Rewarding Learning

ADVANCED
General Certificate of Education
January 2013

Chemistry

Assessment Unit A2 1

assessing

Periodic Trends and Further Organic, Physical and Inorganic Chemistry

[AC212]

AC212

MONDAY 14 JANUARY, AFTERNOON

TIME

2 hours.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.
Answer **all fifteen** 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 five** questions in **Section B**. Write your answers in the spaces provided in this question paper.

INFORMATION FOR CANDIDATES

The total mark for this paper is 120.
Quality of written communication will be assessed in Question **15(a)(iii)**.
In Section A all questions carry equal marks, i.e. **two** marks for each question.
In Section B the figures in brackets printed down the right-hand side of pages indicate the marks awarded to each question or part question.
A Periodic Table of Elements (including some data) is provided.

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

Section A

For each of the following 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   Which one of the following can affect the value of the equilibrium constant for homogeneous reactions?

    A   Addition of a catalyst

    B   Concentration of reactants

    C   Pressure

    D   Temperature

2   The following equilibrium exists in a mixture of concentrated sulfuric and nitric acids.

$$HNO_3 \ + \ 2H_2SO_4 \ \rightleftharpoons \ NO_2^+ \ + \ 2HSO_4^- \ + \ H_3O^+$$

Which one of the following statements is correct about this equilibrium?
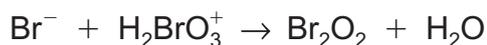
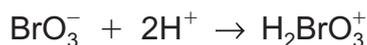   A   The concentration of NO_2^+ is lowered if water is added

    B   The nitric acid acts as an oxidising agent

    C   The species HNO_3 and NO_2^+ are a conjugate acid-base pair

    D   The sulfuric acid acts as a reducing agent

3   How many compounds with asymmetric carbon centres is it possible to prepare by subjecting ethane to repeated chlorination?

    A   0

    B   1

    C   2

    D   3

4 Which one of the following statements about the forward and reverse reactions for the following

$$P + Q \rightleftharpoons R + S$$
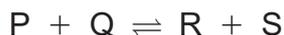
is correct when the system is at equilibrium?

A   The ratio of the rates of the forward reaction to that of the reverse reaction equals the equilibrium constant

B   The rates of both the forward and reverse reactions are equal to zero

C   The rates of the forward and reverse reactions are equal

D   The rate constant for the forward reaction equals the rate constant for the reverse reaction

5 The following is a proposed reaction mechanism for the formation of bromine from bromate ions.

$$BrO_3^- + 2H^+ \rightarrow H_2BrO_3^+$$

$$Br^- + H_2BrO_3^+ \rightarrow Br_2O_2 + H_2O$$

$$Br_2O_2 + 4H^+ + 4Br^- \rightarrow 3Br_2 + 2H_2O$$

Which one of the following is the overall equation for the reaction?

A $BrO_3^- + Br^- + 6H^+ \rightarrow Br_2 + 3H_2O$

B $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

C $2BrO_3^- + 12H^+ \rightarrow Br_2 + 6H_2O$

D $2H_2BrO_3^+ + 8H^+ \rightarrow Br_2 + 6H_2O$

6 The rate of reaction between X and Y is third order. Which one of the following rate equations is **not** correct?

A   Rate = $k [X]^1[Y]^3$

B   Rate = $k [X]^1[Y]^2$

C   Rate = $k [X]^2[Y]^1$

D   Rate = $k [X]^2[Y]^1[Z]^0$

8198   **3**   **[Turn over**

7 Which one of the following is the order of decreasing nucleophilic reactivity of the three species?

A $OH^- > H_2O > H_3O^+$

B $OH^- > H_3O^+ > H_2O$

C $H_2O > H_3O^+ > OH^-$

D $H_2O > OH^- > H_3O^+$

8 Which one of the following reactions has the greatest increase in entropy?

A $X_2(s) + Y_2(g) \rightarrow 2XY(g)$

B $P_2(g) + Q_2(g) \rightarrow 2PQ(g)$

C $M(s) + Z(s) \rightarrow MZ(s)$

D $2A_2(g) + B_2(g) \rightarrow 2A_2B(g)$

9 Which one of the following compounds is formed when the acid below is reduced with excess lithium aluminium hydride?

$$CH_3COCH(CHO)COOH$$

A $CH_3COCH(CH_2OH)_2$

B $CH_3COCH(CHO)CH_2OH$

C $CH_3CHOHCH(CHO)CH_2OH$

D $CH_3CHOHCH(CH_2OH)_2$

10 Which one of the following oxides dissolves in water to form an acid where the central element has an oxidation number of $+6$?

