Please check the examination details below before entering your candidate information

Candidate surname	Other names
StemUp Model Solution	

Pearson Edexcel Level 3 GCE

Centre Number	Candidate Number

Wednesday 19 June 2019

Morning (Time: 2 hours 30 minutes)	Paper Reference **9CH0/03**

Chemistry

Advanced

Paper 3: General and Practical Principles in Chemistry

Candidates must have: Scientific calculator
Data Booklet
Ruler

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **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 This question is about acids and bases.

(a) State what is meant by a Brønsted-Lowry acid.

(1)

A proton (H^+ ion) donor.

(b) Identify the acid-base conjugate pairs in this reaction.

(1)

$$CH_3COOH + HCOOH \rightarrow CH_3COOH_2^+ + HCOO^-$$

base 2 acid 1 acid 2 base 1

(c) Write the expression that defines the pH of a solution.

(1)

$pH = -\log_{10}[H^+(aq)]$

(d) Calculate the concentration of hydrogen ions, in mol dm^{-3}, in a solution with a pH of 2.76

(1)

$[H^+(aq)] = 10^{-pH} = 10^{-2.76}$

$= 1.74 \times 10^{-3}$ mol dm^{-3}

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(e) Explain why the pH of a 1×10^{-8} mol dm^{-3} solution of nitric acid, HNO_3, is not 8.

[Ionic product of water, $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}]

(2)

Water also dissociates, $H_2O \rightleftharpoons H^+ + OH^-$, and the $[H^+]$ from water is $\sqrt{K_w} = \sqrt{(1.00 \times 10^{-14})} = 1.0 \times 10^{-7}$ mol dm^{-3}.

This is not negligible compared with the 1×10^{-8} mol dm^{-3} of H^+ from the acid, so it cannot be ignored: the total $[H^+]$ is greater than 1.0×10^{-7} mol dm^{-3} (about 1.1×10^{-7}).

So the pH is just below 7 (about 6.96). An acid cannot have a pH above 7, as pH 8 is alkaline.

(Total for Question 1 = 6 marks)

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2 This question is about the $Ag^+(aq)|Ag(s)$ half-cell.

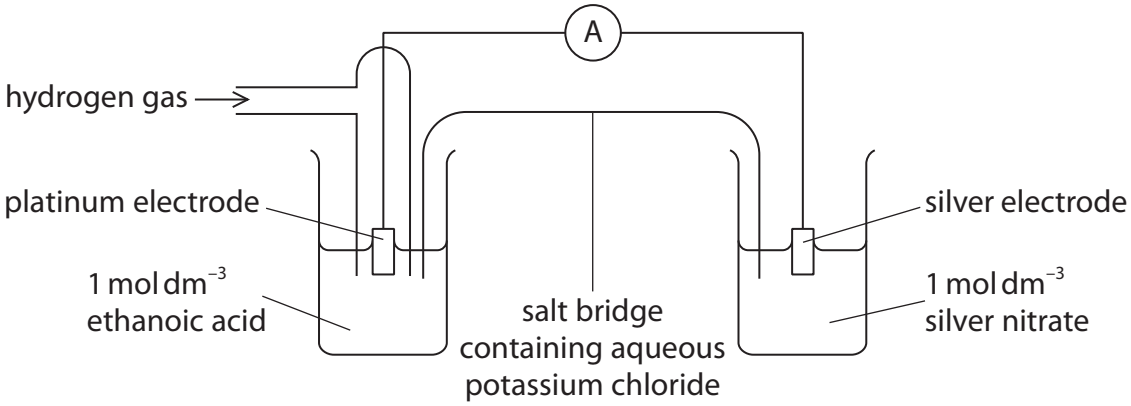
(a) A student was asked to plan an experiment to measure the standard electrode potential of the $Ag^+(aq)|Ag(s)$ half-cell.

(i) State the conditions of temperature and pressure under which standard electrode potentials are measured.

(1)

Temperature of 298 K (25 °C) and a pressure of 100 kPa (1 bar).

(ii) The student drew the diagram shown.



Identify **three** mistakes in this diagram and the modifications that should be made to correct them.

(3)

Mistake in diagram	Modification needed to correct mistake
An ammeter (A) is used, which cannot measure the potential difference.	*Replace the ammeter with a high resistance voltmeter (V).*
The hydrogen half-cell uses 1 mol dm^{-3} ethanoic acid, a weak acid, so $[H^+]$ is not 1 mol dm^{-3}.	*Use 1.0 mol dm^{-3} hydrochloric acid, $HCl(aq)$, so that $[H^+(aq)] = 1.0$ mol dm^{-3}.*
The salt bridge contains potassium chloride: Cl^- ions react with Ag^+ to form a precipitate of $AgCl$.	*Use a salt bridge soaked in aqueous potassium nitrate, $KNO_3(aq)$.*

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(b) The standard electrode potential, $E^{\ominus}$, of the $Ag^+(aq)|Ag(s)$ half-cell is +0.80 V.

The effect of changing the concentration of the ions on the value of the electrode potential, E, in this half-cell is calculated using the equation

$$E = E^{\ominus} + \frac{RT}{96500} \times \ln[Ag^+(aq)]$$

where T is the temperature in kelvin and R is the gas constant.

The electrode potential of a $Ag^+(aq)|Ag(s)$ half-cell was measured at 20 °C and found to be +0.72 V.

Calculate the concentration of silver ions, in mol dm^{-3}, in this half-cell.

