

Chemistry

Advanced

PAPER 3: General and Practical Principles in Chemistry

Total Marks

Friday 23 June 2023 – Morning

Time: 2 hours 30 minutes

In the boxes below, write your name, centre number and candidate number.

Surname					
Other names					
Centre Number					
Candidate Number					

YOU MUST HAVE

Scientific calculator, Data Booklet, ruler

YOU WILL BE GIVEN

Diagram Booklet, Periodic Table

INSTRUCTIONS

Answer ALL questions.

Answer the questions in the spaces provided in this Question Paper or in the separate Diagram Booklet – there may be more space than you need.

INFORMATION

The total mark for this paper is 120.

The marks for EACH question are shown in brackets – use this as a guide as to how much time to spend on each question.

For the question marked with an ASTERISK (*), marks will be awarded for your ability to structure your answer logically, showing the points that you make are related or follow on from each other where appropriate.

A Periodic Table is provided as a separate insert.

There may be spare copies of some diagrams.

ADVICE

Read each question carefully before you start to answer it.

Show all your working in calculations and include units where appropriate.

Check your answers if you have time at the end.

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

1 Alkanes are often used as fuels.

(a) Look at the equation for Question 1(a) in the Diagram Booklet. Complete the equation for the complete combustion of hexane. State symbols are not required. (1 mark)

(b) Identify TWO pollutants produced from the INCOMPLETE combustion of a pure sample of pentane. (2 marks)

(continued on the next page)

1 continued.

- (c) Explain the problem which results from sulfur impurities in fuels.
(2 marks)**

(continued on the next page)

1 continued.

- (d) Adding cyclic hydrocarbons to fuels results in more efficient combustion. These compounds can be made by reforming straight-chain alkanes.**

Write an equation for the reforming of pentane into a cyclic hydrocarbon, using skeletal formulae for the organic compounds.

State symbols are not required.

(2 marks)

(Total for Question 1 = 7 marks)

2 This question is about some reactions of the elements of Group 1 and Group 2 of the Periodic Table and their compounds.

(a) Group 2 metals react vigorously with oxygen when heated.

**(i) Write the equation for the reaction between magnesium and oxygen.
Include state symbols.
(1 mark)**

(continued on the next page)

2(a) continued.

(ii) Explain the trend in reactivity of the elements down Group 2.
(3 marks)

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

(continued on the next page)

Turn over

2 continued.

- (b) (i) State the trend in solubility of the Group 2 sulfates.
(1 mark)**

(continued on the next page)

2(b) continued.

- (ii) Explain why the reaction between calcium and excess sulfuric acid stops before all of the metal has reacted.**

(2 marks)

(continued on the next page)

2 continued.

(c) Sodium nitrate undergoes thermal decomposition to produce oxygen as one of the products.

(i) Describe the test, with the positive result, for oxygen.

(1 mark)

(ii) Write the equation for this decomposition. State symbols are not required.

(1 mark)

(continued on the next page)

Turn over

2(c) continued.

- (iii) Show, by reference to oxidation number changes, that the decomposition of sodium nitrate is a redox reaction.
(2 marks)**

(Total for Question 2 = 11 marks)

3 Ethanol can be dehydrated using concentrated phosphoric(V) acid, concentrated sulfuric acid or aluminium oxide.

(a) Write the equation for the dehydration of ethanol using structural formulae.

State symbols are not required.

(1 mark)

(b) Give the formula of phosphoric(V) acid.

(1 mark)

(continued on the next page)

3 continued.

**(c) Draw the dot-and-cross diagram
of sulfuric acid, H_2SO_4**

**Clearly differentiate between sulfur, oxygen and
hydrogen electrons.**

Show outer shell electrons only.

(2 marks)

(continued on the next page)

Turn over

3 continued.

(d) Ethanol may be dehydrated using the catalyst aluminium oxide, Al_2O_3

Look at the diagram for Question 3(d) in the Diagram Booklet. It shows the apparatus used.