A Cl_2O_7

B P_4O_{10}

C SiO_2

D SO_3

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(Questions continue overleaf)

Section B

Answer **all five** questions in this section in the spaces provided.

11 The concepts of entropy and equilibrium can be used to explain many scientific phenomena.

(a) Explain the meaning of the term **entropy**.

_____

_____ [1]

(b) Explain why the endothermic reaction between ammonium carbonate and ethanoic acid is spontaneous.

_____

_____ [2]

(c) Explain whether reactions which have a negative entropy change and a positive enthalpy change are feasible or not.

_____

_____ [2]

(d) Ammonia is formed by the reaction of nitrogen with hydrogen in an equilibrium reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
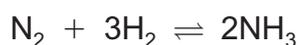
If 1.0 mol of nitrogen was mixed with 3.0 mol of hydrogen at 450 °C and a pressure of 3×10^7 Pa, 1.5 mol of ammonia was produced when equilibrium was reached.

(i) Calculate the mole fraction of each constituent in the equilibrium mixture.

_____

_____

_____

_____ [2]

(ii) Calculate the partial pressures of each constituent.

_____

_____

_____

_____ [2]

(iii) Calculate the value of K_p and state its units.

_____

_____ [2]

[Turn over

12 The chlorides of Period 3 exhibit a variety of formulae, types of bonding and structures.

(a) Complete the table below.

name	formula	approximate pH of solution	type of bonding in the structure
sodium chloride			
magnesium chloride			
aluminium chloride			
phosphorus pentachloride			

[5]

(b) Calculate the oxidation number of each of the elements, sodium, magnesium, aluminium, phosphorus and chlorine, in the chlorides above.

_____

_____ [2]

(c) Write the equation for the reaction of phosphorus pentachloride with water.

_____ [2]

(d) Aluminium chloride is a white solid which has a dimeric structure.

    (i) Suggest the meaning of the term **dimeric**.

_____

_____ [1]

    (ii) Draw a dot and cross diagram for aluminium chloride, using outer electrons only, labelling the coordinate and covalent bonds present.

[3]

(e) Magnesium chloride is slightly hydrolysed by water but sodium chloride is not. Why is magnesium chloride hydrolysed but sodium chloride is not?

_____

_____
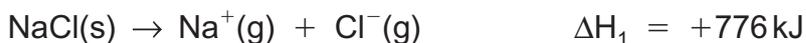
_____ [2]

9

[Turn over

(f) All of the chlorides form solutions when added to water. Sodium chloride dissolves in water by an overall endothermic process. It is explained by the following:

The NaCl(s) separates into its gaseous ions.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_1 = +776\,kJ$$

The gaseous ions dissolve to form aqueous ions.

$$Na^+(g) + Cl^-(g) + aq \rightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H_2 = -771\,kJ$$
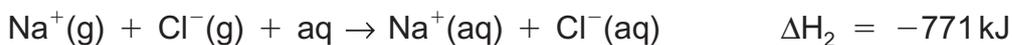
(i) What is the name for the enthalpy value ΔH_1?

_____ [1]

(ii) What is the name for the enthalpy value ΔH_2?

_____ [1]

(iii) ΔH_3 is the enthalpy of solution. Draw a labelled diagram to show the relationship between ΔH_1, ΔH_2 and ΔH_3.

[3]

(iv) Calculate the value of ΔH_3.

_____ [1]

10

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(Questions continue overleaf)

13 Citric acid is found in many fruits especially when they are unripe. It can be obtained from lemon juice which contains about 6–10% citric acid by mass. It crystallises with one molecule of water which is lost at 130 °C, it then melts at 153 °C.

$$CH_2COOH$$
$$|$$
$$C(OH)COOH$$
$$|$$
$$CH_2COOH$$
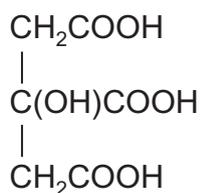
citric acid

(a) Citric acid is a tribasic acid. Suggest the meaning of **tribasic**.

_____

_____ [2]

(b) The extraction of citric acid from lemon juice involves boiling the juice to coagulate proteins and then neutralising the acids present with calcium carbonate.

(i) Explain whether there would be an effect on citric acid when the lemon juice solution is boiled.

_____ [1]

(ii) Write the equation for the reaction of citric acid with excess calcium carbonate.

_____ [2]

(iii) Citric acid is reformed when the calcium citrate is reacted with sulfuric acid. Write the equation for this reaction.

