

Surname <i>StemUp Model Solution</i>	Centre Number	Candidate Number
Other Names		2



GCE A LEVEL

1410U30-1



S19-1410U30-1

TUESDAY, 4 JUNE 2019 – AFTERNOON

CHEMISTRY – A2 unit 3

Physical and Inorganic Chemistry

1 hour 45 minutes

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A 1. to 8.	10	
Section B 9.	15	
10.	15	
11.	12	
12.	15	
13.	13	
Total	80	

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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.

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 (10 marks)** and **Section B (70 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 80.

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.11(b)**.

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

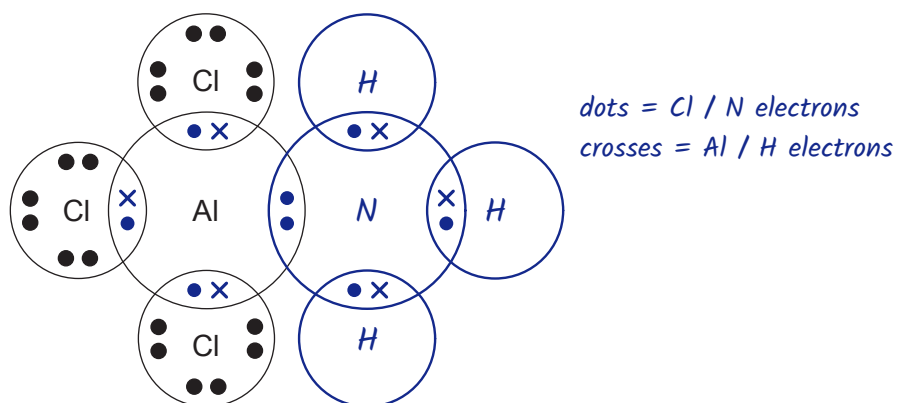
Answer **all** questions in the spaces provided.

1. Complete the electronic structure of the Co^{2+} ion below. [1]

$1s^2 2s^2 2p^6 3s^2 3p^6$ *3d⁷*

2. The compound $\text{AlCl}_3 \cdot \text{NH}_3$ contains both covalent and coordinate bonds. [2]

Complete the dot and cross diagram for this compound.



3. Write the expression for the ionic product of water, K_w . [1]

$$K_w = [\text{H}^+][\text{OH}^-]$$

4. The standard hydrogen electrode and hydrogen fuel cells both use the same metal as an electrode. Name the metal and explain why this metal is suitable. [1]

Platinum, as it is unreactive (inert).



5. When CCl_4 is added to water two separate layers are formed and there is no reaction, whilst SiCl_4 reacts violently with water.

Give the reason for this difference.

[1]

Silicon has available (empty) 3d orbitals whilst carbon does not, so water molecules can bond (donate a lone pair) to the Si atom in SiCl_4 but not to the C atom in CCl_4 .

6. The entropy change of the reaction shown below is positive. Give a reason for this.

[1]



A gas (CO_2) is formed and gases have a greater entropy than liquids and solids (more disorder).

7. Carbon monoxide can be used to extract iron by the reduction of Fe_3O_4 .

(a) Write an equation for this reaction.

[1]



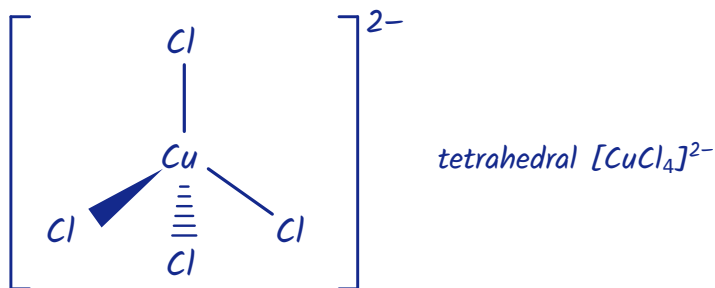
(b) Give a reason why carbon monoxide acts as a reducing agent while the equivalent oxide of lead does not.

[1]

Stability of the +2 oxidation state increases down the group (inert pair effect); carbon is stable as +4 and lead is stable as +2.

8. Draw the **structure** of the copper-containing ion formed when concentrated hydrochloric acid is added to a solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.

