

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



GCE A LEVEL

1410U30-1



S18-1410U30-1

CHEMISTRY – A2 unit 3

Physical and Inorganic Chemistry

TUESDAY, 5 JUNE 2018 – AFTERNOON

1 hour 45 minutes

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A 1. to 7.	10	
Section B 8.	14	
9.	18	
10.	12	
11.	18	
12.	8	
Total	80	

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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. 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.12(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. Give the electronic configuration of a copper atom. [1]

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

2. Excess sodium hydroxide is added to an aqueous solution of chromium(III) chloride, CrCl_3 . Give the formula of the chromium-containing ion formed. [1]

$[\text{Cr}(\text{OH})_6]^{3-}$

3. (a) Write the equation for the reaction of hot concentrated aqueous sodium hydroxide with chlorine. [1]

$6\text{NaOH} + 3\text{Cl}_2 \rightarrow \text{NaClO}_3 + 5\text{NaCl} + 3\text{H}_2\text{O}$

- (b) This is an example of a disproportionation reaction. State what is meant by the term *disproportionation*. [1]

A reaction in which the same element is both oxidised and reduced at the same time (here Cl goes from 0 to +5 and to -1).

4. Give the observation(s) expected when water is added to SiCl_4 . [1]

Steamy (misty) fumes of HCl are given off, and a white precipitate (solid) of SiO_2 forms.



5. A 25.0 cm³ sample of a solution containing iodine is titrated against a sodium thiosulfate solution of concentration 0.0200 mol dm⁻³. This requires 23.25 cm³ of sodium thiosulfate for complete reaction.



Calculate the concentration of the iodine in the solution in g dm⁻³.

[2]

$$n(\text{S}_2\text{O}_3^{2-}) = 0.0200 \times 23.25 \div 1000 = 4.65 \times 10^{-4} \text{ mol}$$

$$n(\text{I}_2) = 4.65 \times 10^{-4} \div 2 = 2.325 \times 10^{-4} \text{ mol}$$

$$[\text{I}_2] = 2.325 \times 10^{-4} \div 0.0250 = 9.30 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{mass conc.} = 9.30 \times 10^{-3} \times 253.8 = 2.36 \text{ g dm}^{-3}$$

Concentration = ... 2.36 g dm⁻³

6. The enthalpy of solution of sodium chloride is +4 kJ mol⁻¹. Explain why this compound is soluble in water despite this value being positive. [1]

Dissolving increases the entropy, as the ordered ionic lattice breaks up into freely moving aqueous ions. This entropy increase overcomes the small endothermic enthalpy change, so $\Delta G = \Delta H - T\Delta S$ is negative.

7. When a solution containing the weak base ammonia is neutralised using the strong acid sulfuric acid, a solution of ammonium sulfate is formed. Suggest a pH for this solution, giving a reason for your answer. [2]

pH $\approx$ 5 (weakly acidic).

The ammonium ion is a weak acid and dissociates to release H⁺ ions: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$.



SECTION B

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

8. (a) Sodium chloride and sodium bromide both react with concentrated sulfuric acid. Describe the observations in both reactions and explain why they are different. [3]

Both reactions give off steamy (misty) fumes of the hydrogen halide (HCl or HBr).

Only sodium bromide also gives orange/brown fumes of Br₂ and a pungent smell of sulfur dioxide.

Bromide is more easily oxidised than chloride: conc. sulfuric acid is a strong enough oxidising agent to oxidise Br⁻ to Br₂ (being reduced to SO₂) but not strong enough to oxidise Cl⁻.

- (b) Fluorine can form the weak acid hydrofluoric acid, HF. This acid has a K_a value of $7.20 \times 10^{-4} \text{ mol dm}^{-3}$.

- (i) Write an expression for the K_a of hydrofluoric acid. [1]

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

- (ii) Calculate the pH of a solution of hydrofluoric acid of concentration $0.100 \text{ mol dm}^{-3}$. [3]

$$[H^+] = [F^-], \text{ so } K_a = [H^+]^2 \div [HF] \text{ and } [H^+]^2 = K_a \times [HF]$$

$$[H^+] = \sqrt{(7.20 \times 10^{-4} \times 0.100)} = 8.49 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(8.49 \times 10^{-3}) = 2.07$$

pH = 2.07



- (iii) The concentration of a solution of hydrofluoric acid can be found by titrating against sodium hydroxide. Not all acid-base indicators would be suitable for this titration. Explain what features would make an indicator suitable for use in a weak acid-strong base titration. [2]

For a weak acid and strong base the vertical (steep) part of the titration curve is in the alkaline region, from about pH 7 to 11.

