Surname	StemUp Model Solution	Centre Number	Candidate Number
First name(s)			2

GCE A LEVEL

A410U10-1

Z22-A410U10-1

MONDAY, 13 JUNE 2022 – MORNING

CHEMISTRY – A level component 1

Physical and Inorganic Chemistry

2 hours 30 minutes

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	Question	Maximum Mark	Mark Awarded
Section A	1. to 8.	15	
Section B	9.	25	
	10.	21	
	11.	15	
	12.	17	
	13.	27	
	Total	120	

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ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.
Do not use gel pen or correction fluid.
You may use a pencil for graphs and diagrams only.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions.
Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

Candidates are advised to allocate their time appropriately between **Section A (15 marks)** and **Section B (105 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 120.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.9**(c)(i) and **Q.13**(a).

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SECTION A

Answer **all** questions.

1. Write the electron configuration of a silicon atom. [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

2. The electronegativity values of some elements are listed in the table.

Element	Al	C	Cl	H	O
Electronegativity value	1.5	2.5	3.0	2.1	3.5

(a) Label the bonds below with δ+ and δ– to show any dipoles that are present. [1]

δ+ δ–
C—Cl

δ+ δ–
H—Cl

δ– δ+
O—Cl

(b) Give a reason why aluminium chloride is covalent. [1]

The difference in electronegativity between Al and Cl (3.0 – 1.5 = 1.5) is not big enough for the compound to be ionic, as it is less than 2.0.

3. Draw a dot-and-cross diagram to show the bonding in the molecule BeF_2. [1]



dots = F electrons, crosses = Be electrons

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4. Explain why the first ionisation energy of nitrogen is higher than that of oxygen. [2]

In N ($2p^3$) the outer electron is unpaired, but in O ($2p^4$) the electron removed is paired with another in the same p orbital.

Paired electrons repel each other more strongly, so less energy is needed to remove one from O.

5. Sodium hydroxide is a strong base.

(a) Calculate the pH of a 0.200 mol dm^{-3} solution of NaOH at 298 K. [2]

$[H^+] = K_w / [OH^-] = 1.00 \times 10^{-14} / 0.200 = 5.00 \times 10^{-14}$ mol dm^{-3}

$pH = -\log(5.00 \times 10^{-14})$

pH = 13.3

(b) Suggest, giving a reason, the pH of a solution of sodium ethanoate. [1]

pH about 9 (alkaline), because sodium ethanoate is the salt of a weak acid and a strong base: the ethanoate sets up the equilibrium $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$, removing H^+ ions.

6. The first ionisation energy of magnesium is 738 kJ mol^{-1}. Calculate the frequency of light that would correspond to this energy. [2]

energy per atom = $738\,000 / 6.02 \times 10^{23} = 1.226 \times 10^{-18}$ J

frequency = $E / h = 1.226 \times 10^{-18} / 6.63 \times 10^{-34}$

Frequency = 1.85×10^{15} Hz

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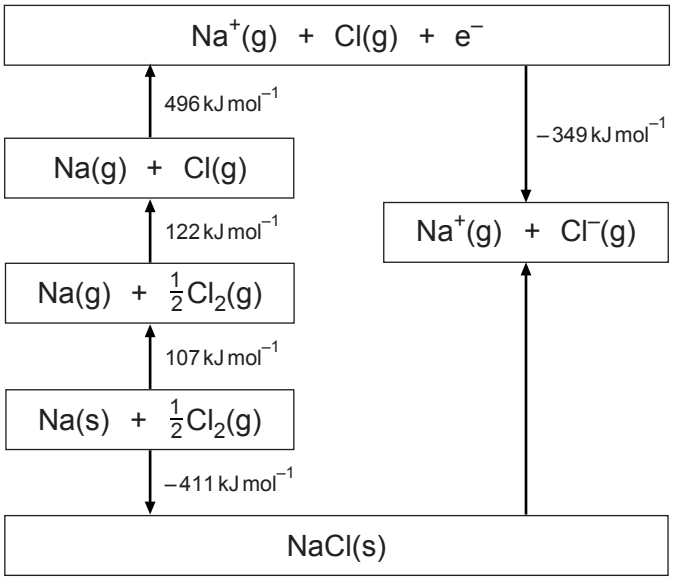
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7. Give the most stable oxidation state of lead, giving a reason why this is more stable than its other common oxidation state. [1]

+2 (Pb^{2+}), due to the inert pair effect (which increases down Group 4): the $6s^2$ electrons are reluctant to take part in bonding.

8. The Born-Haber cycle shown represents the enthalpy changes during the formation of sodium chloride.



(a) State the name of the enthalpy change that has a value of –349 kJ mol^{-1}. [1]

(first) electron affinity of chlorine

(b) Calculate the enthalpy change of lattice breaking of sodium chloride. [2]

ΔH(lattice breaking) = −(−411) + 107 + 122 + 496 + (−349)

Enthalpy change of lattice breaking = *+787* kJ mol^{-1}

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SECTION B

Answer **all** questions.

9. Cerium is a metallic element in the f-block of the Periodic Table.

(a) Cerium has four natural isotopes. The relative isotopic masses and percentage abundances of these isotopes are given in the table.

Isotope	Relative isotopic mass	Percentage abundance
^{136}Ce	135.9	0.19
^{138}Ce	137.9	0.25
^{140}Ce	139.9	88.45
^{142}Ce	141.9	11.11

(i) State what is meant by the term 'relative isotopic mass'. [1]

The mass of an atom of the isotope relative to 1/12 of the mass of an atom of carbon-12.

