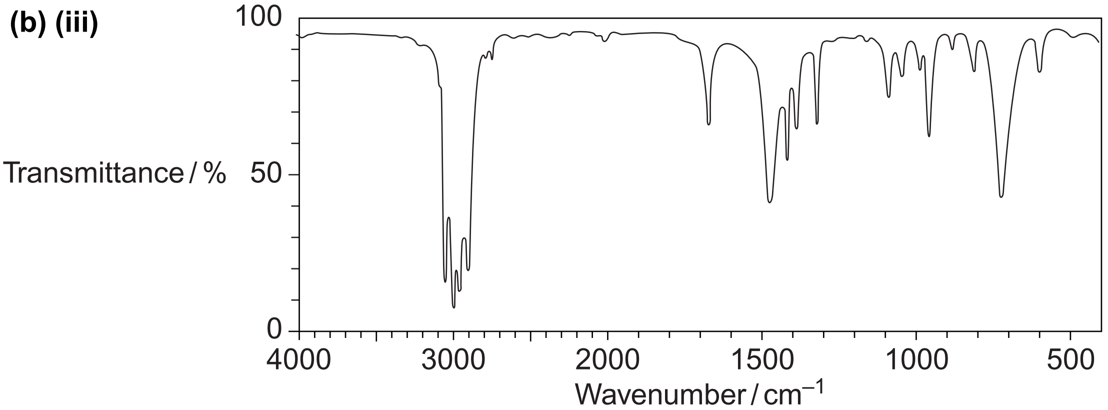
3 (b) (i)



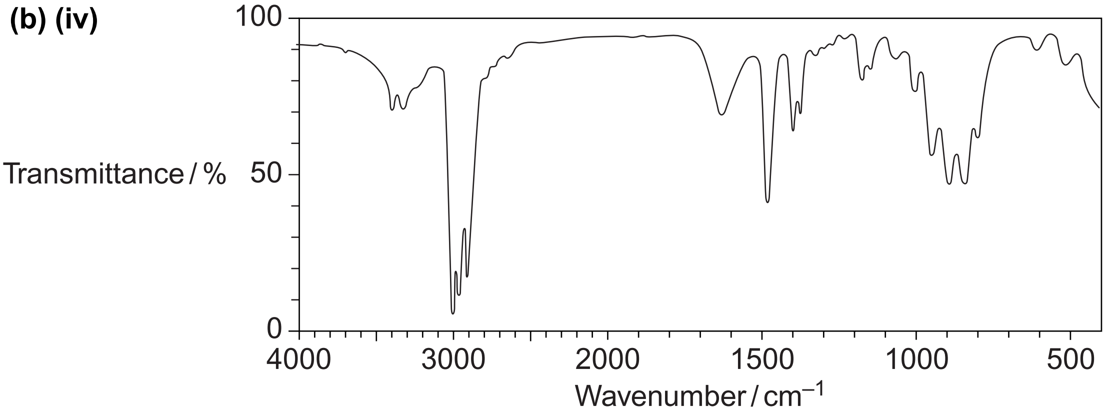
3 (b) (ii)



3 (b) (iii)



3 (b) (iv)



(4 marks)

Question 3 continues on the next page

Turn over ►

3 (c) Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation ....

(2 marks)

3 (d) (i) Outline a mechanism for Reaction **3**.

(4 marks)

3 (d) (ii) State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

....

(1 mark)

3 (d) (iii) Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

(1 mark)

3 (e) **D** is a primary amine which has three peaks in its ^{13}C n.m.r. spectrum.

3 (e) (i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1 mark)

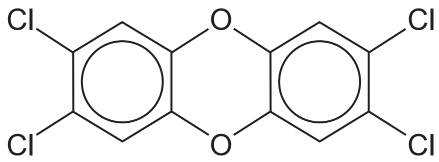
3 (e) (ii) Another isomer of **D** is a tertiary amine. Its ^{1}H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

(1 mark)

17

Turn over ▶

4 In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

4 (a) Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

....

(1 mark)

4 (b) The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$
Chlorine exists as two isotopes ^{35}Cl (75%) and ^{37}Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m*/*z* value of the most abundant molecular ion peak.

Number of molecular ion peaks ....

....

m/*z* value of the most abundant molecular ion peak ....

....

(2 marks)

4 (c) Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

....

....

(1 mark)

4 (d) TCDD can also be analysed using ^{13}C n.m.r.

4 (d) (i) Give the formula of the compound used as the standard when recording a ^{13}C spectrum.

....

(1 mark)

4 (d) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TCDD.

....

(1 mark)

6

Turn over for the next question

5 In this question, give all values of pH to two decimal places.

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is 5.48×10^{-14} mol^2 dm^{-6} at 50 °C.

5 (a) (i) Write an expression for pH.

....

(1 mark)

5 (a) (ii) Write an expression for K_w

....

(1 mark)

5 (b) (i) Calculate the pH of pure water at 50 °C.

....

....

....

(2 marks)

5 (b) (ii) Suggest why this pure water is **not** acidic.

....

....

(1 mark)

5 (b) (iii) Calculate the pH of 0.140 mol dm^{-3} aqueous sodium hydroxide at 50 °C.

....

....

....

....

....

(3 marks)

5 (c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

....

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(6 marks)

5 (d) (i) Write an expression for the acid dissociation constant, K_a, for ethanoic acid.

....

....

(1 mark)

5 (d) (ii) The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C.
Calculate the pH of a 0.136 mol dm^{-3} aqueous solution of ethanoic acid at this temperature.

....

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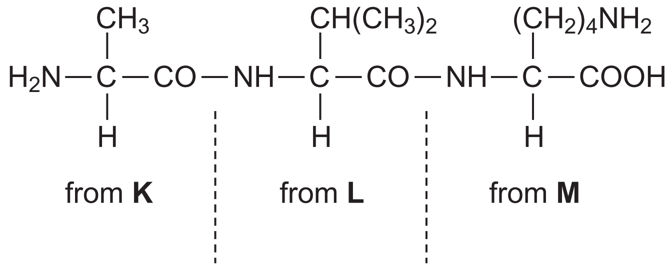
(3 marks)

18

Turn over ▶

6 (a) Consider the tripeptide shown below that is formed from three amino acids, **K**, **L** and **M**.



6 (a) (i) Name the process by which the tripeptide is split into three amino acids.

....

(1 mark)

6 (a) (ii) Give the IUPAC name for the amino acid **K**.

....

(1 mark)

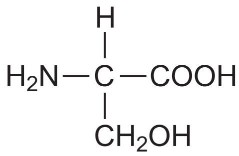
6 (a) (iii) Draw the structure of the zwitterion of amino acid **L**.

(1 mark)

6 (a) (iv) Draw the structure of the species formed by amino acid **M** at low pH.

(1 mark)

6 (b) Consider the amino acid serine.



6 (b) (i) Draw the structure of the product formed when serine reacts with an excess of CH_3Br

(1 mark)

6 (b) (ii) Draw the structure of the dipeptide formed by two molecules of serine.

(1 mark)

6

Turn over for the next question

Answer **all** questions in the spaces provided.

7 Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

7 (a) Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

....

....

....

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....

(4 marks)

7 (b) Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

....

....

....

....

....

....

(3 marks)

7 (c) Name and outline a mechanism for the reaction of CH_3COCl with CH_3OH to form an ester.

(5 marks)

Question 7 continues on the next page

7 (d) The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

....

....

....

....

....

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....

....

(3 marks)

7 (e) Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradeable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

....

....

....

....

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....

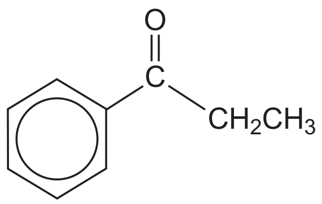
....

(4 marks)

19

Turn over for the next question

8 Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.