The indicator must change colour completely within this vertical region, e.g. phenolphthalein.

- (iv) Addition of 12.5 cm^3 of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide to 25.0 cm^3 of hydrofluoric acid of concentration $0.100 \text{ mol dm}^{-3}$ forms a buffer solution.

- I. Explain how this buffer solution works. [3]

$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ is an equilibrium, with lots of both HF and F^- present.

Adding a small amount of acid: the H^+ reacts with F^- ions, shifting equilibrium to the left. Adding a small amount of base: OH^- removes H^+ and more HF dissociates to replace it, shifting equilibrium to the right; pH stays almost constant.

- II. Calculate the pH of this buffer solution. [2]

$$n(\text{HF}) = 2.50 \times 10^{-3} \text{ mol}; \quad n(\text{NaOH}) = 1.25 \times 10^{-3} \text{ mol}$$

half the HF is neutralised, so $[\text{HF}] = [\text{F}^-]$ (acid = salt)

$$[\text{H}^+] = K_a \times [\text{HF}] \div [\text{F}^-] = 7.20 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(7.20 \times 10^{-4}) = 3.14$$

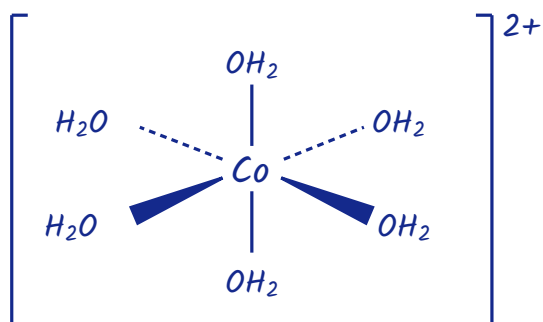
$$\text{pH} = 3.14$$



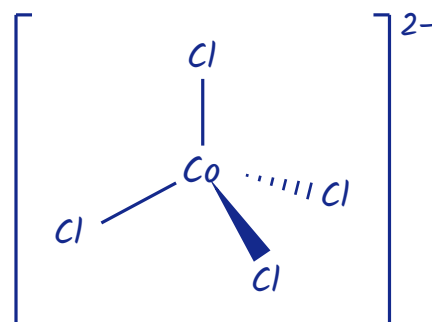
9. Cobalt forms a range of complex ions. Two of these are $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$.

(a) Draw the structures of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$ ions.

[2]



octahedral



tetrahedral

(b) Explain why the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion is coloured.

[3]

The H_2O ligands cause the 3d orbitals of Co^{2+} to split into two energy levels: three lower and two higher energy orbitals.

Electrons absorb energy from visible light of a particular frequency and are promoted from the lower to the higher energy level.

The colour seen is the light that is not absorbed (the complementary colour), so the solution appears pink.



- (c) A student was given a pink-coloured solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions. Upon addition of hydrochloric acid the solution turned blue as $[\text{CoCl}_4]^{2-}$ ions formed according to the equilibrium shown below.



Aqueous silver nitrate was added to the solution containing $[\text{CoCl}_4]^{2-}$.

State and explain the observation(s) expected.

[4]

