cea

Rewarding Learning

ADVANCED
General Certificate of Education
January 2012

Centre Number

Candidate Number

71

Chemistry

Assessment Unit A2 1

assessing

Periodic Trends and Further Organic,
Physical and Inorganic Chemistry

[AC212]

AC212

THURSDAY 26 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 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**. 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(e)**.
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.

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

7648.03**R**

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 as illustrated on the answer sheet.

1   Which one of the following compounds is optically active and incapable of reducing Fehling's solution?

A $CH_3CH(CH_3)CH_2CHO$
B $CH_3CH(C_2H_5)COCH_3$
C $CH_3CHClCH_2CHO$
D $CH_3CH(CH_3)COCH_3$

2   The energy produced when an electron is added to an isolated atom would be the highest for elements in

A   Group I.
B   Group III.
C   Group VII.
D   Group VIII.

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

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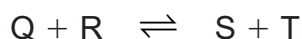
is correct when the system is at equilibrium?

A   The ratio of the rates of the reverse reaction to that of the forward reaction equals the equilibrium constant.
B   The rates of the reverse and forward reactions are equal to zero.
C   The rates of the reverse and forward reactions are equal.
D   The rate constant for the reverse reaction is the same as that of the forward reaction.

4   Which one of the following oxides has a molecular covalent structure?

A Al_2O_3
B Cl_2O_7
C MgO
D Na_2O

5 An organic compound gives an orange crystalline product with 2,4-dinitroph~~enylhydrazi~~ne but does not give a silver mirror with Tollen's reagent. Which one of the follow~~ing molecul~~es is the organic compound?

A ethyl propanoate
B methanal
C propanone
D propanoic acid

6 Ethane reacts with chlorine to form a variety of substituted chloro-compounds ranging from C_2H_5Cl to C_2Cl_6. Which one of the following is the number of optically active compounds formed?

A 0
B 1
C 2
D 4

**7** In the equilibrium between nitrogen and hydrogen to form ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
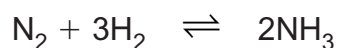
the following partial pressures were obtained.

	nitrogen	hydrogen	ammonia
Relative partial pressure	1	9	1

Which one of the following is the numerical value of the equilibrium constant, K_p?

A 1/729
B 1/9
C 9
D 729

8 Which one of the graphs shown below is that of a first order reaction?

rate of reaction

concentration of reactant
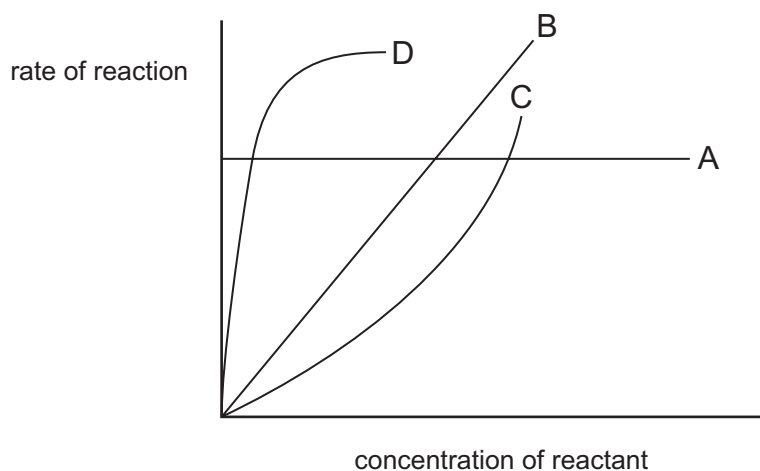
9 Which one of the following always has units?

A K_c
B K_d
C K_p
D K_w

10 The rate equation for the reaction of propanone with iodine in acidic solution is:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

Which one of the following represents the units of k?

A $mol\,dm^{-3}s^{-1}$
B $mol^{-1}dm^3s^{-1}$
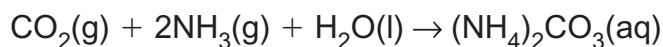C $mol^2dm^{-6}s^{-1}$
D $mol^{-2}dm^6s^{-1}$

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(Questions continue overleaf)

Answer all **six** questions in this section.

11 The formation of ammonium carbonate is being investigated as a possible method to remove carbon dioxide from combustion processes.

$$CO_2(g) + 2NH_3(g) + H_2O(l) \rightarrow (NH_4)_2CO_3(aq)$$

(a) (i) The thermodynamic quantities associated with this reaction are:

$\Delta G = -25\,kJ\,mol^{-1}; \Delta H = -170\,kJ\,mol^{-1}$

$S(CO_2) = +214\,J\,mol^{-1}K^{-1}$
$S(H_2O) = +70\,J\,mol^{-1}K^{-1}$
$S((NH_4)_2CO_3) = +220\,J\,mol^{-1}K^{-1}$
$S(NH_3) = +192\,J\,mol^{-1}K^{-1}$

Use the data provided to calculate the temperature at which the carbon dioxide is being removed.

