Rewarding Learning

ADVANCED
General Certificate of Education
2016

Centre Number

Candidate Number

Chemistry

Assessment Unit A2 1
assessing
Periodic Trends and
Further Organic, Physical
and Inorganic Chemistry

[AC212]

FRIDAY 27 MAY, MORNING

MV18

Time

2 hours, plus your additional time allowance.

Instructions to Candidates

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.
Answer **all sixteen** questions.
Answer **all ten** questions in **Section A**. Record your answers by marking the appropriate letter on the answer sheet provided. Use only the spaces numbered 1 to 10. Keep in sequence when answering.
Answer **all six** questions in **Section B**.
You must answer the questions in the spaces provided.
Complete in blue or black ink only.

Information for Candidates

The total mark for this paper is 120.
Quality of written communication will be assessed in Question **16(a)**.
In Section A all questions carry equal marks, i.e. **two** marks for each question.
In Section B the figures in brackets printed at the end of each question indicate the marks awarded to each question or part question.
A Periodic Table of Elements, containing some data, is included in this question paper.

Section A

For each of the questions only **one** of the lettered responses (A–D) is correct.

Select the correct response in each case and mark its code letter by connecting the dots as illustrated on the answer sheet.

1 For the reaction,

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$$

the rate law is given by the equation, rate = $k[H_2O_2][I^-][H^+]$.

Which one of the following is the factor by which the rate of reaction increases if the concentration of each reactant is doubled?

A 2

B 4

C 8

D 16

2 23 mg of sodium were added to 100 cm^3 of water. Which one of the following is the pH of the solution produced?

A 10

B 11

C 12

D 13

3 Which one of the following is the number of isomers with the molecular formula C_4H_9Br?

A 2

B 3

C 4

D 5

4 Which one of the following oxides produces a slightly alkaline solution when dissolved in water?

A Al_2O_3

B MgO

C Na_2O

D SiO_2

5 Which one of the following does **not** have units?

A ΔS for the boiling of water

B ΔG for the Haber process

C K_w for water at 30 °C

D K_c for the esterification of ethanol

6 Phosphate ions are hydrolysed by water in the following equilibrium:

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + HO^-$$

Which one of the following shows the Brønsted–Lowry bases in the equilibrium?

A PO_4^{3-} and HPO_4^{2-}

B PO_4^{3-} and HO^-

C H_2O and HO^-

D H_2O and HPO_4^{2-}

7 Reactions which have a large activation energy have a

A small entropy change.

B large entropy change.

C small rate constant.

D large rate constant.

8 Which one of the following reagents would **not** be used to distinguish between aldehydes and ketones?

A Acidified potassium dichromate solution

B 2,4-dinitrophenylhydrazine solution

C Fehling's solution

D Tollen's reagent

9 When ammonium chloride is dissolved in water the temperature decreases. Which one of the following shows the changes for ΔH and ΔS?

	ΔH	ΔS
A	negative	negative
B	negative	positive
C	positive	negative
D	positive	positive

10 10 cm^3 of 6 M hydrochloric acid were diluted to form 0.5 M hydrochloric acid. Which one of the following is the volume of water to be added?

A 50 cm^3

B 110 cm^3

C 120 cm^3

D 290 cm^3

Section B

Answer **all six** questions in this section

11 Write equations for the reaction of the following oxides and chlorides of the third period with water. [5 marks]

oxide/chloride	**equation**
sodium oxide	
sulfur trioxide	
chlorine(VII) oxide	
phosphorus(V) oxide	
phosphorus(V) chloride	

12 The concentration of carbon dioxide in the atmosphere was stated in older textbooks to be 0.03**%**. Today that figure is nearer to 0.04**%**. Many processes increase or decrease the amount of carbon dioxide.

(a) (i) Name **two** non-renewable hydrocarbon fuels.
[2 marks]

_____

_____

(ii) Explain how these hydrocarbon fuels increase the concentration of carbon dioxide in the atmosphere.
[1 mark]

_____

_____

_____

(b) State and explain the effect of the following on the concentration of carbon dioxide in the atmosphere.