[1]



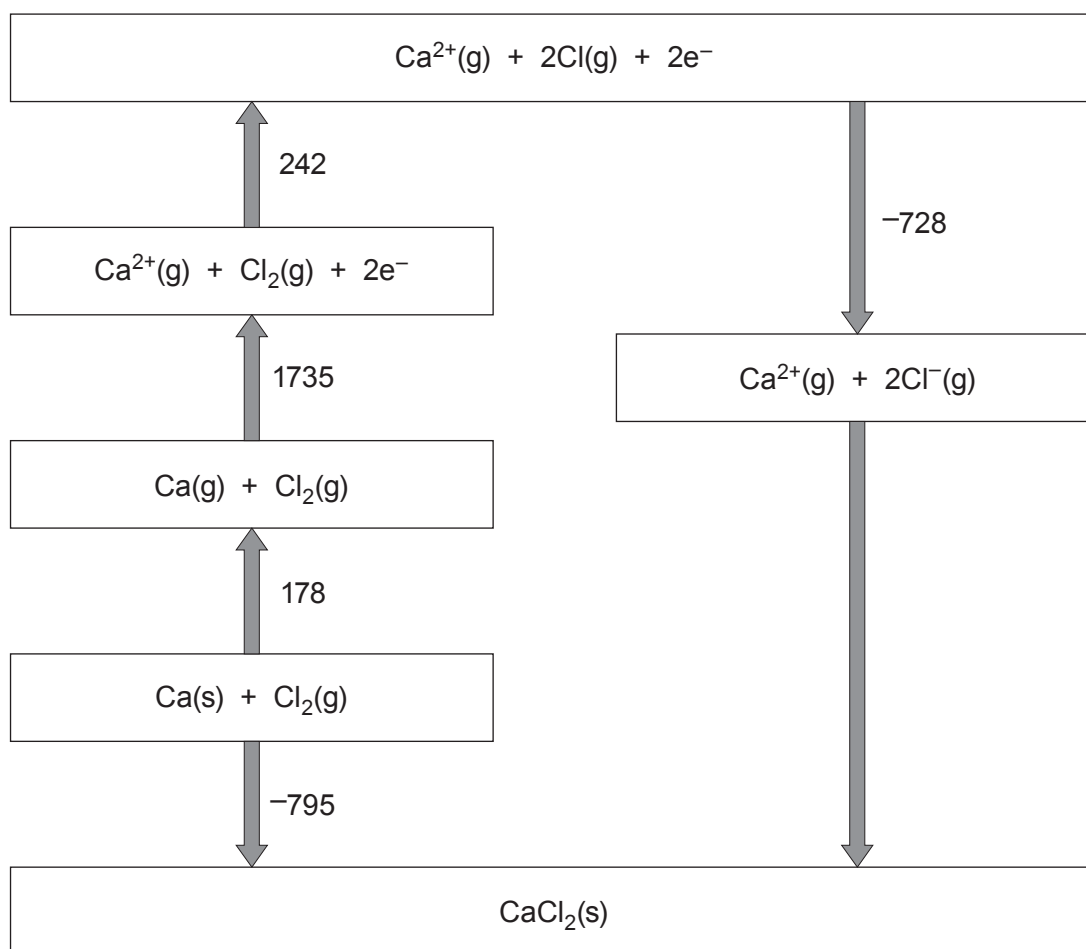
SECTION B

Answer all questions in the spaces provided.

9. Calcium chloride is an ionic solid that is used as a drying agent due to its ability to absorb water and form a range of hydrated crystals.

(a) The Born-Haber cycle below shows the formation of calcium chloride from its elements.

All values shown are standard enthalpy changes and are given in kJ mol^{-1} .



- (i) Give the value of the standard enthalpy change of atomisation of chlorine. [1]

.....121..... kJ mol^{-1}

- (ii) Calculate the standard enthalpy of lattice formation of CaCl_2 . [2]

$$\Delta_{\text{latt form}} H = -(-728) - 242 - 1735 - 178 + (-795)$$

$$= 728 - 242 - 1735 - 178 - 795$$

$$\Delta_{\text{latt form}} H^\theta = \text{.....-2222.....} \text{ kJ mol}^{-1}$$

- (iii) A student incorrectly states that the second ionisation energy of calcium is 1735 kJ mol^{-1} as this is the energy needed to form $\text{Ca}^{2+}(\text{g})$ in the Born-Haber cycle.

