Please check the examination details below before entering your candidate information

Candidate surname	Other names
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Centre Number | Candidate Number

Pearson Edexcel Level 3 GCE

Friday 23 June 2023

Morning (Time: 2 hours 30 minutes)

Paper reference **9CH0/03**

Chemistry

Advanced
PAPER 3: General and Practical Principles in Chemistry

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

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 ▶

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

1 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} + 9½ O_2 → 6 CO_2 + 7 H_2O

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

(2)

Carbon monoxide, CO

Carbon (soot / particulates), C

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

(2)

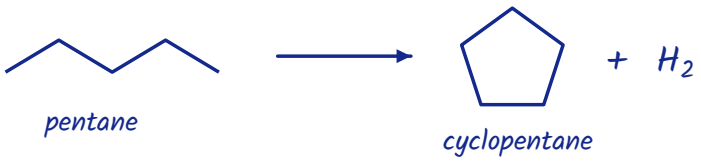
When the fuel burns, the sulfur forms sulfur dioxide, SO_2 (and SO_3), which is released into the atmosphere.

The SO_2 dissolves in rain water forming sulfuric acid, so acid rain is formed, which also causes breathing difficulties.

(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)

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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)

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

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

(3)

Reactivity increases down Group 2 (barium is the most reactive) because the ionisation energies decrease, so the outer electrons are lost more easily.

This is because the atomic radius increases, so the outer (valence) electrons are further from the nucleus.

The outer electrons are also more shielded by the extra inner shells of electrons, so the attraction between the nucleus and the outer electrons is weaker.

(b) (i) State the trend in solubility of the Group 2 sulfates.

(1)

The solubility of the Group 2 sulfates decreases down the group ($BaSO_4$ is the least soluble).

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

(2)

Calcium sulfate, $CaSO_4$, forms and it is only sparingly soluble (insoluble), so a solid layer forms on the surface of the calcium.

This layer is a barrier that prevents the sulfuric acid from coming into contact with the calcium, so the reaction stops.

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(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)

Put a glowing splint into the gas: the glowing splint relights.

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

(1)

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

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

(2)

Oxygen is oxidised: its oxidation number increases from −2 (in $NaNO_3$) to 0 (in O_2).

Nitrogen is reduced: its oxidation number decreases from +5 (in $NaNO_3$) to +3 (in $NaNO_2$).

(Total for Question 2 = 11 marks)

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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)

$CH_3CH_2OH \rightarrow CH_2=CH_2 + H_2O$

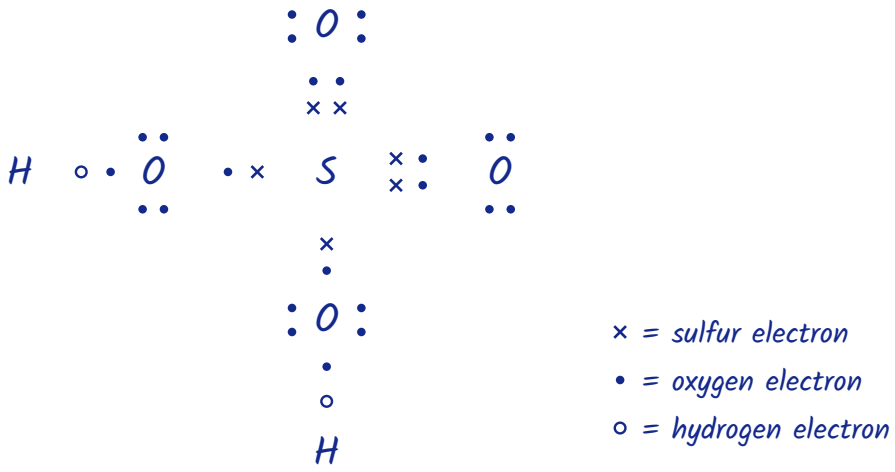
(b) Give the formula of phosphoric(V) acid.

(1)

