Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL – NEW

A410U10-1

S17-A410U10-1

CHEMISTRY – A level component 1
Physical and Inorganic Chemistry

TUESDAY, 13 JUNE 2017 – AFTERNOON

2 hours 30 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 9.**	**15**	
Section B	**10.**	**19**	
	11.	**20**	
	12.	**11**	
	13.	**18**	
	14.	**14**	
	15.	**11**	
	16.	**12**	
	Total	**120**	

A410U101
01

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.

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

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

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.13***(b)* and **Q.14***(b)*(iii).

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.

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SECTION A

Answer **all** *questions in the spaces provided.*

1. Show the electronic structure of silicon using arrows in boxes. [1]

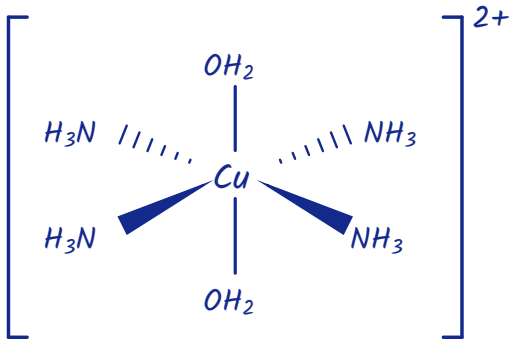


2. Write the equation for the **second** ionisation energy of boron. [1]

$B^+(g) \rightarrow B^{2+}(g) + e^-$

3. When excess ammonia solution is added to aqueous copper(II) sulfate a colour change occurs. Give the colour of the solution formed and draw the complex ion that causes this colour, showing its shape clearly. [2]

Colour dark (royal) blue



octahedral, bond angles 90°

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

4. When dilute sulfuric acid is added to a solution of barium chloride a white precipitate forms. Write the **ionic** equation for this reaction. [1]

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

5. In the atomic emission spectrum of hydrogen the frequency of the convergence point of the Lyman series is 3.28×10^{15} Hz. Calculate the ionisation energy of hydrogen in kJ mol^{-1}. [2]

$E = hf = 6.63 \times 10^{-34} \times 3.28 \times 10^{15} = 2.17 \times 10^{-18}$ J per atom

$IE = 2.17 \times 10^{-18} \times 6.02 \times 10^{23} \div 1000 = 1309$ kJ mol^{-1}

Ionisation energy = 1309 kJ mol^{-1}

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6. Carbon monoxide can be used as a reducing agent. Explain **why** carbon monoxide is a reducing agent and give an equation for a reaction where carbon monoxide acts in this way. [2]

Carbon is more stable in the +4 oxidation state than in the +2 state, so CO is readily oxidised to CO_2 (C: +2 to +4), donating electrons so the other species is reduced.

Equation $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

7. Helium is an example of an ideal gas. Use the ideal gas equation to find the volume of 0.267 mol of helium at –30 °C and 1 atm. [2]

$T = -30 + 273 = 243\ K$; $p = 1\ atm = 1.01 \times 10^5\ Pa$

$pV = nRT$ so $V = nRT \div p = 0.267 \times 8.314 \times 243 \div 1.01 \times 10^5$

$V = 5.34 \times 10^{-3}\ m^3$

Volume = 5.34×10^{-3} m^3

A410U101 03

8. Explain why solid sodium chloride can dissolve in water even though the process is endothermic. [2]

To be feasible, $\Delta G = \Delta H - T\Delta S$ must be negative (total entropy must increase). On dissolving, the ions become free to move in solution, so entropy increases greatly; $T\Delta S$ outweighs the positive ΔH, so $\Delta G < 0$.

9. Suggest a pH value for a dilute solution of ammonium chloride, giving a reason for your answer. [2]

pH ≈ 5 (weakly acidic).

The ammonium ion releases H^+ ions in solution, $NH_4^+ \rightleftharpoons NH_3 + H^+$, making the solution acidic (salt of a weak base and strong acid).