Suggest a possible value for the second ionisation energy of calcium, giving a reason for your answer. [2]

About 1145 kJ mol^{-1} (any value between 900 and 1600). 1735 kJ

mol^{-1} is the sum of the first and second ionisation energies.

Successive ionisation energies increase, so the second ionisation energy is greater than the first and must be more than half of 1735.



- (b) The reaction occurring when calcium chloride is used as a drying agent is shown below.



- (i) A laboratory manual suggests a **minimum** temperature of 200 °C to remove all the water from the hydrated calcium chloride. At this temperature the reaction occurring is as follows.



A student calculates the enthalpy change when calcium chloride becomes dehydrated as 78.0 kJ mol⁻¹.

Assuming that this data is correct, calculate a value for the entropy change when calcium chloride becomes dehydrated at this temperature. [3]

At the minimum temperature $\Delta G = 0$, so $\Delta H = T\Delta S$ and $\Delta S = \Delta H \div T$

$$T = 200 + 273 = 473 \text{ K}, \quad \Delta H = 78.0 \text{ kJ mol}^{-1} = 78\,000 \text{ J mol}^{-1}$$

$$\Delta S = 78\,000 \div 473 = 164.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = \dots\dots\dots 165 \dots\dots\dots \text{ J K}^{-1} \text{ mol}^{-1}$$

- (ii) In the drying process 5.20 g of hydrated calcium chloride forms 3.15 g of anhydrous calcium chloride.

Calculate the value of x in the original $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$. [3]

$$\text{moles CaCl}_2 = 3.15 \div 111.1 = 0.0284 \text{ mol}$$

$$\text{mass of water} = 5.20 - 3.15 = 2.05 \text{ g}$$

$$\text{moles H}_2\text{O} = 2.05 \div 18.02 = 0.1138 \text{ mol}$$

$$\text{ratio H}_2\text{O} : \text{CaCl}_2 = 0.1138 \div 0.0284 = 4.0$$

$$x = \dots\dots\dots 4 \dots\dots\dots$$

- (iii) State the colour observed in a flame test using calcium chloride. [1]

Brick-red



- (c) Calcium halides react with concentrated sulfuric acid in a similar manner to sodium halides.

State the observation(s) when concentrated sulfuric acid is added to calcium chloride and calcium bromide. Explain why the observations are different. [3]

CaCl₂: misty (steamy) fumes of HCl are seen, and a white solid forms.

CaBr₂: misty fumes and a white solid, but orange (brown) fumes / an orange solution of Br₂ are also produced.

Bromide ions are easier to oxidise than chloride ions (Br⁻ is a stronger reducing agent), so bromide can be oxidised to Br₂ by the concentrated sulfuric acid but chloride cannot.

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10. Iodomethane, CH_3I , reacts with a range of nucleophiles. The rate of its reaction with thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, has been studied at a range of temperatures.

- (a) The reaction is found to be first order with respect to iodomethane and has a rate constant of $3.10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at a particular temperature.

- (i) Write the rate equation for this reaction. [2]

$$\text{rate} = k[\text{CH}_3\text{I}][\text{S}_2\text{O}_3^{2-}]$$

- (ii) The activation energy for this reaction is 81.1 kJ mol^{-1} with a frequency factor, A , of $5.62 \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Find the temperature used for this reaction. [3]

$$E_a = 81.1 \text{ kJ mol}^{-1} = 81\,100 \text{ J mol}^{-1}$$

$$k = Ae^{-E_a/RT} \text{ so } \ln(k/A) = -E_a/RT$$

$$T = \frac{-E_a}{R \ln(k/A)} = \frac{-81\,100}{8.31 \times \ln(3.10 \div 5.62 \times 10^{12})}$$

$$\ln(5.516 \times 10^{-13}) = -28.23$$

$$T = 81\,100 \div (8.31 \times 28.23) = 345.8$$

$$T = \dots\dots\dots 346 \dots\dots\dots \text{ K}$$



(b) One method of performing this experiment involves sampling and quenching.

- (i) Explain what is meant by the term 'quenching' and why it needs to be carried out. [2]

Quenching is the sudden stopping (or significant slowing) of the chemical reaction in a sample, e.g. by rapid cooling or dilution.

It ensures the composition of the sample does not change between taking the sample and analysing it, or during the analysis.