P

8 (a) Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

....

....

....

....

....

....

(3 marks)

8 (b) Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

(3 marks)

8 (c) Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

....

....

....

....

....

....

(2 marks)

8

END OF QUESTIONS

GCE Chemistry Data Sheet

Table 1
Infrared absorption data

Bond	Wavenumber /cm^{-1}
N—H (amines)	3300–3500
O—H (alcohols)	3230–3550
C—H	2850–3300
O—H (acids)	2500–3000
C≡N	2220–2260
C=O	1680–1750
C=C	1620–1680
C—O	1000–1300
C—C	750–1100

Table 2
^{1}H n.m.r. chemical shift data

Type of proton	δ/ppm
RO**H**	0.5–5.0
RC**H**$_3$	0.7–1.2
RN**H**$_2$	1.0–4.5
R_2C**H**$_2$	1.2–1.4
R_3C**H**	1.4–1.6
R—C(=O)—C(—**H**)—	2.1–2.6
R—O—C(—**H**)—	3.1–3.9
RC**H**$_2$Cl or Br	3.1–4.2
R—C(=O)—O—C(—**H**)—	3.7–4.1
R(—)C=C(—)**H**	4.5–6.0
R—C(=O)—**H**	9.0–10.0
R—C(=O)—O—**H**	10.0–12.0

Table 3
^{13}C n.m.r. chemical shift data

Type of carbon	δ/ppm
—**C**—**C**—	5–40
R—**C**—Cl or Br	10–70
R—C(=O)—**C**—	20–50
R—**C**—N<	25–60
—**C**—O— alcohols, ethers or esters	50–90
>**C**=**C**<	90–150
R—**C**≡N	110–125
benzene ring	110–160
R—**C**(=O)— esters or acids	160–185
R—**C**(=O)— aldehydes or ketones	190–220

The Periodic Table of the Elements

Key

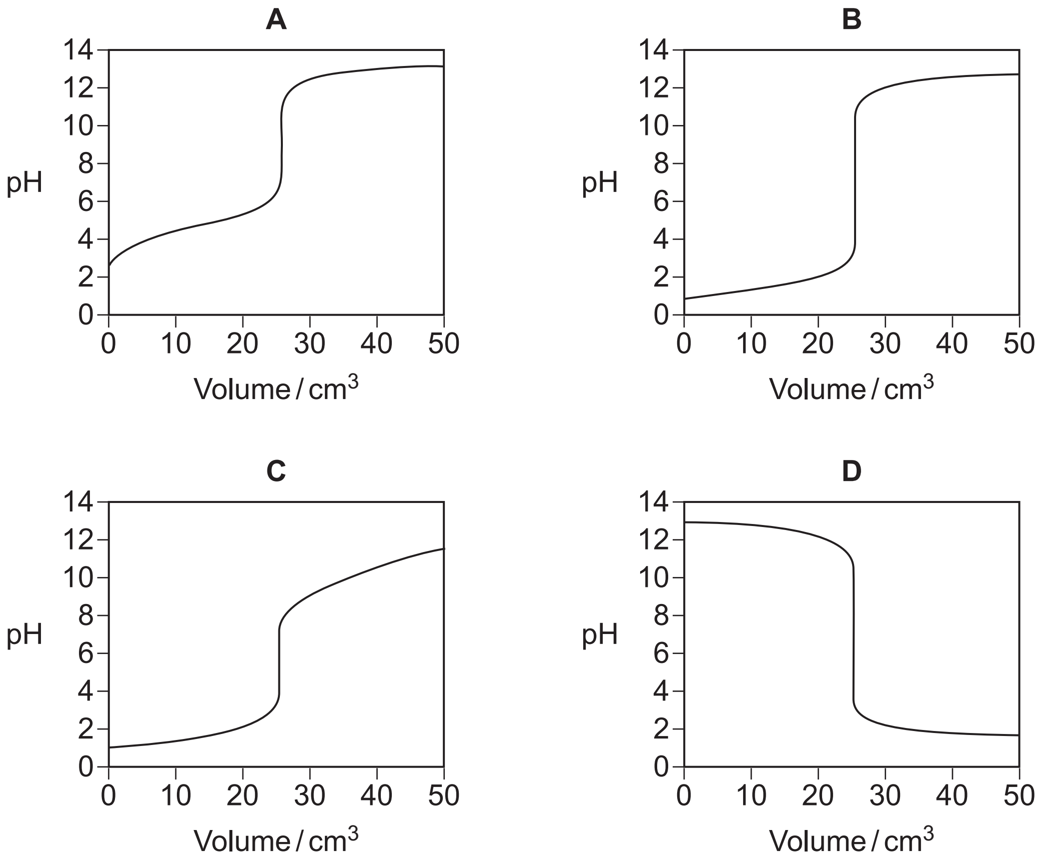
relative atomic mass **symbol** name atomic (proton) number

1	2											3	4	5	6	7	0
(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	96.0 **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	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

* 58 – 71 Lanthanides	140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71
† 90 – 103 Actinides	232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

Answer **all** questions in the spaces provided.

1 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.
All solutions have a concentration of 0.1 mol dm^{-3}.



1 (a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3 marks)

1 (b) A table of acid–base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	**pH range**	**Colour in acid**	**Colour in alkali**
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

1 (b) (i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

....

(1 mark)

1 (b) (ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

....

(1 mark)

5

Turn over for the next question

2 This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

....

(1 mark)

2 (a) (ii) Write an expression for the ionic product of water, K_w

....

(1 mark)

2 (a) (iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72
Calculate the value of K_w at 10 °C.

....

....

....

....

(2 marks)

(Extra space) ....

....

2 (b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (b) (i) Write an expression for K_a for ethanoic acid.

....

....

(1 mark)

2 (b) (ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

....

....

....

....

....

....

(3 marks)

(Extra space) ....

....

....

Question 2 continues on the next page

Turn over ▶

2 (c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (c) (i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

....

....

....

....

....

....

....

(4 marks)

(Extra space) ....

....

....

....

2 (c) (ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

....

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....

(4 marks)

(Extra space) ....

....

....

....

16

Turn over for the next question

3 The following dynamic equilibrium was established at temperature T in a closed container.

$$P(g) + 2Q(g) \rightleftharpoons 2R(g) \qquad \Delta H^{\ominus} = -50\ \text{kJ mol}^{-1}$$

The value of K_c for the reaction was 68.0 mol^{-1} dm^{3} when the equilibrium mixture contained 3.82 mol of **P** and 5.24 mol of **R**.

3 (a) Give the meaning of the term *dynamic equilibrium*.

....

....

....

....

(2 marks)

(Extra space) ....

....

3 (b) Write an expression for K_c for this reaction.

....

....

(1 mark)

3 (c) The volume of the container was 10.0 dm^{3}.

Calculate the concentration, in mol dm^{-3}, of **Q** in the equilibrium mixture.

....

....

....

....

....

....

(4 marks)

(Extra space) ....

....

3 (d) State the effect, if any, on the equilibrium amount of **P** of increasing the temperature. All other factors are unchanged.

....

(1 mark)

3 (e) State the effect, if any, on the equilibrium amount of **P** of using a container of larger volume. All other factors are unchanged.

....

(1 mark)

3 (f) State the effect, if any, on the value of K_c of increasing the temperature. All other factors are unchanged.

....

(1 mark)

3 (g) State the effect, if any, on the value of K_c of using a container of larger volume. All other factors are unchanged.

....

(1 mark)

3 (h) Deduce the value of the equilibrium constant, at temperature T, for the reaction

$$2R(g) \rightleftharpoons P(g) + 2Q(g)$$

....

....

(1 mark)

12

Turn over for the next question

Turn over ▶

4 The amide or peptide link is found in synthetic polyamides and also in naturally-occurring proteins.

4 (a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2 marks)

4 (a) (ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

....