**(i) Give a possible reason for the boiling tube to be clamped at the angle shown.
(1 mark)**

(continued on the next page)

3(d) continued.

- (ii) Describe the problem if the ethanol is heated instead of the catalyst.
(1 mark)**

(continued on the next page)

3(d) continued.

- (iii) Identify a safety issue if the heat source was moved to the position labelled **X** on the diagram.
(1 mark)**

(continued on the next page)

3(d) continued.

- (iv) Give a possible reason for the use of the Bunsen valve in the apparatus.
(1 mark)**

(continued on the next page)

3(d) continued.

(v) Describe a test, with the positive result, which would confirm the presence of an alkene in the test tube.

(1 mark)

(continued on the next page)

3(d) continued.

- (vi) Calculate the volume of 2.759×10^{20} molecules of alkene gas at room temperature and pressure (r.t.p.).
(2 marks)**

(Total for Question 3 = 11 marks)

Turn over

- 4 This question is about hydrated magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

*(a) Devise an experimental procedure to determine the enthalpy change of solution for hydrated magnesium sulfate.



Details of the method of calculation are not required.

(6 marks)

Answer space continues on the next 5 pages.

4(a) continued.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

Turn over

4(a) continued.

[illegible]

Turn over

4(a) continued.

[illegible]

Turn over

4(a) continued.

[illegible]

Turn over

4(a) continued.

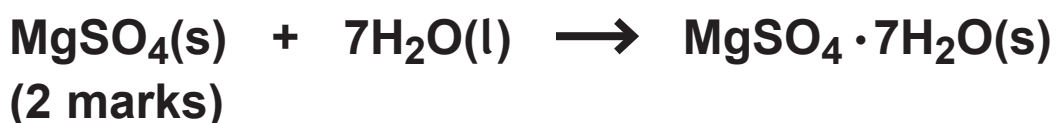
(continued on the next page)

4 continued.

- (b) The enthalpy changes of solution for anhydrous and hydrated magnesium sulfate were found by experiment to be



Calculate, using Hess's law, the enthalpy change for the hydration of anhydrous magnesium sulfate. Include a sign and units in your answer.



4 continued.

- (c) Explain how the enthalpy change of hydration of magnesium ions in magnesium sulfate is different from the enthalpy change of hydration of calcium ions in calcium sulfate.
(2 marks)**

(Total for Question 4 = 10 marks)

5 This question is about electrochemical cells.

- (a) Look at the diagram for Question 5(a) in the Diagram Booklet. It shows the apparatus that is used to measure the emf of a cell with a zinc/zinc(II) electrode and an acidified manganese(II)/manganate(VII) electrode system.**

Complete the labels **Y and **Z** by naming the substances needed.**

**Temperature and concentrations are not required.
(3 marks)**

Y _____

Z _____

(continued on the next page)

5 continued.

- (b) Excess zinc is added to an acidified solution of sodium dichromate(VI). Look at the table for Question 5(b) in the Diagram Booklet. It gives some electrode data.**

Explain, using only the data in the table, the final oxidation state of chromium that is formed when zinc is added to acidified dichromate(VI) ions.

Include $E_{\text{cell}}^{\ominus}$ values where appropriate. Equations are not required.

(5 marks)

Answer lines continue on the next 2 pages.

Turn over

5(b) continued.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

Turn over

5(b) continued.

(continued on the next page)

5 continued.

(c) A cell diagram is shown.



$$E_{\text{cell}}^{\ominus} = +1.06 \text{ V}$$

Deduce the reduction half-equation.

State symbols are not required.

(1 mark)

(continued on the next page)

5 continued.

- (d) Look at the diagram for Question 5(d) in the Diagram Booklet. It shows a hydrogen-oxygen fuel cell. State the direction of the electron flow in the diagram. Justify your answer by reference to the redox processes in the cell.**

(2 marks)

(continued on the next page)

5 continued.