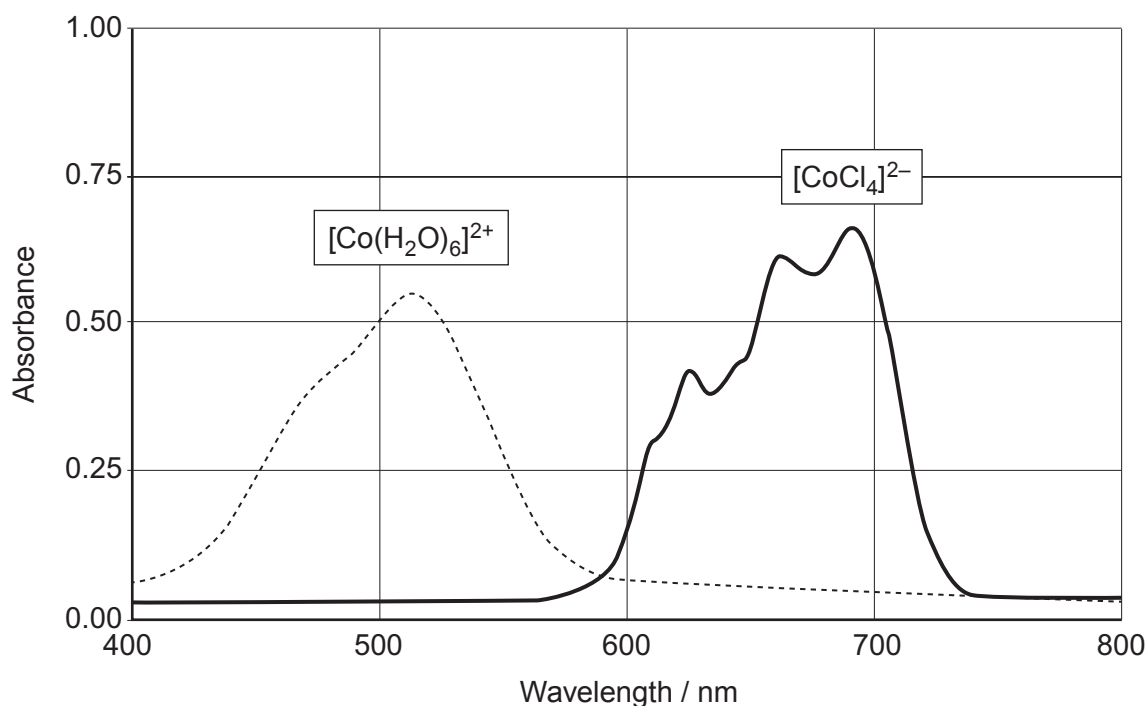
A white precipitate forms: silver chloride, as Ag^+ ions react with the Cl^- ions

($\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$).

The solution turns from blue to pink: removing Cl^- ions causes the equilibrium to shift to the left, re-forming $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (d) These two cobalt-containing ions absorb different frequencies of light. The spectra below show the absorbance at different wavelengths of visible light by the two ions.



- (i) The maximum absorbance for the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion occurs at a wavelength of 518 nm. Calculate the energy of this absorbance in kJ mol^{-1} . [3]

$$f = c \div \lambda = 3.00 \times 10^8 \div 518 \times 10^{-9} = 5.79 \times 10^{14} \text{ Hz}$$

$$E = hf = 6.63 \times 10^{-34} \times 5.79 \times 10^{14} = 3.84 \times 10^{-19} \text{ J}$$

$$\text{per mole: } 3.84 \times 10^{-19} \times 6.02 \times 10^{23} = 2.31 \times 10^5 \text{ J mol}^{-1}$$

$$= 231 \text{ kJ mol}^{-1}$$

$$\text{Energy} = \dots\dots\dots 231 \dots\dots\dots \text{ kJ mol}^{-1}$$

- (ii) A colorimeter was used to study the equilibrium between the two ions.

Suggest, giving a reason, an appropriate wavelength to use for the experiment. [1]

About 690 nm (above 600 nm), as this light is strongly absorbed by $[\text{CoCl}_4]^{2-}$ but hardly absorbed by $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (iii) Write the expression for the equilibrium constant, K_c , for this reaction **giving its unit**. [2]



$$K_c = \frac{[\text{CoCl}_4]^{2-} [\text{H}_2\text{O}]^6}{[\text{Co}(\text{H}_2\text{O})_6]^{2+} [\text{Cl}^-]^4}$$

Unit $\text{mol}^2 \text{dm}^{-6}$

- (iv) A student carries out an experiment starting with separate non-aqueous solutions of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and Cl^- .

When the two solutions are mixed the initial concentrations of both $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and Cl^- in the mixture are $0.720 \text{ mol dm}^{-3}$. When the mixture reaches equilibrium the concentration of the water is $0.744 \text{ mol dm}^{-3}$.

