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

1 Determination of the value of *n* in IO_n^-

IO_n^- is an oxoanion of iodine. It can react with iodide ions, I^-, in an acidic medium, to produce only molecular iodine and water.

This amount of iodine can be analysed via titration with sodium thiosulfate, $Na_2S_2O_3$.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

In this question, you will perform an experiment to determine the stoichiometric ratio between IO_n^- and I_2 and the value of *n* in IO_n^-.

FA 1 is solid hydrated sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$
FA 2 is a solution containing 0.00825 mol dm^{-3} KIO_n
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is 0.25 mol dm^{-3} potassium iodide, KI

You are also provided with starch solution.

(a) Preparation of a standard solution of 0.0484 mol dm^{-3} sodium thiosulfate

(i) Determine the mass of **FA 1** required to prepare 250 cm^3 of sodium thiosulfate solution with a concentration 0.0484 mol dm^{-3}.
[A_r: S, 32.1; O, 16.0; Na, 23.0; H, 1.0]

Amount of $Na_2S_2O_3 = \frac{0.0484}{1000} \times 250 = 0.0121$ mol
M_r of $Na_2S_2O_3 \cdot 5H_2O = 248.2$
Mass of $Na_2S_2O_3 \cdot 5H_2O = 0.0121 \times 248.2 = 3.003 = 3.00$ g

mass of **FA 1** required = …….. g [1]

You will follow the instructions to perform the preparation of the standard solution.

Record your measurements in Table 1.1.

(ii)
1. Using a mass balance, weigh out accurately the mass of **FA 1** determined in **(a)(i)** into a weighing bottle.
2. Dissolve **FA 1** in about 50 cm^3 of deionised water in a 100 cm^3 beaker.
3. Transfer the solution and washings into a 250 cm^3 volumetric flask, using a filter funnel.
4. Top up to the 250 cm^3 mark with deionised water.
5. Stopper the flask and shake to ensure solution is homogeneous. Label this solution as **FA 5**.

Complete Table 1.1 with your mass measurements and calculate the mass of **FA 1** that you used.

Table 1.1

Mass of weighing bottle and **FA 1** / g	
Mass of empty weighing bottle / g	

Mass of **FA 1** / g	3.00

[2]

Records all masses to same number of decimal places (PDO)
Records correctly all masses (PDO)
Mass of **FA 1** measured is ± 0.05 g of that determined in **(a)(i)** (MMO)

(b) Preparation and titration of the reaction mixture

1. Fill a burette with **FA 5**.
2. Using a 25.0 cm^3 pipette, add 25 cm^3 of **FA 2** to a 250 cm^3 conical flask.
3. Using a measuring cylinder, add 10.0 cm^3 of **FA 3**, followed by 10.0cm^3 of **FA 4** to the same conical flask and swirl quickly.
4. **Immediately** titrate the I_2 in the conical flask with **FA 5**. When a pale yellow colour is obtained, add 1 cm^3 of starch solution. The end-point is reached when the blue – black colour of the solution decolourises.
5. Repeat steps **2** to **4** until consistent results are obtained and record your results below.

Results

Final burette reading/cm^3		
Initial burette reading/cm^3		
Volume of FA5/ cm^3	**23.65**	**23.65**

[5]

Records all burette readings to 2 d.p. (MMO)
Has at least 2 titre values ± 0.10 cm^3 (MMO)
Table has appropriate headings and units (PDO)
Accuracy (MMO)

Obtain, from your titration results, a suitable average titre of **FA 5**. Show clearly the titres you used in calculating this average.

Average volume of **FA5** = (23.65 + 23.65)/ 2 = 23.65 cm^3

Average volume of **FA 5** = …….. [1]

Selects at least 2 titre values that are ± 0.20 cm^3 and presents average titre to 2 d.p., with appropriate units (PDO)

Calculations

Show your working and appropriate significant figures in all of your calculations.