(ii) Calculate the relative atomic mass of cerium, giving your answer to **four** significant figures. You **must** show your method. [3]

$A_r = [(135.9 \times 0.19) + (137.9 \times 0.25) + (139.9 \times 88.45) + (141.9 \times 11.11)] / 100$

$= 14\,011.0 / 100 = 140.11$

$A_r(Ce) =$ *140.1*

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(b) Some radioactive isotopes of cerium can be synthesized by nuclear reactions.

Radioisotope of cerium	Type of decay	Half-life
^{134}Ce	electron capture	3 days
^{139}Ce	electron capture	140 days
^{143}Ce	β^- emission	33 hours
^{144}Ce	β^- emission	280 days

(i) Identify the isotopes produced from ^{134}Ce and ^{143}Ce in their radioactive decay processes. [2]

Decay of ^{134}Ce

Element symbol *La* Mass number *134*

Decay of ^{143}Ce

Element symbol *Pr* Mass number *143*

(ii) One method of measuring the half-life of isotopes with half-lives of a few hours to a few days is to take a sample of known composition and record low resolution mass spectra at regular intervals to measure the height of the peaks of each mass.

Suggest why this method would not be suitable for any of these isotopes. [2]

Neither electron capture nor β^- emission changes the mass number, so there is no change in mass.

The parent and daughter isotopes would give one peak at the same m/z in the low resolution mass spectrum, so they cannot be distinguished.

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(iii) Another method of measuring the half-life is to measure the level of radioactivity over time.

An initial sample contained a mixture of equal amounts of ^{139}Ce and ^{144}Ce. After a period of storage, the β^- emission due to ^{144}Ce had dropped to 25% of its initial value.

By considering the decay of both isotopes, calculate the percentage of the cerium remaining that is ^{139}Ce. [3]

^{144}Ce has dropped to 25%, so 2 half-lives have passed = 2 × 280 = 560 days

560 days = 560 / 140 = 4 half-lives of ^{139}Ce, so $(½)^4$ = 6.25% of ^{139}Ce remains

percentage ^{139}Ce = 6.25 / (25 + 6.25) × 100

Percentage = 20 %

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(c) Ce^{4+} ions can be used as oxidising agents in redox titrations, such as those involving the oxidation of Fe^{2+}.

$$Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

(i) A titration requires 250 cm^3 of a standard solution of $Ce(SO_4)_2$ of concentration 0.200 mol dm^{-3}.

Describe how this standard solution could be produced. You should include the mass of $Ce(SO_4)_2$ that would be required. [6 QER]

Moles of $Ce(SO_4)_2$ = 0.200 × 250/1000 = 0.0500 mol. M_r of $Ce(SO_4)_2$ = 140 + 2(32.1 + 64.0) = 332.2, so mass required = 0.0500 × 332.2 = 16.6 g.

1. Weigh 16.6 g of $Ce(SO_4)_2$ accurately into a clean beaker using a balance.

2. Add a small amount of deionised water and stir with a glass rod until all the solid has dissolved.

3. Transfer the solution into a 250 cm^3 volumetric flask using a funnel.

4. Wash the beaker, glass rod and funnel with deionised water and transfer all the washings into the flask so no solid is lost.

5. Add deionised water until the bottom of the meniscus is on the graduation line (last drops with a dropping pipette, line at eye level).

6. Stopper the flask and mix thoroughly by inverting several times.

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(ii) A sample of 0.680 g of an iron ore containing $FeCO_3$ as the only iron-containing compound was dissolved in a suitable acid. This was titrated against the standard $Ce^{4+}(aq)$ solution produced in part (i) and it required 22.45 cm^3 of the standard solution for complete reaction.

Calculate the mass of $FeCO_3$ present in the ore sample. [3]

$n(Ce^{4+}) = 22.45 \times 0.200 / 1000 = 4.49 \times 10^{-3}$ mol

$Ce^{4+} : Fe^{2+} = 1 : 1$, so $n(Fe^{2+}) = n(FeCO_3) = 4.49 \times 10^{-3}$ mol

$M_r(FeCO_3) = 55.8 + 12.0 + 48.0 = 115.8$

mass $= 4.49 \times 10^{-3} \times 115.8$

Mass of $FeCO_3$ = 0.520 g

(iii) A separate ore contains both FeO and $FeCO_3$.

Explain why the method in part (ii) would **not** be suitable for finding the mass of $FeCO_3$ in this ore and outline a method that would be suitable. [3]

The titration measures all the Fe^{2+} present, from FeO as well as $FeCO_3$, not just that in $FeCO_3$.

Instead, add excess acid to a weighed sample of the ore and measure the volume of CO_2 gas produced using a gas syringe. Only $FeCO_3$ gives CO_2, so moles of $FeCO_3$ = moles of CO_2 (V/24.5 at RTP).

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(d) Ce^{4+} ions can be produced in solution by oxidation of Ce^{3+} ions.

Use the data below to identify suitable oxidising agent(s) for this process, giving your reasoning. [2]

	Standard electrode potential, E^{θ}/V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.78
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1.61
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2 + 3H_2O$	+1.52
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.23

H_2O_2: its standard electrode potential (+1.78 V) is more positive than that of Ce^{4+}/Ce^{3+} (+1.61 V), so it is able to oxidise Ce^{3+}. EMF = +1.78 – (+1.61) = +0.17 V, positive, so the reaction is feasible.