(3)

$T = 20 + 273 = 293\ K$

$0.72 = 0.80 + (8.31 \times 293 \div 96500) \times \ln[Ag^+(aq)]$

$\ln[Ag^+(aq)] = (0.72 - 0.80) \times 96500 \div (8.31 \times 293)$

$\ln[Ag^+(aq)] = -3.1707$

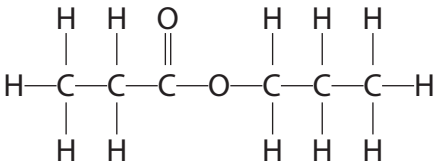
$[Ag^+(aq)] = e^{-3.1707}$

$[Ag^+(aq)] = 0.0420\ mol\ dm^{-3}$

(Total for Question 2 = 7 marks)

3 This question is about esters with the molecular formula $C_6H_{12}O_2$.

(a) Propyl propanoate has the structure shown.



Devise a synthetic pathway to prepare propyl propanoate starting with 1-bromopropane as the **only** organic compound.

Include the reagents for each step in the synthesis, and the names or structures of the intermediate compounds.

(5)

Step 1: heat 1-bromopropane under reflux with aqueous potassium hydroxide, KOH(aq), to form propan-1-ol, $CH_3CH_2CH_2OH$.

$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$

Step 2: oxidise some of the propan-1-ol by heating under reflux with excess potassium dichromate(VI) and dilute sulfuric acid (acidified $K_2Cr_2O_7$) to form propanoic acid, CH_3CH_2COOH.

Step 3: warm the propanoic acid with the rest of the propan-1-ol and a few drops of concentrated sulfuric acid as a catalyst to form propyl propanoate.

$CH_3CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_2CH_3 + H_2O$

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(b) Another ester, **A**, with molecular formula $C_6H_{12}O_2$, was hydrolysed.
It produced ethanoic acid, and an alcohol, **B**, with molecular formula $C_4H_{10}O$.

Alcohol **B** undergoes an elimination reaction to produce a mixture of but-1-ene and but-2-ene.

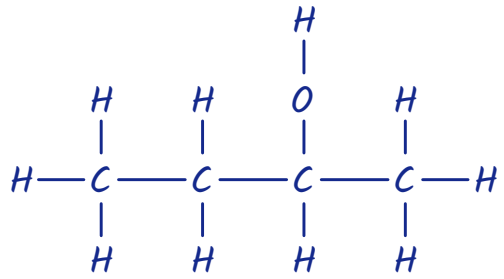
Deduce the structures of **B** and **A**. Justify your structure of **B**.

(3)

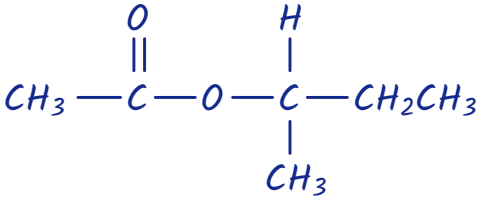
B is butan-2-ol: $CH_3CH_2CH(OH)CH_3$

A is butan-2-yl ethanoate: $CH_3COOCH(CH_3)CH_2CH_3$

B



A



B must be butan-2-ol because the OH group is on the second carbon (a secondary alcohol), so the C=C can form either side of the C bonded to OH: between C1 and C2 to give but-1-ene, or between C2 and C3 to give but-2-ene.

The other $C_4H_{10}O$ alcohols cannot give but-2-ene.

(Total for Question 3 = 8 marks)

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4 Compound **C** is a pink crystalline solid containing two cations and one anion.

(a) Three tests were carried out on **C**. The observation made for each test was recorded in the table.

(i) Complete the statements in the inference column by writing the names or formulae of the species.

(6)

Test	Observation	Inference
Test 1 Aqueous sodium hydroxide was added to solid **C** and the mixture warmed The gas evolved was tested with damp red litmus paper	The red litmus paper turned blue	The gas evolved was *ammonia, NH_3* One of the cations in **C** is *ammonium, NH_4^+*
Test 2 Concentrated hydrochloric acid was added to an aqueous solution of **C**	The pink solution turned blue	The other cation in **C** is *cobalt(II), Co^{2+}* The formula of the complex ion in the blue solution is *$[CoCl_4]^{2-}$*
Test 3 Dilute hydrochloric acid and aqueous barium chloride were added to an aqueous solution of **C**	A white precipitate formed	The white precipitate is *barium sulfate, $BaSO_4$* The anion in **C** is *sulfate, SO_4^{2-}*

(ii) Use the results of the tests in (a)(i) to give a formula of **C**.
Do not include water of crystallisation.

(1)

$(NH_4)_2Co(SO_4)_2$

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(b) Write the **ionic** equation for the reaction between the cation in **C** and sodium hydroxide producing the gas in **Test 1**.
State symbols are not required.

(1)

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

(c) State the type of reaction occurring in **Test 2**.

(1)

Ligand substitution (ligand exchange)

(d) Give a reason why dilute hydrochloric acid is needed in **Test 3**.

(1)

To react with and remove any carbonate (or sulfite) ions, e.g. $2H^+ + CO_3^{2-} \rightarrow H_2O +$ CO_2, which would otherwise also form a white precipitate with Ba^{2+} and give a false positive result.

(Total for Question 4 = 10 marks)

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5 This question is about redox reactions.

(a) Name the ion with formula PO_3^{3-}. Include the relevant oxidation number.

(1)

Phosphate(III) ion

(b) State what happens to a reducing agent during a reaction, in terms of oxidation number **and** electrons.

(1)

A reducing agent loses (donates) electrons, so its oxidation number increases.

(c) Identify the species that is the strongest reducing agent from the list of standard electrode potentials in the Data Booklet.