(c) (i) Calculate the amount, in moles, of $Na_2S_2O_3$ present in the volume of **FA 5** determined in **(b)** and hence the amount of iodine produced.

Amount of $S_2O_3^{2-}$ = conc × volume

Amount of I_2 = Amount of $S_2O_3^{2-} \div 2$

Amount of I_2 = ……..[2]

(ii) Calculate the amount of **FA 2** used in the titration.

Amount of **FA 2** = $\frac{0.00825}{1000} \times 25 = 2.0625 \times 10^{-4}$
$= 2.06 \times 10^{-4}$ mol (ACE)

Amount of **FA 2** = …….. [1]

(d) **(i)** Construct a balanced half-equation, in terms of *n*, for the reduction of IO_n^-.

$IO_n^- + (2n-1)e^- + 2nH^+ \longrightarrow \frac{1}{2} I_2 + nH_2O$

…… [1]

(ii) Hence construct a balanced equation, in terms of *n*, for the reaction between IO_n^- and I^- to give I_2 and H_2O.

$IO_n^- + (2n-1)I^- + 2nH^+ \longrightarrow nI_2 + nH_2O$

…… [1]

(iii) Determine the amount of I_2 produced by one mole of IO_n^- and determine the value of *n* in IO_n^-.

Amount of I_2 produced per mole of IO_n^- = $n = \frac{\text{Answer in (c)(i)}}{\text{Answer in (c)(ii)}}$

n =…….. [1]

(e) **Planning**

The reaction rate between IO_n^- and I^- in an acidic medium can be expressed in the following rate equation:

$$\text{rate} = k\,[IO_n^-]^x\,[I^-]^y\,[H^+]^z$$

If the concentrations of iodide and hydrogen ions are kept constant, the rate equation becomes

$$\text{rate} = k'\,[IO_n^-]^x$$

where $k' = k\,[I^-]^y\,[H^+]^z$

Iodine produced by the reaction gives a dark blue colour in the presence of starch solution.

A small amount of sodium thiosulfate is measured using a burette and added to the reaction mixture prior to the start of the reaction. The sodium thiosulfate reduces the iodine produced and this can be used to monitor the rate of reaction. By changing the initial concentration of IO_n^- and studying how this change influences the reaction rate, its order of the reaction with iodide ions in an acidic medium can be determined.

(i) Plan an investigation, to determine the order of reaction with respect to IO_n^-, in its reaction with iodide ions in an acidic medium.

You may assume that you are provided with
- 100 cm^3 of 0.00825 mol dm^{-3} KIO_n,
- 100 cm^3 of 0.25 mol dm^{-3} potassium iodide, KI,
- 100 cm^3 of 0.0484 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
- 0.5 mol dm^{-3} sulfuric acid, H_2SO_4,
- distilled water,
- starch solution,
- the apparatus normally found in a school or college laboratory.

In your plan you should include details of
- the reagents and apparatus that you would use,
- the procedure that you would follow and the measurements that you would take.

…….. [4]

- Total volume of reaction mixture is constant across different mixtures, with different volume of KIO_n used / other method to ensure concentration of IO_n^- is different in each reaction mixture

- Fixed and small (in relation to volume of KIO_n used, not marking for this) volume of $S_2O_3^{2-}$ used in each reaction mixture (to monitor a fixed amount of iodine produced by the reaction)

- Volumes of KI, KIO_n, H_2SO_4, H_2O measured using measuring cylinders of appropriate capacities

- Start taking time when either KI or KIO_n is poured into reaction mixture containing the rest of the required reagents and stop time when a blue-black colour is observed

(ii) Sketch the graph, with labelled axis, you would expect to obtain from your results in **1(e)(i)**.

Explain your answer.