- (ii) One method of measuring the concentration of thiosulfate ions in solution is by titration using a solution containing iodine. Suggest an indicator for this titration. [1]

Starch

- (iii) A student suggests using gravimetric analysis to measure the amount of iodide ions produced in the reaction by addition of $\text{Pb}^{2+}(\text{aq})$ ions to form a precipitate. Give the colour of this precipitate. [1]

Bright (canary) yellow

(c) Iodomethane is an intermediate in the conversion of methanol to ethanoic acid.

- (i) One catalyst used for this reaction is the iridium-containing complex ion $[\text{Ir}(\text{CO})_2\text{I}_2]^-$. It is an example of a homogeneous catalyst.

- I. State what is meant by a *homogeneous* catalyst. [1]

A catalyst that is in the same physical state (phase) as the reactants.

- II. Explain why transition metal complexes such as $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ can act as homogeneous catalysts. [2]

Transition metals have empty orbitals so they can form bonds to the reactant molecules (form complexes), and they have variable oxidation states so they can oxidise or reduce the reactants.



- (ii) Ethanoic acid is a weak acid with $K_a = 1.76 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of an aqueous solution of ethanoic acid with a concentration of $0.220 \text{ mol dm}^{-3}$. [3]

$$[H^+]^2 = K_a \times [\text{acid}] = 1.76 \times 10^{-5} \times 0.220 = 3.872 \times 10^{-6}$$

$$[H^+] = 1.97 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.97 \times 10^{-3}) = 2.71$$

pH = 2.71

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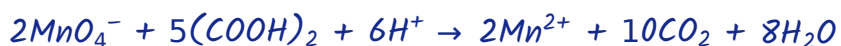
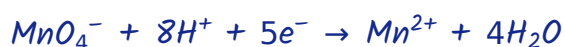
11. Oxalic acid is the common name for ethanedioic acid. It is found in a wide range of plants and when purified it can form a dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. The concentration of a saturated solution of oxalic acid can be found by titration.

(a) A sample of 25.0 cm^3 of a saturated solution of oxalic acid is diluted to form 250.0 cm^3 of an aqueous solution. Samples of 25.0 cm^3 of this diluted solution were heated and titrated using acidified potassium manganate(VII) to oxidise the oxalic acid.

(i) The half-equation for the oxidation of oxalic acid is shown below.



State the half-equation for the reduction of manganate(VII) ions in acid solution and use it to write the equation for the oxidation of oxalic acid by acidified manganate(VII) ions. [2]



- (ii) The titration of 25.0 cm^3 samples of the diluted oxalic acid solution against a potassium manganate(VII) solution of concentration $0.0505\text{ mol dm}^{-3}$ gave the following results.

	1	2	3	4
Volume of KMnO_4 solution / cm^3	31.65	31.30	31.60	31.75

- I. Use appropriate data to find the mean volume of KMnO_4 solution used. [1]

$$(31.65 + 31.60 + 31.75) \div 3 \quad (31.30 \text{ is anomalous})$$

$$\text{Mean volume} = \dots\dots\dots 31.67 \dots\dots\dots \text{ cm}^3$$

- II. Calculate the concentration of the original saturated solution of oxalic acid. [3]

$$\text{moles } \text{MnO}_4^- = 31.67 \times 0.0505 \div 1000 = 1.599 \times 10^{-3} \text{ mol}$$

$$\text{moles } (\text{COOH})_2 \text{ in } 25.0 \text{ cm}^3 = 1.599 \times 10^{-3} \times 5/2 = 4.00 \times 10^{-3} \text{ mol}$$