H_3PO_4

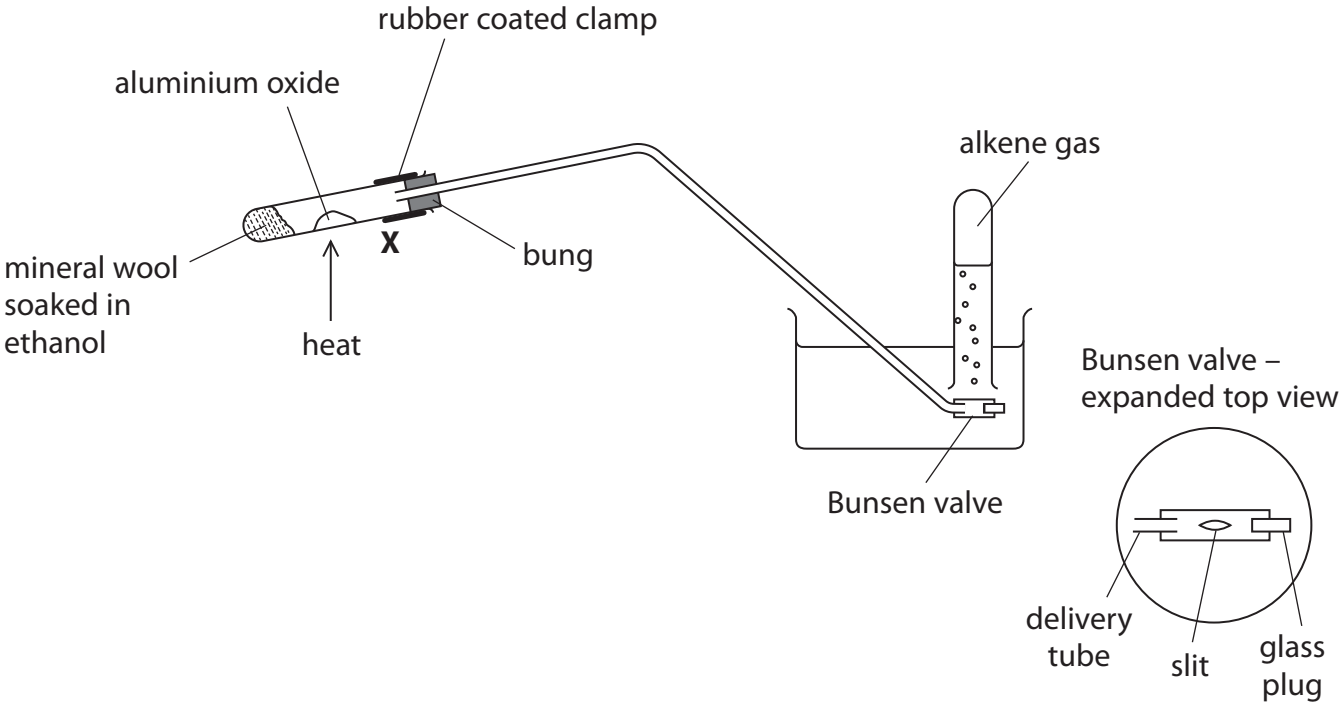
(c) Draw the dot-and-cross diagram of sulfuric acid, H_2SO_4.
Clearly differentiate between sulfur, oxygen and hydrogen electrons.
Show outer shell electrons only.

(2)



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(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)

So that the (liquid) ethanol does not run down the tube onto the hot catalyst, keeping the ethanol in the mineral wool separate from the catalyst.

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

(1)

The ethanol would evaporate and its vapour would pass over the (unheated) catalyst without reacting, so little alkene is made.

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

(1)

The rubber coated clamp and the rubber bung could burn (catch fire) or melt.

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

(1)

The valve lets the alkene gas out but prevents suck-back of water up the delivery tube into the hot boiling tube, which could crack it.

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

(1)

Shake the gas with bromine water: the bromine water is decolourised (orange to colourless).

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

(2)

$n(\text{alkene}) = 2.759 \times 10^{20} \div 6.02 \times 10^{23}$

$= 4.583 \times 10^{-4}$ mol

$V = 4.583 \times 10^{-4} \times 24\,000$

$= 11.0\ cm^3$

Volume = $11.0\ cm^3$ ($0.0110\ dm^3$)

(Total for Question 3 = 11 marks)

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4 This question is about hydrated magnesium sulfate, $MgSO_4 \cdot 7H_2O$.

*(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)

Use a balance to accurately weigh about 5.0 g of hydrated magnesium sulfate in a weighing boat, then reweigh the empty boat so the exact mass added is known.

Measure 50.0 cm^3 (a known mass, 50.0 g) of distilled (deionised) water with a pipette or measuring cylinder and pour it into a polystyrene cup with a lid, standing in a beaker for stability.

The polystyrene cup and lid insulate the solution, reducing heat transfer to or from the surroundings.

Put a thermometer in the water and record the initial temperature of the water every 30 seconds for 3 minutes, before adding the solid, until it is constant.

At the 3rd minute add the magnesium sulfate to the water in the cup, put the lid on and stir continuously so that all the solid dissolves.

Continue to record the temperature every 30 seconds for about 10 minutes, so that the lowest temperature reached (the final temperature) is recorded.

Plot a graph of temperature against time and extrapolate the line back to the time of mixing to find the maximum temperature change, ΔT, which corrects for heat gained from the surroundings.

Repeat the experiment and use the mean ΔT. The enthalpy change of solution can then be found using the mass of water, ΔT and the moles of $MgSO_4 \cdot 7H_2O$ used.