……[3]

Plot lg (rate) = x lg([IO_n^-]) + c
y – axis is lg (rate) or lg(1/t)
- x – axis is lg([IO_n^-]) or lg (V_{FA2})
- c is lg *k*'
- straight line with positive gradient
- rate ∝ $\frac{1}{time}$ since shorter time taken for blue colour to be seen (faster reaction with $S_2O_3^{2-}$), faster the rate of production of iodine / any other reasonable way to determine initial rate

OR

Plots the following graphs (can be drawn or described)
1. Rate vs [IO_n^-] (straight horizontal line) for zero order
   OR
   1/t vs V_{FA2}
2. Rate vs [IO_n^-] (linear with positive gradient) for 1st order
3. Rate vs [IO_n^-]^2 (linear with positive gradient) for 2nd order

- rate ∝ $\frac{1}{time}$ since shorter time taken for blue colour to be seen (faster reaction with $S_2O_3^{2-}$), faster the rate of production of iodine / any other reasonable way to determine initial rate

(iii) Briefly describe how you would use your graph to determine the order with respect to IO_n^-.

Calculate the gradient of the graph in **2(c)(ii)** which will be the order

OR

Match data obtained to one of the three graphs drawn above

……[1]

[Total: 23]

2 Determination of the enthalpy change of neutralisation, ΔH_n

FA 6 is a solution of sodium hydroxide, NaOH, of unknown concentration

According to the *Arrhenius* theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions, in aqueous solution. Using the *Arrhenius* theory, an acid-base neutralisation reaction involves reacting together these two ions to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H_n$$

In this question, you will carry out a series of experiments where different volumes of **FA 3** and **FA 6** are mixed together.

You will determine the temperature change of the mixture, ΔT of each experiment and then analyse your results graphically in order to determine the

- concentration of NaOH in **FA 6**
- maximum temperature change, ΔT_{max}
- value for the enthalpy change of neutralisation, ΔH_n

(a) Determining the change in temperature for a series of reactions between FA 3 and FA 6

(i)

1. Support the styrofoam cup in a 250 cm^3 beaker.
2. Using a measuring cylinder, place 10 cm^3 of **FA 3** into the styrofoam cup.
3. Measure the temperature of **FA 3** in the styrofoam cup. Record the initial temperature of the solution of **FA 3** as $\mathbf{T_{initial}}$.
4. Place 40 cm^3 of **FA 6** into another measuring cylinder.
5. Tip the **FA 6** in the measuring cylinder into the styrofoam cup, stir and record the maximum temperature obtained in the reaction as $\mathbf{T_{max}}$.
6. Rinse and dry the styrofoam cup and the thermometer.
7. Repeat steps **2** to **6** using volumes of **FA 3** listed in Table 2.1. Fill in Table 2.1 with the appropriate volumes of **FA 6** to be used in each experiment such that the total volume of the reaction mixture is 50 cm^3.

Table 2.1

Experiment	**1**	**2**	**3**	**4**	**5**	**6**
Volume of **FA 3** / cm^3	10	20	30	40	15	25
Volume of **FA 6** / cm^3	40	30	20	10	35	25

[1]

In an appropriate format in the space provided, prepare a table in which to record for each experiment

- the initial temperature
- the maximum temperature
- the change in temperature, ΔT

Results

Experiment	Initial Temperature/ ^oC	Final Temperature/ ^oC	ΔT/ ^oC
1	29.0	35.5	6.5
2	29.5	42.0	12.5
3	29.5	38.0	8.5
4	29.5	33.5	4.0
5	30.0	39.0	9.0
6	30.0	40.5	10.5

[3]

(ii) Plot a graph of ΔT (y–axis) against volume of **FA 6** used (x–axis) using the data you have obtained above in **a(i)** on the grid in Fig. 2.1.

By considering the points you have plotted, carry out two more experiments (experiment **5** and **6**) which will enable you to identify the volume of **FA 6** which gives the maximum temperature change, ΔT_{max}.

