NAME Answer slides CLASS 23S

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2024

CHEMISTRY **9729/04**

Higher 2 **13 August 2024**

Paper 4 Practical **2 hours 30 minutes**

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 20 and 21.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	**/ 14**
2	**/ 18**
3	**/ 11**
4	**/ 12**
Total	**/ 55**

This document consists of **21** printed pages.

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

1 Investigation of some inorganic and organic reactions

You are provided with the following samples:

FA 1 is an aqueous solution of an organic compound, **Y**.

FA 2 is an aqueous solution of an organic compound, **Z**, which is an isomer of **Y**.

FA 3 is a solid sample with molecular formula XO_n, where X is a metal.

You will perform tests to identify:

- the structure of **Y** in **FA 1**
- the functional group of **Z** in **FA 2**
- the cation in **FA 3**

(a) (i) Perform the tests described in Table 1.1, and record your observations in the table.

Table 1.1

	tests	observations
1	To 1 cm depth of **FA 1** in a test-tube, add a small piece of sodium. **Redox rxn. H_2? Identify —OH in alcohol, phenol & RCOOH.**	No observable change. No —OH group ⇒ alcohol, phenol & RCOOH absent.
2	To 1 cm depth of aqueous $AgNO_3$ in a test-tube, add 1 cm depth of aqueous NaOH. Then add aqueous NH_3 until the precipitate just dissolves. **Preparing Tollens' reagent, $Ag(NH_3)_2^+(aq)$.** To this mixture, add 1 cm depth of **FA 1**. Heat the mixture in the hot water-bath. **Oxidation. Silver mirror/grey ppt.? Identify aldehydes.**	**Brown ppt.** (✓1) dissolves to give a **colourless solution**. (✓2) Brown $Ag_2O(s)$ dissolves in $NH_3(aq)$ to give colourless $Ag(NH_3)_2^+(aq)$ Tollens' reagent. Upon warming with FA 1, **no silver mirror** (or **no grey ppt.**) (or **no observable change**). (✓3*) Aldehyde absent.
3	To 1 cm depth of **FA 1** in a test-tube, add 10 drops of aqueous sodium hydroxide. Now add aqueous iodine dropwise, until a permanent yellow/orange colour is obtained. Warm the mixture in the hot water bath for 2 minutes. **Iodoform Test. Pale yellow ppt.? Identify ethanal & ketones with $-COCH_3$ and alcohols with $-CH(OH)CH_3$.**	pale **yellow ppt.** (✓4*) formed. CHI_3 ppt. formed. ⇒ ketone with $—COCH_3$ present. **4(✓) [2]; 1(✓*) [1] (✓3*) or (✓4*)**

[2]

(ii) The molecular formula of **Y** is C_3H_6O and it has one functional group. Use your observations in Table 1.1 to deduce the structure of **Y** in **FA 1**.

FA 1 is a ketone with with —$COCH_3$

Structure of **Y** in **FA 1**: CH_3COCH_3. [1]

[1]

(iii) **FA 2** contains an organic compound, **Z**, which is an isomer of **Y**. {M.F. C_3H_6O}

Z contains one functional group.

Devise one confirmatory test, other than those stated in Table 1.1, using the bench reagents provided to identify the functional group present in **Z**.

Carry out the test. Record details of the test performed and observations made in Table 1.2.

Note: Z is isomeric with Y ⇒ M.F. of Z is C_3H_6O.

An alkene or alcohol with C_3H_6O will have 2 functional groups, e.g. $CH_2{=}CHCH_2OH$.

Since Z contains only one functional group, Z is an aldehyde.

Table 1.2

Confirmatory Test	*Observations*
To 1 cm depth of FA 2 in a test-tube, add 1 cm depth of ***dilute sulfuric acid** (or **dilute H_2SO_4**) and a few drops of ***aqueous potassium manganate(VII)** (or **$KMnO_4(aq)$**). **Heat** (or **Warm**) the mixture in the hot water-bath. [1] *State the name or correct formula of the reagent used according to the label on the reagent bottle.	**Purple** $KMnO_4$ **decolourised** [1] upon heating.

The functional group present in **Z**: **aldehyde** [1] with correct test & observations [3]

(b) **(i)** Perform the tests described in Table 1.3, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

FA 3 is a black solid.

Table 1.3

	tests	observations
1	Place 1 cm depth of sulfuric acid in a test-tube. Add a spatula of **FA 3** to this test-tube, followed by another 2 cm depth of aqueous potassium iodide. **Redox rxn? Brown I_2 soln? I^- oxidises to I_2? FA 3 is reduced?** Filter the mixture into a clean test-tube and collect the filtrate. **Filtrate colour? Residue colour?** To the filtrate, add aqueous sodium thiosulfate dropwise, with shaking, until the solution first becomes colourless. **$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ Brown I_2 reduces to colourless I^-.** Divide the resulting solution into two portions. These will be used in tests 2 and 3 respectively.	**Brown/ orange / yellow solution** obtained. (*✓$_1$) I^- oxidises to brown I_2 while FA 3 is reduced. **Brown/orange/yellow filtrate** (*✓$_1$) **Black/ dark brown residue.** (✓$_2$)   Brown/orange/yellow solution turns colourless.
2	To the first portion, add aqueous sodium hydroxide slowly until no further change is seen. Leave the mixture on standing for 2 minutes. **ppt? ppt sol. in xs? colour change of ppt. on standing?**	**Off-white/light brown ppt.**  **insoluble in excess NaOH.** (✓$_3$)  **ppt. turned darker brown** on standing. (*✓$_4$)  Mn^{2+} present in the filtrate.