_____

_____

_____ [3]

(ii) The equilibrium constant for the reaction at 20 °C is 2.5×10^4. At 80 °C it is 0.12. Explain the reason for the drop in the value of K and state how this would affect the CO_2 removal process.

_____

_____ [2]

(b) Ammonium carbonate when added to ethanoic acid undergoes a spontaneous reaction producing great volumes of gas and a dramatic drop in temperature.

(i) Write the equation for the reaction.

_____ [1]

(ii) Explain the meaning of the term **spontaneous** reaction.

_____

_____ [1]

(iii) Why should this reaction proceed when it is endothermic?

_____ [1]

(c) Ammonium ethanoate mixed with ethanoic acid can be used as a buffer solution.

(i) Use an equation to show how the buffer removes added hydrogen ions.

_____ [1]

(ii) Use an equation to show how the buffer removes added hydroxide ions.

_____ [1]

(d) Ammonium ethanoate solid, when heated, dissociates to form the original reactants.

(i) Including state symbols, write an equilibrium equation for the dissociation.

_____ [2]

(ii) Explain why heating ammonium ethanoate in the presence of ethanoic acid prevents the dissociation.
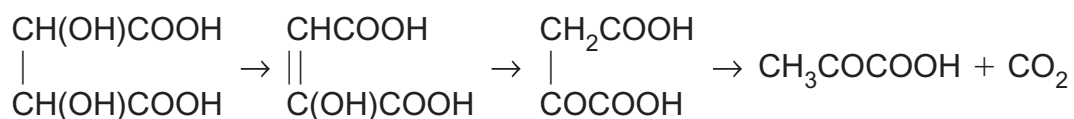
_____

_____ [2]

12 Pyruvic acid is a colourless liquid boiling at 165 °C (with slight decomposition) and has a smell similar to that of ethanoic acid.

$$CH_3COCOOH$$

pyruvic acid

There are several methods used to prepare pyruvic acid.

(a) Tartaric acid when heated with potassium hydrogensulfate forms pyruvic acid. The reaction is believed to take place via the formation of hydroxymaleic acid (structure I) which rearranges to oxalacetic acid (structure II).

```
CH(OH)COOH        CHCOOH          CH2COOH
|          →      ||       →      |         →  CH3COCOOH + CO2
CH(OH)COOH        C(OH)COOH       COCOOH

tartaric acid          I                    II              pyruvic acid
```

(i) How many asymmetric centres are present in tartaric acid?

_____ [1]

(ii) Structure I exists in E and Z structures. Draw the structures and label them as E and Z.

[3]

(iii) The last step in the synthesis involves **decarboxylation**. Suggest a meaning for this term.

_____ [1]

(b) Another method of preparation is the oxidation of lactic acid, $CH_3CHOHCOOH$, using silver oxide suspended in water.

(i) What is the formula of silver oxide?

_____ [1]

(ii) Write the equation for the formation of pyruvic acid from lactic acid using [O] to symbolise the oxidising agent.

_____ [1]

(c) Another method of synthesis is the flow scheme shown below.

$$\begin{array}{ccccc} & A & & B & \\ CH_3COCl & \longrightarrow & CH_3COCN & \longrightarrow & CH_3COCOOH \end{array}$$

Suggest the names of the reagents A and B.

A _____ [1]

B _____ [1]

(d) A further method of preparation is to hydrolyse 2,2-dibromopropanoic acid with water. Write a flow scheme for the reaction showing the intermediate dihydroxy compound.

[2]

(e) Pyruvic acid shows both the reactions of a ketone and a carboxylic acid. Complete the following flow sequences below showing the organic product in each case.