15

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SECTION B

Answer **all** *questions in the spaces provided.*

10. Hydrogen is a key reagent in many chemical processes. Two of the common reactions used in its industrial production are steam reforming of natural gas and the water gas shift reaction.

STEAM REFORMING
(equation 1) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\theta = 205 \text{ kJ mol}^{-1}$

WATER GAS SHIFT REACTION
(equation 2) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H^\theta = -41 \text{ kJ mol}^{-1}$

The mixture of gases produced by steam reforming is often called syngas. This can be used as a starting material for the water gas shift reaction to produce further hydrogen gas.

(a) (i) The atom economy of the steam reforming reaction is 17.8 %. Calculate the atom economy of the water gas shift reaction (equation 2), giving your answer to an appropriate number of significant figures. [2]

$M_r\ H_2 = 2.02$; M_r reactants = 28.01 + 18.02 = 46.03

atom economy = (2.02 ÷ 46.03) × 100 = 4.39%

Atom economy = 4.39 %

(ii) Suggest and explain which of the two routes would be favoured by the principles of green chemistry. You should include **two** advantages and **one** disadvantage of your chosen route. [3]

Steam reforming is favoured.

Advantages: it produces more H_2 per mole and has a much higher atom economy (17.8% compared with 4.39%), so less waste; it does not produce CO_2, and its waste product (CO) can be recycled in the water gas shift reaction.

Disadvantage: it uses methane, a non-renewable fossil fuel, as the starting material, and it is highly endothermic so needs a large energy input.

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(b) The water gas shift reaction (equation 2) requires carbon monoxide as one reactant. This can be provided by adding syngas from the steam reforming reaction or by adding pure carbon monoxide.

Explain why adding pure carbon monoxide is the preferred method. [2]

Syngas already contains H_2, which is a product of the water gas shift reaction.

This H_2 would shift the equilibrium to the left, so less CO would be converted and less H_2 produced; pure CO avoids this.

(c) The water gas shift reaction (equation 2) can be undertaken using two different methods.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H^{\theta} = -41 \text{ kJ mol}^{-1}$$

	Temperature range / °C	Pressure range / Pa	Catalyst mixture	Percentage of CO in equilibrium mixture
Low temperature method	200-250	1.01×10^5 - 8.35×10^6	CuO, ZnO, Al_2O_3	1 %
High temperature method	300-450	1.01×10^5 - 8.35×10^6	Fe_2O_3, Cr_2O_3, MgO	2-4 %

A410U101 05

(i) I. Explain why both catalyst mixtures are classified as heterogeneous catalysts. [1]

The catalysts are solids, which are in a different phase (physical state) from the gaseous reactants.

II. The active components of the catalyst mixtures are CuO and Fe_2O_3. Explain why these transition metal oxides are able to act as catalysts. [2]

The gas molecules are adsorbed onto the catalyst surface (partly filled d-orbitals).

This brings the gases together, and the metal can change oxidation state to oxidise or reduce the gas molecules, making them more reactive.

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(ii) I. The range of pressures used in the water gas shift reaction (equation 2) is large. Explain why this does not affect the equilibrium yield of the desired product. [1]

There are equal numbers of moles of gas on both sides of the equation (2 and 2), so pressure does not affect the position of equilibrium.

II. Suggest **one** reason why some industrial plants might select a lower pressure and **one** reason why some might select a higher pressure. [2]

Lower pressure: reduced energy costs and cheaper equipment (it does not have to withstand high pressures safely).

Higher pressure: increased rate of reaction, so equilibrium is reached in less time.

(iii) I. Explain why the percentage of carbon monoxide in the equilibrium mixture in the water gas shift reaction (equation 2) is lower at low temperature than at high temperature. [2]

The forward reaction is exothermic ($\Delta H = -41$ kJ mol^{-1}).

A higher temperature shifts the equilibrium to the left (endothermic direction), so more CO remains at equilibrium.