[3]

3	To the second portion, add aqueous ammonia slowly until no further change is seen. ppt? ppt sol. in xs?	Off-white/light brown ppt. insoluble in excess NH_3. (✓$_5$) ppt. turned darker brown on standing. (*✓$_4$)
4	Place 3 cm depth of aqueous H_2O_2 into a test-tube. Add a spatula of **FA 3** to this test-tube. O_2 gas bubbles? H_2O_2 oxidises to O_2? $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ or H_2O_2 undergoes catalytic decomposition to give O_2? $2H_2O_2 \rightarrow O_2 + 2H_2O$ Note: With H_2O_2, H_2 gas will not form.	Brisk effervescence noted. (✓$_6$) O_2 (✓$_7$) gas relights a glowing splint. (✓$_8$)  No observable change to **FA 3**. 7-8(✓) [3]; 4-6(✓) [2]; 2-3(✓) [1]

(ii) Identify the metal ion in the filtrate.

metal ion: Mn^{2+} [1]

In Test 1, KI(aq) reduces FA 3 to Mn^{2+}(aq) which is collected in the filtrate.

Since FA 3 has M.F. of XO_n (where X is a metal), X is Mn;
and Mn in FA 3 should have higher oxidation state than +2.

⇒ FA 3 is MnO_2 or MnO_3 (not MnO).

[1]

(iii) Deduce the oxidation state of X in **FA 3**.

oxidation state of X in **FA 3**: +4 or +6. [1] [1]

(iv) Suggest the nature of **FA 3** in the reaction occurring in **Test 1**. Give evidence from the observations in your experiment.

nature of **FA 3**: **oxidising or oxidising agent** **[1]**

evidence:

- **FA 3/MnO_n oxidises I^-/KI to brown/orange/yellow $I_2(aq)$** after adding KI(aq). **[1]**

OR

- **FA 3/MnO_n is reduced to colourless $Mn^{2+}(aq)$** which gives a **off-white/light brown $Mn(OH)_2$ ppt. insoluble in excess NaOH(aq)/$NH_3(aq)$**. The ppt. darkened due to formation of brown $Mn(OH)_3(s)$ when contact in air on standing. **[1]**

[2]

(v) Suggest the role of **FA 3** in the reaction in **Test 4**.

role of **FA 3**: **heterogeneous catalyst** **[1]**

FA 3 is acting as a heterogeneous catalyst to increase the rate of decomposition of H_2O_2. Hence there is a rapid production of O_2 gas (brisk effervescence).

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

[1]

[Total: 14]

2 Determination of the molar enthalpy change of a reaction by an indirect method

Sodium hydroxide and sulfuric acid react according to equation 1.

equation 1
$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \quad \Delta H_1$

Sodium hydroxide and citric acid crystals react according to equation 2.

equation 2
$3NaOH(aq) + C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2Na)_3(aq) + 4H_2O(l) \quad \Delta H_2$

In this question, you will perform two experiments to determine the values for ΔH_1 and ΔH_2. You will use your values of ΔH_1 and ΔH_2 to calculate a value for the enthalpy change shown in equation 3.

equation 3
$C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2^-)_3(aq) + 3H^+(aq) + H_2O(l) \quad \Delta H_3$

In **2(d)**, you will use data provided to determine the concentration of sodium hydroxide in **FA 4**.

You are provided with:

FA 4 is aqueous sodium hydroxide, NaOH
FA 5 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
FA 6 is citric acid crystals, $C_3H_4(OH)(CO_2H)_3 \cdot H_2O$

(a) Experiment 1: Determination of the molar enthalpy change, ΔH_1, for the reaction in *equation 1*

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \quad \Delta H_1$$

You will follow the following instructions to perform the experiment.

Prepare a table in the space provided on the next page and record, to the appropriate level of precision: **(A single table!)**

- all temperatures measured,
- T_{ave} and the change in temperature, ΔT to 1 decimal place.

ΔT should be calculated using the following formula:

$$\Delta T = T_{max} - T_{ave}$$

$$T_{ave} = \frac{(\text{Volume of } \mathbf{FA\ 4} \times T_{FA\ 4}) + (\text{Volume of } \mathbf{FA\ 5} \times T_{FA\ 5})}{\text{Volume of } \mathbf{FA\ 4} + \text{Volume of } \mathbf{FA\ 5}}$$

(i) Method

1. Using a measuring cylinder, transfer 50.0 cm^3 of **FA 4** (an excess) into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
2. Stir and measure the temperature of this **FA 4**, T_{FA4}.
3. Using another measuring cylinder, measure 20.0 cm^3 of **FA 5**.
4. Stir and measure the temperature of this **FA 5**, T_{FA5}.
5. Add the **FA 5** from the measuring cylinder to the **FA 4** in the Styrofoam cup.
6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.