(i) Photosynthesis [2 marks]

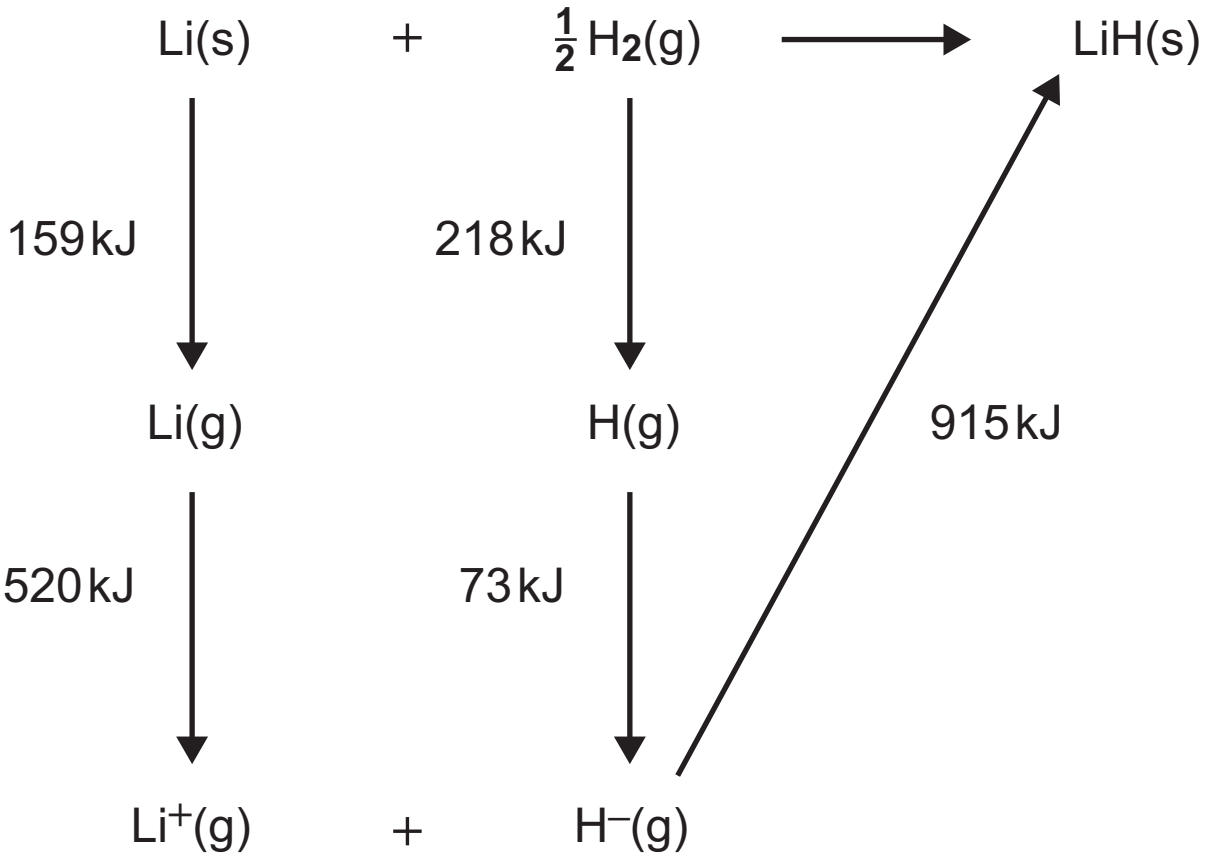
(ii) Respiration [2 marks]

(iii) Surface waters [2 marks]

(c) The concentration of carbon dioxide causes the "greenhouse effect". Explain what is meant by the "greenhouse effect". [3 marks]

13 Lithium hydride is produced by passing hydrogen gas over lithium. The reaction is complete at a temperature of 725 °C. The enthalpy of formation can be determined by using a Born–Haber cycle or Hess's law.

(a) An outline Born–Haber cycle with enthalpy values is shown below. However the enthalpy values have not been given + or – signs.