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10. There are many organic acids produced by living things. These include citric acid in fruit and lactic acid produced during anaerobic respiration.

(a) A solution of citric acid is found to have a pH of 3.2. Calculate the concentration of H^+ ions in this solution. [1]

$[H^+] = 10^{-pH} = 10^{-3.2}$

Concentration = 6.31×10^{-4} mol dm^{-3}

(b) Citric acid is a tribasic acid, represented as H_3(citrate), as it contains three acidic hydrogen atoms in each molecule.

It reacts with sodium hydrogencarbonate in an endothermic reaction.

$$H_3(citrate)(aq) + 3NaHCO_3(s) \longrightarrow Na_3(citrate)(aq) + 3H_2O(l) + 3CO_2(g)$$

(i) Suggest why this reaction is feasible even though the reaction is endothermic. [2]

For a reaction to be feasible ΔG must be negative (overall entropy must increase).

ΔS is positive as a gas is produced, which has a much greater entropy than the reactants, so $-T\Delta S$ is greater than ΔH, making ΔG negative.

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(ii) A sample of 50.0 cm^3 of aqueous citric acid was treated with excess aqueous $NaHCO_3$ and the volume and temperature of the carbon dioxide gas produced was measured.

A total of 72.2 cm^3 of carbon dioxide was produced at a temperature of 16 °C and 1 atm pressure. Calculate the initial concentration of the aqueous citric acid. [3]

$T = 16 + 273 = 289\ K;\ \ V = 72.2 \times 10^{-6}\ m^3;\ \ p = 1.01 \times 10^5\ Pa$

$n(CO_2) = pV / RT = (1.01 \times 10^5 \times 72.2 \times 10^{-6}) / (8.31 \times 289) =$

$3.036 \times 10^{-3}\ mol$

$n(citric\ acid) = 3.036 \times 10^{-3} / 3 = 1.012 \times 10^{-3}\ mol$

$concentration = 1.012 \times 10^{-3} / 0.0500$

Concentration = 2.02×10^{-2} ..... mol dm^{-3}

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(iii) In a separate experiment, a student studies the enthalpy change during the reaction between aqueous citric acid and solid sodium hydrogencarbonate, $NaHCO_3$.

He follows the method below.

1. Measure 50.0 cm^3 of citric acid of concentration 0.500 mol dm^{-3} and place in a polystyrene cup with a lid.
2. Place a thermometer with 0.1 °C divisions through the lid of the cup and measure the temperature of the citric acid every 30 seconds for 3 minutes.
3. At 3 minutes add 2.300 g of powdered $NaHCO_3$ and mix thoroughly.
4. Measure the temperature every 30 seconds for a further 5 minutes.
5. Plot a graph of the data and use this to find the maximum temperature change.

I. Explain why the temperature is measured every 30 seconds for 3 minutes before adding the $NaHCO_3$. [1]

To ensure the temperature has become constant (thermal equilibrium with the surroundings) before the reaction starts.

II. Explain why the temperature is measured every 30 seconds for 5 minutes after adding the $NaHCO_3$. [1]

To allow for adjustment for heat gained from the surroundings, by extrapolating back to 3 minutes.

III. Calculate the number of moles of both citric acid and sodium hydrogencarbonate used in the experiment and hence show which is in excess. [3]

$n(\text{citric acid}) = 0.500 \times 50.0 / 1000 = 0.0250$ mol

$n(NaHCO_3) = 2.300 / 84.0 = 0.0274$ mol

each citric acid reacts with 3 $NaHCO_3$, so 0.0250 mol citric acid can react with $3 \times 0.0250 = 0.0750$ mol $NaHCO_3$

Only 0.0274 mol $NaHCO_3$ is present (less than 0.0750 mol), so citric acid is in excess.

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IV. The maximum temperature change, ΔT, is found to be –2.3 °C.

Calculate the percentage error in this measurement. [1]

% error = (2 × 0.05) / 2.3 × 100

Percentage error = 4.3 ..... %

V. The experiment is repeated using different conditions to produce a larger temperature change. Using 25.0 cm^3 of 0.800 mol dm^{-3} citric acid solution and excess sodium hydrogencarbonate gives a temperature change of –10.1 °C.

Calculate the enthalpy change for the reaction. [3]

H_3(citrate) + $3NaHCO_3$ ⟶ Na_3(citrate) + $3H_2O$ + $3CO_2$

energy = m × c × ΔT = 25.0 × 4.18 × 10.1 = 1055 J (absorbed)

moles reacting = n(citric acid) = 0.800 × 25.0 / 1000 = 0.0200 mol

ΔH = +1055 / 0.0200 = +52 750 J mol^{-1}

ΔH = +52.8 ..... kJ mol^{-1}

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(c) Lactic acid is a weak monobasic acid with a K_a of 1.40×10^{-4} mol dm^{-3}.

(i) Calculate the concentration of a lactic acid solution of pH 2.89. [2]

$[H^+] = 10^{-2.89} = 1.288 \times 10^{-3}$ mol dm^{-3}

$K_a = [H^+]^2 / [HA]$, so $[HA] = [H^+]^2 / K_a$

$= (1.288 \times 10^{-3})^2 / 1.40 \times 10^{-4}$

Concentration = 0.0118 mol dm^{-3}

(ii) A mixture of lactic acid and sodium lactate forms a buffer solution.