Results

T_{FA4} / °C	29.4	Using a 0.2 °C interval thermometer ⇒ precision = 0.1 °C (half interval) ⇒ all T readings to 1 d.p.
T_{FA5} / °C	29.6	
T_{max} / °C	38.2	
T_{ave} / °C	29.5	To 1 d.p. (following the instructions)
ΔT / °C (or K)	8.7 (or +8.7)	

[1] Records all data in a single table with the required 5 correct headers and units + record all temp readings to the nearest 0.1 °C

[1] Calculates T_{ave} and ΔT correctly to 1 d.p.

[1] Accuracy: student's ΔT = 8.3 to 8.9 [3]

(ii) Calculate the heat change, q, for your experiment.

Assume that the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1} and that the density of the solution is 1.00 g cm^{-3}. ⇒ $q = m \times c \times \Delta T$

⇒ m = mass of final solution in the cup giving ΔT_{max}
= total volume of final soln × density of final soln

ΔT of 1 °C = ΔT of 1 K
⇒ ΔT = 8.7 °C = 8.7 K ← (38.2 + 273) – (29.5 + 273)

$q = (50.0 + 20.0) \times 1.00 \times 4.18 \times 8.7$
= 2546 J = 2.546 kJ [1] ans. in J or kJ + ignore sign!

q = 2550 J or 2.55 kJ [1]

(iii) Determine the molar enthalpy change, ΔH_1, for the reaction in equation 1. The sodium hydroxide is in excess.

Include the sign of ΔH_1 in your answer. {heat evolved ⇒ exothermic, ΔH_1<0}

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \quad \Delta H_1$$

FA 4 — 50.0 cm^3; FA 5 (LR) — 20.0 cm^3

ΔH_{neut} is the heat evolved when 1 mole of water is formed from the reaction of an acid and an alkali.

⇒ ΔH_1 is not ΔH_{neut} since the eqn shows 2 mol of H_2O formed. $\Delta H_1 = 2 \times \Delta H_{neut}$

⇒ $\Delta H_1 = -\left(\dfrac{q}{\text{amount of LR}}\right) \times$ stoichiometric coefficient of LR

$n(H_2SO_4)$ reacted $= 1.00 \times \dfrac{20}{1000} = 0.0200$ mol

$\Delta H_1 = -\left(\dfrac{2.546}{0.0200}\right) \times 1 = -127$ kJ mol-1 [1] ecf 'q' with correct sign

ΔH_1 = –127 kJ mol^{-1} [1]

(b) Experiment 2: Determination of the molar enthalpy change, ΔH_2, for the reaction in *equation 2*

$3NaOH(aq) + C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2Na)_3(aq) + 4H_2O(l) \quad \Delta H_2$

You will follow the following instructions to perform the experiment.

In the space provided below, prepare tables **(2 tables)** in which to record for the experiment:

- all weighings and mass of **FA 6** added to an appropriate level of precision,
- all required temperature measurements and ΔT to an appropriate level of precision.

(i) Method

1. Weigh the capped bottle containing **FA 6**.
2. Using a measuring cylinder, transfer 50.0 cm^3 of **FA 4** into the other clean Styrofoam cup. Place this cup inside the used Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 4**, T_{FA4}.
4. Add all the **solid FA 6** to the **FA 4** in the Styrofoam cup.
5. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.
6. Reweigh the empty bottle with its cap.

Results

T_{FA4} / °C	29.2
T_{max} / °C	35.0
ΔT / °C (or K)	5.8 (or +5.8)

Mass of capped bottle with FA 6 /g	7.560
Mass of capped bottle with residual FA 6 / g	5.500
Mass of FA 6 added / g	2.060

[1] Tabulates all required mass readings in a single table with correct headers and units {reject "weight"} + records all mass readings to 3 d.p. + computes mass of FA 6 correctly.

[1] Records all temp data in a single table with the required 3 correct headers and units + records all temp. readings and ΔT to the nearest 0.1 °C + computes ΔT correctly.

[1] Accuracy: student's ($\Delta T/m$) = 2.6 to 3.0 [3]

(ii) Given that:

- sodium hydroxide is used in excess;
- M_r of $C_3H_4(OH)(CO_2H)_3.H_2O$ is 210.0;
- specific heat capacity of the solution is 4.18 J g^{-1} K^{-1};
- density of the solution is 1.00 g cm^{-3},

calculate the heat change, *q*, for your experiment and hence determine a value for the enthalpy change, ΔH_2, for the reaction in equation 2.

Include the sign of ΔH_2 in your answer.{heat evolved ⇒ exothermic, $\Delta H_2 < 0$}

$3NaOH(aq) + C_3H_4(OH)(CO_2H)_3 \cdot H_2O(s) \rightarrow C_3H_4(OH)(CO_2Na)_3(aq) + 4H_2O(l)$ ΔH_2

FA 4 (excess) FA 6 (LR)

50.0 cm^3

$q = m \times c \times \Delta T$

where m = mass of final solution in the cup absorbing the heat

= total volume of final soln × density of final solution

Assume that the added solids do not change the total volume of the final soln.

