

# 19 Practical work

*In this topic, we look at some simple practical techniques that are used in the laboratory, such as titrations and the familiar 'wet' tests for finding out which cations and anions are present in an unknown sample in the test tube. Nowadays these methods are very rarely used in analytical laboratories because modern physical methods are much more sensitive and selective, and can readily be automated, making them less labour intensive. The methods do, however, bring together much of the chemistry that has already been met, so they provide a useful alternative way at looking at inorganic and organic chemistry.*

## Suggested skills

Your practical work will be helped if you are able to:

- take readings with an accuracy determined by the apparatus being used
- produce a numerical result corrected to an appropriate number of significant figures (you are not expected to use statistical methods of analysis or a treatment of errors)
- record clearly and concisely relevant observations (including negative ones)
- draw valid deductions from these observations
- arrive at a likely overall identification of the substance under investigation
- if appropriate, suggest additional experiments (including physical methods of analysis) to confirm your conclusion.

## 19.1 Thermometric measurements

### Measuring enthalpy changes directly

Some reactions, for example neutralisation reactions, take place very quickly. The heat evolved (or absorbed) in these reactions can be measured directly with a thermometer, using an expanded polystyrene cup as a calorimeter.

Examples of such reactions are included in section 5.2.

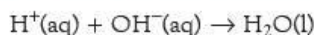
### Measuring enthalpy changes indirectly

Other reactions take place slowly or may require a high temperature to bring them about. The enthalpy change of such a reaction is determined indirectly by carrying out several rapid reactions and then using Hess's Law.

Examples of such reactions are included in section 5.4.

## 19.2 Titrations

### Acid–base titrations

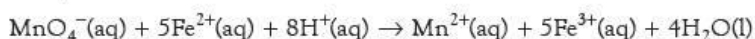


The most common type of titration is the neutralisation of an acid by a base using an indicator to show the equivalence point.

Examples of such titrations are included in sections 6.6 and 6.7.

### Potassium manganate(VII) titrations

For example:

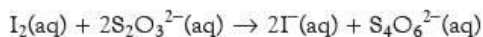


The potassium manganate(VII) solution is placed in the burette. As it is run into the acidified  $\text{Fe}^{2+}(\text{aq})$  solution in the conical flask, its purple colour disappears. The

end-point is when the solution permanently remains pink (that is, pale purple) when the last drop of the manganate(VII) solution is added.

Examples of such titrations are included in section 7.4.

## Iodine–thiosulfate titrations



The sodium thiosulfate solution is added from the burette. The disappearance of the yellow-brown colour of the iodine shows the end-point of these titrations. This end-point is made more obvious by adding a little starch near the end-point; this converts the pale yellow colour into an intense blue colour.

Examples of such titrations are included in section 7.4.

## 19.3 Appearance

### Inorganic

Most inorganic compounds are made up of separate ions, and so they show characteristic reactions associated with each type of ion they contain. Analysing a compound, therefore, involves the separate analysis of cations and of anions.

Since most inorganic compounds are ionic, they are usually solid at room temperature. Much information can be gained from their appearance. Usually, the substance is in the form of a powder. It may be either amorphous, which suggests that it is insoluble in water and has been made by precipitation, or it may be made up of small crystals, which show that it must be soluble, having been prepared by crystallisation from solution. Crystals may absorb moisture from the air – they may be **hygroscopic**. If they are so hygroscopic that they dissolve in the moisture in the air, they are termed **deliquescent**. Some crystals become covered with powder owing to **efflorescence**, that is, the loss of water of crystallisation in a dry atmosphere (see Table 19.1).

**Table 19.1** Information that can be gained from observing the appearance of a powder

Type of powder	Inference	Possible type of substance
amorphous	made by precipitation	insoluble, e.g. oxide or carbonate
crystalline	made by crystallisation	soluble, e.g. Group 1 compounds, nitrates, most sulfates and chlorides
hygroscopic	cation of high charge density	$\text{Li}^+$ and most double and triply charged cations
efflorescent	contains much water of crystallisation	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , alums

If the substance is made up of colourless crystals or a white powder, we may infer that we are dealing with a compound from the s block, or possibly from the p or d