II. Give the expression for the equilibrium constant, K_c, for the water gas shift reaction (equation 2). [1]

$$K_c = \frac{[CO_2(g)]\,[H_2(g)]}{[CO(g)]\,[H_2O(g)]}$$

III. Assuming that the starting mixture contains equimolar amounts of CO and H_2O only, use the data in the table to calculate the value of the equilibrium constant, K_c, for the low temperature method. [3]

Equimolar start, so at equilibrium CO = 1% and H_2O = 1%

CO_2 and H_2 form equally: (100 − 2) ÷ 2 = 49% of each

K_c = (49 × 49) ÷ (1 × 1) = 2401 (volumes cancel)

K_c = 2401

19

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11. The tables below give some data on selected chlorides and oxides of the Period 3 elements.

	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3
Melting temperature / K	987	463	203	179
Electrical conductivity when molten/liquid	conducts	does not conduct	does not conduct	does not conduct

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O
Melting temperature / K	1548	3125	2345	1883	573	200	253
Electrical conductivity when molten/liquid	conducts	conducts	conducts	does not conduct	does not conduct	does not conduct	does not conduct

(a) Phosphorus(V) oxide, P_4O_{10}, reacts with water to form phosphoric(V) acid. Balance the equation for this reaction. [1]

..... P_4O_{10} + ... 6 ..... H_2O ⟶ ..... 4 ..... H_3PO_4

(b) Identify the structures shown by all the oxides in the table and link these to the patterns seen in the melting temperatures. [3]

Na_2O, MgO and Al_2O_3 have giant ionic structures with strong electrostatic forces between the oppositely charged ions, so they have high melting temperatures.

SiO_2 has a giant covalent (macromolecular) structure, so strong covalent bonds must be broken to melt it, giving a high melting temperature.

P_4O_{10}, SO_2 and Cl_2O are simple covalent molecules; only the weak intermolecular forces between the molecules are broken on melting, so their melting temperatures are low.

A410U101 07

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(c) The different properties of aluminium chloride and aluminium oxide are due to the different types of bonding present in these compounds.

(i) State the types of bonding found in aluminium chloride and aluminium oxide. Explain why these compounds have different types of bonding. [2]

Aluminium oxide is ionic and aluminium chloride is covalent.

The difference in electronegativity between Al and O is greater than that between Al and Cl, so electrons are transferred to O but shared with Cl.

(ii) Explain the differences in the electrical conductivity of these two compounds of aluminium. [2]

Aluminium oxide contains charged ions but aluminium chloride (molecules) does not.

When molten, the ions in Al_2O_3 can flow and carry the charge.

(d) Other chlorides and oxides of these elements also exist.

(i) Explain why phosphorus can form two chlorides (PCl_3 and PCl_5) but nitrogen can only form one chloride (NCl_3). [2]

P has available d-orbitals in its outer (third) shell but N does not. This allows phosphorus to expand its octet (10 outer electrons in PCl_5); N is limited to 8.

(ii) Sodium can also form an oxide with formula Na_2O_2. Deduce the oxidation state of the oxygen in this compound, and use it to show that its reaction with water is not a redox reaction. [2]

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

In Na_2O_2 the oxidation state of oxygen is −1. In H_2O_2 oxygen is still −1, Na and H stay +1 and the O of water stays −2: no oxidation states change, so not redox.

(iii) Explain why silicon can form only one chloride ($SiCl_4$) but lead can form two chlorides ($PbCl_2$ and $PbCl_4$). [2]

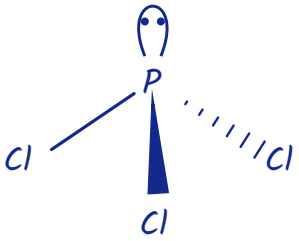
Inert pair effect: the +2 state (s^2 pair not used) becomes more stable down group 4, so it is significant for lead, which forms $PbCl_2$ as well as $PbCl_4$, but Si only forms +4.