....

....

....

....

....

(3 marks)

(Extra space) ....

....

....

4 (b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism..

Mechanism

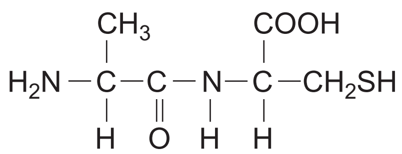
(5 marks)

4 (b) (ii) Give the name of the product containing an amide linkage that is formed in the reaction in part **4 (b) (i)**.

....

(1 mark)

4 (c) The dipeptide shown below is formed from two different amino acids.

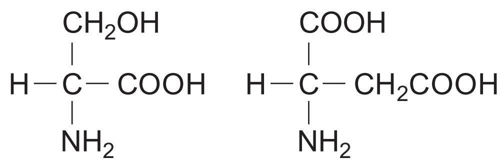


Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1 mark)

Question 4 continues on the next page

4 (d) The amino acids serine and aspartic acid are shown below.



serine   aspartic acid

4 (d) (i) Give the IUPAC name of serine.

....

(1 mark)

4 (d) (ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1 mark)

4 (d) (iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

(1 mark)

4 (d) (iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

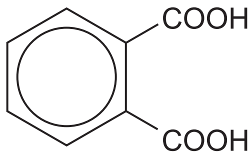
(1 mark)

16

5 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

5 (a) Give the IUPAC name for phthalic acid.

....

(1 mark)

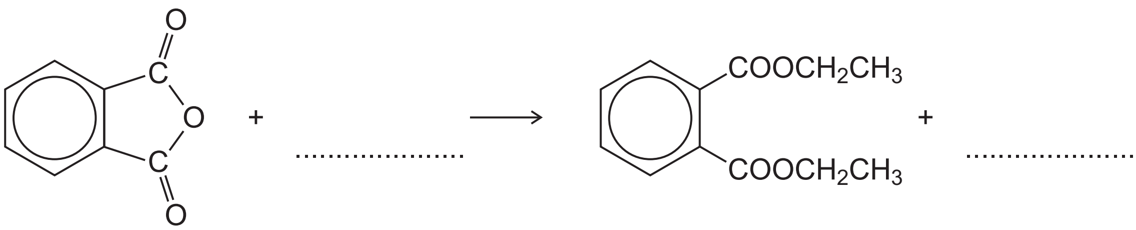
5 (b) Draw the displayed formula of the repeating unit of poly(chloroethene).

(1 mark)

Question 5 continues on the next page

5 (c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

5 (c) (i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2 marks)

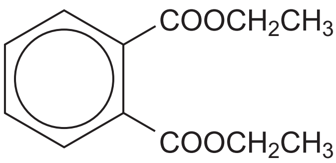
5 (c) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

....

(1 mark)

5 (c) (iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at δ = 62 ppm.
Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

5 (d) The mass spectrum of DEP includes major peaks at m/z = 222 (the molecular ion) and at m/z = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at m/z = 177

....

(2 marks)

5 (e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

'Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.'

5 (e) (i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

....

(1 mark)

5 (e) (ii) Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

(Extra space) ....

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11

6 (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.

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

The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[NO]^2[H_2]$$

The initial rate of reaction was 6.2×10^{-6} mol dm^{-3} s^{-1} when the initial concentration of NO was 2.9×10^{-2} mol dm^{-3} and the initial concentration of H_2 was 2.3×10^{-2} mol dm^{-3}.

6 (a) (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation ....

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....

Units ....

....

(3 marks)

6 (a) (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H_2 both doubled from their original values.

....

....

(1 mark)

6 (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step **1** $NO + NO \longrightarrow X$

Step **2** $X + H_2 \longrightarrow Y$

Step **3** $Y + H_2 \longrightarrow N_2 + 2H_2O$

Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step..

Explanation ....

....

....

(2 marks)

(Extra space) ....

....

6

Turn over for the next question

Answer **all** questions in the spaces provided.

7 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

7 (a) The following compounds can be distinguished by observing what happens in test-tube reactions.

For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

7 (a) (i)

E **F**

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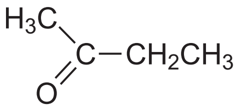
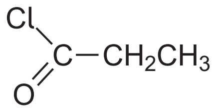
(3 marks)

7 (a) (ii)



G



H

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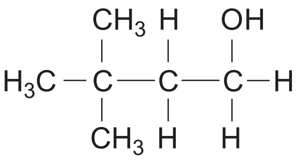
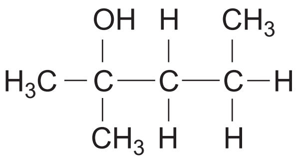
(3 marks)

7 (a) (iii)



J



K

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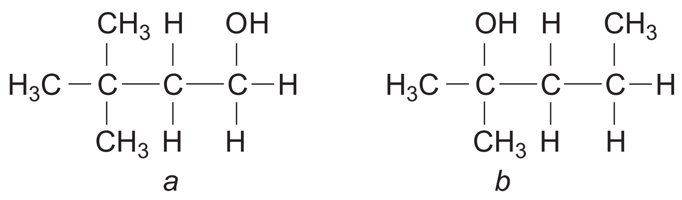
(3 marks)

Question 7 continues on the next page

Turn over ▶

7 (b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



J **K**

7 (b) (i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

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(3 marks)

7 (b) (ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

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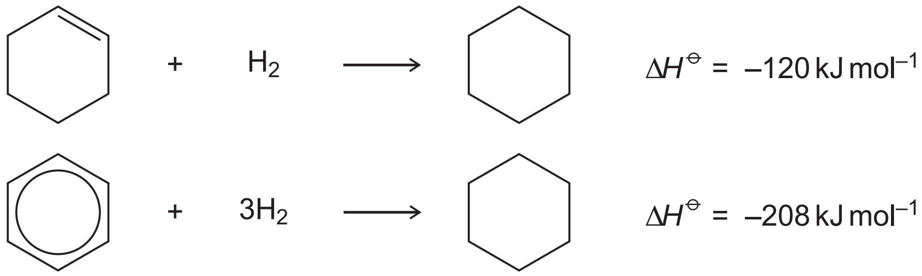
(3 marks)

15

8 The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

8 (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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(4 marks)

(Extra space) ....

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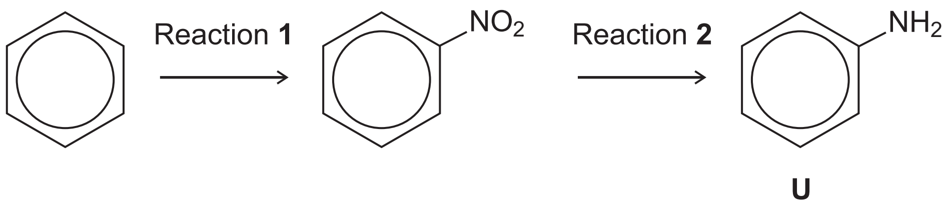
Question 8 continues on the next page

8 (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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(6 marks)

(Extra space) ....

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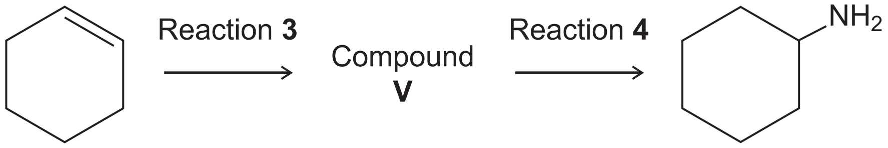
8 (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



W

Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(6 marks)

(Extra space) ....

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Question 8 continues on the next page

Turn over ▶

8 (d) Explain why amine **U** is a weaker base than amine **W**.

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(3 marks)

(Extra space) ....

....