⇒ Do not include the mass of solid!

$q = 50.0 \times 1.00 \times 4.18 \times 5.8$

= 1212 J = 1.212 kJ [1] ans. in J or kJ + ignore sign

ΔH_2 is not ΔH_{neut} since the eqn shows 4 mol of H_2O formed. $\Delta H_2 = 4 \times \Delta H_{neut}$

$\Rightarrow \Delta H_2 = -\left(\frac{q}{\text{amount of LR}}\right) \times$ stoichiometric coefficient of LR

$$n(\text{citric acid}) \text{ reacted} = \frac{2.060}{210.0} = 0.00981 \text{ mol}$$

$$\Delta H_2 = -\left(\frac{1.212}{0.00981}\right) \times 1 = -124 \text{ kJ mol}^{-1}$$ [1] ecf 'q' with correct sign

q = 1210 J or 1.21 kJ

ΔH_2 = −124 kJ mol^{-1} [2]

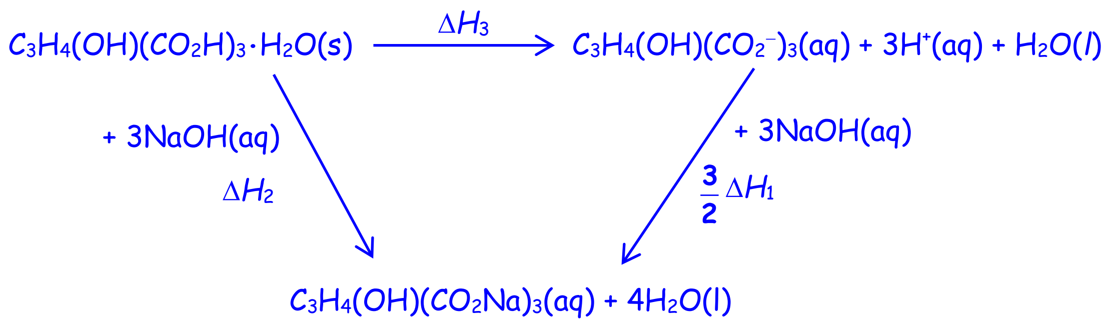
(c) Use your values of ΔH_1 and ΔH_2 to determine a value for the enthalpy change, ΔH_3, for the reaction in equation 3.

Show your working clearly and include the sign of ΔH_3 in your answer.

$C_3H_4(OH)(CO_2H)_3{\cdot}H_2O(s) \rightarrow C_3H_4(OH)(CO_2^-)_3(aq) + 3H^+(aq) + H_2O(l)$ ΔH_3

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ ΔH_1

$3NaOH(aq) + C_3H_4(OH)(CO_2H)_3{\cdot}H_2O(s) \rightarrow C_3H_4(OH)(CO_2Na)_3(aq) + 4H_2O(l)$ ΔH_2



By *Hess' Law*, $\Delta H_3 = \Delta H_2 - \frac{3}{2}\Delta H_1$ **[1] with working**

$= -124 - \frac{3}{2}(-127)$

$=$ **+66.5 kJ mol^{-1}** **[1] with correct sign**

$\Delta H_3 =$ **+66.5 kJ mol^{-1}**

[1] Shows working in all calculations + gives all final answers to 3 sf + gives correct units in all final ans: {for 2(a)(ii)(iii), (b)(ii)q,ΔH2 & (c)}

Any calculation not attempted loses this mark. [3]

(d) The procedure in experiment 1 can be used to determine the concentration of sodium hydroxide in **FA 4**.

A series of seven experiments were performed using different volumes of **FA 4** and **FA 5**. In each experiment, the total volume of the two solutions was kept at 50 cm^3 and the change in temperature, ΔT, was determined.

The results from the experiments were plotted on the grid in Fig. 2.1 below. By taking into account all of the points, two best-fit straight lines were drawn and the lines were extrapolated until they had crossed.