_____ [2]

(c) Citric acid may be synthesised from glycerol by the following reactions.

$$\begin{array}{ccccccccccc}
CH_2OH & & CH_2Cl & & CH_2Cl & & CH_2Cl & & CH_2CN & & CH_2COOH \\
| & A & | & B & | & C & | & KCN & | & D & | \\
CHOH & \rightarrow & CHOH & \rightarrow & CO & \rightarrow & C(OH)CN & \rightarrow & C(OH)CN & \rightarrow & C(OH)COOH \\
| & & | & & | & & | & & | & & | \\
CH_2OH & & CH_2Cl & & CH_2Cl & & CH_2Cl & & CH_2CN & & CH_2COOH
\end{array}$$
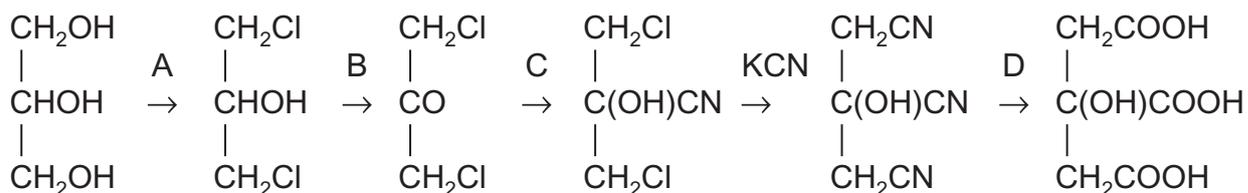
Name reagents A, B, C and D.

A _____ [1]

B _____ [1]

C _____ [1]

D _____ [1]

(d) Citric acid has many uses. Most are based on its acidic properties.

(i) Write the equation for the complete dissociation of citric acid.

_____ [1]

(ii) If the first dissociation constant for citric acid has a pK_a value of 3.05 calculate the pH of a $60\,g\,dm^{-3}$ aqueous solution of citric acid.

_____

_____

_____

_____ [4]

	Examiner Only	
	Marks	Remark

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[Turn over

(e) Citric acid contains an hydroxyl group which means that it can react as an alcohol. Explain whether citric acid is a primary, secondary or tertiary alcohol.

_____

_____ [2]

(f) When heated, citric acid eliminates a molecule of water to form aconitic acid.

$$
\begin{array}{ccc}
CH_2COOH & & CHCOOH \\
| & & \| \\
C(OH)COOH & \rightarrow & C-COOH \quad + \quad H_2O \\
| & & | \\
CH_2COOH & & CH_2COOH
\end{array}
$$
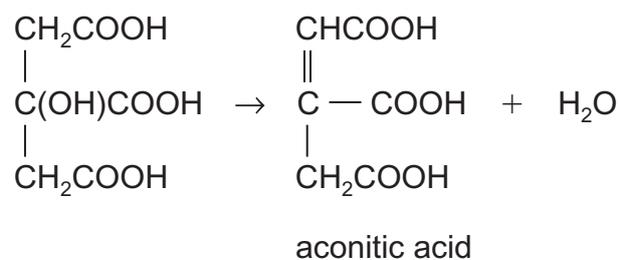
aconitic acid

Draw and label the E and Z isomers of aconitic acid.

[3]

14

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(Questions continue overleaf)

14 Nucleophiles react with carbonyl compounds to form addition products which may then undergo a series of reactions. Both the cyanide ion and amino compounds act as nucleophiles with the initial reaction for both nucleophiles being:

$$\begin{array}{c}\diagdown\\ \diagup\end{array}C=O \;+\; CN^- \;\;\rightarrow\;\; \begin{array}{c}\diagdown\;\diagup O^-\\ C\\ \diagup\;\diagdown CN\end{array}$$

$$\begin{array}{c}\diagdown\\ \diagup\end{array}C=O \;+\; NH_2{-}R \rightarrow \begin{array}{c}\diagdown\;\diagup O^-\\ C\\ \diagup\;\diagdown NH_2^+R\end{array}$$
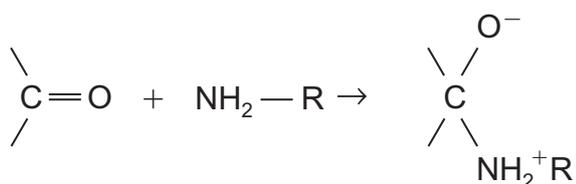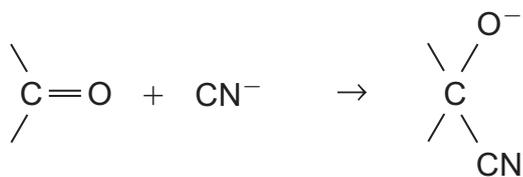
(a) Define the term **nucleophile**.