- (e) State one advantage of the hydrogen-oxygen fuel cell over the use of petrol as fuel in a vehicle.
(1 mark)**

(Total for Question 5 = 12 marks)

6 Amino acids can be separated using chromatography.

(a) State how chromatography separates the components of a mixture.

(1 mark)

(continued on the next page)

6 continued.

- (b) A sample of a tripeptide was hydrolysed and then placed on an 'X' at the bottom right-hand corner of a piece of chromatography paper.**

Look at the diagram for Question 6(b) in the Diagram Booklet. It shows a simplified developed chromatogram.

- (i) Give a possible reason for the presence of only two spots for the tripeptide other than two amino acids have almost identical R_f values.**
(1 mark)

(continued on the next page)

6(b) continued.

- (ii) Some amino acid mixtures cannot be effectively separated in one chromatography 'run'.**

The chromatography paper from the first run is dried but not developed.

The chromatography paper is then rotated clockwise by 90° and placed in a different solvent.

Look at the diagrams for Question 6(b)(ii) in the Diagram Booklet. Complete the simplified diagram of the developed chromatography paper after a second 'run' for a tripeptide of alanine, glycine and valine by adding LABELLED spots for each amino acid.

(3 marks)

(continued on the next page)

6(b) continued.

- (iii) Name a reagent that locates colourless amino acids by producing a coloured compound.
(1 mark)**

- (c) State the technique that is used in conjunction with gas chromatography (GC) when carrying out forensic testing.
(1 mark)**

(Total for Question 6 = 7 marks)

- 7 Hardness in water is measured in terms of the concentration of dissolved calcium compounds.**

Titration experiments can be carried out to determine the hardness of a water sample.

(a) A pipette is used to measure a 50.0 cm^3 water sample for titration.

- (i) Describe how to remove an air bubble from the tip of the pipette.
(1 mark)**

(continued on the next page)

7(a) continued.

- (ii) Calculate the MAXIMUM volume that would be obtained by using a 25.0 cm^3 pipette twice to measure a total volume of 50.0 cm^3 .
The uncertainty in each 25.0 cm^3 pipette measurement is $\pm 0.04\text{ cm}^3$
(1 mark)**

(continued on the next page)

7(a) continued.

- (iii) Compare the percentage uncertainty in using a 25.0 cm^3 pipette twice with using a 50.0 cm^3 pipette once to measure 50.0 cm^3 of water. The uncertainty in the 50.0 cm^3 pipette measurement is $\pm 0.05\text{ cm}^3$ (2 marks)**

(continued on the next page)

7 continued.

(b) About 2 cm^3 of a pH 10 buffer is added to each 50.0 cm^3 water sample.

**(i) State whether or not a 100 cm^3 measuring cylinder is suitable to measure this volume of buffer solution. Justify your answer.
(1 mark)**

(continued on the next page)

7(b) continued.

- (ii) The pH 10 buffer can be made by adding solid ammonium chloride to an aqueous solution of ammonia of concentration 18.1 mol dm^{-3}

The relevant equation is



$$K_a = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$$

Calculate the mass of ammonium chloride that must be added to 100 cm^3 of ammonia solution to make the pH 10 buffer.

Assume that there is no change in the volume on the addition of ammonium chloride.

(4 marks)

Answer space continues on the next page.

7(b)(ii) continued.

(continued on the next page)

7(b) continued.

- (iii) State a necessary laboratory precaution, other than wearing a laboratory coat, gloves and goggles, that must be taken when using concentrated ammonia.
(1 mark)**

(continued on the next page)

7 continued.

(c) The Eriochrome Black T indicator used in this titration forms an octahedral complex with the calcium ions in the water sample.

Look at the diagram for Question 7(c)(i) in the Diagram Booklet. It shows the structure of Eriochrome Black T with a calcium ion.

(i) Complete the diagram to show how Eriochrome Black T forms three dative covalent or coordinate bonds with the calcium ion.