**Table 19.2** Information that can be gained by observing the colour of a compound

Colour	Possible ions or substance present
colourless	s-block elements; $\text{Al}^{3+}$ , $\text{Pb}^{2+}$ ; $d^0$ or $d^{10}$ ions, e.g. $\text{Cu}^+$ or $\text{Zn}^{2+}$
blue	$\text{Cu}^{2+}$ , $\text{VO}^{2+}$ , $\text{Co}^{2+}$
pale green	$\text{Fe}^{2+}$ , $\text{Ni}^{2+}$
dark green	$\text{Cu}^{2+}$ , $\text{Cr}^{3+}$
purple	$\text{Cr}^{3+}$ , $\text{MnO}_4^-$
pale violet	$\text{Fe}^{3+}$ (goes yellow-brown in solution)
pink	$\text{Mn}^{2+}$ , $\text{Co}^{2+}$
yellow	$\text{CrO}_4^{2-}$ , $\text{PbO}$ , S
orange	$\text{Cr}_2\text{O}_7^{2-}$ , $\text{PbO}$
red	$\text{Pb}_3\text{O}_4$ , $\text{Cu}_2\text{O}$
brown	$\text{PbO}_2$ , $\text{Fe}^{3+}$ , $\text{Fe}_2\text{O}_3$
black	$\text{CuO}$ , $\text{MnO}_2$



block. A coloured compound probably indicates the presence of a transition metal (see section 24.5) or an oxide.

## Organic

If the substance is a liquid, it is probably organic. Some organic substances of higher molecular weight are solid, but the most common ones are liquid.

## 19.4 Solubility in water

When finding out if a substance is soluble in water, only a tiny amount or a drop of the substance should be shaken with 1 cm<sup>3</sup> of water. If too much substance is used, it is difficult to see whether any has dissolved.

## Inorganic

The solubility of an inorganic substance depends on the relative values of its lattice enthalpy and enthalpy change of hydration (see sections 20.1 and 20.2).

## Organic

When a drop of an organic liquid is shaken with water, it may form either a clear solution or a cloudy emulsion. This shows whether the substance is soluble in water or not, and gives an indication of what functional groups are present (see Table 19.3).

**Table 19.3** Information that may be deduced about an organic substance from its solubility in water

Solubility in water	Possible functional group present
completely soluble	lower alcohol, carboxylic acid, aldehyde, ketone
slightly soluble	higher alcohol
insoluble – floats on water	hydrocarbon
insoluble – sinks in water	halogenoalkane

## 19.5 Detection of gases

A common analytical test is to observe whether a gas is given off during a reaction and, if so, to identify it. It is important to consider how the gas was produced and, if possible, to write an equation for the reaction. Table 19.4 lists the most likely gases produced. Some of the tests are illustrated in Figure 19.1.

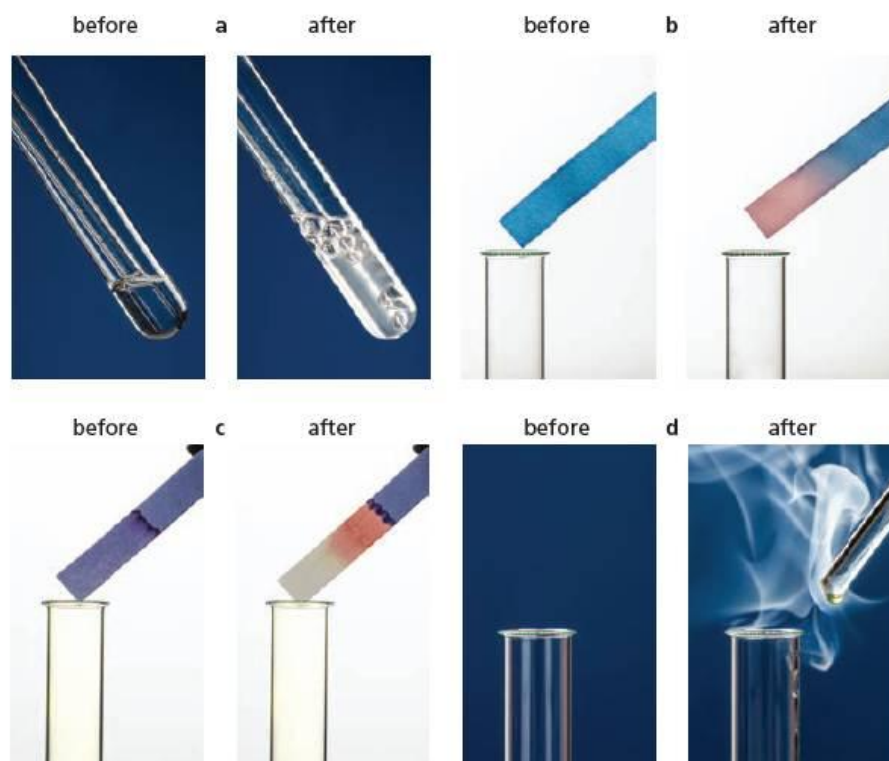
**Table 19.4** The most common gases produced during analysis. Other less common gases include N<sub>2</sub>, CO, SO<sub>3</sub>, N<sub>2</sub>O, NO, Br<sub>2</sub> and I<sub>2</sub>.