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19

END OF QUESTIONS

GCE Chemistry Data Sheet

Table 1

Infrared absorption data

Bond	**Wavenumber /cm^{-1}**
N — H (amines)	3300 – 3500
O — H (alcohols)	3230 – 3550
C — H	2850 – 3300
O — H (acids)	2500 – 3000
C ≡ N	2220 – 2260
C = O	1680 – 1750
C = C	1620 – 1680
C — O	1000 – 1300
C — C	750 – 1100

Table 2

^{1}H n.m.r. chemical shift data

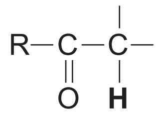
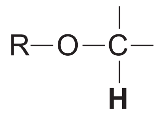
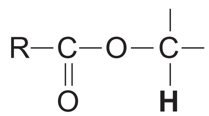
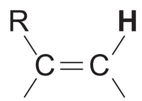
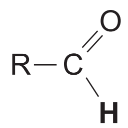
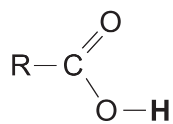
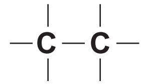
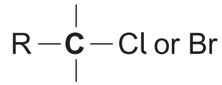
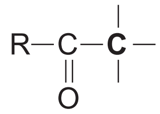
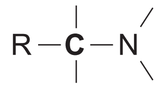
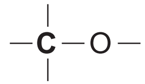
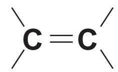
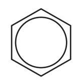
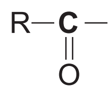
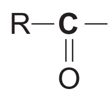
Type of proton	**δ/ppm**
$RO\mathbf{H}$	0.5 – 5.0
$RC\mathbf{H}_3$	0.7 – 1.2
$RN\mathbf{H}_2$	1.0 – 4.5
$R_2C\mathbf{H}_2$	1.2 – 1.4
$R_3C\mathbf{H}$	1.4 – 1.6
	2.1 – 2.6
	3.1 – 3.9
$RC\mathbf{H}_2Cl$ or Br	3.1 – 4.2
	3.7 – 4.1
	4.5 – 6.0
	9.0 – 10.0
	10.0 – 12.0

Table 3

^{13}C n.m.r. chemical shift data

Type of carbon		**δ/ppm**
		5 – 40
		10 – 70
		20 – 50
		25 – 60
	alcohols, ethers or esters	50 – 90
		90 – 150
$R-\mathbf{C}\equiv N$		110 – 125
		110 – 160
	esters or acids	160 – 185
	aldehydes or ketones	190 – 220

The Periodic Table of the Elements

Key

relative atomic mass
symbol
name
atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (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	96.0 **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	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

* **58 – 71** Lanthanides	140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71
† **90 – 103** Actinides	232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

Answer **all** questions in the spaces provided.

1 The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

1 (a) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	1.8×10^{-3}
2	0.40	0.60	
3	0.60		5.4×10^{-3}
4		0.90	12.2×10^{-3}

(3 marks)

(*Space for working*) ....

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1 (b) Use the data from Experiment **1** to calculate a value for the rate constant *k* and deduce its units.

Calculation ....

....

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Units ....

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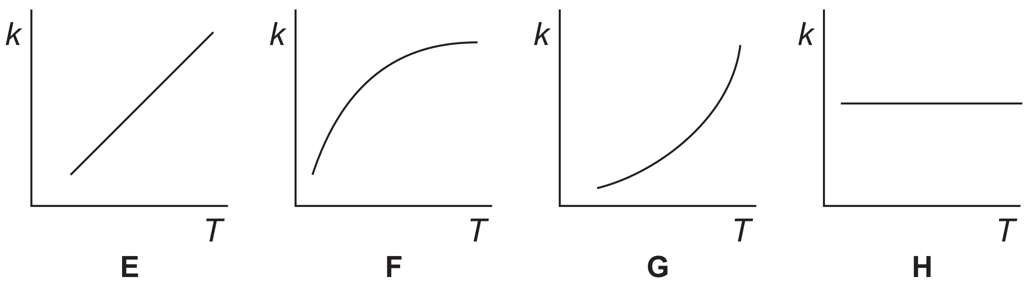
(3 marks)

1 (c) Consider the graphs **E**, **F**, **G** and **H** below.



Write in the box below the letter of the graph that shows how the rate constant *k* varies with temperature.

(1 mark)

7

2 At high temperatures and in the presence of a catalyst, sulfur trioxide decomposes according to the following equation.

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

2 (a) In an experiment, 8.0 mol of sulfur trioxide were placed in a container of volume 12.0 dm^3 and allowed to come to equilibrium.
At temperature T_1 there were 1.4 mol of oxygen in the equilibrium mixture.

2 (a) (i) Calculate the amount, in moles, of sulfur trioxide and of sulfur dioxide in the equilibrium mixture.

Amount of sulfur trioxide ....

Amount of sulfur dioxide ....

(2 marks)

2 (a) (ii) Write an expression for the equilibrium constant, K_c, for this equilibrium.

....

....

(1 mark)

2 (a) (iii) Deduce the units of K_c for this equilibrium.

....

....

(1 mark)

2 (a) (iv) Calculate a value of K_c for this equilibrium at temperature T_1

(If you were unable to complete the calculations in part **(a) (i)** you should assume that the amount of sulfur trioxide in the equilibrium mixture was 5.8 mol and the amount of sulfur dioxide was 2.1 mol. These are **not** the correct values.)

....

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(3 marks)

(Extra space) ....

....

2 (b) The experiment was repeated at the same temperature using the same amount of sulfur trioxide but in a larger container.
State the effect, if any, of this change on:

2 (b) (i) the amount, in moles, of oxygen in the new equilibrium mixture

....

(1 mark)

2 (b) (ii) the value of K_c

....

(1 mark)

2 (c) The experiment was repeated in the original container but at temperature T_2
The value of K_c was smaller than the value at temperature T_1
State which is the higher temperature, T_1 or T_2
Explain your answer.

Higher temperature ....

Explanation ....

....

....

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(3 marks)

(Extra space) ....

....

12

3 Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

3 (a) State the meaning of the term *Brønsted–Lowry base*.

....

....

(1 mark)

3 (b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

....

....

(1 mark)

3 (b) (ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

....

....

(1 mark)

3 (c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base ....

Explanation ....

....

....

....

(3 marks)

(Extra space) ....

....

3 (d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

....

(1 mark)

3 (e) Explain qualitatively how the buffer solution in part **(d)** maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

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....

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(2 marks)

(Extra space) ....

....

9

Turn over for the next question

4 This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

4 (a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

....

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....

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(2 marks)

(Extra space) ....

....

4 (b) HX is a weak monobasic acid.

4 (b) (i) Write an expression for the acid dissociation constant, K_a, for HX.

....

....

(1 mark)

4 (b) (ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

....

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....

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(3 marks)

(Extra space) ....

....

....

4 (c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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(6 marks)

(Extra space) ....

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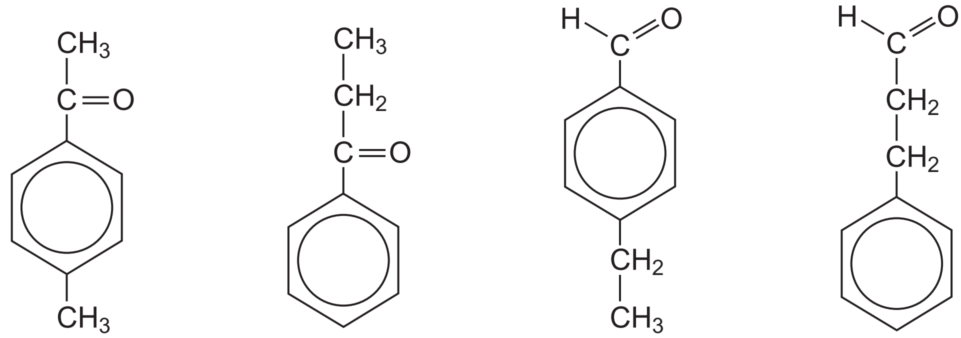
12

Turn over ▶

5 Mass spectrometry is used by organic chemists to help distinguish between different compounds.

Four isomers of $C_9H_{10}O$, shown below, were analysed by mass spectrometry.