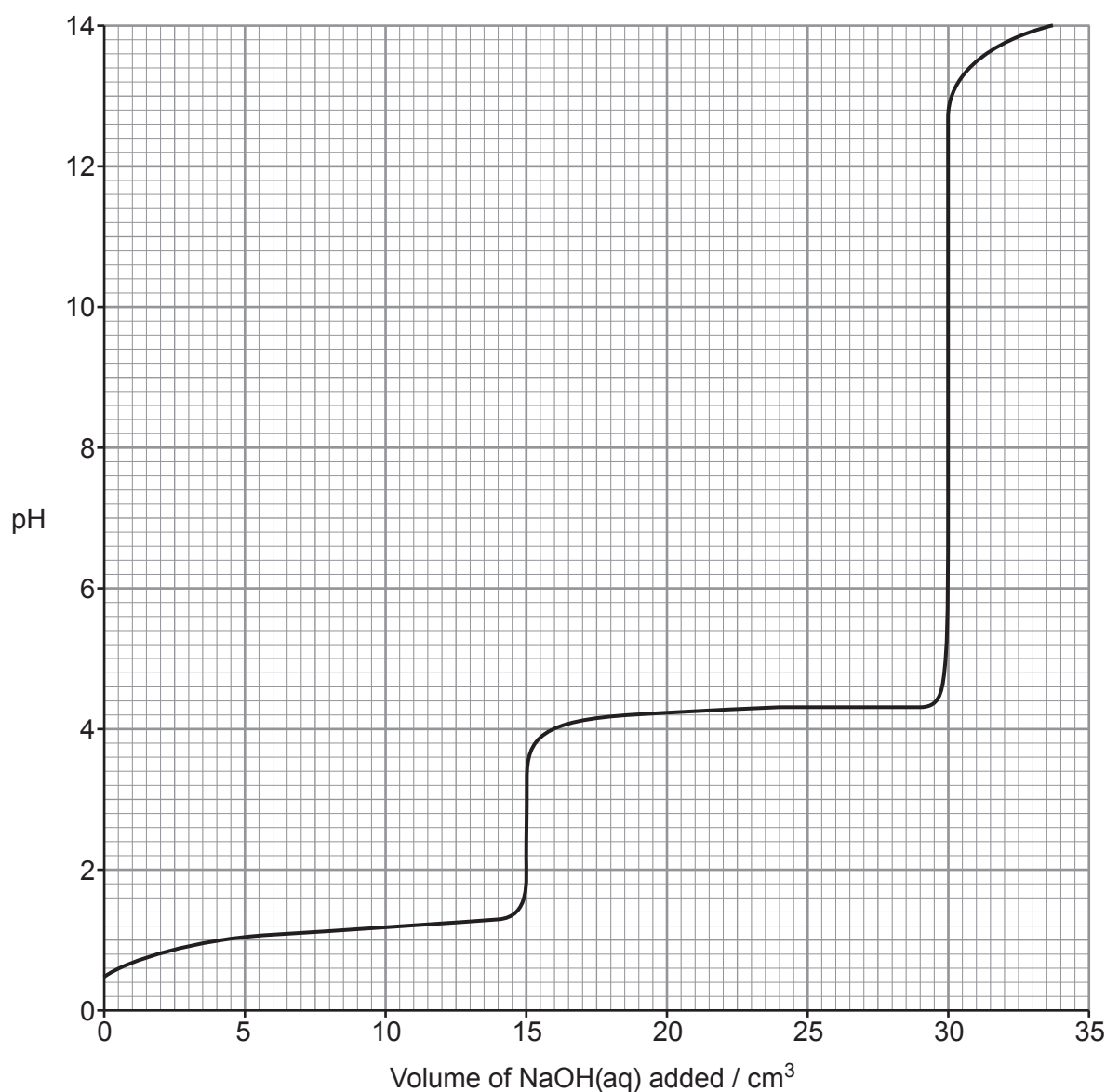
$$\text{concentration of diluted solution} = 4.00 \times 10^{-3} \div 0.0250 = 0.160$$

$$\text{original (diluted } \times 10) = 0.160 \times 10 = 1.60 \text{ mol dm}^{-3}$$

$$\text{Concentration} = \dots\dots\dots 1.60 \dots\dots\dots \text{ mol dm}^{-3}$$



- (b) Oxalic acid solutions may be analysed using acid-base titrations. The simplified pH curve for the titration of a solution of oxalic acid against sodium hydroxide is given below.



Four students undertook the titration in different ways:

- Alice used a pH probe to measure the pH after addition of each portion of sodium hydroxide solution
- Brychan used the indicator phenolphthalein in his titration; phenolphthalein has a pH range of 8.2 to 10.0
- Carys used the indicator methyl orange in her titration; methyl orange has a pH range of 3.2 to 4.4
- David used the indicator cresol red in his titration; cresol red has a pH range of 1.8 to 2.8



State and explain which, if any, of the methods chosen will allow the students to find valid data to calculate the concentration of oxalic acid. Briefly explain why oxalic acid has a pH curve of this shape. [6 QER]

You are not required to carry out any calculations.