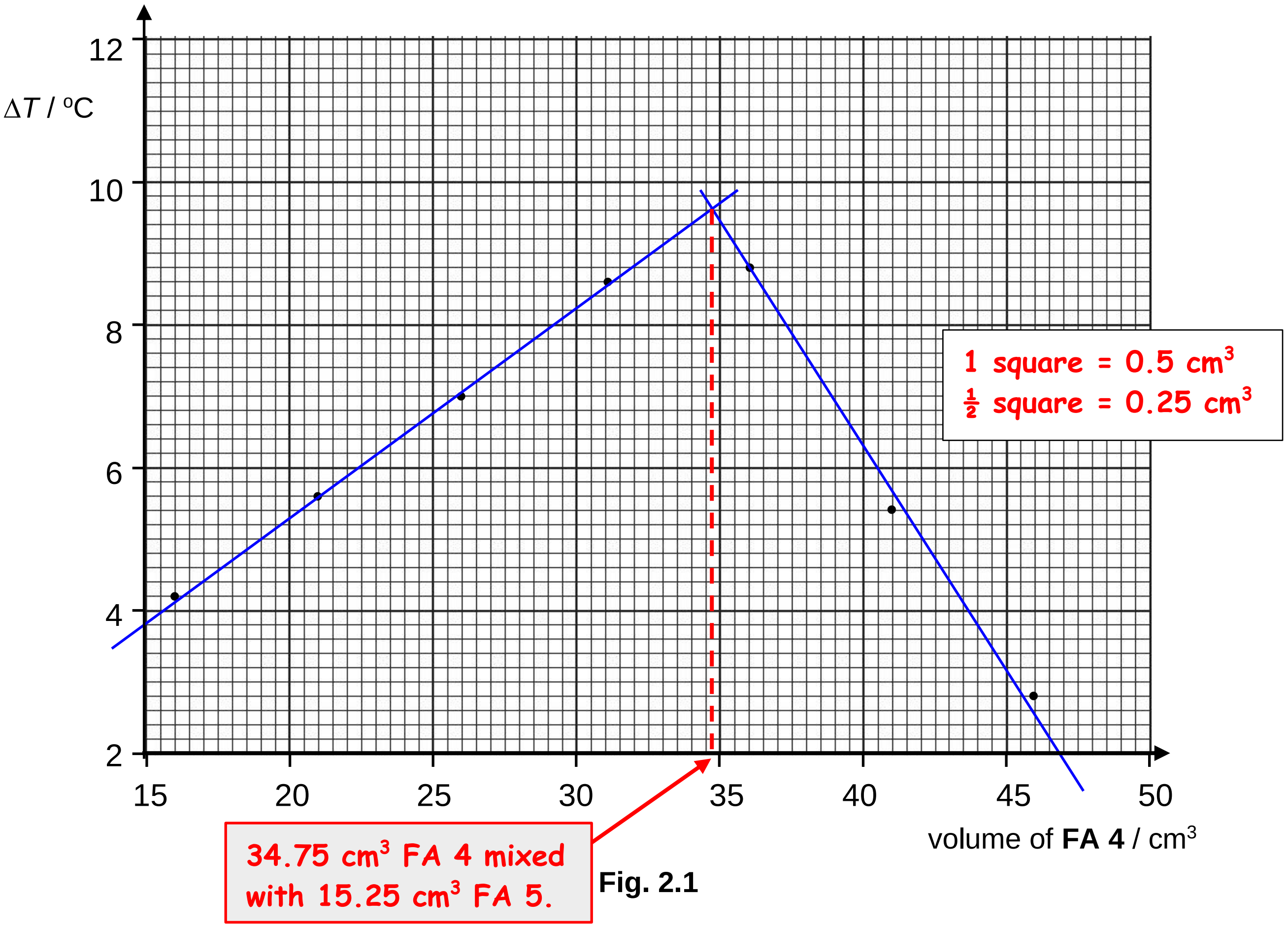


Fig. 2.1

(i) Explain, in terms of the reaction involved, the significance of the point of intersection of the two best-fit lines.

$NaOH(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l) \quad \Delta H_{neut}$

FA 4 FA 5

At this point, the **equivalence point has reached** where the **acid/H_2SO_4 exactly neutralises the base/NaOH present**, **[1]** giving a salt solution.

It gives the **maximum amount of water formed** such that **maximum amount of heat is evolved**. **[1]** [2]

Please refer to **JC1 PC 1** and **JC2 TP2 Q4 (planning)** for further understanding.

(ii) Using your graph, determine the volume of **FA 4** at the point of intersection. Hence, determine the concentration, in mol dm^{-3}, of sodium hydroxide in **FA 4**.

$NaOH(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l)$ ΔH_{neut}

FA 4 — FA 5

34.75 cm^3 — 15.25 cm^3

1.00 mol dm^{-3}

At the point of intersection,

Volume of NaOH = 34.75 cm^3 [1] read to the nearest half square

Volume of H_2SO_4 = 50 – 34.75 = 15.25 cm^3 (✓)

Amount of H_2SO_4 = $\frac{15.25}{1000} \times 1.00$ = 0.01525 mol (✓)

Amount of NaOH = 2 × 0.01525 = 0.0305 mol (✓)

[NaOH] in FA 4 = $\frac{1000}{34.75} \times 0.0305$ = 0.878 mol dm^{-3} (✓)

4(✓) [2], 2-3 (✓) [1]

Volume of NaOH = **34.75** cm^3

Concentration of NaOH = **0.878** mol dm^{-3} [3]

[Total: 18]

3 Determination of the kinetics of a reaction between M^{3+} ions and iodide ions, I^-.

In this experiment, you will investigate how the rate of this reaction is affected by the concentration of M^{3+} and I^- ions.

M^{3+} ions oxidise iodide ions, I^-, to iodine, I_2 as shown in equation 4.

equation 4 **$2M^{3+}(aq) + 2I^-(aq) \rightarrow 2M^{2+}(aq) + I_2(aq)$** immediately reacted away by $S_2O_3^{2-}$

The rate equation is **rate = $k [M^{3+}]^a [I^-]^b$**, where a and b are either 0, 1 or 2.