(1)

Na, sodium

(d) Manganese(IV) oxide, MnO_2, and manganate(VII) ions, MnO_4^-, react in alkaline solution to form manganate(VI) ions, MnO_4^{2-}.

(i) Write the **ionic** equation for this reaction.
State symbols are not required.

(2)

$$MnO_2 + 2MnO_4^- + 4OH^- \rightarrow 3MnO_4^{2-} + 2H_2O$$

(ii) Give a reason why this reaction is **not** disproportionation.

(1)

Disproportionation is when one species is simultaneously oxidised and reduced. Here two different species are involved: Mn in MnO_2 (+4) is oxidised and Mn in MnO_4^- (+7) is reduced, and only one oxidation state (+6) is formed.

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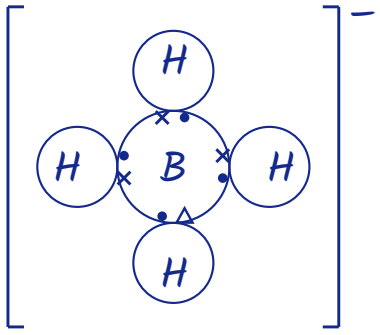
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(e) Sodium tetrahydridoborate(III), $NaBH_4$, is used in organic chemistry.
It is an alternative reagent to lithium tetrahydridoaluminate(III) for the reduction of carbonyl compounds.

(i) Draw a dot-and-cross diagram of the BH_4^- ion.

Use crosses (×) for the boron electrons, dots (•) for the hydrogen electrons and triangles (△) for the additional electron forming the negative ion.

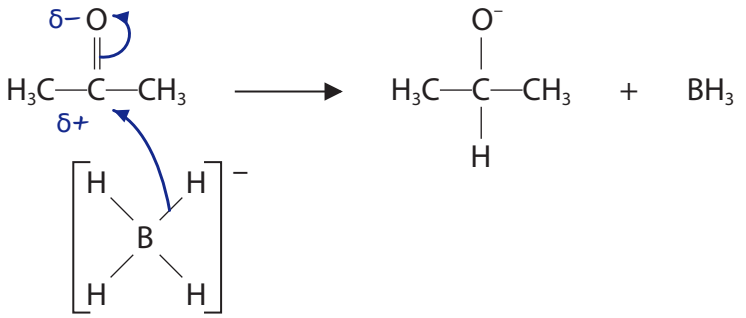
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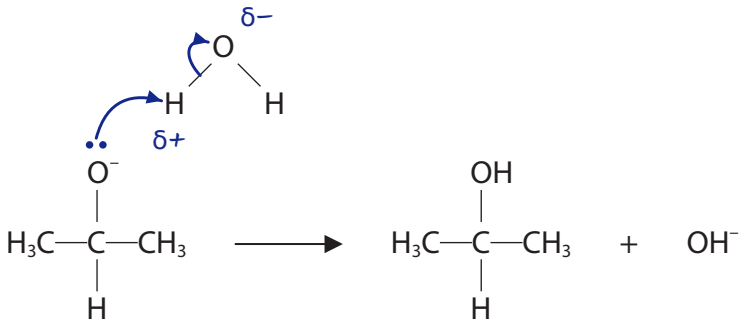


(ii) The BH_4^- ions reduce carbonyl compounds to alcohols in aqueous solution.

Complete the mechanism for the reduction of propanone to propan-2-ol by adding curly arrows, and any relevant lone pairs and dipoles.

(4)





(Total for Question 5 = 11 marks)

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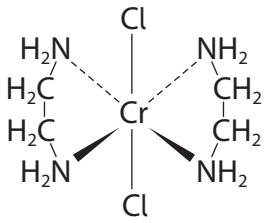
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6 This question is about transition metals and their ions.

(a) The **shape** of a complex ion formed from Cr^{3+} ions is shown.



(i) State the coordination number of Cr^{3+} in this complex ion.

(1)

6 (six)

(ii) State the overall charge on this complex ion.

(1)

1+ (+1)

(b) The complex ions of transition metals have different colours in aqueous solution.

Two factors that affect the colour of the solution are the oxidation number of the central metal ion, and the ligands present.

Give examples to illustrate these factors by referring to complex ions of iron and/or copper. Include the formula and colour of each complex.

An explanation of why transition metal ions are coloured is **not** required.

(3)

Oxidation number: $[Fe(H_2O)_6]^{2+}$ (iron +2) is pale green, but $[Fe(H_2O)_6]^{3+}$ (iron +3) is yellow, with the same ligands.

Ligands: copper(II) with water ligands, $[Cu(H_2O)_6]^{2+}$, is pale blue; with chloride ligands, $[CuCl_4]^{2-}$, it is yellow; with ammonia ligands, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, it is deep (dark) blue. Copper is +2 in all three.

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(c) Tungsten wire catalyses the decomposition of ammonia.