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(e) Use valence shell electron pair repulsion theory (VSEPR) to predict and explain the shape of the PCl_3 molecule. [3]



trigonal pyramidal

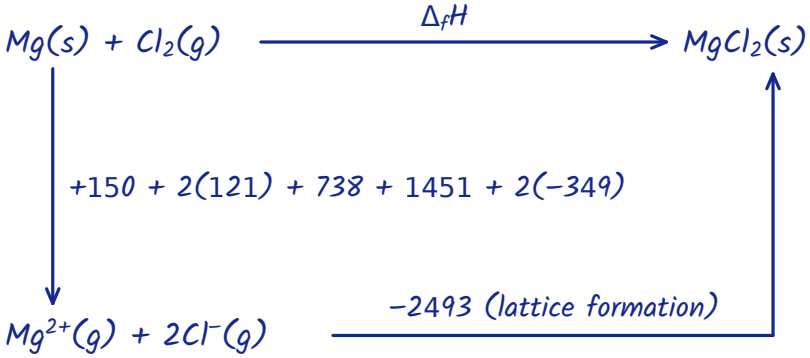
bond angle 107°

P has three bonding pairs (to Cl) and one lone pair: four electron pairs.

These arrange themselves as far apart as possible to minimise repulsion; the lone pair repels more than bonding pairs, so the angle closes from 109.5° to about 107°, giving a pyramidal shape.

(f) Use the values in the table below to calculate the standard enthalpy of formation of magnesium chloride, $MgCl_2$. [3]

	Enthalpy change / kJ mol^{-1}
Standard enthalpy of atomisation of magnesium	150
Standard enthalpy of atomisation of chlorine	121
First ionisation energy of magnesium	738
Second ionisation energy of magnesium	1451
Electron affinity of chlorine	–349
Standard enthalpy of lattice breaking of magnesium chloride	2493



$\Delta_f H = 150 + (2 \times 121) + 738 + 1451 + (2 \times -349) - 2493 = -610$

$\Delta_f H^\theta$ = ... –610 ..... kJ mol^{-1}

20

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A410U101 09

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12. In 2011 a tsunami damaged the Fukushima nuclear plant in Japan. The radioactive material that escaped consisted of many isotopes. Contaminated water from the site was analysed in the immediate aftermath of the incident, with the levels of radioactivity due to each isotope noted.

Isotope	Half-life	Radioactivity / Bq per cm^3 of solution	Type(s) of radioactivity emitted	Product of decay
chlorine-38	37 minutes	1.9×10^6	beta	^{38}Ar
arsenic-74	18 days	3.9×10^2		
yttrium-91	59 days	5.2×10^4	beta	^{91}Zr
iodine-131	8 days	2.1×10^5	beta	^{131}Xe
caesium-134	2 years	1.6×10^5	beta	^{134}Ba
caesium-136	13 days	1.7×10^4	beta	^{136}Ba
caesium-137	30 years	1.8×10^6	beta and gamma	^{137}Ba
lanthanum-140	1.6 days	3.4×10^2	beta	^{140}Ce

(a) The main radioactivity detected was beta radiation. Give a reason why it is unlikely that alpha radiation would be detected from a solution contained in a sample tube. [1]

Alpha particles cannot penetrate the walls of the sample tube; they are absorbed by the solvent.

(b) State what is meant by gamma radiation. [1]

High energy (high frequency) electromagnetic waves emitted from the nucleus.

(c) Give a reason why radioactivity is harmful to living things. [1]

It ionises molecules, damaging DNA and other biological molecules, causing mutations.

(d) Arsenic-74 can decay either by emission of a beta particle or by emission of a positron. Identify the isotope formed by emission of a positron. [1]

Element germanium Mass number 74

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(e) The Becquerel (Bq) is a unit of radioactivity which is equivalent to the decay of 1 nucleus per second.

(i) Calculate the mass of xenon-131 produced per minute from 1 cm^3 of the solution. [3]

atoms decaying per minute = $2.1 \times 10^5 \times 60 = 1.26 \times 10^7$

moles = $1.26 \times 10^7 \div 6.02 \times 10^{23} = 2.09 \times 10^{-17}$ mol

mass = $2.09 \times 10^{-17} \times 131 = 2.74 \times 10^{-15}$ g

Mass = 2.74×10^{-15} g

(ii) Identify which original isotope is present in the greatest concentration in the solution. Explain your answer. [2]

Caesium-137: it has the second highest radioactivity (behind Cl-38) but the longest half-life (30 years), so there must be a much greater amount of Cs-137 to give this activity.