When starch is added to the reaction mixture, a blue colour is immediately seen due to the formation of an iodine-starch complex.

If a small amount of thiosulfate ions, $S_2O_3^{2-}$, is also present in the reaction mixture, the formation of the blue colour is delayed as the iodine produced reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ as shown in equation 5.

equation 5 **$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$**
from rxn 4

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue due to formation of iodine-starch complex.

FA 7 contains 0.0200 mol dm^{-3} metal ions, M^{3+}

FA 8 is 0.0080 mol dm^{-3} aqueous potassium iodide, KI

FA 9 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

Solution S is starch solution

You will perform a series of three experiments. You will add a fixed amount of sodium thiosulfate, **FA 9**, to each of your experiments. You will add an amount of deionised water so that the total volume is 55 cm^3. The time taken for the blue colour to form allows the reaction rate to be determined.

(a) Fill Table 3.1 with the volume of deionised water needed in each experiment.

Table 3.1

experiment	volume of **FA 7** / cm^3	volume of **FA 8** / cm^3	volume of **FA 9** / cm^3	volume of **solution S** / cm^3	volume of deionised water / cm^3	time, t /s
1	20.0	10.0	15.0	10.0	0.0	16.6
2	10.0	10.0	15.0	10.0	10.0	31.3
3	25.0	5.0	15.0	10.0	0.0	53.1

To measure using a 10 cm^3 measuring cylinder.
1 interval = 0.2 cm^3
½ interval = 0.1 cm^3 (∴ record all volumes of H_2O to 1 d.p.)

To the nearest 0.1 s

[1] states correct volume of deionised water such that V_{total} = 55 cm^3
+ records volume of water to 1 d.p.

[1] record t to nearest 0.1 s [1] correct trend ($t_3 > t_2 > t_1$) [3]

Experiment 1

The end-point of the reaction is the **first** appearance of a blue colour.

1. Use an appropriate measuring cylinder to transfer 10.0 cm^3 of **FA 8** into a 100 cm^3 beaker. Place the beaker on the white tile.
2. Use appropriate measuring cylinders, transfer to the beaker.
   - 15.0 cm^3 of **FA 9**
   - 10.0 cm^3 of starch solution
   - appropriate volume of deionised water recorded in Table 3.1.
3. Use the measuring cylinder labelled **FA 7** to transfer a 20.0 cm^3 of **FA 7** to the beaker and start the stopwatch at the instant of mixing.
4. Mix the contents in the beaker by **thoroughly** stirring.
5. Stop the stopwatch when the solution **first** turns blue.
6. Record the time taken, *t*, to nearest 0.1 s in Table 3.1.
7. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

Experiment 2 and 3

Repeat experiment 1 using the volumes of **FA 7, FA 8, FA 9, solution S** and deionised water given in Table 3.1.

You should alternate the use of the two 100 cm^3 beakers.

Record all values of *t* to nearest 0.1 s in Table 3.1.

(b) Calculate the ratio of the time taken in experiment 2, $t_{\text{expt 2}}$, to the time taken in experiment 1, $t_{\text{expt 1}}$, using the expression shown.

Record your answer to 1 decimal place.

$$\text{ratio 1} = \frac{t_{\text{expt 2}}}{t_{\text{expt1}}} = \frac{31.3}{16.6} = \underline{1.9}$$ (✓) with 1 dp

Similarly, calculate and record the ratio of reaction time given below.

$$\text{ratio 2} = \frac{t_{\text{expt 2}}}{t_{\text{expt3}}} = \frac{31.3}{53.1} = \underline{0.6}$$ (✓) with 1 dp 2(✓) [1]

Accuracy: ratio 1 = 1.8 - 2.0 *[1]

Accuracy: ratio 2 = 0.5 - 0.6 *[1]

*Award [0] if the total volume of the two expts is not kept constant. [3]

(c) The rate equation is **rate = k [M^{3+}]^a[I^-]^b**

(i) Deduce the order, a, with respect to [M^{3+}]. Explain your deduction in terms of your experimental results.

- Since the total volume of the reaction mixture is kept constant, initial [reactant] ∝ volume of reactant added.
- Since the same volume of $Na_2S_2O_3$ is used, the same end-point is timed. ∴ rate ∝ 1/t.

Comparing **experiments 1 and 2**, rate ∝ [M^{3+}]^a

Since rate $\propto \frac{1}{t}$, $\frac{rate_{expt\,1}}{rate_{expt\,2}} = \frac{t_{expt\,2}}{t_{expt\,1}} = 1.9 = \frac{(20.0)^a}{(10.0)^a}$

$1.9 = 2^a$

$\Rightarrow a = 0.926 \approx 1$

Or, When **[M^{3+}] is ×2**, **t is ≈** $\times\frac{1}{2}$ and hence **rate is ≈ ×2**.

∴ the **order of reaction w.r.t. [M^{3+}] is 1** or **a = 1**.

[1] with working

[1]

(ii) Deduce the order, b, with respect to [I^-]. Explain your deduction in terms of your experimental results.