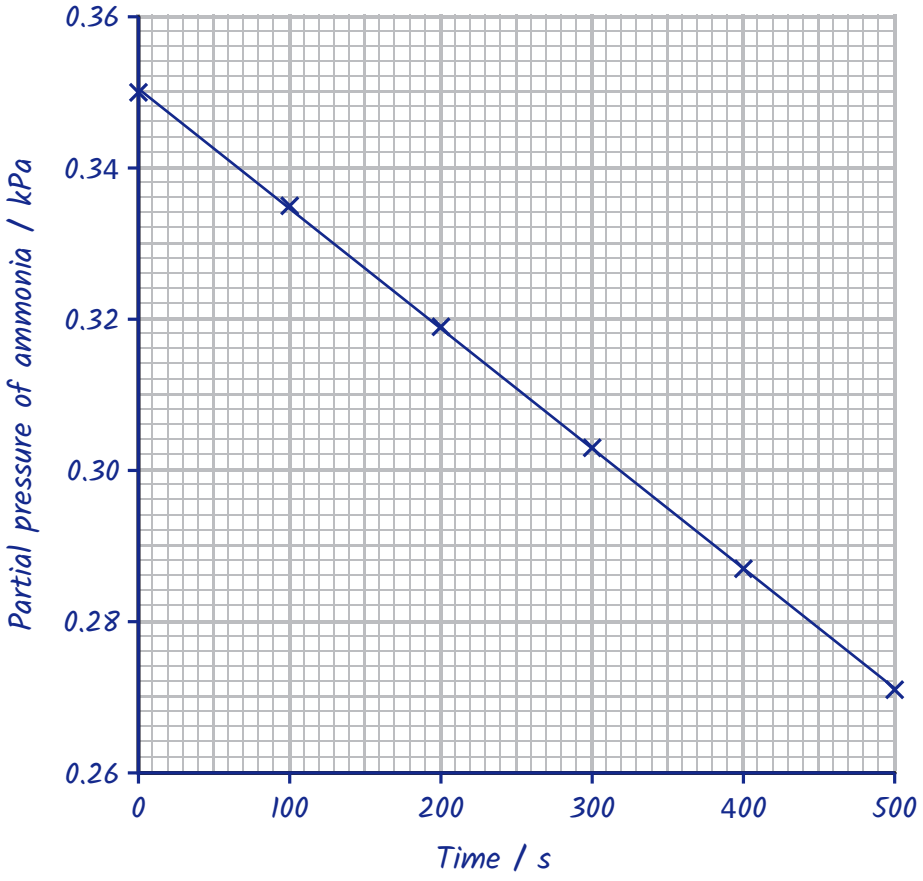
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

In an experiment, the following results were obtained.

Time /s	Partial pressure of ammonia / kPa
0	0.350
100	0.335
200	0.319
300	0.303
400	0.287
500	0.271

(i) Plot a graph of partial pressure of ammonia against time.

(2)



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(ii) Deduce the rate equation for this reaction by using your graph in (c)(i).
Justify your answer.

(2)

rate = k (rate = k $p(NH_3)^0$), so the reaction is zero order with respect to ammonia.

This is because the graph is a straight line, so the gradient (the rate) is constant and independent of the partial pressure of ammonia.

(iii) Use the graph to calculate the rate constant. Include units in your answer.

(2)

gradient = (0.271 − 0.350) ÷ (500 − 0) = -1.58×10^{-4} kPa s^{-1}

rate = k, so k = 1.58×10^{-4} kPa s^{-1}

(iv) Describe the stages in the catalytic decomposition of ammonia by tungsten.

(3)

Ammonia molecules are adsorbed onto the surface of the tungsten catalyst (at the active sites).

This weakens the N–H bonds in the ammonia, which break, and new N≡N and H–H bonds form.

The products, nitrogen and hydrogen, are then desorbed (released) from the surface of the tungsten, freeing the surface for more ammonia to be adsorbed.

(Total for Question 6 = 14 marks)

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7 A group of students analysed a hydrated salt with the formula $KH_3(C_2O_4)_y.zH_2O$ where **y** and **z** are whole numbers.

The students carried out experiments to determine the values of **y** and **z**.

(a) **Experiment 1** – to determine the value of **y**

One student was provided with a 0.0235 mol dm^{-3} solution of the salt.

25.0 cm^3 portions of the salt solution were acidified with excess dilute sulfuric acid and heated to about 60 °C.

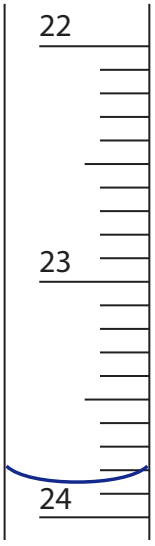
Each portion was titrated with 0.0203 mol dm^{-3} potassium manganate(VII).

The results of four titrations are shown in the table.

Titration number	1	2	3	4
Final burette reading / cm^3	23.85	47.20	24.05	48.10
Initial burette reading / cm^3	0.00	24.00	0.50	25.00
Titre / cm^3	23.85	23.20	23.55	23.10

(i) Complete the diagram to show the final burette reading in **Titration 1**.

(2)



(ii) Explain why this student should use a mean titre of 23.15 cm^3 and not 23.43 cm^3 in the calculation.

(2)

23.15 cm^3 is the mean of the concordant titres only, titres 2 and 4 (23.20 and 23.10 cm^3), which are within 0.10 cm^3 of each other.

23.43 cm^3 should not be used as it includes the non-concordant (inaccurate) titres 1 and 3 (23.85 and 23.55 cm^3).

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(iii) The uncertainty in each burette reading is ±0.05 cm^3.

Calculate the percentage uncertainty in the titre volume of potassium manganate(VII) solution used in **Titration 2**.

(1)

$(2 \times 0.05 \div 23.20) \times 100 = \pm 0.43\ \%$

(iv) The equation for the reaction is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Deduce, by calculation, the value of **y**, to the nearest whole number, in the formula $KH_3(C_2O_4)_{\mathbf{y}}.\mathbf{z}H_2O$.

Use the mean titre of 23.15 cm^3 and other data from **Experiment 1**.

You **must** show your working.