(1 mark)

(ii) State the number of water molecules needed to complete this complex.

(1 mark)

(continued on the next page)

7 continued.

(d) There are two types of water hardness:

TEMPORARY HARDNESS which is removed by boiling as a precipitate forms,
PERMANENT HARDNESS which is unaffected by boiling.

Levels of water hardness are expressed as the concentration of calcium ions in mg dm^{-3}

A student carried out a series of experiments to determine the hardness of a sample of water. 50.0 cm^3 samples of the water were titrated with EDTA.

Further 50.0 cm^3 samples of water were taken after boiling and then titrated with EDTA.

- (i) Name the process needed before titrating the sample of boiled water.
(1 mark)

(continued on the next page)

7(d) continued.

- (ii) The mean titre of $0.0100 \text{ mol dm}^{-3}$ EDTA^{4-} with a 50.0 cm^3 water sample before boiling was 12.80 cm^3

After boiling the mean titre was 5.15 cm^3

There is a 1 : 1 ratio in the reaction between EDTA^{4-} ions and Ca^{2+} ions.

Calculate, in this water, the levels of permanent and temporary hardness in mg dm^{-3} of calcium ions.

(6 marks)

Answer space continues on the next page.

7(d)(ii) continued.

(Total for Question 7 = 19 marks)

8 This question is about reaction kinetics and the Arrhenius equation.

(a) Different iodine clock reactions are often used to investigate reaction kinetics.

(i) The iodine clock reaction with hydrogen peroxide involves the reaction shown.



Deduce TWO possible experimental techniques which could be used to monitor the progress of this reaction.

(2 marks)

(continued on the next page)

8(a) continued.

- (ii) The iodate(V) reaction has the rate determining step



Give a possible reason why this is the slowest step.

(1 mark)

(continued on the next page)

8(a) continued.

(iii) The chlorate(V) reaction has the rate determining step



Deduce the rate equation for this iodine clock reaction.

(1 mark)

(continued on the next page)

Turn over

8 continued.

(b) Look at the graph for Question 8(b) in the Diagram Booklet. It shows a sketch of the Maxwell-Boltzmann curve for the distribution of molecular energies of a reaction mixture at temperature 298 K.

- (i) Add a curve to show the distribution at a temperature of 308 K.
(1 mark)**

(continued on the next page)

8(b) continued.

- (ii) Explain why a temperature rise from 298 K to 308 K results in a large increase in the rate of reaction.
Refer to the Maxwell-Boltzmann distribution in your answer.
(2 marks)**

(continued on the next page)

8 continued.

- (c) The Arrhenius equation may be written in a logarithmic or an exponential form.

$$\ln k = -\frac{E_a}{RT} + \ln A \quad k = A e^{-\frac{E_a}{RT}}$$

A is a constant.

- (i) The rate constant, k , for the isomerisation of cyclopropane to propene was measured at various temperatures.
Look at the graph for Question 8(c) in the Diagram Booklet. The data obtained were used to draw the graph shown.

Determine the activation energy, E_a , from the gradient of the graph.
Include units in your answer.
(3 marks)

8(c) continued.

- (ii) At a temperature T, the fraction of molecules with energy equal to or greater than the activation energy is given by the expression**

$$\text{fraction of molecules} = e^{-\frac{E_a}{RT}}$$

When a catalyst is added, the activation energy for a reaction is lowered.

Explain, using calculations, why lowering the activation energy from $50\,000\text{ J mol}^{-1}$ to $25\,000\text{ J mol}^{-1}$ at 298 K results in a large increase in the rate of reaction.

(3 marks)

Answer space continues on the next page.

8(c)(ii) continued.

(Total for Question 8 = 13 marks)

9 This is a question about isomers of $C_8H_8O_2$

(a) One of these isomers, methyl benzoate, is hydrolysed by alkali or by acid.