I. State what is meant by a 'buffer solution'. [1]

A solution that keeps the pH (relatively) constant when small amounts of acid or base are added.

II. Calculate the pH of a buffer solution formed by mixing 100 cm^3 of 0.20 mol dm^{-3} aqueous lactic acid with 50 cm^3 of 0.20 mol dm^{-3} aqueous sodium lactate. [3]

n(lactic acid) = $0.100 \times 0.20 = 0.020$ mol; n(lactate) = $0.050 \times 0.20 = 0.010$ mol

same volume, so [acid] = 2 × [salt]

$[H^+] = K_a \times [acid] / [salt] = 1.40 \times 10^{-4} \times 2 = 2.80 \times 10^{-4}$ mol dm^{-3}

$pH = -\log(2.80 \times 10^{-4})$

pH = 3.55

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11. Seawater contains a wide range of compounds formed from atoms of many different elements. The ten most abundant elements are shown in the table.

Element	Abundance / g dm^{-3}
oxygen	857
hydrogen	108
chlorine	19.4
sodium	10.8
magnesium	1.29
sulfur	0.905
calcium	0.412
potassium	0.399
bromine	0.0673
carbon	0.0281

(a) Seawater contains a range of oxyanions such as carbonate and sulfate which contain a small proportion of the oxygen atoms present.

Assuming all hydrogen atoms present are contained in water molecules, use the data in the table to calculate the percentage of the oxygen atoms that are present in water molecules. [2]

oxygen atoms in water = (108 / 1.01) × ½ = 53.465 mol

total oxygen atoms = 857 / 16.0 = 53.5625 mol

percentage = 53.465 / 53.5625 × 100

Percentage of oxygen atoms = *99.8* ..... %

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(b) Flame tests can identify many of the metal ions present in seawater.

(i) Give the colours expected in flame tests for each of the metal ions present. [2]

sodium golden yellow

magnesium no colour

calcium brick red

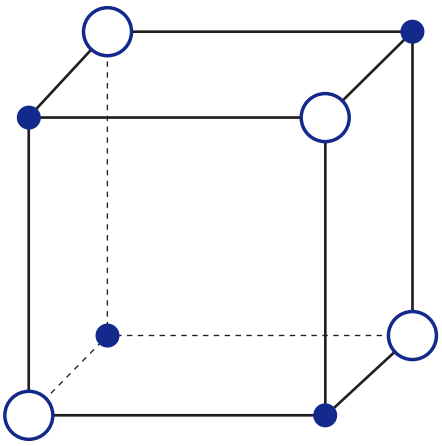
potassium lilac

(ii) Suggest why flame tests are not always effective for identifying the metal ions present in **mixtures** like seawater. [1]

In a mixture the colours can mask (hide) each other, e.g. intense yellow sodium hides the others.

(c) It is possible to form crystals of sodium chloride by evaporation of seawater.

Complete and label the diagram below to show the crystal structure of sodium chloride. [2]



● = Na^+ ion

○ = Cl^- ion

ions alternate at the corners (face centred cubic)

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(d) Evaporation of seawater can also form hydrated salts, $MX_n.aH_2O$, that include common ions formed from the elements listed in the table. One such salt has several different hydrated forms, including a=6, a=4 and a=2.

A sample of $MX_n.6H_2O$ is heated and loses 16.44% of its initial mass as it forms $MX_n.4H_2O$. Identify MX_n. You **must** show your working. [3]

mass lost = $2H_2O$ = 2 × 18.02 = 36.04, which is 16.44% of M_r of $MX_n.6H_2O$

$M_r(MX_n.6H_2O)$ = 36.04 × 100 / 16.44 = 219.2

$M_r(MX_n)$ = 219.2 − (6 × 18.02) = 111.1

$CaCl_2$ = 40.1 + (2 × 35.5) = 111.1, so the salt is calcium chloride

Identity of salt ..... $CaCl_2$ (as $CaCl_2.6H_2O$) .....

(e) Bubbling chlorine gas through seawater causes an orange colouration to appear as small amounts of $Br_2(aq)$ are formed.

(i) Write an ionic equation for this process. [1]

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

(ii) Excess chlorine is bubbled through a sample of seawater and 0.0673 g dm^{-3} of Br_2 is produced. Find the concentration of $Br_2(aq)$ in mol dm^{-3}. [1]

concentration = 0.0673 / (2 × 79.9) = 0.0673 / 159.8

Concentration = ... 4.21×10^{-4} ..... mol dm^{-3}

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(f) The carbon present in seawater exists as dissolved carbon dioxide, HCO_3^- ions and CO_3^{2-} ions. There are complex equilibria between these species, which can be simplified as follows.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

These equilibria are important when discussing the effects of increased atmospheric carbon dioxide and climate change.

More carbon dioxide in the atmosphere can lead to a decrease in the pH of the oceans. This can cause problems for marine creatures that form shells out of carbonate minerals. Use the equilibria to explain why this is so. [3]

A decrease in pH means a higher concentration of H^+ ions (more CO_2 dissolves and reacts with water, shifting the first two equilibria to the right). The increased concentration of H^+ shifts the equilibrium $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ to the left. This produces less CO_3^{2-}, so marine creatures cannot form their carbonate shells.

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12. A transition metal compound $[ML_n]X_2$ was analysed and the following observations were made.