(4)

$mol\ MnO_4^- = 23.15 \times 0.0203 \div 1000 = 4.6995 \times 10^{-4}\ mol$

$mol\ C_2O_4^{2-}\ in\ 25.0\ cm^3 = 4.6995 \times 10^{-4} \times 5/2 = 1.1749 \times 10^{-3}\ mol$

$mol\ salt\ in\ 25.0\ cm^3 = 0.0235 \times 25.0 \div 1000 = 5.875 \times 10^{-4}\ mol$

$ratio\ salt : C_2O_4^{2-} = 5.875 \times 10^{-4} : 1.1749 \times 10^{-3} = 1 : 1.9998$

$so\ y = 2$

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(b) **Experiment 2** – to determine the value of **z**

Another student wrote an account of the method for this experiment.

A crucible was weighed.

A sample of the hydrated salt was added to the crucible and it was reweighed.

The crucible and salt were heated to remove the water of crystallisation and then allowed to cool.

The crucible and contents were weighed again.

Results

Mass of crucible	*= 19.56 g*
Mass of crucible + $KH_3(C_2O_4)_y.\mathbf{z}H_2O$	*= 22.97 g*
Mass of crucible + $KH_3(C_2O_4)_y$	*= 22.52 g*

(i) Deduce, by calculation, the value of **z**, to the nearest whole number, in the formula $KH_3(C_2O_4)_y.\mathbf{z}H_2O$.

You must use the data from **Experiment 2** and your value of **y** in (a)(iv).

You **must** show your working.

(3)

mass of anhydrous salt = 22.52 − 19.56 = 2.96 g

mass of water = 22.97 − 22.52 = 0.45 g

M_r of $KH_3(C_2O_4)_2$ = 39.1 + 3.0 + 2(88.0) = 218.1

mol anhydrous salt = 2.96 ÷ 218.1 = 0.013572 mol

mol H_2O = 0.45 ÷ 18.0 = 0.025 mol

ratio salt : H_2O = 0.013572 : 0.025 = 1 : 1.84

so z = 2

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(ii) A third student carried out Experiment 2 and calculated a value of **z** that was lower than expected.

This student evaluated the experiment and gave two suggestions for **z** being lower.

Suggestion **1**
"Some of the crystals jumped out of the crucible while it was being heated."

Suggestion **2**
"It was difficult to tell when all the water of crystallisation had been lost."

Evaluate these two suggestions to decide whether they could account for the lower value of **z** obtained from the experimental results.

Include an explanation of the effect each suggestion would have on the calculated value of **z** and how the method could be improved to prevent these errors.

(5)

Suggestion 1: if crystals jump out of the crucible, the loss in mass is greater, so it appears that more water was lost than really was. The calculated mass of water is too large, so the value of z would increase. Suggestion 1 does not account for the lower value of z.

This error can be prevented by placing a lid on the crucible (partly covering it) and heating more gently.

Suggestion 2: if not all the water of crystallisation is lost, less mass is lost than expected, so the calculated mass of water is too small (and the mass of anhydrous salt too large).

This makes the value of z decrease, so Suggestion 2 does account for the lower value of z.

This can be prevented by heating to constant mass: heat, cool and reweigh repeatedly until two consecutive masses are the same.

(Total for Question 7 = 17 marks)

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8 1-bromobutane can be prepared from butan-1-ol and hydrogen bromide.

$$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

Hydrogen bromide can be made from sodium bromide and 50% concentrated sulfuric acid.

(a) The steps for the preparation of impure 1-bromobutane are summarised.

Step **1** Dissolve the sodium bromide in distilled water in a pear-shaped flask and then add 20.0 cm^3 of butan-1-ol.

Step **2** Surround the flask with an ice bath to **cool the mixture**, before adding concentrated sulfuric acid drop by drop.

Step **3** Remove the flask from the ice bath and add a few **anti-bumping granules** to the reaction mixture.

Step **4** Set up the apparatus for **heating under reflux**. Heat the mixture in the flask for 30 minutes and then allow the apparatus to cool.

Step **5** Rearrange the apparatus for distillation and heat the mixture until no more 1-bromobutane distils over.

(i) Parts of the method are given in **bold** type in Steps **2**, **3** and **4**. Give a reason why each of these parts is necessary.

(3)

Cool the mixture: adding concentrated sulfuric acid is very exothermic (releases a lot of heat), so the ice bath removes this heat.

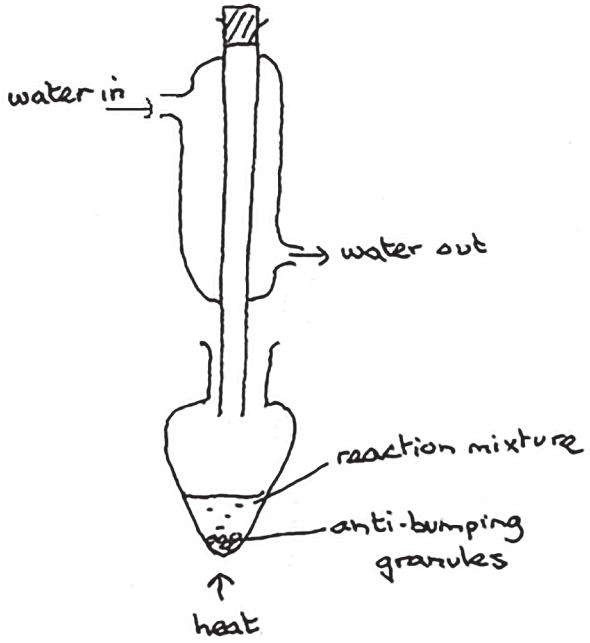
Anti-bumping granules: they provide a rough surface for small bubbles to form, so the mixture boils smoothly, preventing sudden violent boiling (superheating).

Heating under reflux: the vapour condenses and returns to the flask, preventing the loss of the volatile reactants and products (butan-1-ol and 1-bromobutane), so the reaction can go to completion.