(f) After studying the data, it was suggested that the affected area around the reactor would be safe after 60 years as this is twice the half-life of the longest lived isotope in the sample. Give **two** reasons why this suggestion is incorrect. [2]

After two half-lives a quarter of the Cs-137 is still present (still radioactive). Decay products may be radioactive with longer half-lives, or undetected isotopes with longer half-lives may be present.

A410U101 11

11

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13. A class of students is provided with a mixture of the strong base sodium hydroxide and the weak base sodium carbonate. They are asked to carry out an experiment to find the percentage by mass of each in the sample using the following method.

- Prepare a standard solution of the solid mixture in a 250 cm^3 volumetric flask.
- Measure 25.00 cm^3 of this mixture into a conical flask and add a small amount of an appropriate indicator.
- Add 0.105 $mol\,dm^{-3}$ hydrochloric acid from a burette whilst swirling the mixture until a permanent colour change occurs. At this point all the sodium hydroxide has reacted.
- Record the results and calculate the volume required to reach the first end-point (volume **A**).
- Add a few drops of a different indicator.
- Add more of the hydrochloric acid from the burette whilst swirling the mixture until a permanent colour change occurs. At this point all the sodium carbonate has reacted.
- Record the results and calculate the additional volume required to reach the second end-point (volume **B**).

(a) The results of the titrations are shown below.

	1	2	3	4
Initial burette reading / cm^3	0.00	0.00	1.20	5.55
Burette reading at first end-point / cm^3	22.35	22.00	23.25	27.55
Burette reading at second end-point / cm^3	33.55	32.65	33.80	38.00
Volume required to reach first end-point (volume **A**) / cm^3	22.35	22.00	22.05	22.00
Additional volume required to reach second end-point (volume **B**) / cm^3	11.20	10.65	10.55	10.45

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(i) Complete the table and calculate the mean volume required to reach the first end-point, and the mean additional volume required to reach the second end-point. [3]

Titration 1 is not concordant, so use titrations 2, 3 and 4:

mean A = (22.00 + 22.05 + 22.00) ÷ 3 = 22.02 cm^3

mean B = (10.65 + 10.55 + 10.45) ÷ 3 = 10.55 cm^3

Mean volume for first end-point = ... 22.02 ..... cm^3

Mean additional volume for second end-point = ... 10.55 ..... cm^3

(ii) The class teacher tells the students that the data show that the value for volume **A** is more reliable than the value for volume **B**. Give **two** reasons for this. [2]

The repeat values of volume A are closer together (concordant, less scatter) than those of B.

A is larger, so its percentage error is smaller; and B needs two colour changes (two end-points) to find it, but A only one.

(iii) Calculate the mass of sodium carbonate present in the original solid mixture. [3]

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

M_r 106.0

moles HCl = 10.55 × 0.105 ÷ 1000 = 1.108×10^{-3} mol

moles Na_2CO_3 in 25.00 cm^3 = $1.108 \times 10^{-3} \div 2 = 5.54 \times 10^{-4}$ mol

in 250 cm^3: $5.54 \times 10^{-4} \times 10 = 5.54 \times 10^{-3}$ mol

mass = $5.54 \times 10^{-3} \times 106.0 = 0.587$ g

Mass = ... 0.587 ..... g

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(b) Explain how an indicator works and give reasons why two different indicators are used to identify the end-points for neutralisation of sodium hydroxide and sodium carbonate. Suggest how you would select appropriate indicators for this experiment. [6 QER]

An indicator is a weak acid, HIn, whose protonated (HIn) and deprotonated (In^-) forms are different colours: $HIn \rightleftharpoons H^+ + In^-$. Adding acid or alkali shifts this equilibrium, so the indicator changes colour over a range of about 2 pH units.

Different indicators change colour over different pH ranges, and an indicator is only useful if its colour change range lies within the vertical (steep) section of the titration curve.