_____

_____ [2]

(b) Explain why the carbonyl group is susceptible to attack by a nucleophile.

_____

_____ [1]

(c) Draw a flow scheme to show the mechanism for the reaction of hydrogen cyanide with methanal.

[2]

16

(d) The reaction of carbonyl compounds with amino compounds is used as a means of identifying the carbonyl compound. Initially, the reaction of carbonyl compounds with hydrazine, NH_2NH_2, was used. Later it was the reaction with phenylhydrazine and today it is the reaction with 2,4-dinitrophenylhydrazine.

(i) Write the equation for the reaction of propanone with hydrazine.

_____ [2]

(ii) Suggest the first step in the mechanism for the reaction of propanone with hydrazine.

[1]

(iii) Draw the structural formula for 2,4-dinitrophenylhydrazine.

[1]

(iv) In terms of intermolecular forces suggest the advantages of using 2,4-dinitrophenylhydrazine compared to hydrazine when preparing derivatives of the carbonyl compound.

_____

_____

_____

_____ [3]

17

[Turn over

(e) Hydroxylamine, NH_2OH, may be used to form oximes which were also used for identification purposes. Write the equation for the condensation reaction of propanal with hydroxylamine.

_____ [2]

(f) Aldehydes can be distinguished from ketones using the following reagents.

(i) Complete the following table.

reagent	formula of metal/ion before test	formula of metal/ion after a positive test
Fehling's solution		
Tollen's reagent		

[2]

(ii) Which reagent(s) will give a positive test for ethanal?

_____ [1]

(g) Technological methods have removed the need to form derivatives for identification purposes. Outline how they can be used to determine the identity of an organic compound.
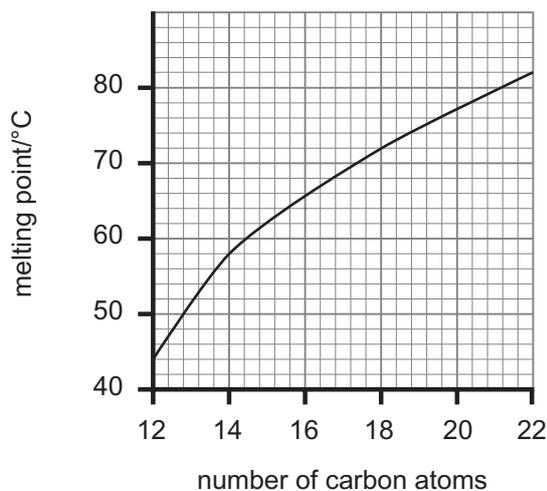
_____

_____

_____

_____

_____ [3]

18

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(Questions continue overleaf)

15 The higher carboxylic acids which occur in nature have straight chains and usually contain an even number of carbon atoms.
The melting points of some of the acids are shown below.

(a) (i) What is the general formula of a carboxylic acid?

_____ [1]

(ii) Explain why there is a gradual increase in melting point of the acids.

_____

_____ [2]

(iii) Giving full experimental details explain how you would determine the melting point of one of these acids.

_____

_____

_____

_____

_____

_____ [4]

Quality of written communication [2]

(b) Palmitic acid, $C_{15}H_{31}COOH$, forms the triglyceride palmitin when it reacts with glycerol.

(i) What is the empirical formula for palmitic acid?

_____ [1]

(ii) Write the equation for the reaction of palmitic acid with glycerol.

[2]

(iii) Explain what is meant by the term **saponification value**.

_____

_____

_____ [3]

(iv) Calculate the saponification value of palmitin which has a relative molecular mass of 806.

_____

_____

_____

_____ [3]

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[Turn over

(c) Palmitin is described as a "saturated fat".

   (i) Explain the meaning of the term **saturated**.

_____

_____ [2]

   (ii) Explain whether palmitin has an iodine value.

_____

_____ [2]

   (iii) Explain whether palmitin, present in foods, contributes to a healthy or an unhealthy diet.

_____

_____

_____

_____

_____ [3]

(d) Palmitin may be hydrolysed. Name **two** chemicals, with very different pH values, which may be used to carry out the hydrolysis.

_____ [2]

_____

THIS IS THE END OF THE QUESTION PAPER

_____

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