## Instructions

- Use **black** ink or ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer all questions.
- Answer the questions in the spaces provided
  - 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 printed on the back cover of this paper.

## **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.

Turn over ▶







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

- Alkanes are often used as fuels.
  - (a) Complete the equation for the complete combustion of hexane. State symbols are not required.

(1)

$$C_6H_{14}$$
 + ..... $O_2$   $\rightarrow$  ..... $CO_2$  + ..... $H_2O$ 

(b) Identify **two** pollutants produced from the **incomplete** combustion of a pure sample of pentane.

(2)

(c) Explain the problem which results from sulfur impurities in fuels.

(2)

(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)

(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)
	(ii) Explain the trend in reactivity of the elements down Group 2.	(3)
	(b) (i) State the trend in solubility of the Group 2 sulfates.	(1)
		(1)
	(ii) Explain why the reaction between calcium and excess sulfuric acid stops before all of the metal has reacted.	(2)



(c) Sodium nitrate undergoes thermal decomposition to produce oxygen as the products.	one of
(i) Describe the test, with the positive result, for oxygen.	(1)
(ii) Write the equation for this decomposition. State symbols are not required.	(1)
(iii) Show, by reference to oxidation number changes, that the decomposi sodium nitrate is a redox reaction.	ition of (2)
(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)

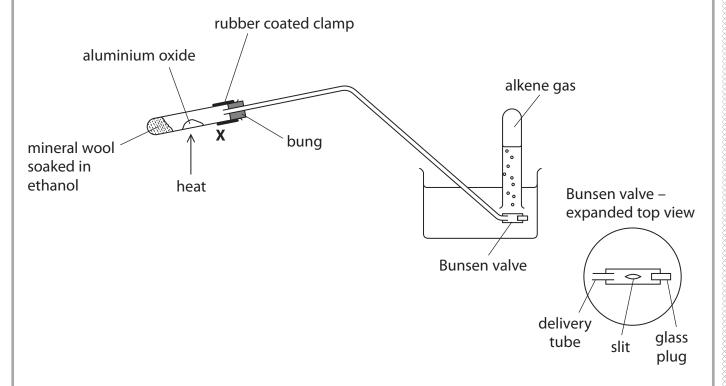
(b) Give the formula of phosphoric(V) acid.

(1)

(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)

(d) Ethanol may be dehydrated using the catalyst aluminium oxide,  $Al_2O_3$ . The apparatus is shown.



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

(1)

(ii) Describe the problem if the ethanol is heated instead of the catalyst.

(1)

(iii) Identify a safety issue if the heat source was moved to the position labelled  ${\bf X}$  on the diagram.

(1)

6

(iv) Give a possible reason for the use of the Bunsen valve in the apparatus.	(1)
(v) Describe a test, with the positive result, which would confirm the presence of an alkene in the test tube.	(1)
(vi) Calculate the volume of $2.759 \times 10^{20}$ molecules of alkene gas at room temperature and pressure (r.t.p.).	
at room temperature and pressure (i.t.p.).	(2)
(Total for Question 3 = 11 m	arks)



- 4 This question is about hydrated magnesium sulfate, MgSO<sub>4</sub>•7H<sub>2</sub>O.
  - \*(a) Devise an experimental procedure to determine the enthalpy change of solution for hydrated magnesium sulfate.

$$MgSO_4 \cdot 7H_2O(s) + aq \rightarrow MgSO_4(aq)$$

Details of the method of calculation are not required.

(6)




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

$$MgSO_4(s)$$
 + aq  $\rightarrow$   $MgSO_4(aq)$   $\Delta_r H = -63.2 \text{ kJ mol}^{-1}$ 

$$MgSO_4 \cdot 7H_2O(s) + aq \rightarrow MgSO_4(aq)$$
  $\Delta_r H = +15.7 \text{ kJ mol}^{-1}$ 

Calculate, using Hess's law, the enthalpy change for the hydration of anhydrous magnesium sulfate.

Include a sign and units in your answer.

$$MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4 \cdot 7H_2O(s)$$

(2)

(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.

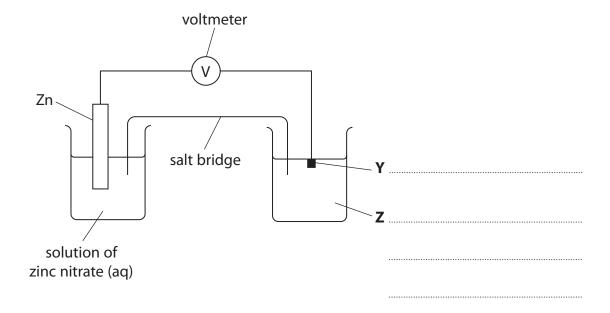
(2)

(Total for Question 4 = 10 marks)

- 5 This question is about electrochemical cells.
  - (a) A diagram is shown of 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)



(b) Excess zinc is added to an acidified solution of sodium dichromate(VI). Some electrode data are given in the table.