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(ii) A student drew a diagram of the apparatus used for heating under reflux in Step **4**. There are three errors in the apparatus shown in the diagram. Assume the apparatus is suitably clamped.



Identify the three errors, including the effect of each error.

(3)

1. There is a gap between the flask and the condenser (the joint is not sealed), so vapour of the reactants and product escapes and the yield of 1-bromobutane is lower.

2. The water flows the wrong way through the condenser; it should go in at the bottom and out at the top. Otherwise the condenser does not fill with water, so cooling and condensation are inefficient.

3. There is a stopper on top of the condenser. If the joint were sealed, there would be a build-up of pressure, so the stopper could blow off or the apparatus could explode.

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(iii) The student corrected the errors.
While the mixture was heating under reflux, the student noticed a small amount of a brown vapour was formed.

Explain why the brown vapour forms.

(2)

The brown vapour is bromine, Br_2.

Concentrated sulfuric acid is an oxidising agent: it oxidises some of the bromide ions (HBr) to bromine, $2Br^- \rightarrow Br_2 + 2e^-$.

(b) The distillate collected in Step **5** is a mixture consisting of two layers.
There is an aqueous layer and a layer containing impure 1-bromobutane.

Data

Densities:

water	1.00 g cm^{-3}
butan-1-ol	0.81 g cm^{-3}
1-bromobutane	1.27 g cm^{-3}

Boiling temperature of 1-bromobutane = 102 °C

The steps for the purification of the 1-bromobutane are summarised.

Step **6** Transfer the mixture from Step **5** to a separating funnel and remove the aqueous layer.

Step **7** Wash the impure 1-bromobutane with concentrated hydrochloric acid in the separating funnel. Remove the aqueous layer.

Step **8** Add aqueous sodium hydrogencarbonate to the impure 1-bromobutane in the separating funnel.

Step **9** Shake the mixture in the separating funnel and, from time to time, invert the funnel and open the tap.

Step **10** Collect the 1-bromobutane layer from Step **9** in a small conical flask. Add anhydrous sodium sulfate and swirl the flask until the liquid becomes clear.

Step **11** Decant the 1-bromobutane into a clean pear-shaped flask and redistil it. Measure the volume of 1-bromobutane produced.

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(i) State the position of the aqueous layer in the separating funnel at the start of Step **6**. Justify your answer.

(1)

The aqueous layer is on top, because water has a lower density (1.00 g cm^{-3}) than 1-bromobutane (1.27 g cm^{-3}).

(ii) Concentrated hydrochloric acid is used to remove any unreacted butan-1-ol in the mixture in Step **7**.

Give the reasons for carrying out Steps **8**, **9** and **10**.

(3)

Step 8: aqueous sodium hydrogencarbonate neutralises (reacts with and removes) the remaining hydrochloric acid (H^+ ions) in the mixture.

Step 9: this reaction produces carbon dioxide gas, so the tap is opened to release the CO_2 and prevent a build-up of pressure in the funnel.

Step 10: anhydrous sodium sulfate is a drying agent; it absorbs (removes) water from the 1-bromobutane, so the cloudy liquid becomes clear.

(iii) Give a suitable temperature **range** over which to collect the pure 1-bromobutane in the redistillation in Step **11**.

(1)

100 °C to 104 °C

(iv) The volume of 1-bromobutane collected was 12.0 cm^3.

Calculate the number of molecules of 1-bromobutane produced in this experiment.

Give your answer to an appropriate number of significant figures.

(2)

mass = 12.0 × 1.27 = 15.24 g

mol 1-bromobutane = 15.24 ÷ 136.9 = 0.11132 mol

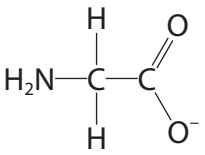
molecules = 0.11132 × 6.02 × 10^{23} = 6.70 × 10^{22}

(Total for Question 8 = 15 marks)

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9 Some organic compounds contain metals.

(a) Glycinate ions are formed from the amino acid glycine.



glycinate ion

(i) Explain the effect, if any, of an aqueous solution containing glycinate ions on plane-polarised monochromatic light.

(2)

The glycinate ion has no chiral carbon: the central carbon is bonded to two H atoms, so it does not have four different groups attached and is superimposable on its mirror image (no optical isomers).

So the solution has no effect: the plane of polarisation of the light is not rotated.

(ii) A hot aqueous solution of glycine is added to a hot solution of copper(II) ethanoate.
When the mixture is cooled, crystals of copper(II) glycinate are formed.

Write the equation for this reaction.
State symbols are not required.

(2)

$$(CH_3COO)_2Cu + 2NH_2CH_2COOH \rightarrow (NH_2CH_2COO)_2Cu + 2CH_3COOH$$

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(iii) In an experiment, the crystals are filtered, weighed and the percentage yield calculated.

Student **1** obtained a yield of 102.6%.

Student **2** obtained a yield of 56.4%.

The expected yield is 82% and the students carried out the calculation correctly.

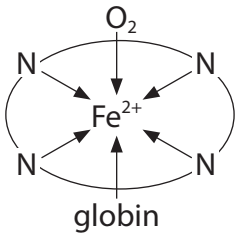
Discuss possible reasons for the yields obtained by these students.

(4)

Student 1 (102.6 %, more than 100 %): the crystals were not dry (still damp) when they were weighed, and/or the crystals contained impurities such as unreacted glycine, which added to the mass.

Student 2 (56.4 %): the reaction may have been incomplete, or not all of the copper(II) glycinate crystallised, so some was left in solution in the filtrate. Some crystals may also have been lost, e.g. left on the walls of the beaker or lost during filtration and transfer.