The two equivalence points occur at different pH values: when all the NaOH has reacted the solution is basic (about pH 8 to 9), but when all the Na_2CO_3 has reacted (dissolved CO_2) it is acidic (about pH 4). So one indicator cannot show both end-points.

To select indicators, calculate the pH at each equivalence point, or find it experimentally by plotting a pH curve with a pH probe, and find the pH of each vertical region. Then compare these with literature values of indicator pH ranges: e.g. phenolphthalein (pH 8.3 to 10) for the first end-point and methyl orange (pH 3.1 to 4.4) for the second.

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(c) One student suggests using 0.100 mol dm^{-3} ethanoic acid for this titration method, however his partner suggests that a different method would be needed.

(i) Calculate the pH of 0.100 mol dm^{-3} ethanoic acid. [2]

(K_a for ethanoic acid = 1.76×10^{-5} mol dm^{-3})

$[H^+]^2 = K_a \times [CH_3COOH] = 1.76 \times 10^{-5} \times 0.100 = 1.76 \times 10^{-6}$

$[H^+] = 1.33 \times 10^{-3}$ mol dm^{-3}

$pH = -\log[H^+] = -\log(1.33 \times 10^{-3}) = 2.88$

pH = 2.88

(ii) Suggest how the equivalence point for the titration of a weak acid and a weak base such as sodium carbonate can be found experimentally. [2]

Use a pH probe (pH meter) to measure the pH as the acid is added in small portions.

Plot pH against volume of acid and find the equivalence point from the curve, as there is no sharp increase (jump) in pH for an indicator to detect.

18

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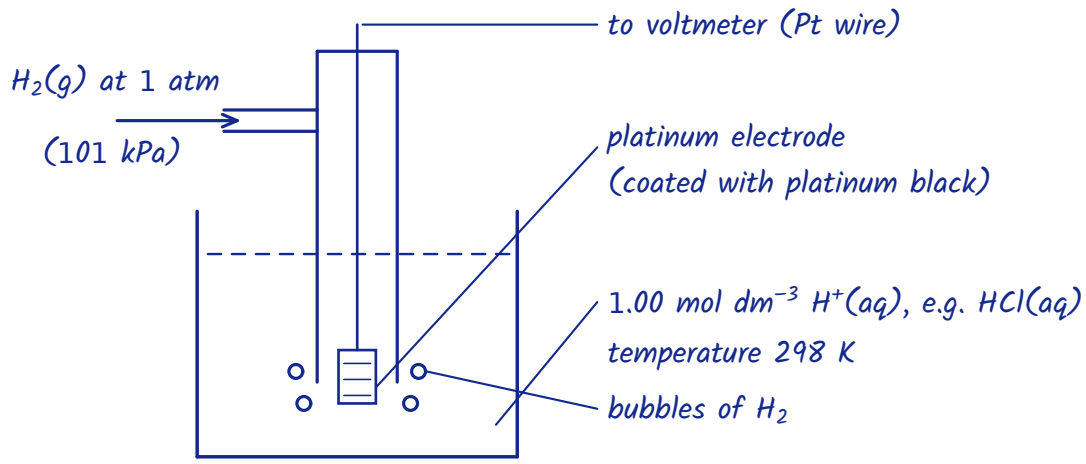
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14. *(a)* The usual method for measuring the standard electrode potential of a half-cell is to connect it to a standard hydrogen electrode using a high resistance voltmeter and a salt bridge.

(i) State the function of the salt bridge. [1]

It completes the circuit, allowing ions to flow between the half-cells without the solutions mixing.

(ii) Draw a labelled diagram of the standard hydrogen electrode. [3]



(iii) When measuring the standard electrode potential for the $Zn^{2+}(aq) \mid Zn(s)$ system a piece of zinc metal is placed in an aqueous solution containing $Zn^{2+}(aq)$. Explain why a similar method would not be appropriate for the $Li^+(aq) \mid Li(s)$ system. [1]

Lithium is very reactive and would react with the water in the solution (forming LiOH and H_2).