Hence, complete the expression for the rate equation.

Comparing **Experiment 2 and 3**, rate ∝ [M^{3+}][I^-]^b

Since rate $\propto \frac{1}{t}$, $\frac{rate_{expt\,3}}{rate_{expt\,2}} = \frac{t_{expt\,2}}{t_{expt\,3}} \approx 0.6 = \frac{(25.0)(5.0)^b}{(10.0)(10.0)^b}$

$0.24 = 0.5^b$

$\Rightarrow b = \lg(0.24)/\lg(0.5)$
$= 2.06 \approx 2$

[1] with working

Or, Comparing **Experiment 1 and 3**, rate ∝ [M^{3+}][I^-]^b

Since rate $\propto \frac{1}{t}$, $\frac{rate_{expt\,1}}{rate_{expt\,3}} = \frac{\frac{1}{16.6}}{\frac{1}{53.1}} = \frac{(20.0)(10.0)^b}{(25.0)(5.0)^b}$

$4.00 = 2^b$

$\Rightarrow b = 2$

[1] with working

∴ **rate = k [M^{3+}][I^-]^2** **[1] ecf**

[2]

(d) **(i)** Instead of washing the beaker as required before performing the next experiment, a student simply just poured away the reaction mixture. There was some leftover reaction mixture in the beaker when he performed the subsequent experiment.

State, and explain, how the value of ***t*** would be affected.

reaction 4: $2M^{3+}(aq) + 2I^{-}(aq) \rightarrow 2M^{2+}(aq) + I_2(aq)$

reaction 5: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

from rxn 4

For reaction 4, rate = $k[M^{3+}][I^{-}]^2$

$Na_2S_2O_3$ is not the reactant for rxn 4 and hence the rate of qn 4 does not depend on $[Na_2S_2O_3]$.

However, **t will change if the amount of $S_2O_3^{2-}$ added is changed** since a fixed amount of $Na_2S_2O_3$ is added as a "marker" to control the amount of I_2 that is needed to be produced for the appearance of blue-black colour.

The residual I_2 left (or I_2 produced from residual reactants) in the beaker will react with $S_2O_3^{2-}$ added (✓1) for the new experiment.

Since less $S_2O_3^{2-}$ is left in the reaction mixture, less I_2 is needed to be produced (✓2) for the appearance of blue colour.

Hence t will be smaller/shorter (✓3). [1]

(ii) Instead of adding 15.0 cm^3 of **FA 9** in each experiment, a student used only 7.5 cm^3 of **FA 9**. (Total volume is still constant)

State, and explain, how the value of **t** would be affected.

Since amount of $Na_2S_2O_3$ present in the reaction mixture is halved, half the amount of iodine is needed to be produced (✓4) for the appearance of blue colour.

Hence t will be smaller/shorter (✓5).

2-3(✓) [1], 4-5(✓) [2]

Reject 't becomes faster' as fast/slow is describing rate, not length of time. [1]

[Total: 11]

4 Planning

The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^-\,(aq)$$

The equilibrium constant for the above solubility equilibrium, K_{sp}, is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$$

This solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate.

The exact concentration of IO_3^- ions is determined by titration. Excess aqueous KI and aqueous H^+ is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-\,(aq) + 5I^-\,(aq) + 6H^+\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate, $Na_2S_2O_3$ of known concentration.

$$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

(a) Using the information given above, you are required to write a plan to determine the solubility product, K_{sp}, of calcium iodate, $Ca(IO_3)_2$, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$ (M_r = 248.2)
- solid calcium iodate, $Ca(IO_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol dm^{-3}
- aqueous hydrochloric acid, HC*l*, of about 1 mol dm^{-3}
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm^3 of 0.075 mol dm^{-3} aqueous $Na_2S_2O_3$;
- the preparation of about 100 cm^3 of a saturated solution of calcium iodate, $Ca(IO_3)_2$ at 20 °C;
- the essential details of the titration process.

To prepare 250.0 cm^3 of 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$:

Mass of $Na_2S_2O_3.5H_2O$ required = $\frac{250}{1000} \times 0.075 \times 248.2$ = *4.654 g

1. **Weigh** accurately ***4.654/4.64 g of solid $Na_2S_2O_3.5H_2O$ into a weighing bottle** using an **electronic weighing balance**.
   (OR, **Weigh accurately *4.654/4.64 g of solid $Na_2S_2O_3.5H_2O$ into a small beaker** using an **electronic weighing balance**.)

[1] step 1: accurately weigh the required mass of solid in 2-3 d.p.

2. **Transfer all the weighed solid into a small beaker** and **dissolve the solid completely with** about 60 cm^3 **deionised water**.
   (OR, **Add** about 60 cm^3 of **deionised water into the beaker to dissolve the solid completely**).
3. Using a filter funnel, carefully **transfer the solution and all washings into a 250.0 cm^3 graduated/volumetric flask**. **Make up to the graduated mark with deionised water**. **Stopper and shake the flask well** to obtain a homogeneous solution.

[1] step 2 & 3: accurately prepares 250 cm^3 of standard soln with complete transfer (no loss of $S_2O_3^{2-}$).