Crystal structure	The compound contains an octahedral transition metal complex with anions X^- formed from single atoms.
Addition of sodium hydroxide solution and warming	A pungent-smelling gas is released that turns moist red litmus paper blue. A precipitate with an unfamiliar colour forms when the solution cools. This precipitate does not dissolve in excess sodium hydroxide.
Addition of concentrated sulfuric acid	Coloured fumes are released with a smell of rotten eggs.
Addition of ligand $H_2NCH_2CH_2NH_2$, represented by the abbreviation 'en'	A new complex is formed with formula $[M(en)_3]X_2$. The mass of this compound is 18.82% greater than the original compound.

(a) State which anions, X^-, are present in the compound, giving a reason for your answer. [2]

Iodide ions, I^-, because the anion is monatomic and it produces a smell of rotten eggs (H_2S) and coloured (purple) iodine fumes with concentrated H_2SO_4.

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(b) The compound forms a coloured precipitate when sodium hydroxide is added.

(i) Explain why transition metals form coloured compounds. [3]

The ligands split the d-orbitals into two higher energy and three lower energy orbitals.

Electrons absorb a specific amount of energy from visible light to move from the lower to the higher energy level.

The colour seen is the remaining colours that are not absorbed, which are transmitted or reflected.

(ii) The precipitate does not dissolve when excess sodium hydroxide is added. State what information this provides about metal M. [1]

M (its hydroxide) is not amphoteric.

(c) State which ligands, L, are present in the complex ion, giving a reason for your answer. [2]

Ammonia, NH_3, because the gas released on warming with NaOH, which turns moist red litmus blue, is ammonia.

(d) State the value of n, the number of ligands present in the complex. [1]

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(e) Use the reaction with $H_2NCH_2CH_2NH_2$ to calculate M_r for $[ML_n]X_2$ and hence find the identity of the transition metal, M.

You **must** show your working. [3]

mass of six NH_3 ligands = 6 × 17.03 = 102.18

mass of three en ligands ($C_2H_8N_2$) = 3 × 60.08 = 180.24

difference = 180.24 − 102.18 = 78.06, which is 18.82% of the original M_r

original M_r = 78.06 × 100 / 18.82 = 414.8

M_r due to metal = 414.8 − 102.18 − (2 × 127) = 58.6, so M is nickel

M_r = *414.8*

M is *nickel, Ni*

(f) Write the formula of the complex cation, $[ML_n]^{a+}$. [1]

$[Ni(NH_3)_6]^{2+}$

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(g) The metal hydroxide produced on reaction with sodium hydroxide, $M(OH)_2$, decomposes on heating in a similar manner to the decomposition of Group 2 hydroxides.

(i) Write an equation for the thermal decomposition of $M(OH)_2$. [1]

$Ni(OH)_2 \rightarrow NiO + H_2O$

(ii) Give the trend in the thermal stability of the hydroxides in Group 2. [1]

The hydroxides become more thermally stable down the group.

(iii) The Group 2 metal carbonates also decompose upon heating.

Calculate the minimum temperature required to decompose $MgCO_3$. [2]

$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$ $\quad \Delta H^\theta = 117\,kJ\,mol^{-1}$

$\Delta S^\theta = 175\,J\,K^{-1}\,mol^{-1}$

at the minimum temperature ΔG = 0, so T = ΔH / ΔS

T = 117 000 / 175

Temperature = *669* K

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13. The elements of Group 5 react with hydrogen to form compounds of formula XH_3. Some information regarding the physical properties of these compounds is shown in the table.

Compound	Formula	Boiling temperature / °C	Solubility in water / g dm^{-3}
ammonia	NH_3	–33	470
phosphane	PH_3	–83	0.312
arsane	AsH_3	–63	0.710
stibane	SbH_3	–17	4.24

(a) Identify and explain the patterns seen in these physical properties. [6 QER]

Boiling temperature drops from ammonia (–33 °C) to phosphane (–83 °C), then increases from phosphane to arsane to stibane (–17 °C). Ammonia is much more soluble in water than the others, which have very low solubility. NH_3 has H bonded to very electronegative N, creating a large dipole with an exposed hydrogen nucleus, so ammonia forms hydrogen bonds between its molecules. PH_3, AsH_3 and SbH_3 cannot form hydrogen bonds and only have van der Waals forces between molecules.

Hydrogen bonds are stronger than van der Waals forces, so more energy is needed to overcome the forces between ammonia molecules than phosphane molecules, giving ammonia a higher boiling temperature.

Going down the group from PH_3 to SbH_3 the molecules contain more electrons, so there are stronger van der Waals forces between molecules, giving a higher boiling temperature.

Ammonia can form hydrogen bonds with water molecules so it is very soluble; the others cannot, so they are almost insoluble.

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(b) Use VSEPR theory to predict the shape of the PH_3 molecule, giving reasons for your answer. [3]

P has three bond pairs and one lone pair of electrons.

Electron pairs repel to be as far from each other as possible, and the lone pair repels more than bond pairs.

So the shape is pyramidal (bond angle less than 109.5°).