Calculate the value of the equilibrium constant, K_c . [3]

$$[\text{CoCl}_4]^{2-} = 0.744 \div 6 = 0.124 \text{ mol dm}^{-3}$$

$$[\text{Co}(\text{H}_2\text{O})_6]^{2+} = 0.720 - 0.124 = 0.596 \text{ mol dm}^{-3}$$

$$[\text{Cl}^-] = 0.720 - (4 \times 0.124) = 0.224 \text{ mol dm}^{-3}$$

$$K_c = (0.124 \times 0.744^6) \div (0.596 \times 0.224^4) = 14.0$$

$$K_c = 14.0 \text{ mol}^2 \text{dm}^{-6}$$



10. (a) (i) Tin and carbon are both more stable in oxidation state +4 whilst lead is more stable as +2. Explain the difference in the stabilities of these oxidation states. [1]

The inert pair effect becomes more significant down the group: the $6s^2$ pair in Pb is not used in bonding, so +2 is more stable for lead.

- (ii) Lead(IV) oxide can act as an oxidising agent when it reacts with concentrated hydrochloric acid. Write an equation for this reaction. [1]



- (b) Tin(II) ions can be used to reduce iron(III) ions in **acidic** solution.



$[Fe^{3+}] / \text{mol dm}^{-3}$	$[Sn^{2+}] / \text{mol dm}^{-3}$	pH	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
0.200	0.100	0	1.4×10^{-2}
0.300	0.200	0	2.8×10^{-2}
0.400	0.100	1	1.4×10^{-3}
0.400	0.200	1	2.8×10^{-3}

- (i) Find the rate equation for this reaction. [3]

Exp 3 to 4: $[Sn^{2+}]$ doubles and rate doubles: 1st order in Sn^{2+}

Exp 1 to 2: rate only doubles (due to Sn^{2+}): 0 order in Fe^{3+}

Exp 1 to 3: $[H^+]$ falls $10 \times$ (pH 0 to 1), rate falls $10 \times$:

1st order in H^+ rate = $k[H^+][Sn^{2+}]$

- (ii) Calculate the value of the rate constant, k , for this reaction. [2]

$k = \text{rate} \div [H^+][Sn^{2+}]$

$= 1.4 \times 10^{-2} \div (1.00 \times 0.100) = 0.14$

$k = 0.14 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$



- (iii) A student suggests that the rate determining step for this reaction is:



State, giving a reason, whether this is a possible rate determining step for this reaction. [2]

No, it is not possible: the rate determining step should include one H^+ ion and one Sn^{2+} ion and no Fe^{3+} ion (zero order), but this step has Fe^{3+} and no H^+ .

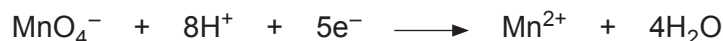
- (c) The rate of this reaction can be followed using sampling and quenching.

- (i) Explain what is meant by *sampling and quenching*. [1]

Samples are removed from the reaction mixture at set time intervals and the reaction in each is then stopped (quenched), e.g. by adding a large volume of cold water, before analysis.

- (ii) A 5.00 cm^3 sample of the solution was analysed by titration against acidified potassium manganate(VII). The sample required 27.20 cm^3 of manganate(VII) solution of concentration $0.00205\text{ mol dm}^{-3}$ for complete reaction.

Calculate the concentration of Fe^{2+} in the solution. [2]



$$n(\text{MnO}_4^-) = 0.00205 \times 27.20 \div 1000 = 5.576 \times 10^{-5} \text{ mol}$$

$$\text{reacting ratio } 5\text{Fe}^{2+} : 1\text{MnO}_4^-$$

$$n(\text{Fe}^{2+}) = 5 \times 5.576 \times 10^{-5} = 2.788 \times 10^{-4} \text{ mol}$$

$$[\text{Fe}^{2+}] = 2.788 \times 10^{-4} \div 0.00500 = 0.0558 \text{ mol dm}^{-3}$$