To prepare about 100 cm^3 of $Ca(IO_3)_2$ saturated solution at 20 °C:

4. Use a **100 cm^3 measuring cylinder** to **transfer 100 cm^3 of deionised water into a** 250 cm^3 **conical flask**.
5. Using a spatula, **add** a few tips of **solid $Ca(IO_3)_2$ into the conical flask**. **Stopper the flask and shake the flask** for a few minutes. Keep adding more solid $Ca(IO_3)_2$, with shaking after each addition, **until some $Ca(IO_3)_2$ solids are left undissolved**.

[1] step 4 & 5: correctly prepares a saturated soln of $Ca(IO_3)_2$ {allow stirring using a glass rod or swirling in place of shaking; allow the use of a beaker or other appropriate apparatus.)

6. To ensure that the solution is saturated, shake the flask at intervals and **leave the conical flask in a *thermostat controlled water bath set at 20 °C** for some time/30 min. There must be **some solids left undissolved**.

[1] step 6: ensures saturated soln reached eqm at 20 °C using a thermostat controlled water bath

7. To remove undissolved solids, **filter the saturated solution into a dry conical flask using a dry filter funnel and a piece of dry filter paper**.

[1] step 7: performs a dry filtration to remove undissolved solids and collect the filtrate in a dry flask.

Titration procedure:

8. Fill a burette with 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$.
9. Pipette *25.0 cm^3 of the saturated solution into a conical flask.
10. Use separate measuring cylinders to add to the conical flask 10 cm^3 of HCl(aq) and 10 cm^3 of KI(aq).

[1] step 8-10: accurately prepares titrant and analyte in a conical flask with minimum 10 cm^3 of KI & minimum 5 cm^3 of H^+.

11. Titrate the liberated I_2 in the mixture with $Na_2S_2O_3$(aq) from the burette until the solution turns pale yellow. Then add about 1 cm^3 of starch indicator and continue to titrate until the dark blue-black colour just disappears/ turns colourless at the end-point.
12. Repeat the titration to obtain two consistent titres within 0.10 cm^3 in difference.

[1] step 11: correct titration procedure using starch indicator with end-point colour change correctly stated.

[7]

(b) Outline how you would use your mean titre value to determine the solubility product of $Ca(IO_3)_2$.

In your calculations, you should let **V** cm^3 be your mean titre and express your final mathematical expression in terms of **V**.

$n(S_2O_3^{2-})$ required $= \dfrac{V}{1000} \times 0.075 = 7.5 \times 10^{-5}\ V$ mol

$n(IO_3^-)$ in *25.0 cm^3 saturated soln

$= \dfrac{1}{6} \times 7.5 \times 10^{-5} V = 1.25 \times 10^{-5}\ V$ mol [1]

IO_3^- : I_2 : $S_2O_3^{2-}$
1 : 3 : 6

$[IO_3^-]$ in saturated solution

$= \dfrac{1000}{*25.0} \times 1.25 \times 10^{-5} V = 5 \times 10^{-4}\ V$ mol dm^{-3} [1]

*volume of saturated soln used in titration.

	$Ca(IO_3)_2$ (s)	⇌	Ca^{2+} (aq)	+	$2IO_3^-$ (aq)
eqm conc.	-		2.5×10^{-4} V		5×10^{-4} V
			x		2x

K_{sp} $(Ca(IO_3)_2) = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$

$= (2.5\times10^{-4}\ V)(5\times10^{-4}\ V)^2$

$= 6.25 \times 10^{-11}\ V^3$ mol^3 dm^{-9}

(OR $= 4x^3 = 4\left(\dfrac{5\times10^{-4}V}{2}\right)^3 = 6.25 \times 10^{-11}\ V^3$ mol^3 dm^{-9}

[1]

[3]

(c) The experiment described in your plan in **(a)** is repeated using 0.1 mol dm^{-3} aqueous $Ca(NO_3)_2$ solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V). **{the solvent contain common Ca^{2+} ions}**

State and explain how, if at all, the titre values and calculated K_{sp} would be expected to differ from that obtained in **(a)**.

Assume that both the experiments were carried out under the same conditions.

Presence of **common ion Ca^{2+}** from $Ca(NO_3)_2(aq)$ **increases $[Ca^{2+}(aq)]$ and causes the position of equilibrium of $Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$ to shift left**. ∴ the **solubility of $Ca(IO_3)_2$ is reduced**. **[1]**

With a **lower $[IO_3^-]$ in saturated solution**, the **titre values will be smaller**. However, **since the temperature is kept constant**, the calculated **K_{sp} value would remain the same/unchanged**. **[1]** [2]

[Total: 12]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of Aqueous Cations

cation	*Reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no. ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off–white ppt. rapidly turning brown on contact with air insoluble in excess	off–white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of Anions

Anion	***Reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
choride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$);
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$);
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$);
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in excess dilute strong acids)

(c) Tests for Gases

gas	***Test and test results***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns acidified aqueous potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas/liquid	orange	orange–red
iodine, I_2	black solid/purple gas	brown	purple