SOCl₂

NH₂NH—⬡

PCl₅

CH₃COCOOH

excess
LiAlH₄

HCN

[6]
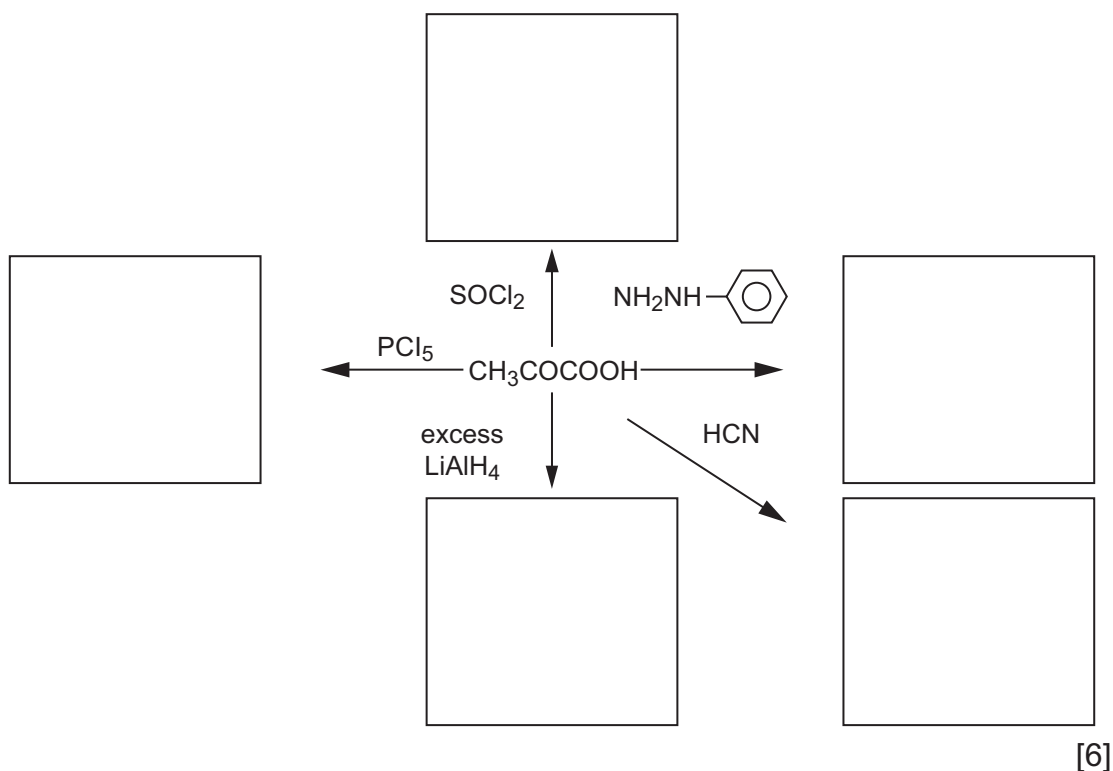
(f) Pyruvic acid is quite a strong acid with an acid dissociation constant of 0.56. It is also miscible in water.

(i) Write the expression for the acid dissociation constant of pyruvic acid.

_____ [1]

(ii) Calculate the pH of a 0.25 M solution of pyruvic acid.

_____

_____

_____ [3]

(iii) Suggest the meaning of the term **miscible**.
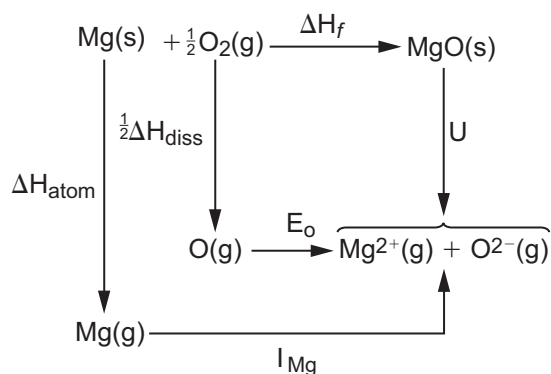
_____ [1]

(iv) Suggest why pyruvic acid is miscible in water.

_____

_____ [2]

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(Questions continue overleaf)

13 The Born-Haber cycle can be written in many different ways. One of those ways is shown below.

The values of the terms shown in the scheme are:

ΔH_f = $-602\,\text{kJ}\,\text{mol}^{-1}$
ΔH_{diss} = $+498\,\text{kJ}\,\text{mol}^{-1}$
ΔH_{atom} = $+148\,\text{kJ}\,\text{mol}^{-1}$
I_{Mg} = $+2189\,\text{kJ}\,\text{mol}^{-1}$
E_o = $+657\,\text{kJ}\,\text{mol}^{-1}$

(a) Explain the meanings of the following terms.

(i) ΔH_{diss}

_____ [1]

(ii) ΔH_{atom}

_____ [1]

(iii) I_{Mg}

_____ [1]

(b) (i) Calculate the value of U for magnesium oxide.

_____

_____ [2]

(ii) Using the Born-Haber cycle explain why magnesium oxide is very stable.