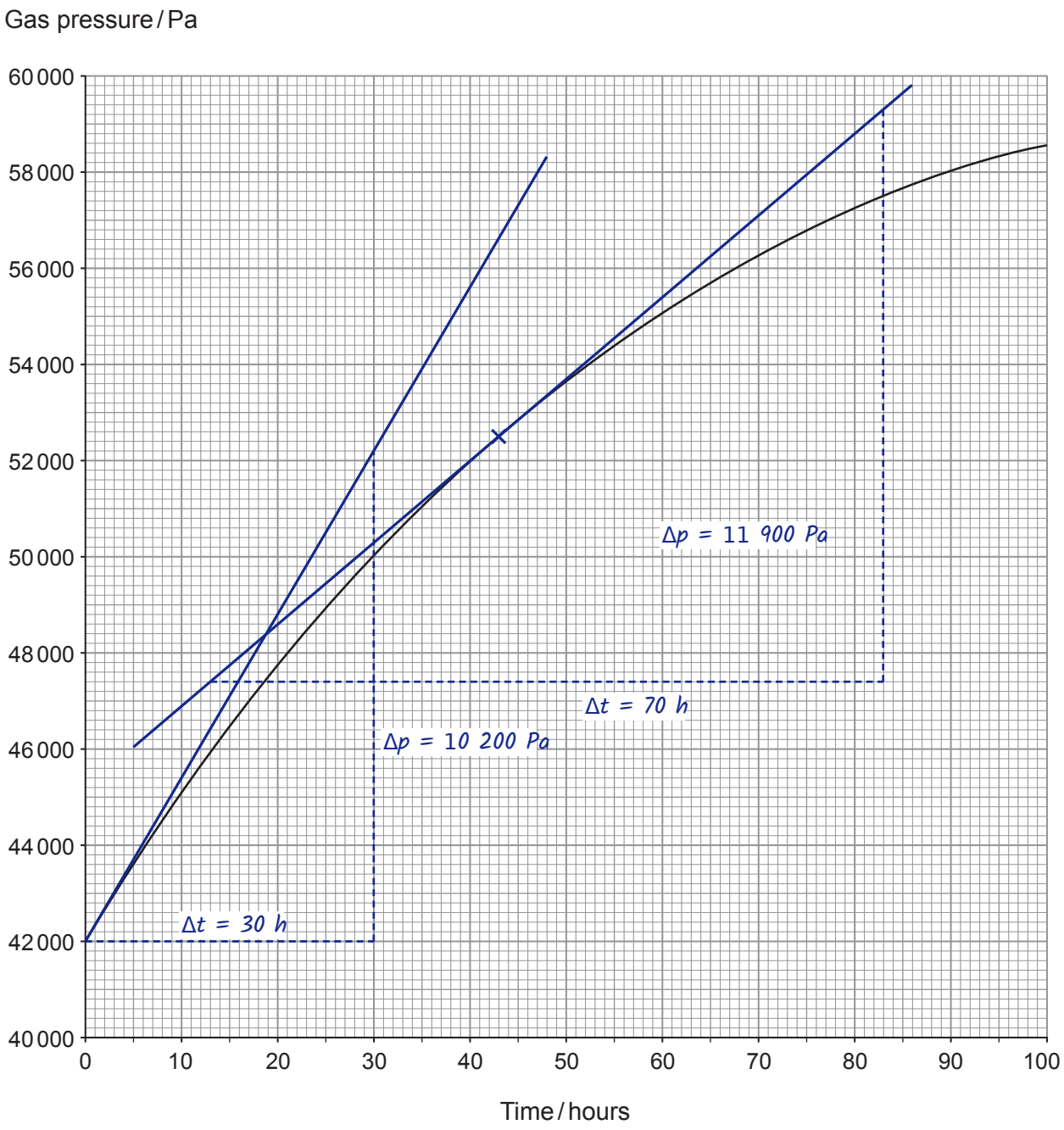
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(c) Stibane is a gas that decomposes slowly at a temperature of 350 °C.

$$2SbH_3(g) \longrightarrow 2Sb(s) + 3H_2(g)$$

The decomposition of stibane was studied in a sealed vessel, with the pressure measured over a period of 100 hours. The results are shown on the graph.



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(i) The initial pressure in the vessel was 42 000 Pa. Calculate the pressure in the vessel when all the stibane had decomposed. [2]

$2SbH_3 \rightarrow 3H_2$: 2 mol of gas give 3 mol of gas, so the final pressure is 1½ times the initial

pressure = 1.5 × 42 000

Pressure = 63 000 Pa

(ii) Calculate the initial rate of change of pressure in $Pa\,hr^{-1}$. [2]

tangent drawn at t = 0 on the graph:

gradient = (52 200 − 42 000) / (30 − 0) = 10 200 / 30

Rate of change of pressure = 340 $Pa\,hr^{-1}$

(iii) Use the initial pressure and your answer to part (i) to calculate the pressure in the vessel when half the stibane had decomposed.

Use this and the graph to show that the reaction is first order with respect to stibane. [4]

pressure = (42 000 + 63 000) / 2

Pressure when half the stibane had decomposed = 52 500 Pa

tangent at 52 500 Pa (t = 43 h):

rate of change of pressure = 11 900 / 70 = 170 Pa hr^{-1}

initial rate of change of pressure from part (ii) = 340 Pa hr^{-1}

When the concentration of SbH_3 is halved the rate is halved, so rate ∝ $[SbH_3]$: first order.

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(d) Ammonia is produced industrially using the Haber process.

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

The reaction traditionally used iron-based catalysts which reduce the activation energy of the reaction to 101.4 kJ mol^{-1}. Newer catalysts have been developed using ruthenium which reduce the activation energy further to 64.0 kJ mol^{-1}.