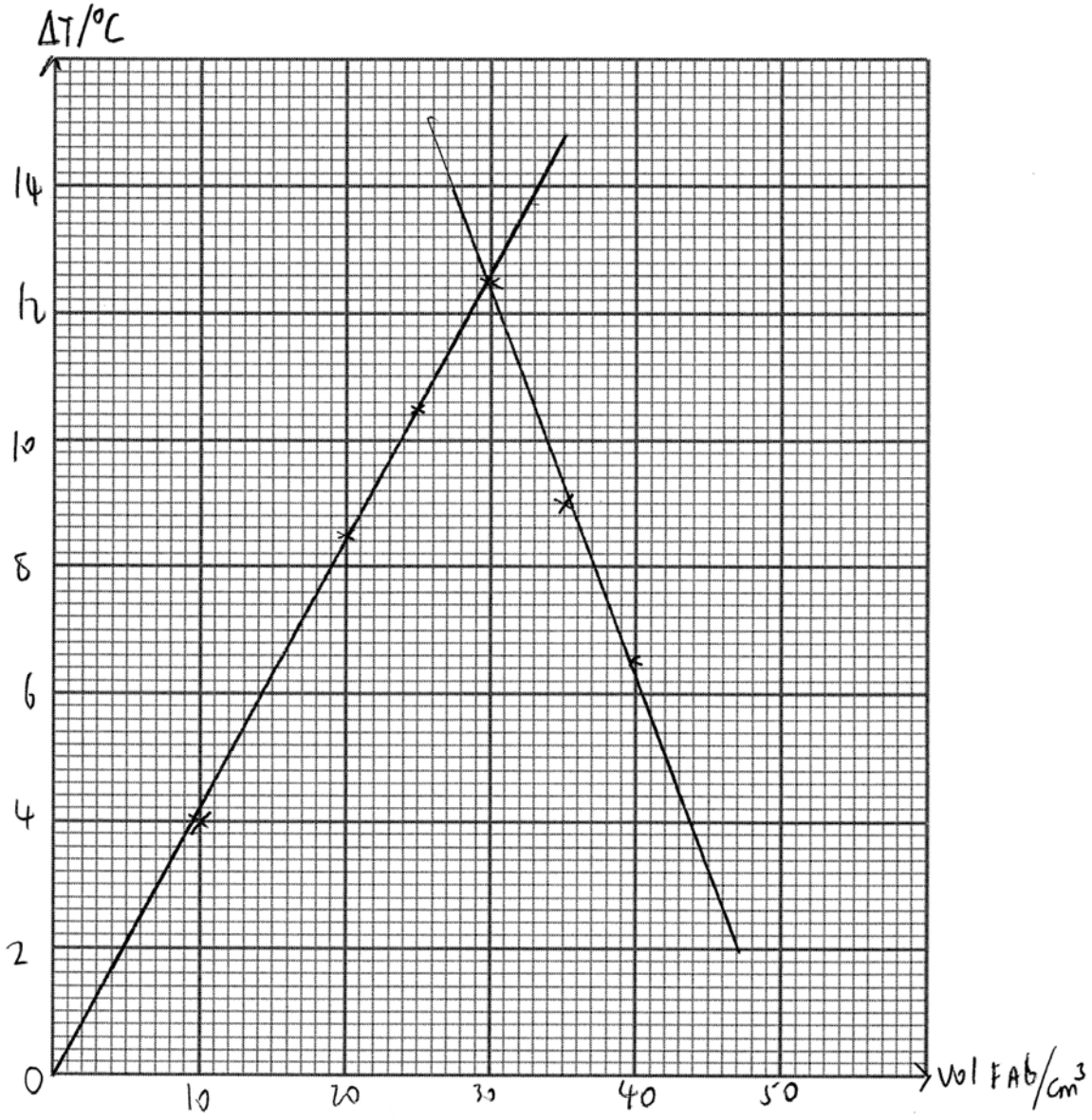

Fig. 2.1 [2]

(iii) Draw two straight lines of best fit. The first best fit line should be drawn using the plotted points where ΔT is increasing and the second best fit line should be drawn using the plotted points where ΔT is decreasing. Extrapolate these two lines until they cross. [1]

(iv) From your graph, determine the maximum temperature change, ΔT_{max}, and the volume of **FA 6** required to obtain this.