Gas	Appearance and properties	Test and equation
O <sub>2</sub>	colourless, odourless	glowing splint glows more brightly and may be rekindled
H <sub>2</sub>	colourless, odourless	when lit, burns at mouth of test tube*: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
CO <sub>2</sub>	colourless, almost odourless	limewater turns milky: $\text{Ca}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$
H <sub>2</sub> O	condenses on cooler part of test tube	blue cobalt chloride paper turns pink: $\text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$
SO <sub>2</sub>	colourless, choking, acidic	acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> turns green: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) + 3\text{SO}_2(\text{g}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 3\text{SO}_4^{2-}(\text{aq})$
<sup>†</sup> HCl	colourless, choking, acidic steamy fumes in moist air	forms white fumes with ammonia gas: $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
Cl <sub>2</sub>	pale green, very choking	moist litmus paper is bleached (it may turn red first): $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Cl}(\text{aq}) + \text{HClO}(\text{aq})$
NO <sub>2</sub>	brown, choking, acidic	moist litmus paper turns red
NH <sub>3</sub>	colourless, choking, pungent	the only common alkaline gas; forms white fumes with HCl: $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

\*When pure, hydrogen burns with a quiet, colourless flame. It is nearly always mixed with air and hence burns with a mild explosion. The flame is often tinged with yellow from the sodium ions in the glass of the test tube.

<sup>†</sup>HBr and HI give the same tests as HCl, but are nearly always given off in the presence of either bromine or iodine, which are easily identified by their colours.

**Figure 19.1** Positive tests for **a** carbon dioxide, **b** water vapour, **c** chlorine and **d** ammonia



The source of the gases is important because it tells us something about the substance under investigation. Table 19.5 lists the most common sources of these gases.