Electrode system	E⊕/V
$Cr^{2+}(aq) + 2e^{-} \rightleftharpoons Cr(s)$	-0.91
$Cr^{3+}(aq) + e^{-} \rightleftharpoons Cr^{2+}(aq)$	-0.41
$\frac{1}{2}Cr_{2}O_{7}^{2-}(aq) + 7H^{+}(aq) + 3e^{-} \rightleftharpoons Cr^{3+}(aq) + 3\frac{1}{2}H_{2}O(l)$	+1.33
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76

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 $E_{cell}^{\oplus}$ values where appropriate. Equations are not required.

(5)

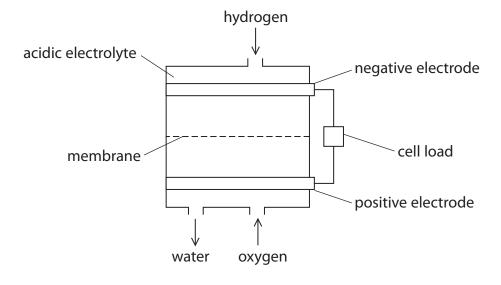
(c) A cell diagram is shown.

$$Ni(s) \mid Ni^{2+}(aq) \mid \mid [NO_{3}^{-}(aq) + 2H^{+}(aq)], [NO_{2}(g) + H_{2}O(l)] \mid Pt(s) \qquad E_{cell}^{\ominus} = +1.06 \text{ V}$$

Deduce the reduction half-equation. State symbols are not required.

(1)

(d) State the direction of the electron flow in the hydrogen-oxygen fuel cell shown. Justify your answer by reference to the redox processes in the cell.



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

(1)

(2)

(Total for Question 5 = 12 marks)

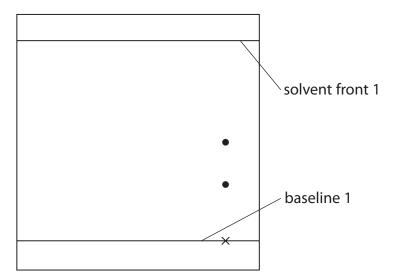


- **6** Amino acids can be separated using chromatography.
  - (a) State how chromatography separates the components of a mixture.

(1)

(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.

A simplified diagram of a developed chromatogram is shown.



(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)





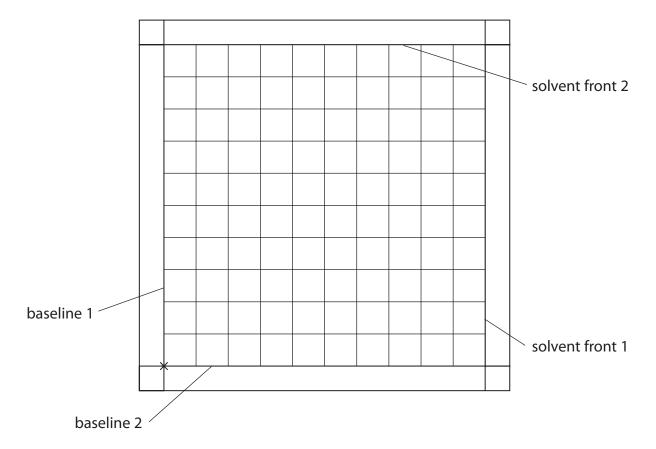
(ii) Some amino acid mixtures cannot be effectively separated in one chromatography 'run'.

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.

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.

Amino acid	$R_{\rm f}$ in solvent 1	R <sub>f</sub> in solvent 2
alanine	0.38	0.43
glycine	0.33	0.26
valine	0.39	0.58

(3)



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

(1)

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

(1)

(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<sup>3</sup> water sample for titration.
  - (i) Describe how to remove an air bubble from the tip of the pipette.

(1)

(ii) Calculate the **maximum** volume that would be obtained by using a 25.0 cm<sup>3</sup> pipette twice to measure a total volume of 50.0 cm<sup>3</sup>. The uncertainty in each 25.0 cm<sup>3</sup> pipette measurement is ±0.04 cm<sup>3</sup>.

(1)

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

(2)



- (b) About 2 cm<sup>3</sup> of a pH 10 buffer is added to each 50.0 cm<sup>3</sup> water sample.
  - (i) State whether or not a 100 cm<sup>3</sup> measuring cylinder is suitable to measure this volume of buffer solution. Justify your answer.

(1)

(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<sup>-3</sup>.

The relevant equation is

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

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

Calculate the mass of ammonium chloride that must be added to 100 cm<sup>3</sup> 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)

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

(1)

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

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

(1)



(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<sup>-3</sup>.