_____

_____ [2]

(c) Explain why a Born-Haber cycle cannot be constructed for phosphorus(V) oxide.

_____ [1]

14 Sulfur dioxide and a small amount of sulfur trioxide are formed when sulfur burns in air. The presence of sulfur trioxide accounts for the foggy appearance of the sulfur dioxide.

(a) Write equations for the reaction of sulfur with oxygen to form sulfur dioxide and sulfur trioxide.

(i) sulfur dioxide

_____ [1]

(ii) sulfur trioxide

_____ [1]

(b) Sulfur dioxide and sulfur trioxide dissolve in water to form sulfurous acid and sulfuric acid. Write equations for the reactions.

(i) sulfur dioxide

_____ [1]

(ii) sulfur trioxide

_____ [1]

(c) Both of these acids react with sodium hydroxide to form sodium salts. These salts dissolve in water to produce solutions of different pH.

Write the equations for the reactions of sulfurous acid and sulfuric acid with excess sodium hydroxide to produce the sodium salts.
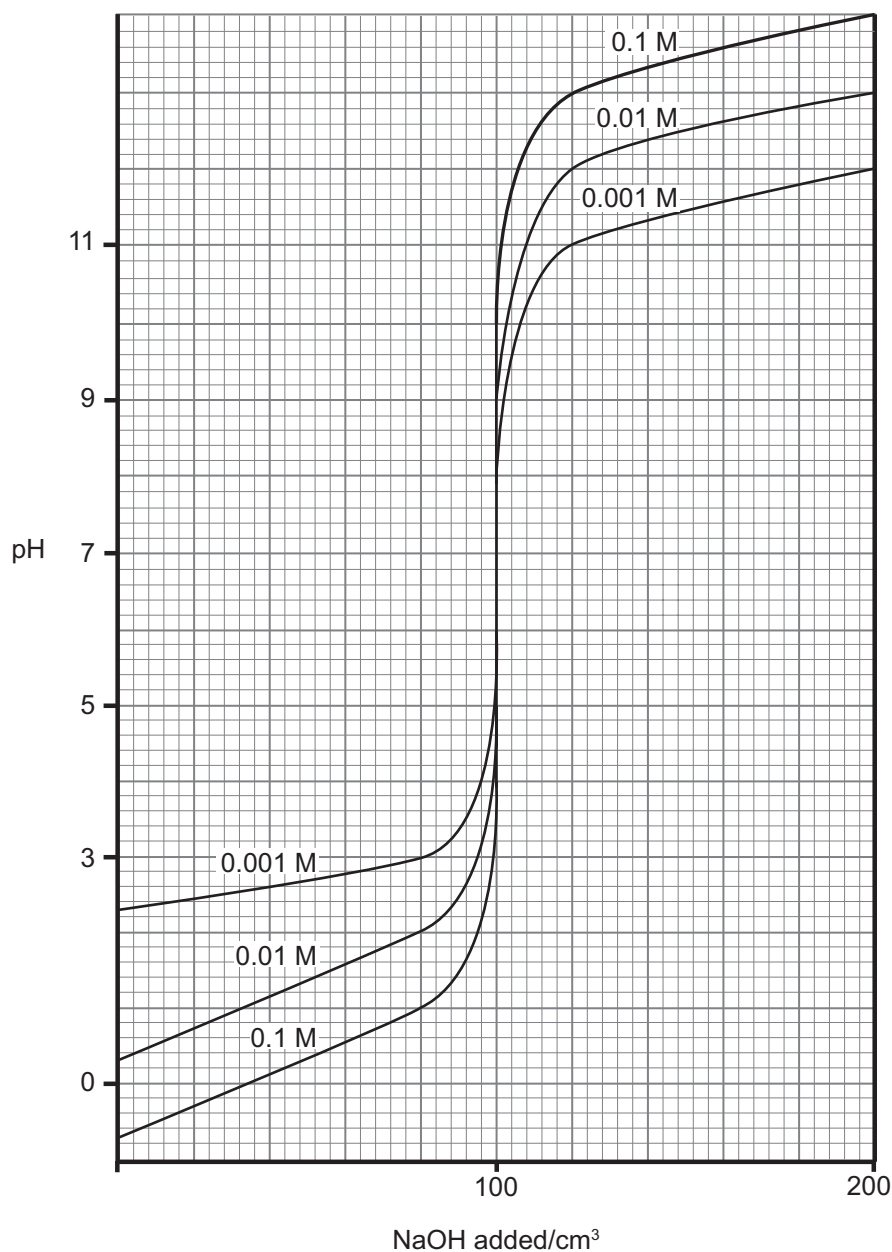
(i) sulfurous acid

_____ [1]

(ii) sulfuric acid

_____ [1]

(d) Explain why a saturated solution of sodium sulfite has a pH of 9 and sodium sulfate has a pH of 7.