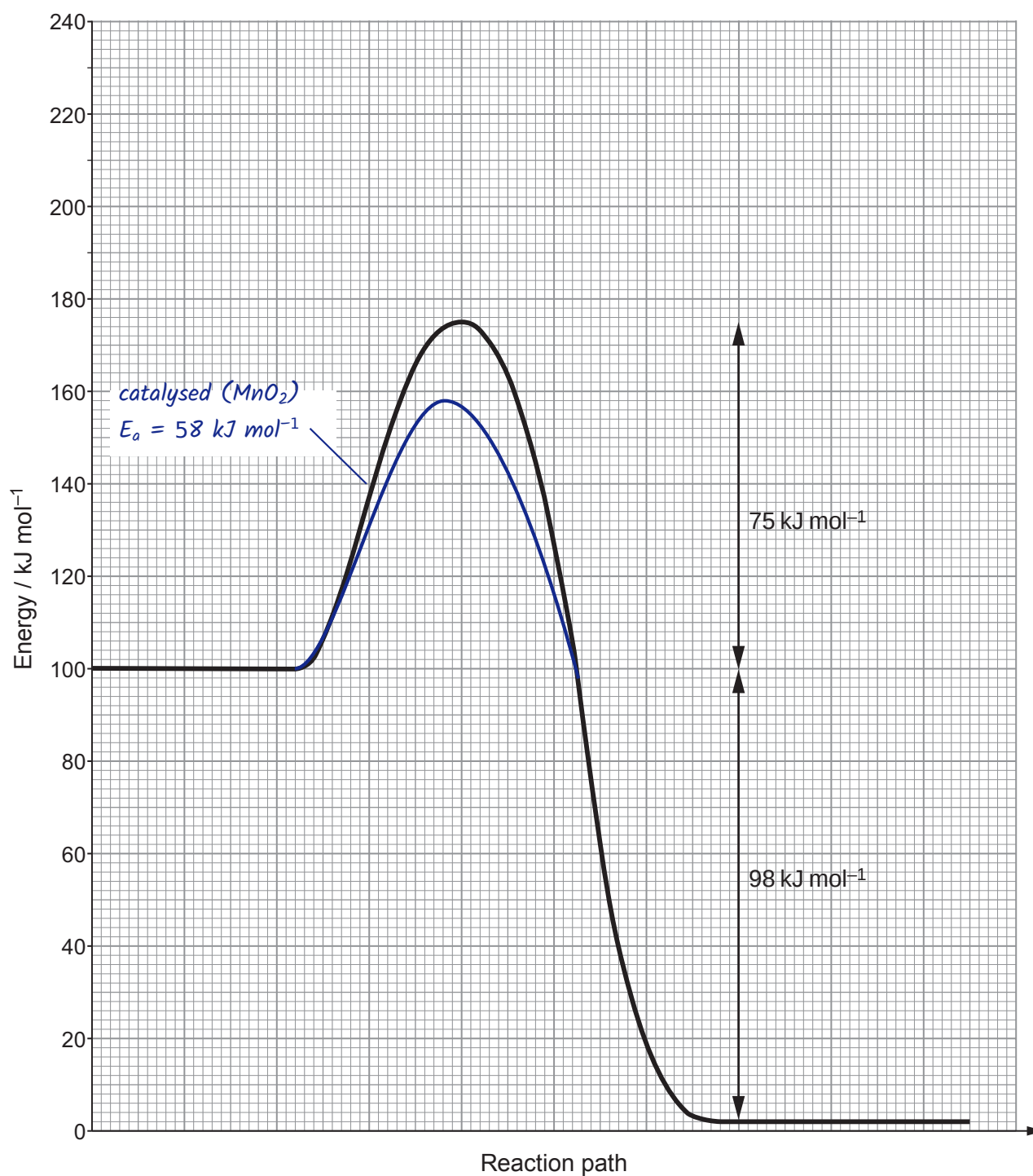
Concentration of Fe^{2+} = 0.0558 mol dm^{-3}



11. Hydrogen peroxide, H_2O_2 , decomposes slowly at 300 K to form water and oxygen gas.



The reaction profile for this reaction is shown below.



- (a) The rate of decomposition of hydrogen peroxide can be influenced by a range of catalysts. The activation energy when using MnO_2 as a catalyst is 58 kJ mol^{-1} .

Draw the reaction profile for the catalysed reaction **on the grid opposite**. [1]

- (b) Another catalyst was used and this gave a value for the rate constant, k , of $1.68 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the frequency factor, A , of $1.41 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at a temperature of 300 K .