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

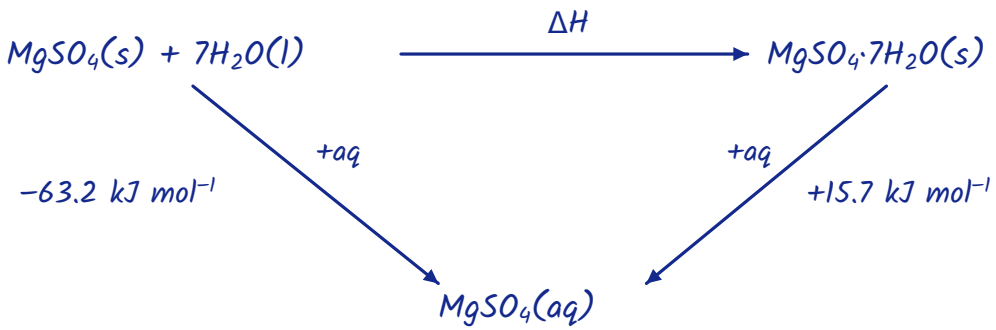
$MgSO_4(s) + aq \rightarrow MgSO_4(aq) \quad \Delta_r H = -63.2\,kJ\,mol^{-1}$

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

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)



$\Delta H = -63.2 - (+15.7)$

$\Delta H = -78.9\ kJ\ mol^{-1}$

(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)

The enthalpy change of hydration of the magnesium ion is more exothermic (more negative) than that of the calcium ion.

This is because the Mg^{2+} ion is smaller than the Ca^{2+} ion but has the same charge, so it has a greater charge density and attracts the water molecules more strongly.

(Total for Question 4 = 10 marks)

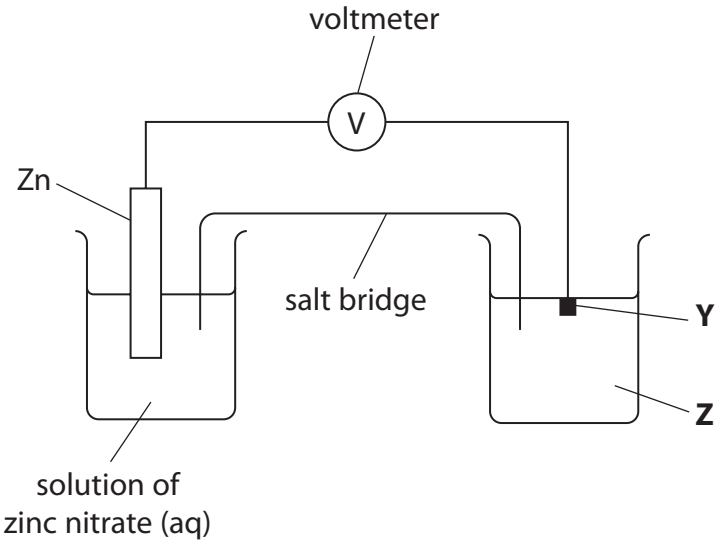
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5 This question is about electrochemical cells.

(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)



Y platinum, Pt

Z potassium manganate(VII), manganese(II) sulfate and sulfuric acid (aq)

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

Electrode system	$E^{\ominus}$ / V
$Cr^{2+}(aq) + 2e^- \rightleftharpoons Cr(s)$	−0.91
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.41
$\frac{1}{2}Cr_2O_7^{2-}(aq) + 7H^+(aq) + 3e^- \rightleftharpoons Cr^{3+}(aq) + 3\frac{1}{2}H_2O(l)$	+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 $E^{\ominus}_{cell}$ values where appropriate. Equations are not required.

(5)

The chromium is reduced from +6 all the way to +2, so the final oxidation state is +2, chromium(II), Cr^{2+}.

Cr(VI) to Cr(III): $E^{\ominus}_{cell}$ = +1.33 − (−0.76) = +2.09 V

Cr(III) to Cr(II): $E^{\ominus}_{cell}$ = −0.41 − (−0.76) = +0.35 V

Cr(II) to Cr(0): $E^{\ominus}_{cell}$ = −0.91 − (−0.76) = −0.15 V

The first two reductions are feasible (they occur) because $E^{\ominus}_{cell}$ is positive in both cases, so zinc reduces $Cr_2O_7^{2-}$ to Cr^{3+} and then reduces Cr^{3+} to Cr^{2+}.

The final reduction, Cr^{2+} to Cr, is not feasible (does not occur) because $E^{\ominus}_{cell}$ is negative, so the chromium stays as chromium(II), oxidation state +2.

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(c) A cell diagram is shown.

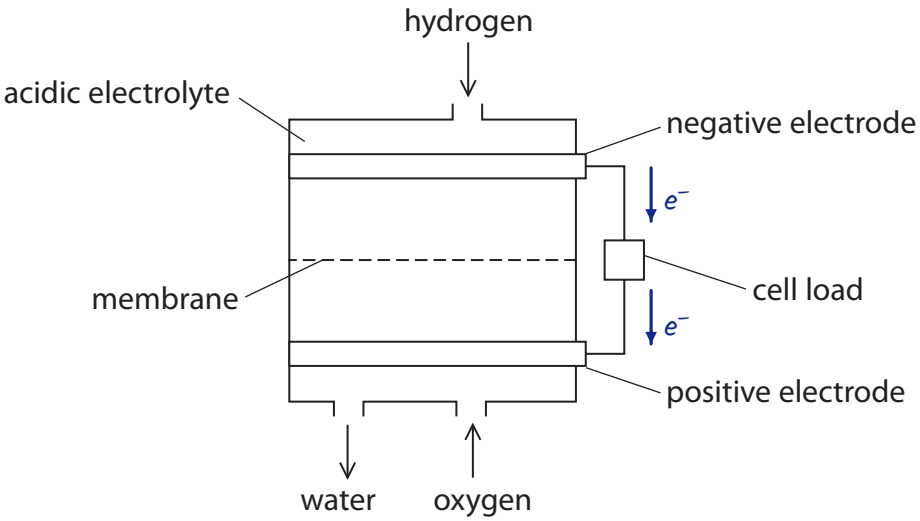
$$Ni(s) \mid Ni^{2+}(aq) \mid\mid [NO_3^-(aq) + 2H^+(aq)], [NO_2(g) + H_2O(l)] \mid Pt(s) \qquad E^{\ominus}_{cell} = +1.06\,V$$

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

(1)

$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$

(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.