(b) Haemoglobin is an iron(II) complex. It carries oxygen around the body.
Part of the structure of haemoglobin is shown.



The four nitrogen atoms are part of a multidentate ligand in the haem group.

Explain why inhaling carbon monoxide can be fatal.

(2)

CO replaces (displaces) the O_2 as a ligand on the Fe^{2+} ion. CO binds much more strongly, almost irreversibly, to Fe^{2+}, so haemoglobin cannot carry oxygen around the body to the cells.

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*(c) Grignard reagents contain a metal.

Discuss how Grignard reagents are formed and used in adding one or more carbon atoms to the carbon chain in 1-bromopropane to produce primary, secondary and tertiary alcohols and a carboxylic acid.

Include a suitable example for each reaction and give reagents, conditions and products. You may include equations in your answer.

(6)

Grignard reagents are formed by reacting a halogenoalkane with magnesium in dry ether (dry ethoxyethane), warming under reflux. The ether must be dry because Grignard reagents react with water.

$CH_3CH_2CH_2Br + Mg \rightarrow CH_3CH_2CH_2MgBr$ (propylmagnesium bromide)

The Grignard reagent is then reacted, still in dry ether, with a carbonyl compound or carbon dioxide. The propyl group bonds to the carbon atom of the C=O, so the carbon chain is lengthened. The intermediate formed is then hydrolysed by adding dilute hydrochloric acid, $H^+(aq)$, to give the product.

Primary alcohol: react with methanal, HCHO, then dilute acid, to form butan-1-ol, $CH_3CH_2CH_2CH_2OH$ (one carbon atom added).

$CH_3CH_2CH_2MgBr + HCHO \rightarrow CH_3CH_2CH_2CH_2OMgBr$, then $+ H_2O \rightarrow CH_3CH_2CH_2CH_2OH + Mg(OH)Br$

Secondary alcohol: react with ethanal, CH_3CHO, then dilute acid, to form pentan-2-ol, $CH_3CH_2CH_2CH(OH)CH_3$ (two carbon atoms added).

Tertiary alcohol: react with a ketone, propanone, CH_3COCH_3, then dilute acid, to form 2-methylpentan-2-ol, $CH_3CH_2CH_2C(OH)(CH_3)CH_3$ (three carbon atoms added).

Carboxylic acid: react with carbon dioxide (dry ice, solid CO_2), then dilute acid, to form butanoic acid, $CH_3CH_2CH_2COOH$ (one carbon atom added).

$CH_3CH_2CH_2MgBr + CO_2 \rightarrow CH_3CH_2CH_2COOMgBr$, then $+ H^+ \rightarrow CH_3CH_2CH_2COOH$

So the number of carbon atoms added, and the type of product, depend on the carbonyl compound (or CO_2) chosen.

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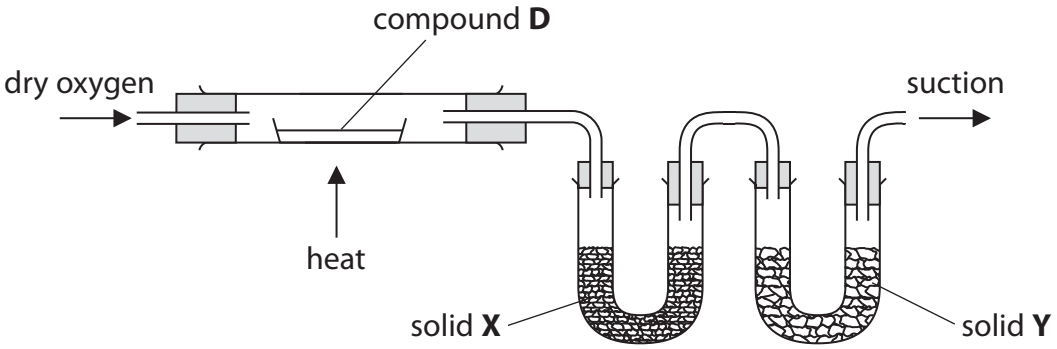
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(Total for Question 9 = 16 marks)

10 Organic compound **D** contains the elements carbon, hydrogen, oxygen and nitrogen only.

(a) A sample of **D** was burned completely in the apparatus shown.
Solid **X** absorbed the water formed in the combustion.
Solid **Y** absorbed the carbon dioxide.



(i) The masses of solids **X** and **Y** increased during the experiment.

Explain the effect, if any, on the changes in mass of **X** and **Y** if the oxygen gas was not dry.

(3)

The increase in mass of X would be greater, but the increase in mass of Y would stay the same.

This is because X would absorb the water (moisture) in the oxygen as well as the water formed in the combustion.

Y stays the same because the moisture has already been absorbed by X, and Y only absorbs carbon dioxide, the amount of which does not change.

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(ii) On combustion in dry oxygen, 3.36 g of **D** produced 0.72 g of water and 5.28 g of carbon dioxide.
This sample of **D** also contained 0.56 g of nitrogen.

Use these data to calculate the empirical formula of compound **D**.

You **must** show your working.