(b) The values for some standard electrode potentials are listed in the table below.

	Standard electrode potential, E^θ / V
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	–0.04
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

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(i) Give the **formula** of the strongest reducing agent in the table. [1]

Li

(ii) Calculate the EMF of the cell formed when the $Br_2(l) \mid Br^-(aq)$ half-cell is connected to the $Zn^{2+}(aq) \mid Zn(s)$ half-cell. [2]

$EMF = E^\ominus(Br_2/Br^-) - E^\ominus(Zn^{2+}/Zn)$

$EMF = 1.09 - (-0.76) = 1.85\ V$

EMF = 1.85 V

(iii) Use the values in the table to explain why the reaction between gaseous iodine and heated iron wire produces iron(II) iodide whilst chlorine gas and iron wire produce iron(III) chloride. Your answer should include:

- An explanation of the products formed in the two reactions using the standard electrode potentials listed.
- Chemical equations for both reactions.
- A prediction of the product that would be formed when bromine gas reacts with heated iron wire, including a reason.
- An explanation of why the prediction made using the standard electrode potentials above may not be correct.

[6 QER]

Chlorine ($E^\ominus$ = +1.36 V) is a stronger oxidising agent than Fe^{3+} (Fe^{3+}/Fe^{2+} = +0.77 V), as its electrode potential is more positive. So chlorine can oxidise iron all the way to Fe^{3+} (EMF = 1.36 − 0.77 = +0.59 V, positive): $2Fe + 3Cl_2 \rightarrow 2FeCl_3$

Fe^{3+} is a stronger oxidising agent than iodine, as $E^\ominus$ for Fe^{3+}/Fe^{2+} (+0.77 V) is more positive than for I_2/I^- (+0.54 V). So iodine cannot oxidise Fe^{2+} to Fe^{3+} (any Fe^{3+} would be reduced to Fe^{2+} by I^-): $Fe + I_2 \rightarrow FeI_2$

Bromine (+1.09 V) is a stronger oxidising agent than Fe^{3+} (+0.77 V), so I predict iron(III) bromide forms: $2Fe + 3Br_2 \rightarrow 2FeBr_3$

This prediction may not be correct because $E^\ominus$ values only apply under standard conditions (aqueous solutions, 1 mol dm^{-3}, 298 K), but here the iron is heated, the halogens are gases and the products are solids, not solutions.

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15. The wide range of mobile technology available to us today has relied on the development of ways to store and utilise energy efficiently. Many mobile devices use batteries based on lithium ions as they have a large charge density.

(a) A lithium ion battery can sustain a current over an extended period of time so that a total charge of 1.2×10^4 C has flowed. Calculate the mass of lithium that has reacted in this time, giving your answer to an appropriate number of significant figures. [3]

electrons = $1.2 \times 10^4 \div 1.60 \times 10^{-19} = 7.5 \times 10^{22}$

moles of electrons = $7.5 \times 10^{22} \div 6.02 \times 10^{23} = 0.1246$ mol

$Li \rightarrow Li^+ + e^-$, so moles of Li = 0.1246 mol

mass = $0.1246 \times 6.94 = 0.86$ g (2 s.f.)

Mass = ...0.86.... g

(b) Many lithium ion batteries contain electrodes made of compounds of formula $Li_aM_b(PO_4)_c$ where M can be one of a range of metals from the first row of the *d*-block elements.

A university student undertook a series of experiments to analyse the compound used as an electrode in a given lithium ion battery.

The relative formula mass of the compound was approximately 158.

2.70 g of the solid were dissolved in hot acid and a solution containing calcium ions was added. All the phosphate ions were precipitated from the hot mixture as calcium phosphate (M_r 310.3). The calcium phosphate was washed and heated to constant mass, with 2.66 g produced.

A small amount of the original compound was dissolved in hot solvent to give a solution of concentration 1.90×10^{-6} mol dm^{-3}. Atomic absorption spectroscopy was used to measure the concentration of lithium ions in this solution and it was found to be 13.2 μg dm^{-3}.