(i) These are examples of heterogeneous catalysts.

State what is meant by a 'heterogeneous' catalyst. [1]

A catalyst that is in a different physical state (phase) from the reactants.

(ii) State, giving a reason, the effect of changing the catalyst on the position of this equilibrium. [2]

No effect on the position of equilibrium.

The catalyst increases the rate of both the forward and reverse reactions equally.

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(iii) The Haber process typically uses a temperature of 500 °C.

Replacing the iron-based catalyst with a newer ruthenium-based catalyst increases the initial rate of reaction by a factor, **f**, at this temperature.

Use the Arrhenius equation to calculate the value of **f**.

You may assume that the frequency factor in both cases is the same. [3]

$T = 500 + 273 = 773$ K; $E_a(Fe) = 101\ 400$ J mol^{-1}; $E_a(Ru) = 64\ 000$ J mol^{-1}

$k = Ae^{-Ea/RT}$, and A is the same for both catalysts, so

$f = Ae^{-Ea(Ru)/RT} \div Ae^{-Ea(Fe)/RT} = e^{-Ea(Ru)/RT} \div e^{-Ea(Fe)/RT}$

$f = e^{(101\ 400 - 64\ 000)/(8.31 \times 773)} = e^{5.822}$

f = 338

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(e) When water is added to gaseous phosphane no visible reaction occurs. However, studies using isotopes of hydrogen have shown that hydrogen atoms are exchanged between the phosphane and water.

The following gas phase equilibrium occurs, where D represents deuterium, a hydrogen isotope with a mass number of 2.

$$PH_2D(g) + H_2O(g) \rightleftharpoons PH_3(g) + HDO(g)$$

A sealed vessel of volume 500 cm^3 contained 1.00×10^{-3} mol of $PH_2D(g)$. A sample of 4.90×10^{-4} mol of $H_2O(g)$ was added and the mixture allowed to reach equilibrium.

The mass spectrum of the equilibrium mixture shows that 36% of the phosphorus is present in PH_3 and 64% of the phosphorus is present in PH_2D.

Calculate the value of the equilibrium constant K_c for this reaction. [4]

initial: $[PH_2D] = 1.00 \times 10^{-3} / 0.500 = 2.00 \times 10^{-3}$ mol dm^{-3}

$[H_2O] = 4.90 \times 10^{-4} / 0.500 = 9.80 \times 10^{-4}$ mol dm^{-3}

equilibrium: $[PH_3] = [HDO] = 0.36 \times 2.00 \times 10^{-3} = 7.20 \times 10^{-4}$ mol dm^{-3}

$[PH_2D] = 0.64 \times 2.00 \times 10^{-3} = 1.28 \times 10^{-3}$ mol dm^{-3}

$[H_2O] = 9.80 \times 10^{-4} - 7.20 \times 10^{-4} = 2.60 \times 10^{-4}$ mol dm^{-3}

$K_c = [PH_3][HDO] / [PH_2D][H_2O]$

$= (7.20 \times 10^{-4})^2 / (1.28 \times 10^{-3} \times 2.60 \times 10^{-4})$

$K_c =$ 1.56

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END OF PAPER

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GCE A LEVEL

A410U10-1A

Z22-A410U10-1A

MONDAY, 13 JUNE 2022 – MORNING

CHEMISTRY – A level component 1
Data Booklet

Avogadro constant	N_A	$= 6.02 \times 10^{23}\ \text{mol}^{-1}$
molar gas constant	R	$= 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$
molar gas volume at 273 K and 1 atm	V_m	$= 22.4\ \text{dm}^3\ \text{mol}^{-1}$
molar gas volume at 298 K and 1 atm	V_m	$= 24.5\ \text{dm}^3\ \text{mol}^{-1}$
Planck constant	h	$= 6.63 \times 10^{-34}\ \text{J s}$
speed of light	c	$= 3.00 \times 10^{8}\ \text{m s}^{-1}$
density of water	d	$= 1.00\ \text{g cm}^{-3}$
specific heat capacity of water	c	$= 4.18\ \text{J g}^{-1}\ \text{K}^{-1}$
ionic product of water at 298 K	K_w	$= 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$
fundamental electronic charge	e	$= 1.60 \times 10^{-19}\ \text{C}$

temperature (K) = temperature (°C) + 273

$1\ \text{dm}^3 = 1000\ \text{cm}^3$
$1\ \text{m}^3 = 1000\ \text{dm}^3$
1 tonne = 1000 kg
$1\ \text{atm} = 1.01 \times 10^5\ \text{Pa}$

Multiple	Prefix	Symbol
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

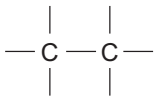
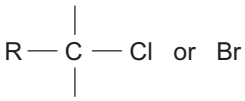
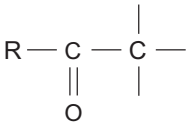
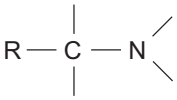
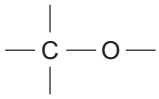
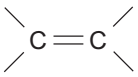
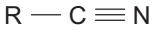
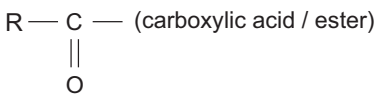
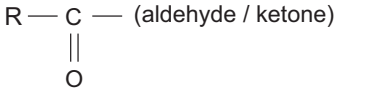
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Infrared absorption values