(2)

Electrons flow from the negative to the positive electrode (through the external circuit), because H_2 is oxidised (loses electrons) at the negative electrode and O_2 is reduced (gains electrons) at the positive electrode.

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

(1)

The only product is water, so no pollutants such as CO, CO_2 or NO_x are produced.

(Total for Question 5 = 12 marks)

6 Amino acids can be separated using chromatography.

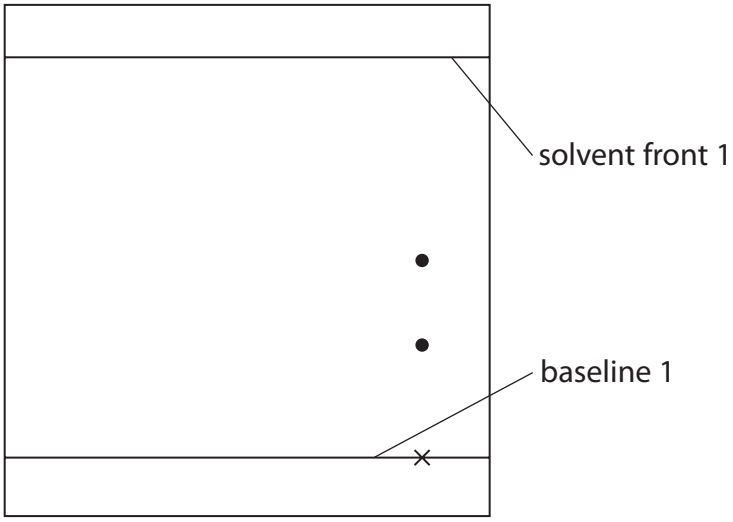
(a) State how chromatography separates the components of a mixture.

(1)

Each component is attracted to both the mobile phase and the stationary phase, but more strongly to one than to the other, so they move different distances.

(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)

Two of the three amino acids in the tripeptide are the same.

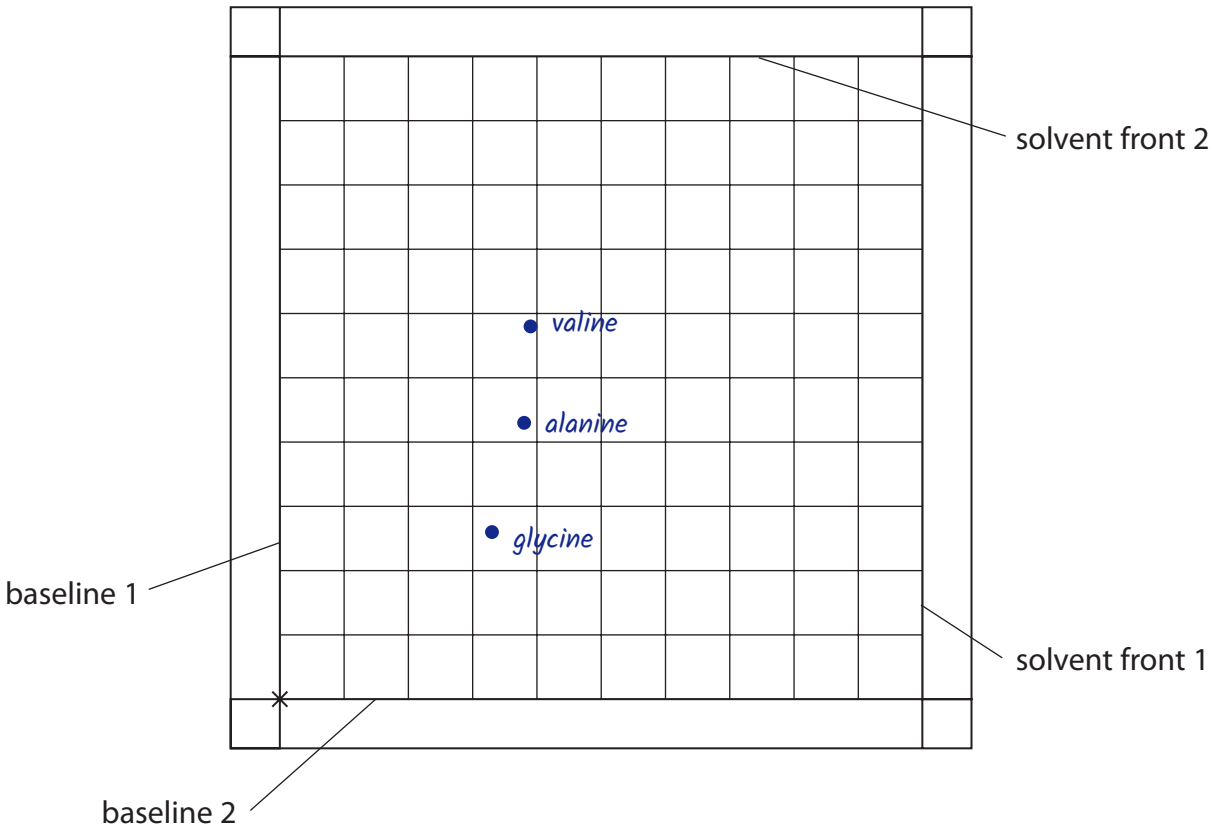
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(ii) Some amino acid mixtures cannot be effectively separated in one chromatography 'run'.
The chromatography paper from the first run is dried but not developed.
The chromatography paper is then rotated clockwise by 90° and placed in a different solvent.