**Table 19.5** Possible sources of some common gases

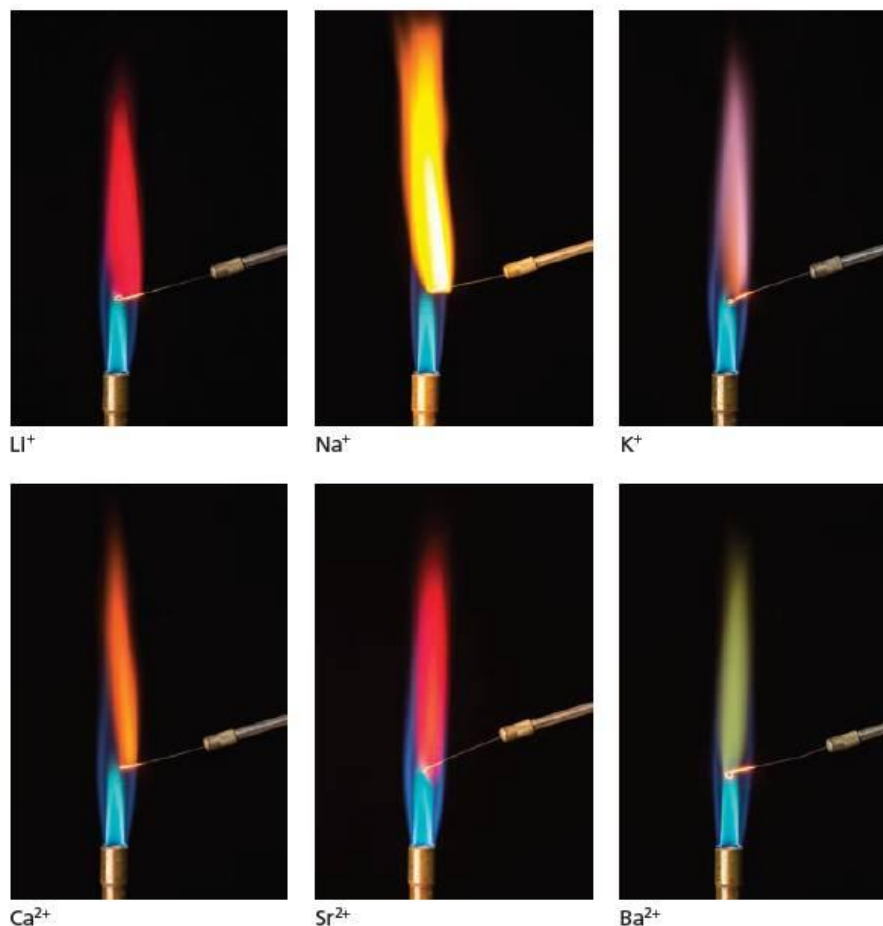
Gas	Likely source	Typical equation
O <sub>2</sub> + NO <sub>2</sub> (H <sub>2</sub> O if nitrate is hydrated)	heating nitrates	$\text{Ca}(\text{NO}_3)_2(\text{s}) \rightarrow \text{CaO}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) + 2\text{NO}_2(\text{g})$
H <sub>2</sub>	HCl(aq) on metal	$\text{Mg}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$
CO <sub>2</sub>	heating carbonates or HCl(aq) on carbonates	$\text{CuCO}_3(\text{s}) \rightarrow \text{CuO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
H <sub>2</sub> O	heating hydrated salts	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{g})$
SO <sub>2</sub>	HCl(aq) on sulfites	$\text{Na}_2\text{SO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$
HCl	H <sub>2</sub> SO <sub>4</sub> (l) on chlorides	$\text{KCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{KHSO}_4(\text{s}) + \text{HCl}(\text{g})$
Cl <sub>2</sub>	HCl(aq) with oxidising agents	$4\text{HCl}(\text{aq}) + \text{MnO}_2(\text{s}) \rightarrow \text{MnCl}_2(\text{aq}) + \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup> and NaOH(aq)	$\text{NH}_4\text{Cl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$

## 19.6 Flame tests

Some cations, particularly those of the s block, give characteristic colours in the flame of a Bunsen burner. A nichrome wire or porcelain rod is first cleaned by dipping it into concentrated hydrochloric acid and heating it in the blue part of the Bunsen burner flame until there is no persistent yellow colour (due to sodium impurities). A speck of the solid to be tested is mixed with a drop of concentrated hydrochloric acid on the end of the wire or rod and heated. The function of the hydrochloric acid is to convert non-volatile substances such as oxides and carbonates into the more volatile chlorides. Typical flame colours are listed in Table 19.6 and shown in Figure 19.2.

**Table 19.6** Some typical flame test colours

Colour of flame	Likely ion present
intense scarlet red	$\text{Li}^+$ or $\text{Sr}^{2+}$
persistent, intense yellow	$\text{Na}^+$
lilac	$\text{K}^+$
intermittent brick-red	$\text{Ca}^{2+}$
pale green	$\text{Ba}^{2+}$
blue-green	$\text{Cu}^{2+}$

**Figure 19.2** Flame tests

All substances emit light at various visible frequencies, which appear as lines in the spectrum (see section 24.5). Often the lines are distributed across the spectrum and there is no overall predominant colour. Sodium has a single line at 590 nm, which can easily be identified with a direct vision spectroscope. Many substances contain sodium as an impurity and it is difficult to eliminate the yellow colour entirely. Its effect can be partially masked by viewing the colours through blue cobalt glass.



## 19.7 Precipitation reactions for cations

Hydroxides, except those of Group 1 and ammonium, are insoluble in water and often have characteristic appearances. Some are amphoteric and dissolve in excess sodium hydroxide; others dissolve in excess ammonia to form a complex ion. The addition of aqueous sodium hydroxide (see Table 19.7) or aqueous ammonia (see Table 19.8) to an aqueous solution of the unknown (the tests are useless on the solid) gives valuable information about the cations present.