A **B** **C** **D**

The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m*/*z* = 134

The data in the table below show the *m*/*z* values greater than 100 for the **major** peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

Spectrum	*m*/*z* values for major peaks	No major peak at *m*/*z*
I	119	133, 105
II	133, 119 and 105	
III	133, 105	119
IV	105	133, 119

5 (a) Two of the molecular ions fragmented to form an ion with *m*/*z* = 133 by losing a radical. Identify the radical that was lost.

....

(1 mark)

5 (b) Two of the molecular ions fragmented to form an ion with *m*/*z* = 119 by losing a radical. Identify the radical that was lost.

....

(1 mark)

5 (c) Three of the molecular ions fragmented to form ions with *m*/*z* = 105 by losing a radical with M_r = 29

Identify **two** different radicals with M_r = 29 that could have been lost.

Radical 1 ....

Radical 2 ....

(2 marks)

5 (d) Consider the structures of the four isomers and the fragmentations indicated in parts **(a)** to **(c)**.
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

Spectrum I ☐

Spectrum II ☐

Spectrum III ☐

Spectrum IV ☐

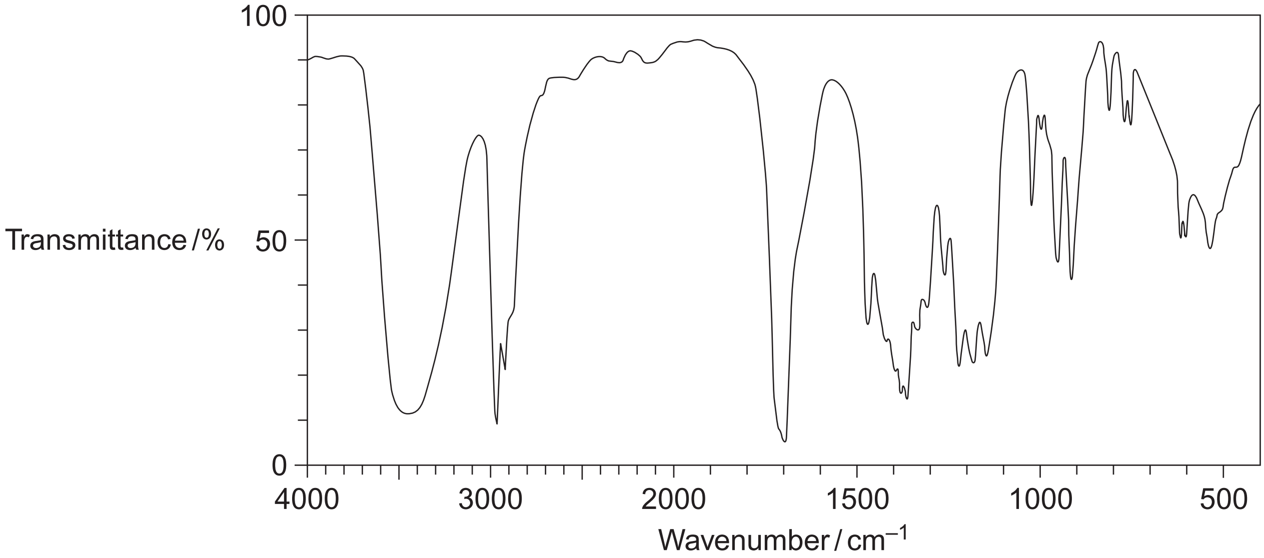
(4 marks)

8

Turn over for the next question

6 Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

6 (a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450 cm^{-1} in the spectrum.

....

(1 mark)

6 (b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ/ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

6 (b) (i) The peak at $\delta = 2.6$

....

(1 mark)

6 (b) (ii) The peak at $\delta = 2.2$

....

(1 mark)

6 (b) (iii) The peak at $\delta = 1.2$

....

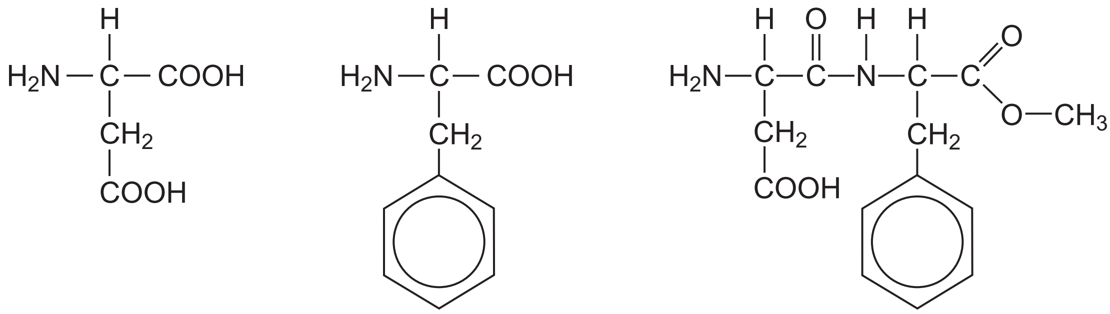
(1 mark)

6 (b) (iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

(1 mark)

5

7 The amino acids aspartic acid and phenylalanine react together to form a dipeptide. This dipeptide can be converted into a methyl ester called aspartame.



Aspartame has a sweet taste and is used in soft drinks and in sugar-free foods for people with diabetes.

Hydrolysis of aspartame forms methanol initially. After a longer time the peptide link breaks to form the free amino acids. Neither of these amino acids tastes sweet.

7 (a) Apart from the release of methanol, suggest why aspartame is **not** used to sweeten foods that are to be cooked.

....

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(1 mark)

(Extra space) ....

....

7 (b) Give the IUPAC name of aspartic acid.

....

(1 mark)

7 (c) Draw the organic species formed by aspartic acid at high pH.

(1 mark)

7 (d) Draw the zwitterion of phenylalanine.

(1 mark)

7 (e) Phenylalanine exists as a pair of stereoisomers.

7 (e) (i) State the meaning of the term *stereoisomers*.

....

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(2 marks)

7 (e) (ii) Explain how a pair of stereoisomers can be distinguished.

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(2 marks)

(Extra space) ....

....

8

8 Common substances used in everyday life often contain organic compounds.

8 (a) State an everyday use for each of the following compounds.

8 (a) (i) $CH_3(CH_2)_{17}COO^- Na^+$ ....

(1 mark)

8 (a) (ii) $CH_3(CH_2)_{19}COOCH_3$ ....

(1 mark)

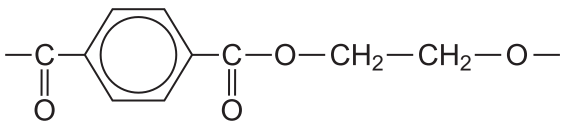
8 (a) (iii) $[C_{16}H_{33}N(CH_3)_3]^+ Br^-$ ....

(1 mark)

8 (b) The following structures are the repeating units of two different condensation polymers.

For each example, name the type of condensation polymer. Give a common name for a polymer of this type.

8 (b) (i)

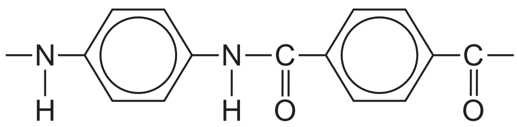


Type of condensation polymer ....

Common name ....

(2 marks)

8 (b) (ii)



Type of condensation polymer ....

Common name ....