(i) Write + or – before each enthalpy value on the diagram. [2 marks]

(ii) Calculate the molar enthalpy of formation for lithium hydride. [2 marks]

(iii) The lattice enthalpies for the other Group I hydrides are shown below in kJ mol^{-1}:

NaH +864;

KH +729;

RbH +704;

CsH +656

In terms of the Born–Haber cycle, suggest why these values decrease. [2 marks]

(b) The molar enthalpy of formation for lithium hydride can be determined using the reactions of lithium and lithium hydride with water.

$2Li + 2H_2O \longrightarrow 2LiOH + H_2 \qquad \Delta H = -440\ kJ$

$LiH + H_2O \longrightarrow LiOH + H_2 \qquad \Delta H = -130\ kJ$

Calculate the molar enthalpy of formation of lithium hydride using the enthalpy values above. [2 marks]

(c) Using the equation $\Delta G = \Delta H - T\Delta S$ explain why the free energy change for the formation of lithium hydride has a negative value. [2 marks]

(d) Lithium hydride is used to make lithium aluminium hydride, $LiAlH_4$ (lithal). This reduces aldehydes and ketones using hydride ions, H^-. The mechanism for these reductions is similar to that of their reactions with cyanide ions.

(i) Explain why the hydride ion is a nucleophile. [1 mark]

(ii) Draw the mechanism for the reduction of propanone with hydride ions.
The intermediate is reacted with water to form the organic product. [3 marks]

(iii) Name the organic product from the reduction of propanone. [1 mark]

(iv) Carboxylic acids are also reduced by lithal.
Write an equation for the reduction of propanoic acid with lithal using [H] as the reducing agent.
[2 marks]

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(Questions continue overleaf)

14 Cyanoethanoic acid, $CH_2CNCOOH$, is an important intermediate in the production of "superglue". It is a white solid with a melting point of 65–67 °C. It is a stronger acid than ethanoic acid.

(a) Cyanoethanoic acid is prepared by the reaction of potassium chloroethanoate with potassium cyanide. The cyanoethanoic acid is liberated by the addition of hydrochloric acid.

Write equations for the **two** reactions taking place. [2 marks]

(b) Cyanoethanoic acid is very soluble in water and may be purified by recrystallisation. However, it cannot be distilled at atmospheric pressure since at 160 °C it is decarboxylated to form ethanenitrile, CH_3CN.

(i) Explain how you would choose a suitable solvent to recrystallise cyanoethanoic acid. [4 marks]

(ii) Write the equation for the decarboxylation of cyanoethanoic acid. [1 mark]

(c) Cyanoethanoic acid can be esterified by reaction with alcohols. The methyl ester has a boiling point of 205–207 °C and the ethyl ester has a boiling point of 208–210 °C.

(i) Comment on these boiling points with regard to intermolecular forces. [4 marks]

(ii) Write an equation for the formation of the methyl ester. [1 mark]

(iii) Name a catalyst for the reaction. [1 mark]

(d) Ethyl cyanoethanoate reacts with formaldehyde to give a cyanoacrylic ester which is the basis of "superglue".