## Reactions with aqueous sodium hydroxide

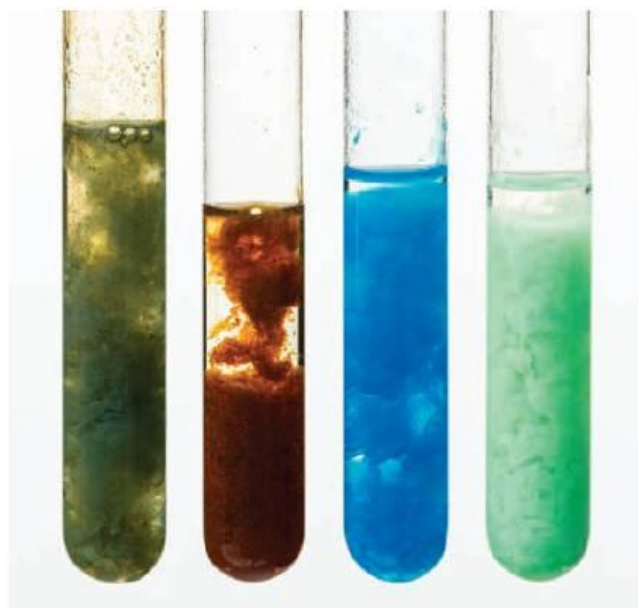
**Table 19.7** A few drops of aqueous sodium hydroxide are added to a solution of the unknown. If a precipitate forms, further sodium hydroxide is added until it is in excess.

Cation		On addition of a few drops of NaOH(aq)	On addition of excess NaOH(aq)
	$\text{NH}_4^+$	no ppt, but smell of $\text{NH}_3$ , especially on warming	—
<b>Group 1</b>	$\text{Li}^{+*}, \text{Na}^+, \text{K}^+$	no ppt	—
<b>Group 2</b>	$\text{Mg}^{2+}, \text{Ca}^{2+}$	white ppt	not soluble
	$\text{Sr}^{2+*}, \text{Ba}^{2+*}$	no ppt	—
<b>Groups 13 and 14</b>	$\text{Al}^{3+}, \text{Pb}^{2+}$	white ppt	soluble
<b>d block</b>	$\text{Cr}^{3+}$	green ppt	soluble
	$\text{Mn}^{2+}$	off-white ppt <sup>†</sup>	not soluble
	$\text{Fe}^{2+}$	pale green ppt <sup>†</sup>	not soluble
	$\text{Fe}^{3+}$	brown ppt	not soluble
	$\text{Co}^{2+}$	pink or blue ppt	not soluble
	$\text{Ni}^{2+}$	green ppt	not soluble
	$\text{Cu}^{2+}$	blue ppt	not soluble
	$\text{Zn}^{2+}$	white ppt	soluble
	$\text{Ag}^+$	brown ppt	not soluble

\*If the solutions are concentrated,  $\text{Li}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  may give a slight precipitate because their hydroxides are not very soluble (see section 10.4).

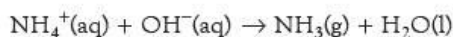
<sup>†</sup>On exposure to air, the off-white precipitate of  $\text{Mn}(\text{OH})_2$  turns to brown  $\text{MnO} \cdot \text{OH}$ , and the green precipitate of  $\text{Fe}(\text{OH})_2$  turns to brown  $\text{FeO} \cdot \text{OH}$ .

**Figure 19.3** Hydroxide precipitate colours. Can you determine the cation present in each of these solutions?

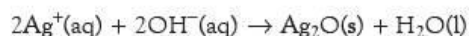


### Summary of equations

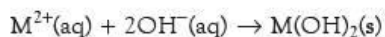
- For  $\text{NH}_4^+$  ions:



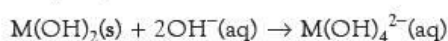
- For  $\text{Ag}^+$  ions:



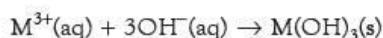
- For divalent  $\text{M}^{2+}$  ions:



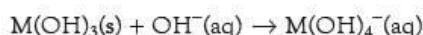
If the precipitate is soluble in excess:



- For trivalent  $\text{M}^{3+}$  ions:



If the precipitate is soluble in excess:



## Reactions with aqueous ammonia

**Table 19.8** A few drops of aqueous ammonia are added to a solution of the unknown. If a precipitate forms, further ammonia solution is added until it is in excess.