Oxalic acid is a diprotic acid; it has two acidic protons (two COOH groups), which are removed in two stages.

The K_a (ease of removal) of each proton is different, the first being lost more easily, so the curve has two separate vertical regions.

The first vertical region (15 cm^3) occurs at half the volume of the second (30 cm^3) as each occurs after removing the same number of moles of protons.

The flat regions from about 5 to 10 cm^3 and 20 to 25 cm^3 are due to the formation of buffer solutions.

Indicators only work if they change colour fully within a vertical region, so Alice, Brychan and David's methods will work but Carys's will not.

Alice: the pH probe lets her plot the curve, so the first and second equivalence points can both be found.

Brychan: phenolphthalein (8.2 to 10.0) changes colour fully during the second vertical region.

David: cresol red (1.8 to 2.8) changes colour fully during the first vertical region.

Carys: methyl orange (3.2 to 4.4) is not within a whole vertical region; it would change colour gradually as the NaOH is added, so there is no sharp end point.



12. (a) A student planned to distinguish between the following eight compounds.

magnesium hydroxide	magnesium carbonate
iron(II) hydroxide	iron(II) carbonate
chromium(III) hydroxide	chromium(III) carbonate
lead(II) hydroxide	lead(II) carbonate

He used the following method.

Step 1 Add dilute acid until all the solid has disappeared. Record any effervescence.

Step 2 Add 1 cm³ of sodium hydroxide solution to each solution formed in step 1. Record any precipitate observed.

(i) State which compound(s) would give effervescence and why they do so. [2]

All four carbonates (Mg, Fe(II), Cr(III) and Pb(II) carbonates).

Acids react with metal carbonates to form carbon dioxide gas.

(ii) The student plans to use dilute hydrochloric acid in step 1. His teacher tells him that this is **not** the correct acid to use.

Explain why hydrochloric acid should not be used and suggest an appropriate acid to use in its place. [2]

Hydrochloric acid would form an insoluble compound (PbCl₂ precipitate)

with Pb²⁺, so the lead compounds would not dissolve.

Use nitric acid (or ethanoic acid) instead.



- (iii) Give the colours of the precipitates formed when sodium hydroxide solution is added to solutions containing the following ions. [2]

$\text{Mg}^{2+}(\text{aq})$ *white precipitate*

$\text{Fe}^{2+}(\text{aq})$ *(dark) green precipitate*

$\text{Cr}^{3+}(\text{aq})$ *(grey) green precipitate*

$\text{Pb}^{2+}(\text{aq})$ *white precipitate*

- (iv) The method given opposite is incomplete.

Suggest an additional step that would allow the remaining solutions formed in step 2 to be identified. Give the expected observations. State the property of the metals that allows them to be distinguished in this way. [3]

Add excess sodium hydroxide solution to each precipitate.

Magnesium hydroxide white precipitate remains but lead hydroxide white precipitate dissolves, giving a colourless solution.

Iron(II) hydroxide green precipitate remains but chromium(III) hydroxide precipitate dissolves, giving a dark green solution.

Lead and chromium hydroxides are amphoteric (iron and magnesium are not).



- (b) Many rocks that contain carbonate anions also contain a mixture of cations. Atomic absorption spectroscopy can be used to find the ratio of the amounts of different cations present.

Analysis of an acid solution formed from the carbonate mineral huntite shows that it contains 91 ng cm^{-3} of magnesium ions and 50 ng cm^{-3} of calcium ions. These are the only two metal cations present.

- (i) Find the formula of the mineral huntite. [3]

$$\text{Mg}^{2+}: 91 \div 24.3 = 3.745$$

$$\text{Ca}^{2+}: 50 \div 40.1 = 1.247$$

$$\text{ratio Mg : Ca} = 3.745 \div 1.247 : 1 = 3 : 1$$

$$\text{charge } 3(2+) + 2+ = 8+, \text{ so } 4 \times \text{CO}_3^{2-} \text{ needed}$$