(i) Explain why the solid calcium phosphate precipitate must be heated to constant mass. [1]

Heating to constant mass ensures all the water has been removed, so the sample is completely dry.

(ii) Find the value of c, the number of phosphate ions present in the molecular formula.

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

moles $Ca_3(PO_4)_2 = 2.66 \div 310.3 = 8.57 \times 10^{-3}$ mol

moles $PO_4^{3-} = 2 \times 8.57 \times 10^{-3} = 0.0171$ mol

moles of solid = $2.70 \div 158 = 0.0171$ mol (0.017088)

PO_4^{3-} : solid = 0.0171 : 0.0171 = 1 : 1

c = ...1....

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(iii) Find the value of a, the number of lithium ions present in the molecular formula. [2]

$[Li^+] = 13.2 \times 10^{-6}\ g\ dm^{-3} \div 6.94 = 1.90 \times 10^{-6}\ mol\ dm^{-3}$

this equals the concentration of the solid, so Li : compound = 1 : 1

a = 1

(iv) Identify the first row *d*-block element M, and the number of atoms of this present in the molecular formula, b, and hence write the molecular formula of the compound. [2]

M_r of M = 158 − 6.94 − (31.0 + 4 × 16.0) = 158 − 6.94 − 95.0 = 56.1

this matches iron (A_r 55.8), so M = Fe and b = 1

Molecular formula $LiFePO_4$

11

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16. The reaction between ethoxide ions ($C_2H_5O^-$) and iodoethane produces ethoxyethane. The reaction was studied at various temperatures and the percentage of products formed every 10 s was measured for the first 50 s.

Temperature / °C	Percentage conversion of reactants to products				
	10 s	20 s	30 s	40 s	50 s
10	2 %	3 %	5 %	6 %	7 %
20	5 %	10 %	15 %	19 %	24 %
30	16 %	30 %	41 %	50 %	58 %
40	41 %	65 %	79 %	88 %	93 %
50	77 %	95 %	99 %	100 %	100 %

(a) The initial rate of reaction can be calculated approximately using the formula:

$$\text{rate} = \frac{\text{percentage conversion}}{\text{time taken}}$$

(i) One student chose to use the data at 50 s to calculate the rate at 40 °C. Suggest and explain why this will **not** give an appropriate value of initial rate. [2]

By 50 s 93% has reacted, so the concentration of reactants has fallen greatly, so the rate changes significantly over this time: it gives an average rate, far below the initial rate.

(ii) A second student chose to use the data at 10 s to calculate the rate. Give a reason why the percentage error at lower temperatures may be more significant. [2]

At lower temperatures the values measured at 10 s are very small (e.g. 2% at 10 °C), so the uncertainty is a larger proportion of them: percentage errors are larger than in other measurements.

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(b) The rate constant for the reaction in solution at 30 °C is 1.752×10^{-2} dm^3 mol^{-1} s^{-1}.

(i) Give the overall order of the reaction. [1]

Second order

(ii) Explain what information about the mechanism can be found from:

- the overall order of reaction
- the orders with respect to each reactant [3]

Rate data tell us about the rate-determining (slowest) step of the mechanism.

The overall order (2) shows the total number of molecules/ions in the rate-determining step (two); the order for each reactant shows how many of each reactant molecule are in that step.

(iii) State the Arrhenius equation. [1]

$k = Ae^{-Ea/RT}$

(iv) The frequency factor for the reaction under these conditions is found to be 1.49×10^{11} dm^3 mol^{-1} s^{-1}. Use this value to calculate the activation energy of the reaction in kJ mol^{-1}. [3]

$\ln k = \ln A - E_a/RT$, so $E_a = -RT \ln(k/A)$

$E_a = -8.314 \times 303 \times \ln(1.752 \times 10^{-2} \div 1.49 \times 10^{11})$

$E_a = -8.314 \times 303 \times (-29.77) = 7.50 \times 10^4$ J mol^{-1}

$E_a = 75.0$ kJ mol^{-1}

Activation energy = 75.0 kJ mol^{-1}

12

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