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_f in solvent 1	R_f in solvent 2
alanine	0.38	0.43
glycine	0.33	0.26
valine	0.39	0.58

(3)



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

(1)

Ninhydrin

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

(1)

Mass spectrometry (GC-MS)

(Total for Question 6 = 7 marks)

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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)

Expel some of the solution from the pipette to remove the air bubble, then suck the solution up again above the line with the tip under the surface of the solution.

(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 ±0.04 cm^3.

(1)

25.04 + 25.04 = 50.08 cm^3

(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 ±0.05 cm^3.

(2)

Two 25.0 cm^3: % uncertainty = (2 × 0.04) ÷ 50.0 × 100 = 0.16 %

One 50.0 cm^3: % uncertainty = 0.05 ÷ 50.0 × 100 = 0.10 %

0.16 % > 0.10 %, so using the 25.0 cm^3 pipette twice has the greater percentage uncertainty (by 0.06 %).

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(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)

No, it is unsuitable; 2 cm^3 is too small to measure in a 100 cm^3 measuring cylinder, as the graduations are too large, so the percentage uncertainty would be too high.

(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

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

$K_a = 5.62 \times 10^{-10}$ 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)

$K_a = [NH_3][H^+] \div [NH_4^+]$

$[H^+] = 10^{-pH} = 10^{-10} = 1.0 \times 10^{-10}$ mol dm^{-3}

$[NH_4^+] = (18.1 \times 1.0 \times 10^{-10}) \div 5.62 \times 10^{-10} = 3.22$ mol dm^{-3}

$n(NH_4Cl) = 3.22 \times (100 \div 1000) = 0.322$ mol

$M(NH_4Cl) = 14.0 + 4.0 + 35.5 = 53.5$ g mol^{-1}

mass = $0.322 \times 53.5 = 17.2$ g

Mass of ammonium chloride = 17.2 g

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

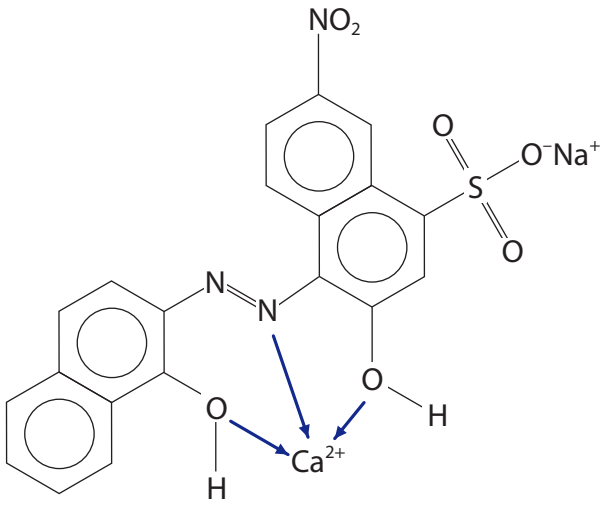
(1)

Use the concentrated ammonia in a fume cupboard.

(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)

3

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(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)

Filtration (filter off the precipitate)

(ii) The mean titre of 0.0100 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)

Before boiling (total hardness):

$n(EDTA^{4-}) = (12.80 \div 1000) \times 0.0100 = 1.28 \times 10^{-4}$ mol = $n(Ca^{2+})$ in 50.0 cm^3

$n(Ca^{2+})$ in 1 $dm^3 = 1.28 \times 10^{-4} \times 20 = 2.56 \times 10^{-3}$ mol

mass of $Ca^{2+} = 2.56 \times 10^{-3} \times 40.1 = 0.10266$ g, total = 102.66 mg dm^{-3}

After boiling (permanent hardness):

$n(EDTA^{4-}) = (5.15 \div 1000) \times 0.0100 = 5.15 \times 10^{-5}$ mol = $n(Ca^{2+})$

$n(Ca^{2+})$ in 1 $dm^3 = 5.15 \times 10^{-5} \times 20 = 1.03 \times 10^{-3}$ mol

mass of $Ca^{2+} = 1.03 \times 10^{-3} \times 40.1 \times 1000 = 41.3$ mg

Permanent hardness = 41.3 mg dm^{-3}

Temporary hardness = 102.66 − 41.30 = 61.4 mg dm^{-3}

(Total for Question 7 = 19 marks)

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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)

Colorimetry: measure the absorbance, which increases as the (yellow-brown) iodine forms.