(i) Hydrolysis with aqueous sodium hydroxide is followed by acidification to form benzoic acid.

Give a reason why acidification is required after hydrolysis.

(1 mark)

(continued on the next page)

9(a) continued.

- (ii) Write an equation, using structural formulae, for the acid hydrolysis of methyl benzoate. (1 mark)**

(continued on the next page)

Turn over

9 continued.

(b) Four other $\text{C}_8\text{H}_8\text{O}_2$ isomers were investigated.

- **W** and **X** are mono-substituted aromatic compounds with the same functional group as methyl benzoate but only **W** is made from methanoic acid
- **Y** is a mono-substituted aromatic compound which reacts with sodium carbonate to give carbon dioxide
- **Z** is a disubstituted aromatic compound with six peaks in its ^{13}C NMR spectrum and forms a sweet-smelling compound on reaction with ethanol

Deduce the structures of isomers **W**, **X**, **Y** and **Z**.
Justify your answers.
(7 marks)

Answer space continues on the next 4 pages.

9(b) continued.

9(b) continued.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

Turn over

9(b) continued.

[illegible]

Turn over

9(b) continued.

(continued on the next page)

9 continued.

(c) Piceol is found in the needles of Norway spruce trees. Look at the diagram for Question 9(c) in the Diagram Booklet. It shows the structure of piceol.

(i) Piceol can be produced from the reaction of ethanoyl chloride and phenol. Assume the mechanism for the reaction with phenol is similar to that with benzene and involves the use of an aluminium chloride catalyst, which produces the electrophile $[\text{CH}_3\text{C}=\text{O}]^+$.

Complete the diagram, including curly arrows, to show the mechanism for this reaction to produce piceol.

Include the regeneration of the catalyst.

(4 marks)

(continued on the next page)

9(c) continued.

- (ii) Piceol can be distinguished from $\text{HOC}_6\text{H}_4\text{CH}_2\text{CHO}$ using simple chemical tests.**

**Give the reagents for a chemical test, and the observation that would only be positive for piceol.
(2 marks)**

(Total for Question 9 = 15 marks)

10 The Mond Process is an industrial method of purifying nickel.

(a) The first step involves the reaction of nickel oxide with hydrogen gas at 473 K.



The nickel is not pure because the impurities also react with the hydrogen gas.

Complete the electronic configuration of the Ni^{2+} ion.

(1 mark)

1s² _____

(continued on the next page)

10 continued.

- (b) The second step involves passing carbon monoxide over impure nickel at 323 K. The impurities do not react. The nickel reaction is



- (i) Look at the table for Question 10(b)(i) in the Diagram Booklet. Calculate the total entropy change, $\Delta S_{\text{total}}^\ominus$, for this reaction. Include a sign and units in your answer. (5 marks)

Answer space continues on the next page.

10(b)(i) continued.

(continued on the next page)

10(b) continued.

- (ii) Predict the sign of the Gibbs Free Energy change, ΔG , for this reaction and justify your choice. No calculation is required.
(1 mark)**

(continued on the next page)

10(b) continued.

(iii) 50.0 mol of carbon monoxide is mixed with excess impure solid nickel at 323 K in an industrial reactor.

At equilibrium, 0.750 mol of carbon monoxide remains. The pressure is maintained at 1.5 atm throughout.

Calculate the value of K_p at 323 K. Include units with your answer.

(6 marks)

Answer space continues on the next page.

10(b)(iii) continued.

(continued on the next page)

10 continued.

- (c) The final stage of the Mond Process is the thermal decomposition of the nickel carbonyl gas, Ni(CO)_4 , to give pure nickel and carbon monoxide. The reaction mixture is heated to 523 K.**

Explain, in qualitative terms, why the entropy change of the system, $\Delta S_{\text{system}}^\ominus$, for this decomposition reaction is positive.
(2 marks)

(Total for Question 10 = 15 marks)

TOTAL FOR PAPER = 120 MARKS
END OF PAPER