- (i) State the Arrhenius equation. [1]

$$k = A e^{-E_a/RT}$$

- (ii) Calculate the activation energy using this catalyst and hence state whether it is a more effective catalyst than MnO_2 . [3]

$$e^{-E_a/RT} = k \div A = 1.68 \div 1.41 \times 10^4 = 1.19 \times 10^{-4}$$

$$-E_a \div RT = \ln(1.19 \times 10^{-4}) = -9.035$$

$$E_a = 9.035 \times 8.31 \times 300 = 22\,524 \text{ J mol}^{-1}$$

$$= 22.5 \text{ kJ mol}^{-1}$$

Activation energy = 22.5 kJ mol^{-1}

Its activation energy (22.5 kJ mol^{-1}) is lower than with MnO_2 (58 kJ mol^{-1}), so this catalyst is more effective.

- (c) The standard enthalpy change of formation, $\Delta_f H^\theta$, of water is -286 kJ mol^{-1} .

Use this information and the graph to calculate the standard enthalpy change of formation of hydrogen peroxide. [2]

$$\Delta_r H = 2\Delta_f H(\text{H}_2\text{O}) - 2\Delta_f H(\text{H}_2\text{O}_2) = -98 \text{ kJ mol}^{-1} \text{ (graph)}$$

$$2\Delta_f H(\text{H}_2\text{O}_2) = 2(-286) - (-98) = -474$$

$\Delta_f H^\theta(\text{H}_2\text{O}_2) = \underline{-237} \text{ kJ mol}^{-1}$

- (d) State whether you would expect the entropy change for the decomposition of hydrogen peroxide to be positive or negative. Give a reason for your answer. [1]

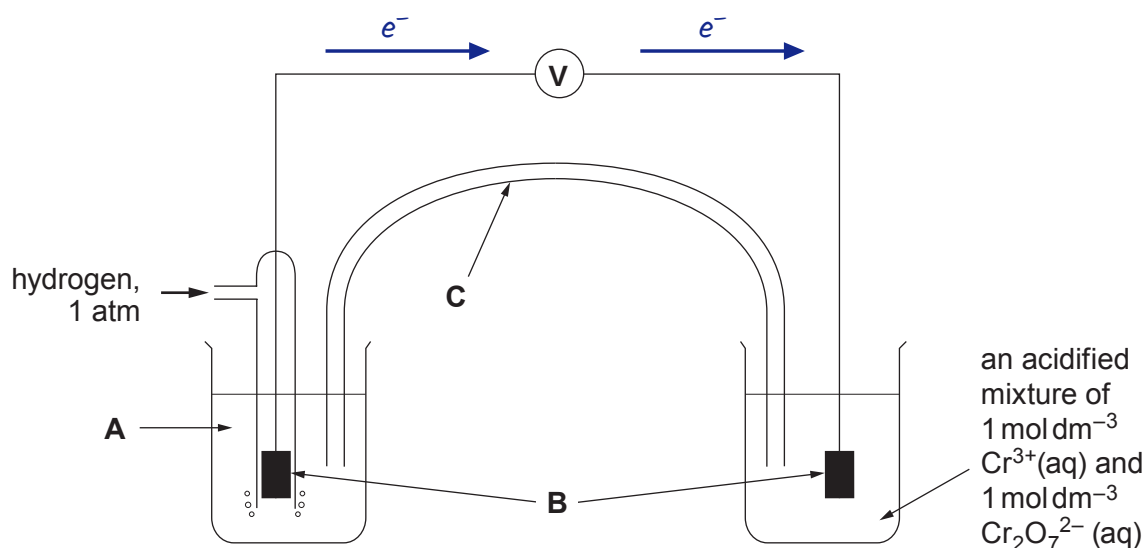
Positive: a gas (O_2) is formed from liquids, and gases have a higher entropy than liquids.



(e) One way of assessing whether a reaction is feasible is to use standard electrode potentials.

	Standard electrode potential / V
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.77
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33

- (i) The apparatus below can be used to measure the standard electrode potential for the $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half-cell.



- I. State what is represented by **A** and **B** on the diagram. [1]

A 1 mol dm⁻³ HCl / H⁺(aq)

B platinum (Pt) electrode

- II. **On the diagram** show the direction of flow of electrons in the external circuit. [1]



III. State what is represented by **C** on the diagram and state its function. [1]

Salt bridge ($\text{KNO}_3(\text{aq})$): it completes the circuit, letting ions flow, without allowing the solutions to mix.