Electrical conductivity: the conductivity decreases as the I^- and H^+ ions are used up.

(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)

Four ions must collide at the same time, which is unlikely, and the negative ions repel each other.

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

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

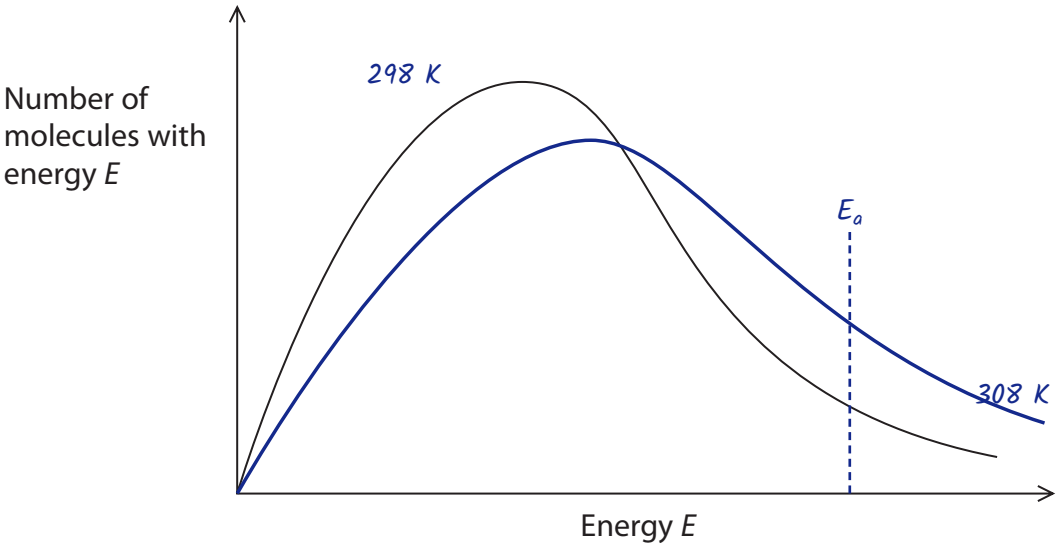
Deduce the rate equation for this iodine clock reaction.

(1)

rate = $k[ClO_3^-][H^+]^2[I^-]$

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(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)

At 308 K the area under the curve to the right of the activation energy, E_a, increases substantially (it roughly doubles).

So a much greater proportion of the molecules have energy greater than or equal to the activation energy, so there are many more successful collisions per second.

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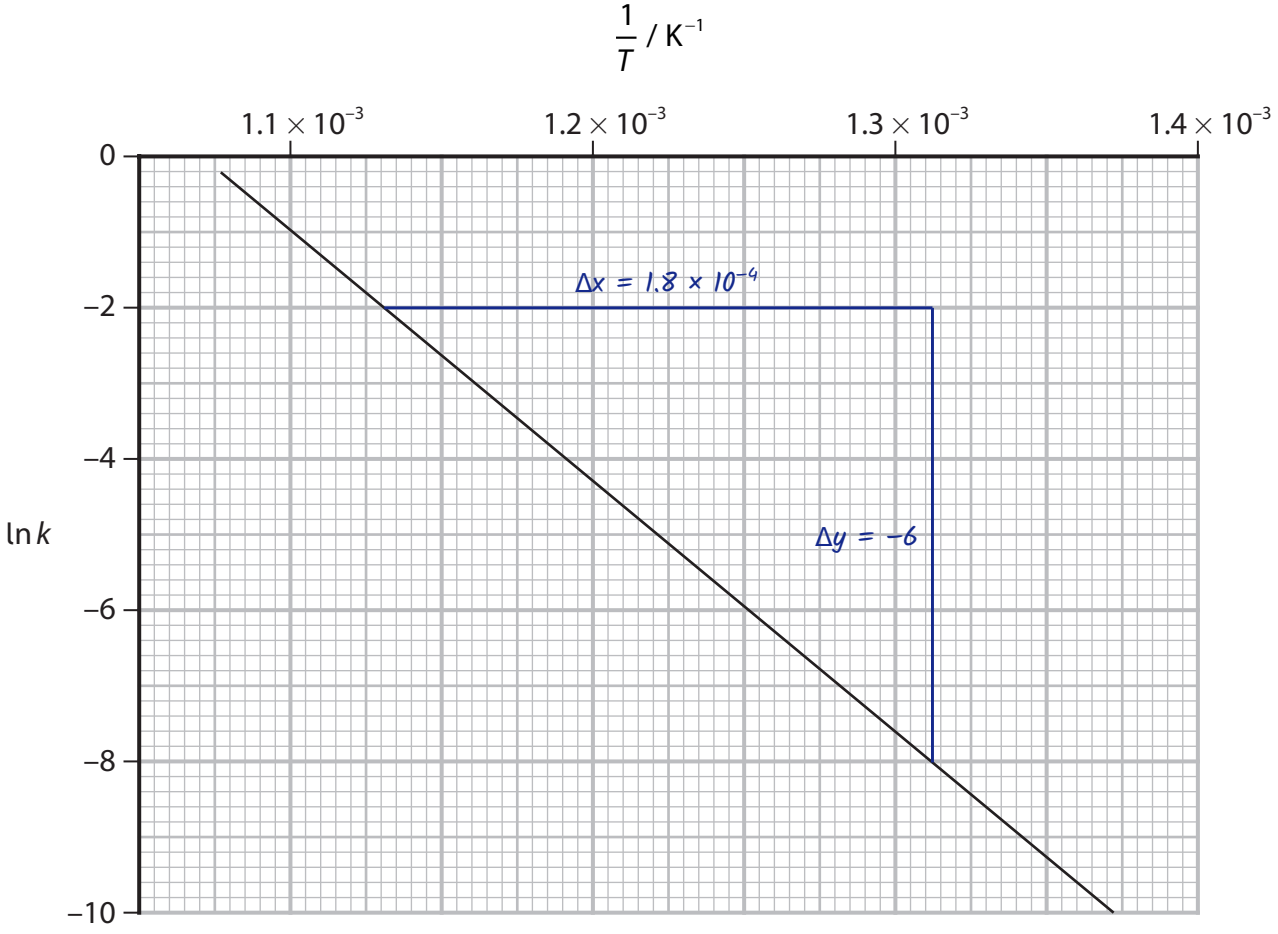
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(c) The Arrhenius equation may be written in a logarithmic or an exponential form.