_____

_____

_____ [3]

(e) Titration curves for the reaction of sulfuric acid with excess sodium hydroxide are shown below.

NaOH added/cm³

(i) Explain why the length of the vertical sections of the curves decreases with decreasing concentrations of the acid.

_____ [1]

(ii) Explain how you would choose a suitable indicator for the titration of 0.001 M sulfuric acid with 0.1 M NaOH.

_____

_____ [2]

(f) At the end point the addition of 0.1 cm^3 of 2 M sodium hydroxide to a solution of 1 M sulfuric acid causes a dramatic change in pH. The table below shows the changes in pH.

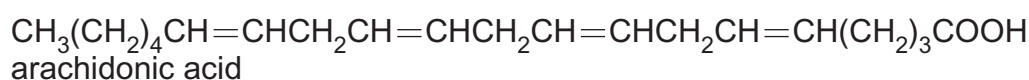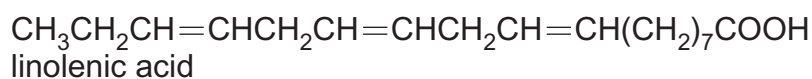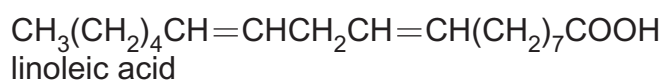| volume of sulfuric acid/cm^3	volume of sodium hydroxide solution added/cm^3	pH of solution
100	99.9	
100	100.0	7.0

Calculate the missing pH of the solution shown in the table.

_____

_____

_____

_____ [3]

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(Questions continue overleaf)

15 Some common unsaturated fatty acids found in oils and fats are shown below. The vast majority of unsaturated linkages are *cis*.

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
oleic acid

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
linoleic acid

$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
linolenic acid

$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH$
arachidonic acid
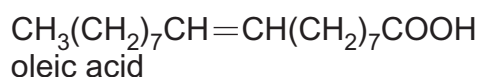
(a) Explain which of these acids are monounsaturated and which are polyunsaturated.

_____

_____ [2]

(b) All the double bonds in arachidonic acid are *cis*. Draw the structure of the acid.

[2]

(c) Write the equation for the reaction of oleic acid with molecular iodine.

_____ [2]

(d) (i) It is possible to determine the iodine value of a fatty acid. Define the term **iodine value**.

_____

_____

_____ [2]

(ii) Calculate the iodine value of linolenic acid.

_____

_____

_____

_____ [4]

(iii) State and explain which one of the acids has the highest iodine value.

_____

_____ [2]

(e) Explain the contribution of polyunsaturated oils or fats to the diet.
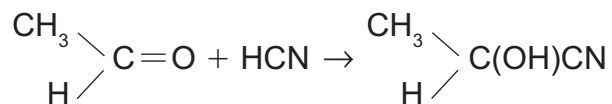
_____

_____

_____

_____

_____

_____ [4]

Quality of written communication [2]

(f) All of these acids can be catalytically hydrogenated in the same way as oils and fats. Name the catalyst and state the conditions used.

_____

_____

_____ [3]

16 Ethanal reacts with hydrogen cyanide to form a cyanohydrin

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=O + HCN \rightarrow \begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C(OH)CN$$

(a) The first step is the reaction of the cyanide ion with the carbonyl group to form an intermediate. This is the rate determining step.

(i) Draw the structure of the intermediate.

[1]

(ii) Explain the meaning of the term **rate determining step**.

_____

_____ [1]

(iii) Write the rate equation and state the meaning of the symbol k.

_____

_____ [2]

(iv) What is the order of the reaction.

_____ [1]

(b) The second step is the protonation of the intermediate.

(i) Write the equation for this step involving the reaction of hydrogen cyanide with the intermediate.

[2]

(ii) Explain whether you would expect this to be a slow or fast step.

_____

_____ [2]

(c) Suggest why this equation shows that the cyanide ion could be regarded as a catalyst in cyanohydrin formation.

_____

_____ [1]

(d) The structure of the intermediate in the mechanism leads to the production of an optically inactive product.

(i) Explain the meaning of the term **optically inactive**.

_____

_____ [2]

(ii) Draw the 3D structures of the two cyanohydrin isomers.

[2]

(iii) Explain why the cyanohydrin product is optically inactive.

_____

_____ [2]

THIS IS THE END OF THE QUESTION PAPER

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