Formula $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$

- (ii) The initial solution was prepared using $220 \mu\text{g}$ of huntite. Calculate the volume of aqueous acid used to form the solution for analysis. [3]

$$\text{concentration of huntite} = [\text{Ca}^{2+}] = 50 \times 10^{-9} \text{ g cm}^{-3}$$

$$= 50 \times 10^{-6} \text{ g dm}^{-3} \div 40.1 = 1.25 \times 10^{-6} \text{ mol dm}^{-3}$$

$$M_r \text{ Mg}_3\text{Ca}(\text{CO}_3)_4 = 3(24.3) + 40.1 + 4(60.0) = 353$$

$$\text{moles of solid} = 220 \times 10^{-6} \div 353 = 6.232 \times 10^{-7} \text{ mol}$$

$$\text{volume} = 6.232 \times 10^{-7} \div 1.247 \times 10^{-6} = 0.500 \text{ dm}^3$$

Volume = 0.500 dm^3



13. (a) Potassium dichromate(VI) is used as a reagent in acid solution in a wide range of redox reactions. The dichromate(VI) ions can be reduced using **excess** metallic zinc in acid conditions.

- Elfed performs the experiment in a sealed tube under an atmosphere of pure nitrogen gas
- Fatima performs the experiment in a standard test tube

The final products are different in each case. Use the standard electrode potentials below to identify the products in both cases. Give reasons for your answers. [4]

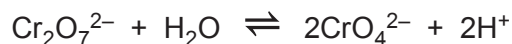
	Standard electrode potential, $E^\ominus$ /V
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.78
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.42
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33

Elfed's reaction produces Cr^{2+} . Zinc reduces dichromate(VI) to Cr^{3+} and then further to Cr^{2+} , as the $E^\ominus$ values for these two processes (+1.33 V and -0.42 V) are more positive than that for Zn^{2+}/Zn (-0.76 V): EMF = +2.09 V and +0.34 V. Cr^{3+} is not reduced to Cr as -0.78 V is more negative.

Fatima's reaction produces Cr^{3+} . Oxygen from the air oxidises Cr^{2+} back to Cr^{3+} , as $E^\ominus$ for O_2/OH^- (+0.40 V) is more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$: EMF = +0.82 V.



- (b) Chromium(VI) is present in the anions dichromate(VI), $\text{Cr}_2\text{O}_7^{2-}$, and chromate(VI), CrO_4^{2-} . These ions can be interconverted in solution with the following equilibrium being established.



The equilibrium constant, K_c , for this reaction is $2.42 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$.

In general, dichromate(VI) is the main species in acid solution and chromate(VI) is the main species in alkaline solution.

- (i) Write an expression for the equilibrium constant, K_c , for this reaction. [1]

$$K_c = \frac{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2}{[\text{Cr}_2\text{O}_7^{2-}] [\text{H}_2\text{O}]}$$

- (ii) The mass of the water in 1.00 cm^3 of a dilute aqueous solution is 1.00 g . Show that the concentration of water in any dilute aqueous solution is 55.5 mol dm^{-3} . [2]

$$1 \text{ dm}^3 = 1000 \text{ cm}^3 \text{ contains } 1000 \text{ g of water}$$

$$\text{moles of water} = 1000 \div 18.02 = 55.5 \text{ mol}$$

$$\text{so } [\text{H}_2\text{O}] = 55.5 \text{ mol dm}^{-3}$$



- (iii) A solution was prepared containing equal concentrations of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} . The concentration of each was $0.057 \text{ mol dm}^{-3}$. A student predicted that a solution containing equal amounts of both must be neutral. Is the student correct? Use calculation(s) to justify your answer. [4]

$$[\text{H}^+]^2 = K_c \times [\text{Cr}_2\text{O}_7^{2-}] \times [\text{H}_2\text{O}] \div [\text{CrO}_4^{2-}]^2$$

$$= 2.42 \times 10^{-15} \times 0.057 \times 55.5 \div 0.057^2$$

$$[\text{H}^+]^2 = 2.356 \times 10^{-12}, [\text{H}^+] = 1.535 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.535 \times 10^{-6}) = 5.81$$

The student is incorrect: the pH is 5.81, which is below 7, so this solution is acidic, not neutral.

- (iv) The value of the equilibrium constant for this reaction increases when the mixture is warmed. State and explain what information this provides about the enthalpy change of the reaction. [2]

If K_c increases on warming, the equilibrium is shifting to the right

(more products).

A reaction that shifts to the right when heated must be endothermic, so ΔH is positive.

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