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

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)

gradient = $\Delta y \div \Delta x = (-8 - (-2)) \div (1.31 \times 10^{-3} - 1.13 \times 10^{-3})$

$= -6 \div 1.8 \times 10^{-4} = -33\,333$ K

gradient = $-E_a \div R$, so E_a = −gradient × $R = 33\,333 \times 8.31$

$E_a = +277\,000$ J mol^{-1} = +277 kJ mol^{-1}

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(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 J mol^{-1} to 25 000 J mol^{-1} at 298 K results in a large increase in the rate of reaction.

(3)

Uncatalysed: fraction = $e^{-50\,000 \div (8.31 \times 298)} = e^{-20.19} = 1.70 \times 10^{-9}$

Catalysed: fraction = $e^{-25\,000 \div (8.31 \times 298)} = e^{-10.10} = 4.13 \times 10^{-5}$

Increase = $4.13 \times 10^{-5} \div 1.70 \times 10^{-9} = 24\,300$

So the fraction of molecules with energy ≥ E_a (able to react) increases about 24 000 times, so there are many more successful collisions and the rate increases greatly.

(Total for Question 8 = 13 marks)

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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)

Hydrolysis with NaOH forms the sodium salt, sodium benzoate (the benzoate ion, $C_6H_5COO^-$), not benzoic acid.

The H^+ ions from the acid protonate the benzoate ion to form benzoic acid:

$C_6H_5COO^- + H^+ \rightarrow C_6H_5COOH$

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

(1)

$C_6H_5COOCH_3 + H_2O \rightleftharpoons C_6H_5COOH + CH_3OH$

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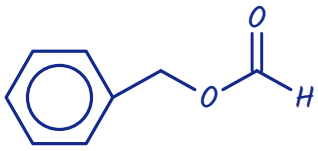
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(b) Four other $C_8H_8O_2$ isomers were investigated.

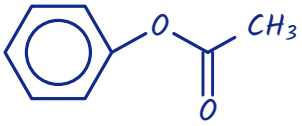
- **W** and **X** are mono-substituted aromatic compounds with the same functional group as methyl benzoate but only **W** is made from methanoic acid
- **Y** is a mono-substituted aromatic compound which reacts with sodium carbonate to give carbon dioxide
- **Z** is a disubstituted aromatic compound with six peaks in its ^{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.

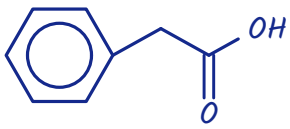
(7)



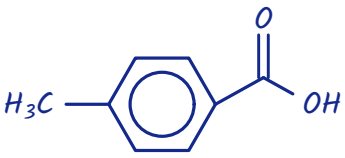
W (benzyl methanoate)



X (phenyl ethanoate)



Y (phenylethanoic acid)



Z (4-methylbenzoic acid)

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W and X both contain the ester group, –COO–, the same functional group as methyl benzoate, and both are mono-substituted (only one group on the benzene ring).

W is made from methanoic acid, so it is a methanoate ester with the HCOO– group: W is benzyl methanoate, $HCOOCH_2C_6H_5$.

X is not a methanoate; it is made from ethanoic acid (and phenol): X is phenyl ethanoate, $CH_3COOC_6H_5$.

Y reacts with sodium carbonate to give carbon dioxide, so it contains a carboxylic acid group, –COOH. As it is mono-substituted, Y is phenylethanoic acid, $C_6H_5CH_2COOH$.