(5)

C: mol CO_2 = 5.28 ÷ 44.0 = 0.12 mol, so mol C = 0.12 (mass C = 1.44 g)

H: mol H_2O = 0.72 ÷ 18.0 = 0.04 mol, so mol H = 0.08 (mass H = 0.08 g)

N: mol N = 0.56 ÷ 14.0 = 0.04 mol

O: mass O = 3.36 − (1.44 + 0.08 + 0.56) = 1.28 g

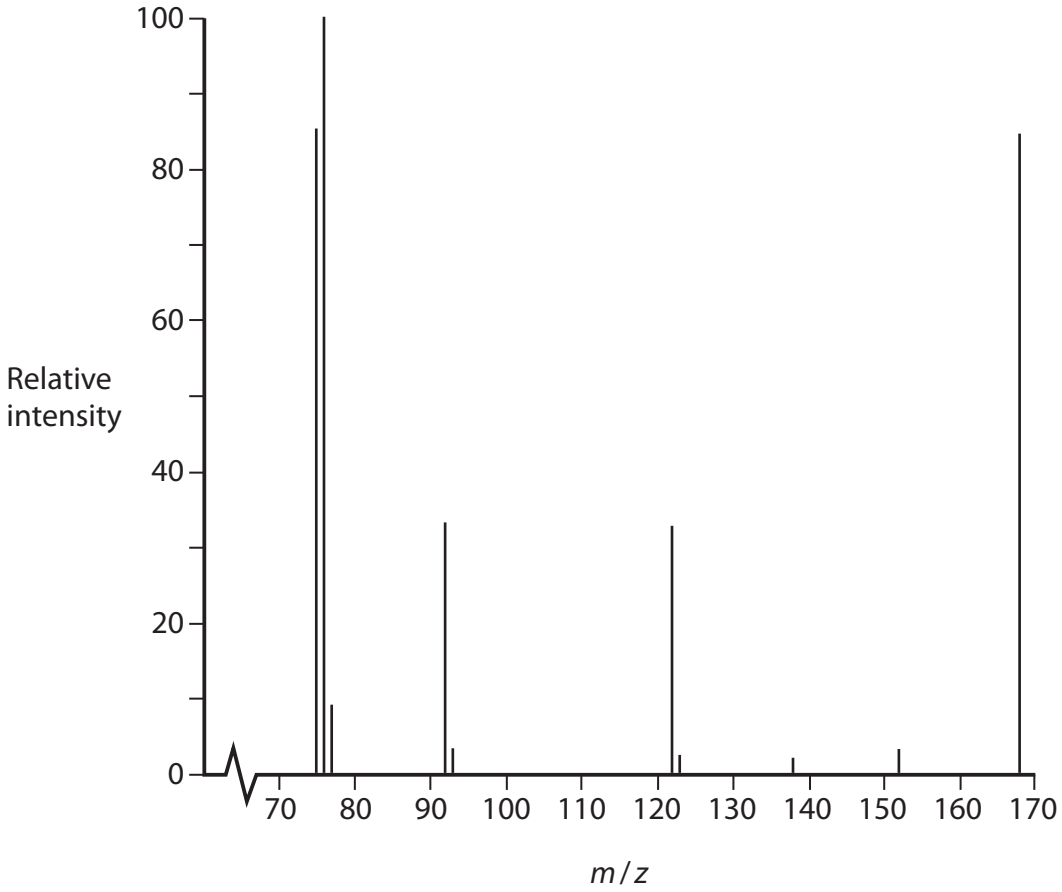
mol O = 1.28 ÷ 16.0 = 0.08 mol

C : H : N : O = 0.12 : 0.08 : 0.04 : 0.08 = 3 : 2 : 1 : 2

Empirical formula = $C_3H_2NO_2$

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(b) Part of the mass spectrum of **D** is shown.



Deduce the molecular formula of **D**. Justify your answer.

(2)

The molecular ion peak is at m/z = 168, so the M_r of D is 168.

M_r of $C_3H_2NO_2$ = 84, and 168 ÷ 84 = 2, so the molecular formula is $C_6H_4N_2O_4$.

(c) Compound **D** contains a benzene ring.

(i) Give the molecular formula of the species that causes the peak at $m/z = 76$ in the mass spectrum of **D**.

(1)

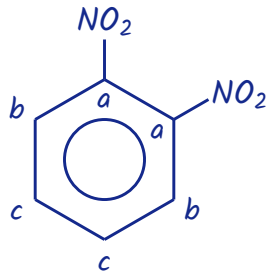
$C_6H_4^+$

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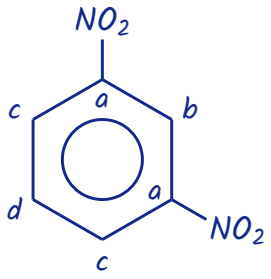
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(ii) Draw the structures of the **three** possible isomers of **D** containing a benzene ring.

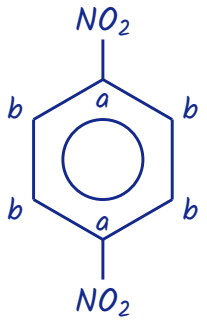
(2)



1,2-dinitrobenzene



1,3-dinitrobenzene



1,4-dinitrobenzene

(iii) The ^{13}C NMR spectrum of compound **D** has four peaks.

Identify the structure of **D**. Justify your answer by labelling the different carbon environments in **all** the structures drawn in (c)(ii).

(3)

The carbon environments are labelled a, b, c, d on the structures in (c)(ii).

D is 1,3-dinitrobenzene, because it is the only isomer with four different carbon environments (a, b, c and d), so it gives four peaks.

1,2-dinitrobenzene has only three carbon environments (a, b, c) and 1,4-dinitrobenzene has only two (a, b), so they would give three and two peaks.

(Total for Question 10 = 16 marks)

TOTAL FOR PAPER = 120 MARKS

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The Periodic Table of Elements

1 (1)	2 (2)											3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
6.9 Li lithium 3	9.0 Be beryllium 4											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							

Key: relative atomic mass / **atomic symbol** / name / atomic (proton) number

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

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
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

* Lanthanide series

* Actinide series

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