IV. The concentrations of both $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} ions are 1 mol dm^{-3} . State and explain how the value shown on the high resistance voltmeter would change if the concentration of the Cr^{3+} ions were increased whilst the concentration of the $\text{Cr}_2\text{O}_7^{2-}$ was left unchanged. [2]

The reading becomes less positive (smaller). Increasing $[\text{Cr}^{3+}]$ shifts the equilibrium $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ to the left, so the half-cell accepts electrons less readily.

(ii) It is suggested that hydrogen peroxide could be used to oxidise Cr^{3+} ions in acidic solution to form dichromate ions.

I. Write an equation for this proposed reaction. [1]



II. Use the standard electrode potential values given to predict whether this reaction is feasible. [2]

Feasible: $E^\ominus$ for H_2O_2 (+1.77 V) is more positive than for $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ (+1.33 V), so $\text{EMF} = 1.77 - 1.33 = +0.44 \text{ V}$; a positive value means the reaction is feasible.

III. Another method of finding whether a reaction is feasible is to use the Gibbs free energy calculated from standard enthalpy of formation and standard entropy values.

State, giving a reason, whether Gibbs free energies or electrochemical methods are more appropriate for finding whether this reaction is feasible. [2]

Electrochemical methods are better, because the reaction takes place in aqueous solution, whereas standard enthalpies of formation (and entropies) refer to standard states, not solutions.



12. A student was provided with five ionic solids containing familiar cations and anions. Each solid contains a different **cation**. The solids were labelled **A**, **B**, **C**, **D** and **E**.

The student attempted to dissolve all five solids in water. She then attempted to dissolve those that did not dissolve in water in a stoichiometric amount of acid.

The results are given below.

Solid	Addition of water	Addition of dilute sulfuric acid to solid	Addition of dilute nitric acid to solid
A	dissolves giving colourless solution 1		
B	dissolves giving colourless solution 2		
C	does not dissolve	pale blue solution 3 forms upon warming with the acid	
D	does not dissolve	effervescence and solution 4 forms	
E	does not dissolve	some effervescence but the solid does not dissolve	effervescence and solution 5 forms

Pairs of the solutions formed were mixed and the observations recorded.

	Solution 5	Solution 4	Solution 3	Solution 2
Solution 1 (formed by dissolving solid A)	no visible change	white precipitate	white precipitate	bright yellow precipitate
Solution 2 (formed by dissolving solid B)	no visible change	no visible change	brown solution with a white solid	
Solution 3 (formed by reacting solid C with acid)	thick white precipitate	no visible change		
Solution 4 (formed by reacting solid D with acid)	thick white precipitate			

Flame tests

Flame tests carried out on solutions **1**, **2**, **3**, **4** and **5** gave no colour with one solution, an apple-green flame with another and a lilac flame with a third. The student noted unfamiliar flame test colours for the other two solutions.



- (a) Suggest which anion is present in substances **D** and **E**. Give a reason for your answer. [2]

Carbonate, CO_3^{2-} : D and E both effervesce with acid, as carbonates react with acids to release carbon dioxide gas.

- (b) Use **all** the information provided to suggest identities for compounds **A-E**.

Explain clearly how you identified compounds **A** and **C**.

[6 QER]

A *lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$*

B *potassium iodide, KI*

C *copper(II) oxide, CuO*

D *magnesium carbonate, MgCO_3*

E *barium carbonate, BaCO_3*

Explanation

Solution 1 + solution 2 gives a bright yellow precipitate of PbI_2 , so one contains lead(II) ions and the other iodide ions.

C is insoluble and does not fizz with acid, so it is an oxide (or hydroxide). It forms a pale blue solution with H_2SO_4 , so it contains copper(II) ions: C is copper(II) oxide.

Solution 2 + solution 3 gives a brown solution (I_2) and a white solid (CuI):

Cu^{2+} oxidises iodide, so B contains I^- ions, and its lilac flame shows K^+ , so B is KI . So A must contain Pb^{2+} ; the only soluble lead salt is lead(II) nitrate, which gives white PbSO_4 with solutions 3 and 4.

E gives an apple-green flame (Ba^{2+}) and stops fizzing in H_2SO_4 as insoluble BaSO_4 forms; solution 5 gives thick white BaSO_4 with sulfate solutions 3 and 4. D gives no flame colour and a soluble sulfate, so D is MgCO_3 .

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Examiner
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