Bond	Wavenumber / cm^{-1}
C — Br	500 to 600
C — Cl	650 to 800
C — O	1000 to 1300
C = C	1620 to 1670
C = O	1650 to 1750
C ≡ N	2100 to 2250
C — H	2800 to 3100
O — H (carboxylic acid)	2500 to 3200 (very broad)
O — H (alcohol / phenol)	3200 to 3550 (broad)
N — H	3300 to 3500

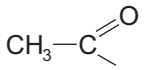
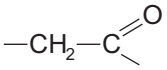
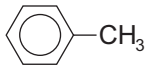
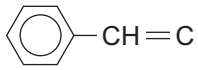
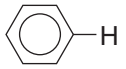
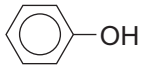
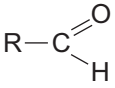
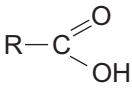
^{13}C NMR chemical shifts relative to TMS = 0

Type of carbon	Chemical shift, δ (ppm)
	5 to 40
	10 to 70
	20 to 50
	25 to 60
	50 to 90
	90 to 150
	110 to 125
	110 to 160
	160 to 185
	190 to 220

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^{1}H NMR chemical shifts relative to TMS = 0

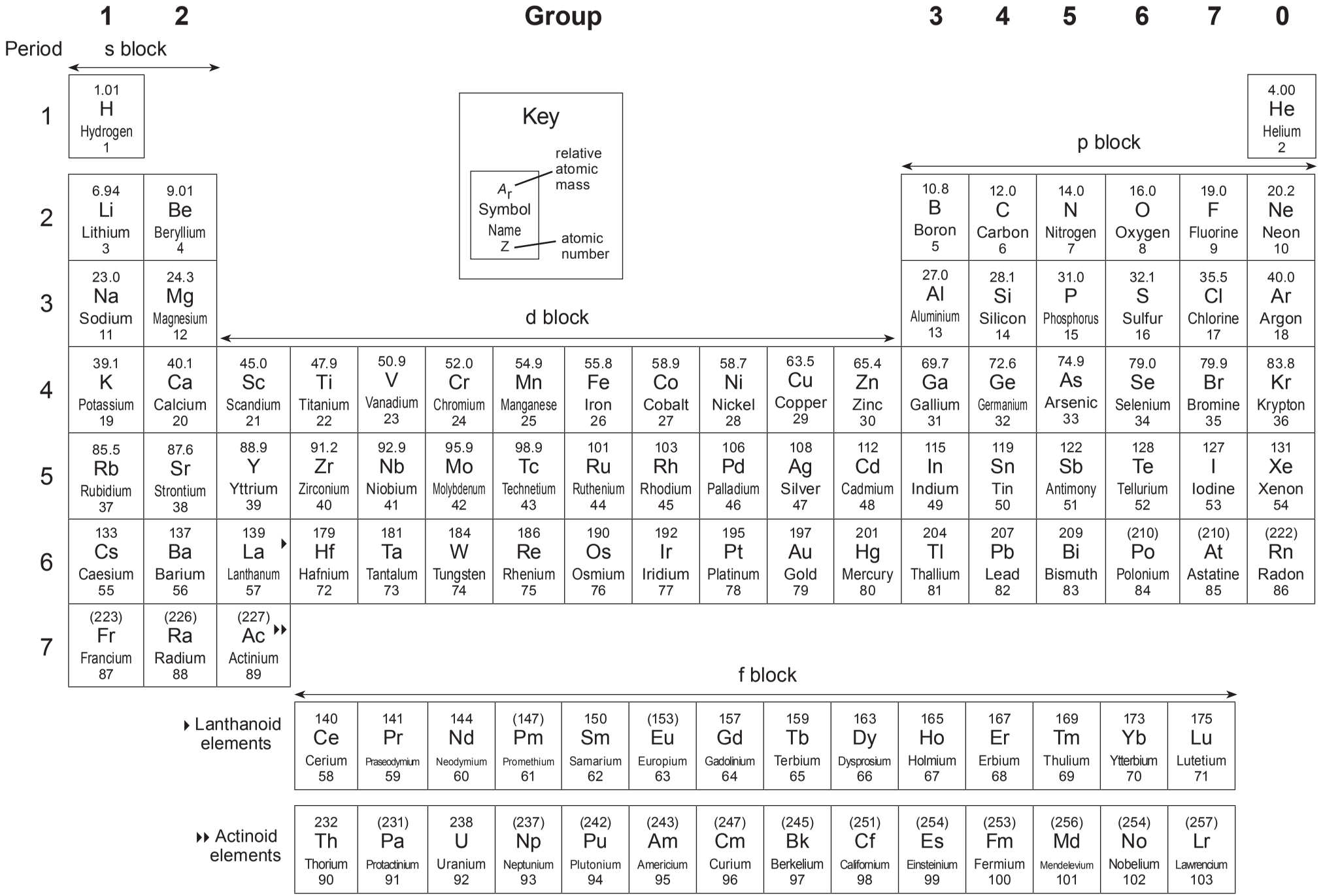
Type of proton	Chemical shift, δ (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
HC — Cl or HC — Br	3.1 to 4.3
HC — O	3.3 to 4.3
R — OH	4.5 *
— C ═ CH	4.5 to 6.3
— C ═ CH — CO	5.8 to 6.5
	6.5 to 7.5
	6.5 to 8.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

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THE PERIODIC TABLE



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