(2 marks)

8 (b) (iii) Explain why the polymer in part **(b) (ii)** has a higher melting point than the polymer in part **(b) (i)**.

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(2 marks)

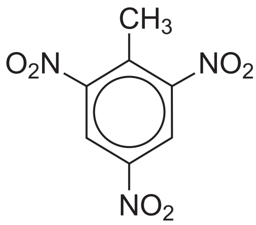
(Extra space) ....

....

9

Turn over for the next question

9 Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



9 (a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.

9 (a) (i) Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents ....

....

Equation ....

....

(3 marks)

9 (a) (ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3 marks)

9 (b) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TNT.

....

(1 mark)

9 (c) Deduce the number of peaks in the ^{1}H n.m.r. spectrum of TNT.

....

(1 mark)

9 (d) Using the molecular formula ($C_7H_5N_3O_6$), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

....

(1 mark)

9

Turn over for the next question

Answer **all** questions in the spaces provided.

10 The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of CH_3CH_2COCl and of $CH_3CH_2CH_2Cl$ with ammonia.

10 (a) For the reaction of CH_3CH_2COCl with ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

(Extra space) ....

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10 (b) For the reaction of $CH_3CH_2CH_2Cl$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

(Extra space) ....

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Question 10 continues on the next page

Turn over ▶

10 (c) Suggest **one** reason why chlorobenzene (C_6H_5Cl) does **not** react with ammonia under normal conditions.

....

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....

(1 mark)

(Extra space) ....

....

13

11 Chemists have to design synthetic routes to convert one organic compound into another.

Propanone can be converted into 2-bromopropane by a three-step synthesis.

Step 1: propanone is reduced to compound **L**.
Step 2: compound **L** is converted into compound **M**.
Step 3: compound **M** reacts to form 2-bromopropane.

Deduce the structure of compounds **L** and **M**.

For each of the three steps, suggest a reagent that could be used and name the mechanism.

Equations and curly arrow mechanisms are **not** required.

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(8 marks)

(Extra space) ....

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8

END OF QUESTIONS

GCE Chemistry Data Sheet

Table 1
Infrared absorption data

Bond	Wavenumber /cm^{-1}
N—H (amines)	3300 – 3500
O—H (alcohols)	3230 – 3550
C—H	2850 – 3300
O—H (acids)	2500 – 3000
$C\equiv N$	2220 – 2260
C=O	1680 – 1750
C=C	1620 – 1680
C—O	1000 – 1300
C—C	750 – 1100

Table 2
[1]H n.m.r. chemical shift data

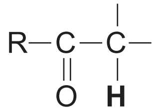
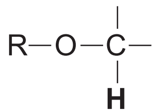
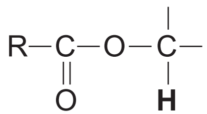
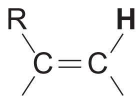
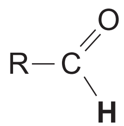
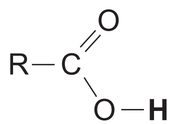
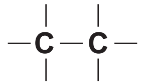
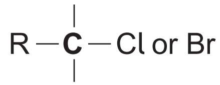
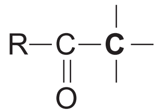
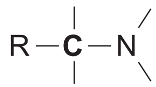
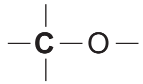
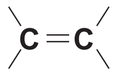
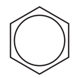
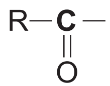
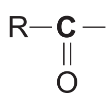
Type of proton	δ/ppm
RO**H**	0.5 – 5.0
RCH_3	0.7 – 1.2
RNH_2	1.0 – 4.5
R_2CH_2	1.2 – 1.4
R_3CH	1.4 – 1.6
	2.1 – 2.6
	3.1 – 3.9
RCH_2Cl or Br	3.1 – 4.2
	3.7 – 4.1
	4.5 – 6.0
	9.0 – 10.0
	10.0 – 12.0

Table 3
[13]C n.m.r. chemical shift data

Type of carbon		δ/ppm
		5 – 40
		10 – 70
		20 – 50
		25 – 60
	alcohols, ethers or esters	50 – 90
		90 – 150
R—**C**≡N		110 – 125
		110 – 160
	esters or acids	160 – 185
	aldehydes or ketones	190 – 220

The Periodic Table of the Elements

Key

relative atomic mass **symbol** name atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (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	96.0 **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	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

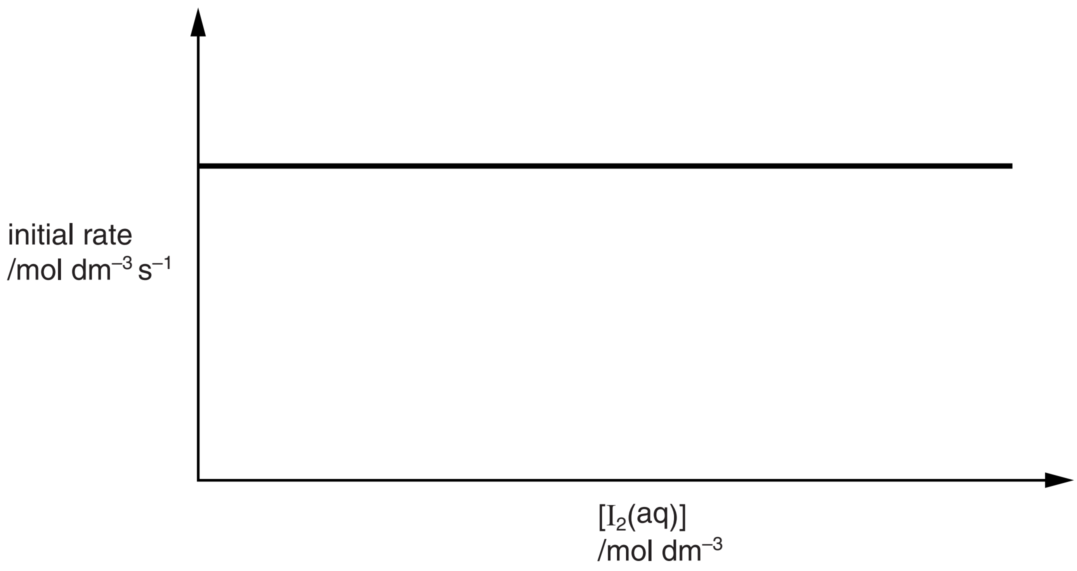
* **58 – 71** Lanthanides	140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71
† **90 – 103** Actinides	232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

Answer **all** the questions.

1 A student investigates the reaction between iodine, I_2, and propanone, $(CH_3)_2CO$, in the presence of aqueous hydrochloric acid, $HCl(aq)$.

The results of the investigation are shown below.

Rate–concentration graph



Results of initial rates experiments

experiment	$[(CH_3)_2CO(aq)]$ / mol dm^{-3}	$[HCl(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.50×10^{-3}	2.00×10^{-2}	2.10×10^{-9}
2	3.00×10^{-3}	2.00×10^{-2}	4.20×10^{-9}
3	3.00×10^{-3}	5.00×10^{-2}	1.05×10^{-8}

(a) Determine the orders with respect to I_2, $(CH_3)_2CO$ and HCl, the rate equation and the rate constant for the reaction.

Explain all of your reasoning.

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.... **[9]**

(b) The student then investigates the reaction of hydrogen, H_2, and iodine monochloride, ICl.

The equation for this reaction is shown below.