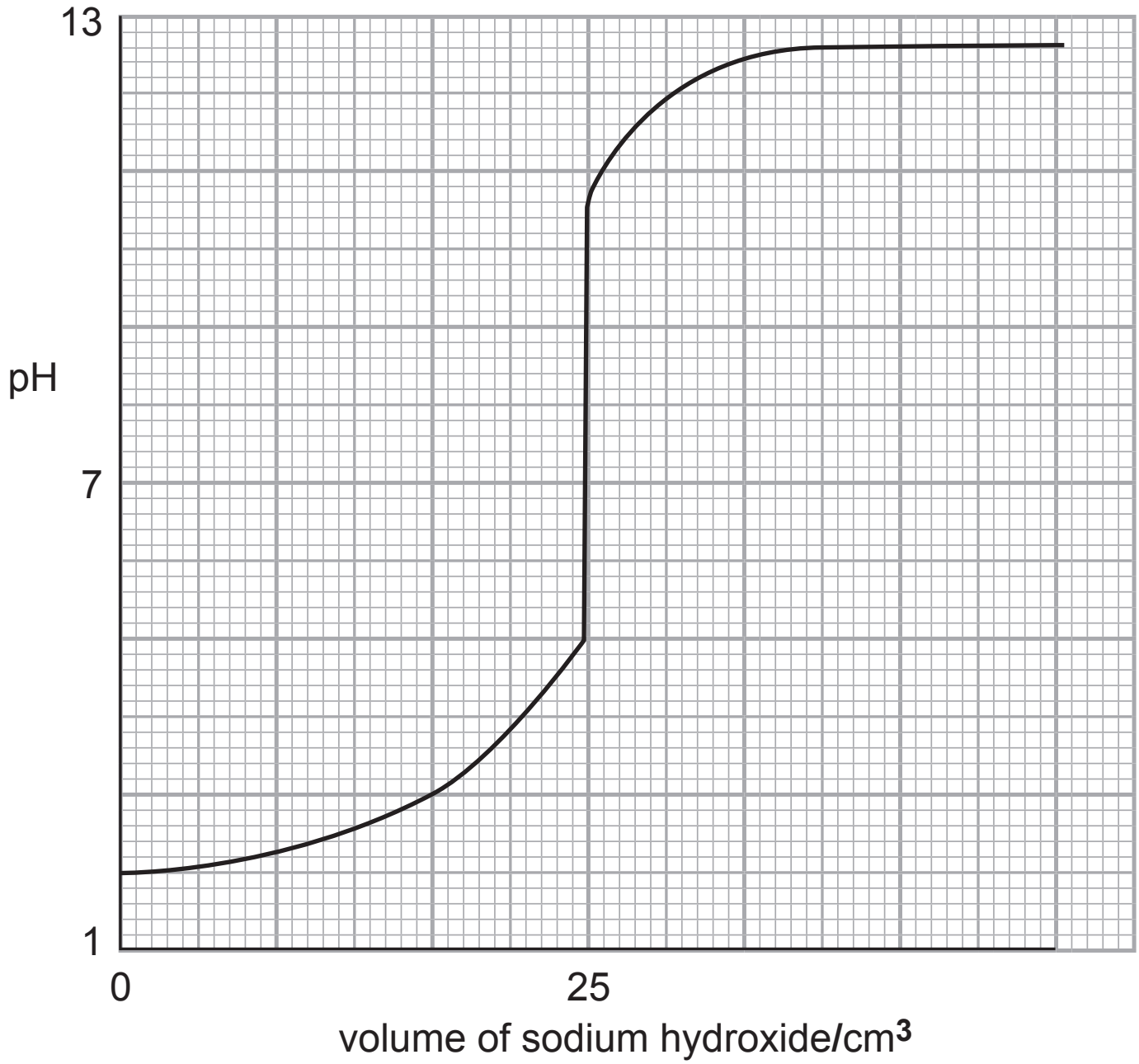
$$CH_2{=}O + CH_2CNCO_2C_2H_5 \longrightarrow CH_2{=}C(CN)CO_2C_2H_5 + H_2O$$

(i) Give the systematic name for formaldehyde. [1 mark]

(ii) Draw the structure of the cyanoacrylic ester, showing **all** the bonds present and explain whether it has E/Z isomers. [3 marks]

(iii) Draw the polymeric structure formed from the cyanoacrylic ester showing **three** repeating units. [2 marks]

(e) The titration curve for the reaction of cyanoethanoic acid with sodium hydroxide is shown below.



The cyanoethanoic acid reacts to form a salt.
The pH of the solution is given by the equation:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

(i) Write the equation for the dissociation constant, K_a, of cyanoethanoic acid. [2 marks]

(ii) The concentration of the salt is the same as the concentration of the acid when the titration is half-complete. Use the titration curve to determine the pK_a and consequently the K_a. [2 marks]

(iii) Explain which indicator would be suitable for this titration. [2 marks]

15 Oils and fats react with potassium hydroxide and are saponified. The carboxylic acids from the oil/fat form potassium salts.