ΔT_{max} = ……12.5…….°C

V_{FA6} = …..……30.0……...cm^3 [1]

(b) Using your answers in **a(iv)**,

(i) calculate the concentration of NaOH in **FA 6**

Using V_{FA6} = 30.0 cm^3

volume of H_2SO_4 reacted = 50.0 – 30.0 = 20.0 cm^3

Amount of H_2SO_4 reacted = 20.0/1000 x 1.00 = 0.0200 mol

Amount of NaOH reacted = 0.0200 x 2 = 0.0400 mol

Concentration of NaOH = 0.0400 / (30.0/1000) = 1.33 mol dm^{-3}

concentration of NaOH in **FA 6** = …1.33 mol dm^{-3}……..[2]

(ii) calculate the heat change at $\Delta T_{max.}$

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and that the density is 1.00 g cm^{-3}.

heat change = 50 x 4.18 x 12.5= 2610 J

heat change = ……..[1]

(c) Using your answers in **(b)**, calculate the enthalpy change of neutralisation, ΔH_n.

Amount of water produced = amount of NaOH reacted = 0.0400 mol

ΔH_n = –2610/0.0400 = –65300 J mol^{-1}

ΔH_n = ……..[1]

[Total: 12]

3 Qualitative Analysis

(a) You are to perform the tests given in Table 3.1 on **FA 9** and **FA 10**.

Record details of any colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should be identified by a test, described in the appropriate place in the table provided. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Table 3.1

Tests		Observations	
		FA 9	**FA 10**
1	To 0.5 cm depth of solution in a test-tube, add equal volume of aqueous sulfuric acid.	Brown gas (NO_2) is evolved	
	Then add three to four drops of potassium iodide solution.	black solid/brown solution	
	Then add a few drops of aqueous starch.	blue-black/dark blue colour	
2	Add 2 drops of aqueous potassium manganate(VII) to a test tube followed by 2 drops of sulfuric acid.		
	Then add about 5 drops of **FA 9**.	Purple to colourless	
3	To 1 cm depth of **FA10** in a test-tube, add aqueous sodium hydroxide dropwise, until it is in excess.		Red brown ppt, insoluble in excess

4	To 0.5 cm depth of **FA 10** in a test-tube, add aqueous silver nitrate		white ppt /cream/pale yellow ppt
5	To 0.5 cm depth of **FA 10** in a test-tube, add aqueous sodium carbonate.		Reddish brown /brown ppt Effervescence seen. Gas formed white ppt in limewater. CO_2 evolved

[5]

(b) (i) **FA 9** can act both as an oxidising or a reducing agent. Based on your observations in test 1 and 2, state the role of **FA 9** in each of the tests.

role of **FA 9** in test 1……**oxidising agent**…….....

role of **FA 9** in test 2……**reducing agent**…….....[2]

(ii) Give the ionic equation, with state symbols, for the reaction of the metal cation in **FA 10** with aqueous sodium hydroxide in test 3.

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

……[1]

(iii) The observation you made in test 4 when aqueous silver nitrate was added to **FA 10** does not allow the anion in **FA 10** to be identified with certainty.

Explain why you cannot be certain about the identity of the anion.

Difficult to distinguish the colour of the ppt due to the colour of FA 10 itself
……
OR
……
Cannot be certain whether the ppt with $AgNO_3$ is white (AgCl) or cream(AgBr) or yellow(AgI)
……[1]

(iv) A student suggested that the anion in **FA 10** could be identified with more certainty if excess ammonia solution was added after the aqueous silver nitrate.