A student carried out a series of experiments to determine the hardness of a sample of water. 50.0 cm<sup>3</sup> samples of the water were titrated with EDTA. Further 50.0 cm<sup>3</sup> 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)

(ii) The mean titre of 0.0100 mol dm<sup>-3</sup> EDTA<sup>4-</sup> with a 50.0 cm<sup>3</sup> water sample before boiling was 12.80 cm<sup>3</sup>.

After boiling the mean titre was 5.15 cm<sup>3</sup>.

There is a 1:1 ratio in the reaction between EDTA<sup>4-</sup> ions and Ca<sup>2+</sup> ions.

Calculate, in this water, the levels of permanent and temporary hardness in mg dm<sup>-3</sup> of calcium ions.

(6)

(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.

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

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

(2)

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

$$IO_3^- + 3HSO_3^- \rightarrow I^- + 3HSO_4^-$$

Give a possible reason why this is the slowest step.

(1)

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

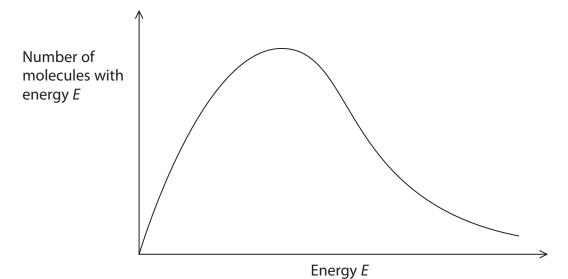
$$ClO_3^- + 2H^+ + I^- \rightarrow HIO + HClO_2$$

Deduce the rate equation for this iodine clock reaction.

(1)



(b) The diagram 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)

(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)


ln k

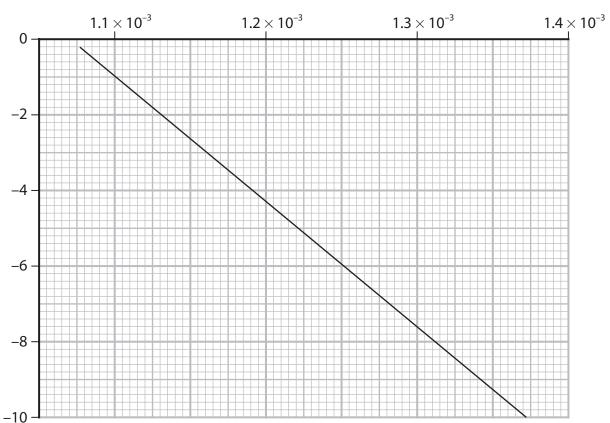
(c) The Arrhenius equation may be written in a logarithmic or an exponential form.

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

A is a constant.

(i) The rate constant, k, for the isomerisation of cyclopropane to propene was measured at various temperatures.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)



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

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  $50\,000\,\mathrm{J\,mol^{-1}}$  to  $25\,000\,\mathrm{J\,mol^{-1}}$  at  $298\,\mathrm{K}$  results in a large increase in the rate of reaction.

(3)

(Total for Question 8 = 13 marks)

- **9** This is a question about isomers of C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>.
  - (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)

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

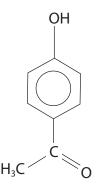
(1)

- (b) Four other  $C_8H_8O_2$  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 <sup>13</sup>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)** 

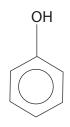
(c) Piceol is found in the needles of Norway spruce trees. Its structure is shown.



(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 [CH<sub>3</sub>C=O]<sup>+</sup>.

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





$$H_3C - C^{\dagger}$$

(ii) Piceol can be distinguished from HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CHO using simple chemical tests.

Give the reagents for a chemical test, and the observation that would only be positive for piceol.

(2)

(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.

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

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

Complete the electronic configuration of the Ni<sup>2+</sup> ion.

(1)

1s

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

Ni(s) + 4CO(g) 
$$\rightarrow$$
 Ni(CO)<sub>4</sub>(g)  $\Delta_r H^{\oplus} = -191 \text{ kJ mol}^{-1}$ 

(i) Calculate the total entropy change,  $\Delta S_{\text{total}}^{\oplus}$ , for this reaction. Include a sign and units in your answer.

Substance	S <sup>⊕</sup> / Jmol <sup>-1</sup> K <sup>-1</sup>
Ni(s)	+29.9
CO(g)	+197.6
Ni(CO) <sub>4</sub> (g)	+313.4

(5)

(ii) Predict the sign of the Gibbs Free Energy change,  $\Delta G$ , for this reaction and justify your choice. No calculation is required.

(1)

(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)

30

(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)							
(Total for Question 10 = 15 marks)									
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**TOTAL FOR PAPER = 120 MARKS** 



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