$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$

The rate equation for this reaction is shown below.

$$\text{rate} = k[H_2(g)]\,[ICl(g)]$$

Predict a possible two-step mechanism for this reaction. The first step should be the rate-determining step.

step 1 ....

step 2 .... **[2]**

[Total: 11]

Turn over

2 Lattice enthalpies can be calculated indirectly using Born–Haber cycles.

Table 2.1 shows enthalpy changes needed to calculate the lattice enthalpy of sodium oxide, Na_2O.

letter	enthalpy change	energy /kJ mol^{-1}
A	1st electron affinity of oxygen	–141
B	2nd electron affinity of oxygen	+790
C	1st ionisation energy of sodium	+496
D	atomisation of oxygen	+249
E	atomisation of sodium	+108
F	formation of sodium oxide	–414
G	lattice enthalpy of sodium oxide	

Table 2.1

(a) Define the term *lattice enthalpy*.

....

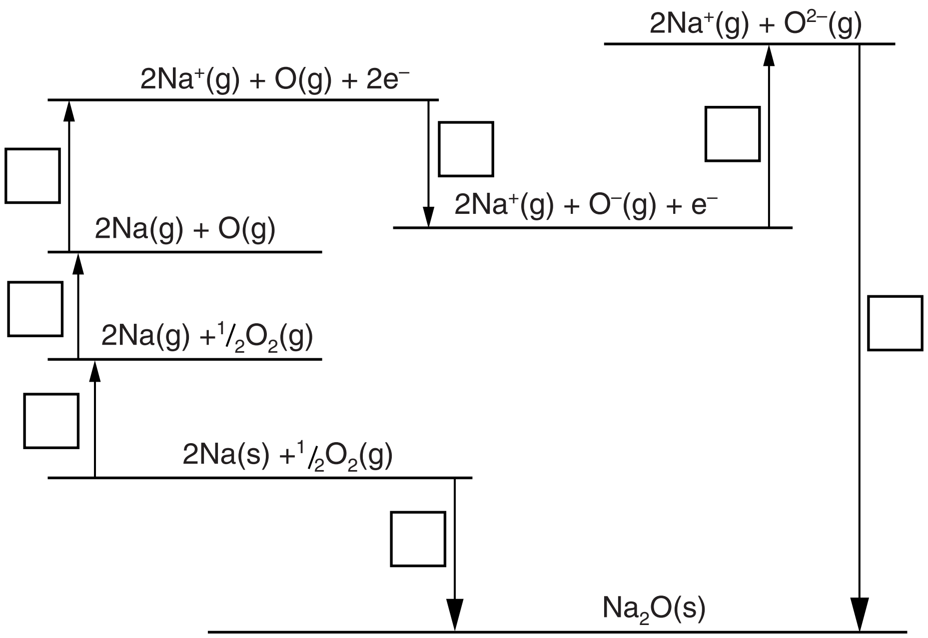
....

....

.... **[2]**

(b) The Born–Haber cycle below links the lattice enthalpy of sodium oxide with its enthalpy change of formation.

(i) On the Born–Haber cycle, write the correct letter from **Table 2.1** in each box.



[3]

(ii) Calculate the lattice enthalpy of sodium oxide, **G**.

answer = ... kJ mol^{-1} **[2]**

(c) Explain why it is difficult to predict whether the lattice enthalpy of magnesium sulfide would be more or less exothermic than the lattice enthalpy of sodium oxide.

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.... **[3]**

Turn over

(d) A student wanted to determine the lattice enthalpy of sodium carbonate, Na_2CO_3. Unfortunately this is very difficult to do using a similar Born–Haber cycle to that used for sodium oxide in **(b)**.

(i) Suggest why this is very difficult.

....

....

....

.... **[1]**

(ii) The student thought that he could determine the lattice enthalpy of Na_2CO_3 using a Born–Haber cycle that links lattice enthalpy with enthalpy change of solution.
The enthalpy change of solution of Na_2CO_3 is exothermic.

- Sketch this Born–Haber cycle,
- Explain how the lattice enthalpy of Na_2CO_3 could be calculated from the enthalpy changes in the cycle.

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.... **[3]**

[Total: 14]

3 Cobalt is a transition element. Solid compounds of cobalt are often complexes and in solution, complex ions are formed.

(a) In its complexes, the common oxidation numbers of cobalt are +2 and +3.

Complete the electron configurations of cobalt as the element and in the +3 oxidation state:

cobalt as the element: $1s^2\ 2s^2\ 2p^6$ ....

cobalt in the +3 oxidation state: $1s^2\ 2s^2\ 2p^6$ .... **[2]**

(b) State **one** property of cobalt(II) and cobalt(III), other than their ability to form complex ions, which is typical of ions of a transition element.

....

.... **[1]**

(c) Complex ions contain ligands.

State the meaning of the term *ligand*.

....

....

.... **[1]**

(d) Aqueous cobalt(II) sulfate, $CoSO_4$(aq), takes part in the following reactions.

For each reaction, state the formula of the transition element species formed and the type of reaction taking place.

(i) Aqueous cobalt(II) sulfate, $CoSO_4$(aq), reacts with aqueous sodium hydroxide.

transition element species formed: ....

type of reaction: .... **[2]**

(ii) Aqueous cobalt(II) sulfate, $CoSO_4$(aq), reacts with concentrated hydrochloric acid.

transition element species formed: ....

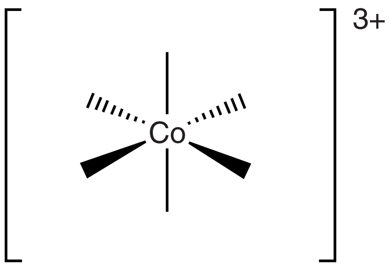
type of reaction: .... **[2]**

(e) Cobalt(III) chloride, $CoCl_3$, reacts with ammonia to form a range of complexes. These complexes contain different amounts of ammonia. Information about these complexes is summarised below.

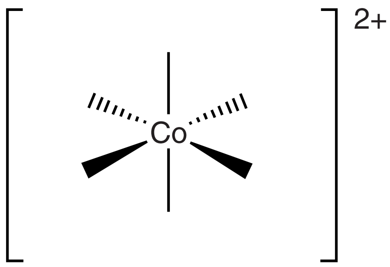
The complex ions **C** and **D** are stereoisomers.

complex	formula	formula of complex
A	$CoCl_3(NH_3)_6$	$[Co(NH_3)_6]^{3+}\ 3Cl^-$
B	$CoCl_3(NH_3)_5$	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$
C	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$
D	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$

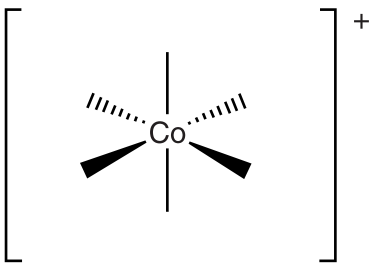
(i) Complete the diagrams below to suggest possible structures for the complex ion in complexes **A** to **D**.



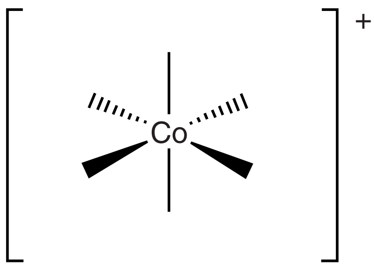
complex ion in A



complex ion in B



complex ion in C



complex ion in D

[4]

(ii) Chemists provided evidence for the formulae of these complexes from their reactions with aqueous silver nitrate. Aqueous silver nitrate reacts with aqueous halide ions in a precipitation reaction.

An excess of silver nitrate solution was reacted with 0.0100 mol of one of the complexes **A** to **D**. 2.868 g of a precipitate was formed.

Determine which complex was reacted.

In your answer you should explain how the result of the experiment would allow the formula of the complex to be identified.

.... **[3]**

[Total: 15]

4 This question looks at acids, bases and buffer solutions.

(a) Nitric acid, HNO_3, is a strong Brønsted–Lowry acid.
Nitrous acid, HNO_2, is a weak Brønsted–Lowry acid with a K_a value of 4.43×10^{-4} mol dm^{-3}.

(i) What is the difference between a strong acid and a weak acid?