Explain why this suggestion is **not** correct.

Ammonia would form ppt with Fe^{3+} ions, thus masking the effect of ammonia on the silver halide ppt
……
Or
……
Ammonia would form ppt with Fe^{3+} ions so the ppt of AgCl would not appear to dissolve.
……[1]

(v) Suggest a pH value of solution **FA 10** based on your observations in test 5. Write an equation to account for your suggested pH value.

suggested pH value…**Any value below 7**……

equation…….
$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$.
……

……[2]

[Total: 12]

4 Preparation of cyclohexene from cyclohexanol

Cyclohexene is prepared by dehydration of cyclohexanol using concentrated phosphoric acid as a catalyst.

$$C_6H_{11}OH(l) \longrightarrow C_6H_{10}(l) + H_2O(l)$$

Data about cyclohexanol and cyclohexene are given in the table below.

property	cyclohexanol	cyclohexene
density/ g cm^{-3}	0.96	0.81
molar mass/ g mol^{-1}	100.0	82.0
boiling point/ ^oC	161.0	83.3

Preparation of impure cyclohexene

0.1 mol of cyclohexanol and 3 cm^3 of concentrated phosphoric acid were added together into a round-bottomed distillation flask. The mixture was heated and the impure cyclohexene was collected by distillation. Both cyclohexanol and cyclohexene are flammable.

Purification of impure cyclohexene

The impure cyclohexene was transferred into a separating funnel and an equal volume of saturated sodium chloride solution was added. The funnel was allowed to stand for a few minutes until the layers separated out.

The cyclohexene layer was transferred into a small flask and some anhydrous calcium chloride was added. The mixture was allowed to stand until the cyclohexene became clear.

The dried cyclohexene was decanted into a clean flask and was then fractionally distilled to produce the pure cyclohexene.

(a) (i) Calculate the volume of cyclohexanol to be used in the preparation.

Mass = 0.1 x100 = 10.0 g
Volume = 10/0.96 = 10.4 cm^3

volume of cyclohexanol to be used = ……cm^3 [1]

(ii) Using the information given on the previous page, outline how you would prepare a sample of impure cyclohexene from cyclohexanol.

In your answer, you should

- Give a full description of the procedures you would use to prepare the impure cyclohexene, stating clearly the apparatus used for measuring the reactants.
- State the temperature at which you would conduct the experiment.

…….. [3]

1. **Measure 10.4 cm^3 of cyclohexanol using a <u>50 cm^3 measuring cylinder</u> into a round-bottomed flask.**
2. **Using a <u>10 cm^3 measuring cylinder</u>, add 3 cm^3 of concentrated phosphoric acid into the flask.**
3. **Set up the distillation apparatus with a water-cooled condenser and a thermometer in the neck of a round-bottomed distillation flask and gently heat the mixture in the flask using a water bath or an electrical heater.**
4. **When the thermometer showed about 83°C, the impure cyclohexene distilled over, cooled and is collected.**

(b) (i) When the layers separate out in the separating funnel, suggest whether the cyclohexene will be the upper or lower layer. Hence explain how you would use the separating funnel to transfer the cyclohexene layer into a small flask.

…….. [2]

Upper layer is cyclohexene. Run off lower layer (to waste) by turning the tap of funnel and then pour out the upper layer into a small flask.

(ii) Why is anhydrous calcium chloride added to the cyclohexene?

……..… [1]

It is used as a drying agent to remove any water present in the cyclohexene layer.

(c) The percentage yield of cyclohexene in this preparation is 57.3%.

Suggest a reason why this preparation does not produce a 100% yield.

……..[1]

- **Reaction may not be complete**
- **Side reactions and other products might be formed**
- **Some of the cyclohexene might have stayed in the aqueous layer.**

[Total: 8]

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

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, 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 Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (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 dilute strong acids)

(c) Tests for gases

gas	*test and test result*
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 aqueous acidified 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