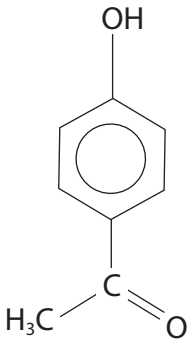
Z forms a sweet-smelling ester with ethanol, so Z also contains a carboxylic acid group, –COOH.

Z is disubstituted with a $-CH_3$ group and a –COOH group. Six peaks in the ^{13}C NMR spectrum means six different carbon environments, so the two groups must be in the 1,4 (para) positions.

So Z is 4-methylbenzoic acid, $CH_3C_6H_4COOH$. (The 1,2 and 1,3 isomers would have eight carbon environments, so eight peaks.)

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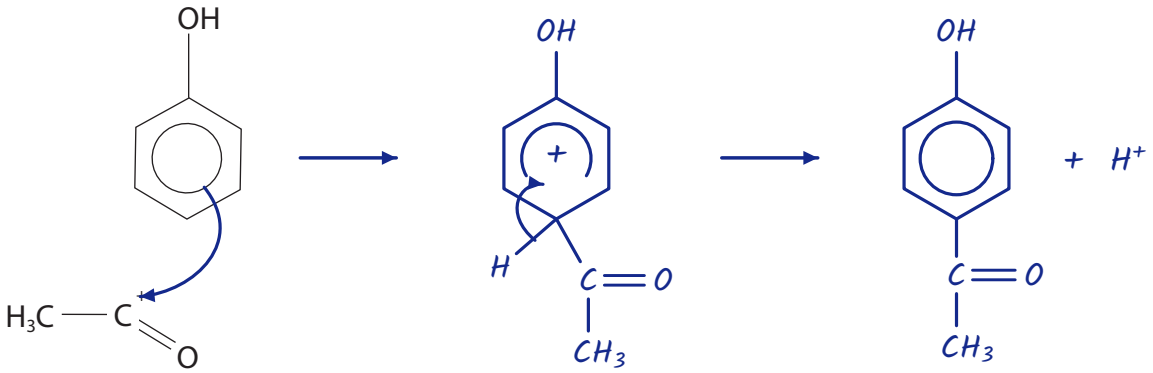
(c) Piceol is found in the needles of Norway spruce trees. Its structure is shown.



(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 $[CH_3C{=}O]^+$.

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

(4)



$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

(ii) Piceol can be distinguished from $HOC_6H_4CH_2CHO$ using simple chemical tests.

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

(2)

Warm with iodine and sodium hydroxide solution (alkaline iodine).

Only piceol (a methyl ketone, CH_3CO- group) gives a pale yellow precipitate (of CHI_3) with an antiseptic smell.

(Total for Question 9 = 15 marks)

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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^{2+} ion.

(1)

$1s^2$ $2s^2 2p^6 3s^2 3p^6 3d^8$

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

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g) \qquad \Delta_r H^{\ominus} = -191\ kJ\,mol^{-1}$$

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

Substance	$S^{\ominus}$ / J mol^{-1} K^{-1}
Ni(s)	+29.9
CO(g)	+197.6
$Ni(CO)_4(g)$	+313.4

(5)

$\Delta S_{system} = 313.4 - (29.9 + 4 \times 197.6) = 313.4 - 820.3$

$\Delta S_{system} = -506.9\ J\ mol^{-1}\ K^{-1}$

$\Delta S_{surroundings} = -\Delta H \div T = -(-191\ 000) \div 323 = +591.3\ J\ mol^{-1}\ K^{-1}$

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = -506.9 + 591.3$

$\Delta S_{total} = +84.4\ J\ mol^{-1}\ K^{-1}$

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

(1)

ΔG is negative, because ΔS_{total} is positive ($\Delta G = -T\Delta S_{total}$), so the reaction is feasible at 323 K, as expected for an industrial process.

(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)

CO reacted = 50.0 − 0.750 = 49.25 mol

$n(Ni(CO)_4)$ = 49.25 ÷ 4 = 12.3125 mol

total moles of gas = 0.750 + 12.3125 = 13.0625 mol

$x(CO)$ = 0.750 ÷ 13.0625 = 0.057416

$x(Ni(CO)_4)$ = 12.3125 ÷ 13.0625 = 0.942584

$p(CO)$ = 0.057416 × 1.5 = 0.086124 atm

$p(Ni(CO)_4)$ = 0.942584 × 1.5 = 1.413876 atm

$K_p = p(Ni(CO)_4) \div p(CO)^4$

$K_p = 1.413876 \div (0.086124)^4 = 25\,700$

$K_p = 25\,700\ atm^{-3}$

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(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, $\Delta S^{\ominus}_{system}$, for this decomposition reaction is positive.

(2)

In $Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$ the number of moles of gas increases from 1 to 4, and gases have high entropy (more disorder).

Although solid nickel (low entropy) forms, the increase in entropy from forming 4 mol of CO gas is larger than the decrease from forming solid Ni, so ΔS_{system} is positive.

(Total for Question 10 = 15 marks)

TOTAL FOR PAPER = 120 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
																	(18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

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