....

....

.... **[1]**

(ii) What is the expression for the acid dissociation constant, K_a, of nitrous acid, HNO_2?

[1]

(iii) Calculate the pH of 0.375 mol dm^{-3} nitrous acid, HNO_2.

Give your answer to **two** decimal places.

pH = ... **[2]**

(iv) A student suggests that an acid–base equilibrium is set up when nitric acid is mixed with nitrous acid.

Complete the equation for the equilibrium that would be set up and label the conjugate acid–base pairs.

HNO_3 + HNO_2 $\rightleftharpoons$ .... + ...

....

[2]

(b) Calcium hydroxide, $Ca(OH)_2$, is a strong Brønsted–Lowry base.

(i) Explain what is meant by the term *Brønsted–Lowry base*.

....

.... **[1]**

(ii) Calculate the pH of 0.0400 $mol\,dm^{-3}$ $Ca(OH)_2$.

Give your answer to **two** decimal places.

pH = ... **[3]**

(c) Aqueous calcium hydroxide is added to nitrous acid, HNO_2.

Write the overall equation and the ionic equation for the reaction that takes place.

overall: ....

ionic: .... **[2]**

(d) Carbonic acid, H_2CO_3, is a weak Brønsted–Lowry acid formed when carbon dioxide dissolves in water. Healthy blood is buffered to a pH of 7.40. The most important buffer solution in blood is a mixture of carbonic acid and hydrogencarbonate ions, HCO_3^-.

(i) Explain how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH.

In your answer you should explain how equilibrium allows the buffer solution to control the pH.

.... **[5]**

(ii) Healthy blood at a pH of 7.40 has a hydrogencarbonate : carbonic acid ratio of 10.5 : 1. A patient is admitted to hospital. The patient's blood pH is measured as 7.20.

Calculate the hydrogencarbonate : carbonic acid ratio in the patient's blood.

[5]

[Total: 22]

5 Redox reactions can be used to generate electrical energy from electrochemical cells.

(a) A student carries out an investigation based on the redox systems shown in **Table 5.1** below.

	redox system	$E^{\ominus}$/V
1	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.25
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74

Table 5.1

The student sets up two standard cells to measure two standard cell potentials.

- **Cell A** is based on redox systems **1** and **2.**
- **Cell B** is based on redox systems **1** and **3.**

(i) Draw a labelled diagram to show how the student could have set up **Cell A**, based on redox systems **1** and **2**, to measure the standard cell potential.

[3]

(ii) For each standard cell below,

- what would be the standard cell potential?
- what would be the sign of the Ni electrode?

Cell A based on redox system **1** and **2**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

Cell B based on redox system **1** and **3**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

[2]

(b) The student left each cell in **(a)** connected for a length of time.

For each cell, the student weighed the nickel electrode before connecting the cell and after the cell had been disconnected.

The student made the following observations.

- In **Cell A**, the nickel electrode lost mass.
- In **Cell B**, the nickel electrode gained mass.
- In **both** cells, the measured cell potential slowly changed.

Explain these observations. Include equations in your answer.

....

....

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....

....

.... **[3]**

(c) Nickel metal hydride cells (NiMH cells) are being developed for possible use in cars.
In a NiMH cell, an alloy is used to absorb hydrogen as a metal hydride. For simplicity, the alloy can be represented as M and the metal hydride as MH.

The overall cell reaction in a NiMH cell is shown below.

$$MH + NiO(OH) \rightarrow M + Ni(OH)_2$$

The half-equation at one electrode is shown below.

$$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$$

(i) Deduce the half-equation at the other electrode.

.... **[1]**

(ii) State a method, other than absorption, that is being developed to store hydrogen for possible use as a fuel in cars.

.... **[1]**

[Total: 10]

6 Free energy changes can be used to predict the feasibility of processes.

(a) Write down the equation that links the free energy change with the enthalpy change and temperature.

.... **[1]**

(b) You are provided with equations for five processes.

For each process, predict the sign of ΔS.

process	sign of ΔS
$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	
$NaCl(s) + (aq) \rightarrow NaCl(aq)$	
$H_2O(l) \rightarrow H_2O(s)$	
$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$	
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \bullet 5H_2O(s)$	

[2]

(c) Ammonia can be oxidised as shown in the equation below.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Standard entropies are given in the table below.

substance	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	192	205	211	189

Calculate the standard entropy change, in J K^{-1} mol^{-1}, for this oxidation of ammonia.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

(d) The exothermic reaction below occurs spontaneously at low temperatures but does **not** occur at very high temperatures.

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

Explain why.

....

....

....

....

....

.... **[2]**

(e) An ore of iron contains iron(III) oxide, Fe_2O_3.
Iron is extracted from this ore by heating with carbon.
The equation below shows one of the reactions which takes place.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

$\Delta S = +543\,J\,K^{-1}\,mol^{-1}$ and $\Delta H = +493\,kJ\,mol^{-1}$

Calculate the minimum temperature at which this reaction becomes feasible.

Show **all** your working.

minimum temperature = ... **[3]**

[Total: 10]

7 Dinitrogen tetroxide, $N_2O_4(g)$, and nitrogen dioxide, $NO_2(g)$, coexist in the following equilibrium.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57\,kJ\,mol^{-1}$$

A chemist adds 4.00 mol NO_2 to a container with a volume of 2.00 dm^3. The container is sealed, heated to a constant temperature and allowed to reach equilibrium.

The equilibrium mixture contains 3.20 mol NO_2.

(a) Calculate the value for K_c under these conditions.

[5]

(b) The experiment is repeated but the pressure in the container is doubled.

Explain in terms of K_c the effect on the concentrations of NO_2 and N_2O_4 when the mixture has reached equilibrium.

....

....

....

....

....

....

.... **[3]**

[Total: 8]

Turn over

8 Haematite is the main ore of iron. The percentage of iron in a sample of haematite can be determined using the method below.

Method

Stage 1. An excess of concentrated hydrochloric acid is added to a 3.25 g sample of haematite. The iron(III) oxide in the haematite reacts to form a solution containing Fe^{3+} ions.

Stage 2. An excess of aqueous tin(II) chloride is added. Sn^{2+} reduces the Fe^{3+} present to Fe^{2+}. Excess Sn^{2+} is removed.

Stage 3. The solution is diluted and made up to 250.0 cm^3 in a volumetric flask.

Stage 4. A 25.0 cm^3 sample of this solution is pipetted into a conical flask.

Stage 5. The solution in the conical flask is titrated with 0.0200 mol dm^{-3} aqueous potassium dichromate(VI), $K_2Cr_2O_7$.
The Fe^{2+} ions are oxidised to Fe^{3+} ions.

Stage 6. Stages 4 and **5** are repeated to obtain an average titre of 26.5 cm^3.

You are provided with the following electrode potentials.

You may need to use this information throughout this question.

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^\ominus = +0.15\,V$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\ominus = +1.33\,V$$
$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\,V$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\,V$$

(a) Write an equation for the reaction between iron(III) oxide and concentrated hydrochloric acid, occurring in **Stage 1**.

.... [1]

(b) Write equations for the reactions involving iron ions in **Stages 2** and **5**.

Stage 2 ....

Stage 5 .... [2]

(c) Calculate the percentage by mass of iron in the haematite ore.

percentage iron = ... % **[5]**

(d) Aqueous potassium manganate(VII), $KMnO_4$(aq), is **not** suitable for titrating the solution in this method. Aqueous potassium dichromate(VI), $K_2Cr_2O_7$(aq), is used instead.

Suggest and explain why potassium dichromate(VI), $K_2Cr_2O_7$, is suitable for this titration whereas potassium manganate(VII), $KMnO_4$, is not suitable.

....

....

....

.... **[2]**

[Total: 10]

END OF QUESTION PAPER