(a) The saponification value of a fat was determined by adding 9.0 g of the fat to a round-bottomed flask containing 50.0 cm^3 of 1.00 M ethanolic potassium hydroxide and a few pieces of porous pot. The flask was fitted with a reflux condenser and the mixture boiled for one hour by which time the solution was clear.
The remaining solution was titrated with 0.50 M hydrochloric acid.

(i) Suggest why ethanolic potassium hydroxide was used rather than aqueous potassium hydroxide. [1 mark]

(ii) Explain why the reaction took one hour and was not instantaneous. [1 mark]

(iii) Suggest the purpose of the porous pot. [1 mark]

(iv) Explain why the solution went clear. [1 mark]

(v) Calculate the saponification value of the fat if 15.0 cm^3 of the 0.50 M hydrochloric acid were required. [3 marks]

(b) One mole of an oil/fat, when hydrolysed, produced one mole of glycerol, one mole of oleic acid, $C_{18}H_{34}O_2$, and two moles of palmitic acid, $C_{16}H_{32}O_2$.

(i) Draw the possible structures of the oil/fat. [3 marks]

(ii) Explain whether any of the structures drawn have asymmetric centres. [2 marks]

(c) The relative molecular mass, RMM, of a fatty acid can be determined by the ignition of the silver salt of the fatty acid. A fatty acid suspected of being oleic acid was reacted with silver carbonate. The silver salt was heated to leave only silver.

(i) Write the equation for the reaction of the acid, RCOOH, with silver carbonate. [1 mark]

(ii) 0.130 g of the pure silver salt, when heated to complete decomposition, gave 0.036 g of pure silver. Calculate the RMM of the silver salt. [3 marks]

(iii) Use the RMM calculated in part **(ii)** to confirm the identity of the fatty acid. [1 mark]

(d) Arachidonic acid, $C_{20}H_{32}O_2$, has four double bonds which are listed as 5Z – 8Z – 11Z – 14Z. Suggest a structure of the acid showing the stereochemistry about the double bonds. [2 marks]

(e) Oleic acid is insoluble in water but sodium oleate is soluble.

(i) Explain why oleic acid is insoluble. [1 mark]

(ii) Explain why sodium oleate is soluble. [2 marks]

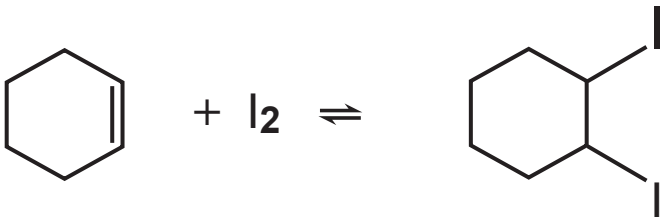
(iii) Explain whether a solution of sodium oleate is alkaline, acidic or neutral. [2 marks]

16 Iodine dissolves in cyclohexane but reacts reversibly with cyclohexene.

(a) Describe, giving experimental details, how you would use 100 cm^3 of cyclohexane to extract as much solid iodine as possible from a solution of iodine in water. [5 marks]

Quality of written communication [2 marks]

(b) The equilibrium equation for the reaction of cyclohexene with iodine is:



The equilibrium constant for the reaction at 25 °C is 20 mol dm^{-3} and at 35 °C is 13 mol dm^{-3}.

(i) Explain whether the forward reaction is endothermic or exothermic. [2 marks]

(ii) Suggest how you could determine the change in the concentration of I_2 with time. [3 marks]

(iii) What happens to the rate of the forward reaction and the reverse reaction when equilibrium is reached? [1 mark]

(iv) Calculate the equilibrium concentration of iodine, I_2, in g dm^{-3} in a system at equilibrium at 35 °C when the equilibrium concentration of $C_6H_{10}I_2$ is 0.001 M and that of C_6H_{10} is 0.01 M. [3 marks]

(c) Bromine water is used to test for the presence of unsaturation. Suggest why iodine is not used. [1 mark]

THIS IS THE END OF THE QUESTION PAPER

DO NOT WRITE ON THIS PAGE

For Examiner's use only	
Question Number	**Marks**
Section A	
1–10	
Section B	
11	
12	
13	
14	
15	
16	
Total Marks	

Examiner Number