Cation		On addition of a few drops of $\text{NH}_3(\text{aq})$	On addition of excess $\text{NH}_3(\text{aq})$
Group 1	$\text{Li}^+, \text{Na}^+, \text{K}^+$	no ppt	—
Group 2	$\text{Mg}^{2+}$	white ppt	not soluble
	$\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+*}$	no ppt	—
Groups 13 and 14	$\text{Al}^{3+}, \text{Pb}^{2+}$	white ppt	not soluble
d block	$\text{Cr}^{3+}$	green ppt	slightly soluble
	$\text{Mn}^{2+}$	off-white ppt	not soluble
	$\text{Fe}^{2+}$	pale green ppt	not soluble
	$\text{Fe}^{3+}$	brown ppt	not soluble
	$\text{Co}^{2+}$	pink or blue ppt	soluble
	$\text{Ni}^{2+}$	green ppt	soluble
	$\text{Cu}^{2+}$	pale blue ppt	soluble
	$\text{Zn}^{2+}$	white ppt	soluble
	$\text{Ag}^+$	brown ppt	soluble

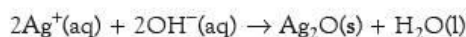
\*Because the  $\text{OH}^-$  concentration is low,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  ions do not produce a precipitate. A concentrated solution of  $\text{Ca}^{2+}$  ions may give a faint precipitate.

The ammonia acts in two ways:

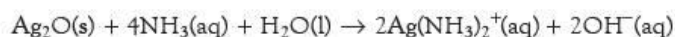
- as a weak base, giving a low concentration of  $\text{OH}^-$  ions, though not sufficient to produce hydroxy complexes
- as a complexing agent, with  $\text{NH}_3$  acting as the ligand.

### Summary of equations

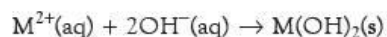
- For  $\text{Ag}^+$  ions:



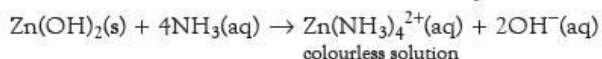
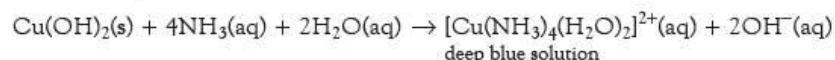
With excess aqueous ammonia:



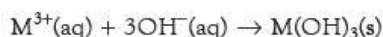
- For divalent  $\text{M}^{2+}$  ions:



With excess aqueous ammonia:



- For trivalent  $\text{M}^{3+}$  ions:



## 19.8 Action of acids

### Hydrochloric acid

Table 19.9 lists the most common gases given off as a result of treating a solid with aqueous hydrochloric acid.

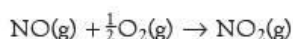
**Table 19.9** Common gases given off when a solid is treated with aqueous hydrochloric acid

Gas evolved	Likely anion present	Typical equation
CO <sub>2</sub>	carbonate, CO <sub>3</sub> <sup>2-</sup> or hydrogencarbonate, HCO <sub>3</sub> <sup>-</sup>	$\text{CuCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CuCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ $\text{NaHCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
SO <sub>2</sub>	sulfite, SO <sub>3</sub> <sup>2-</sup>	$\text{Na}_2\text{SO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
SO <sub>2</sub> (+ S)	thiosulfate, S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	$\text{Na}_2\text{S}_2\text{O}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{SO}_2(\text{g}) + \text{S}(\text{g}) + \text{H}_2\text{O}(\text{l})$
NO <sub>2</sub> + NO	nitrite, NO <sub>2</sub> <sup>-</sup>	$2\text{KNO}_2(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{NO}_2(\text{g}) + \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l})$

Hydrogencarbonates can be distinguished from carbonates, as heating a solid hydrogencarbonate gives water as well as carbon dioxide:



The colourless nitrogen monoxide obtained when nitrite is treated with aqueous hydrochloric acid reacts with oxygen in the air to give more of the brown nitrogen dioxide:



If the solid is insoluble in water but dissolves in aqueous hydrochloric acid, it may be a carbonate (if carbon dioxide is given off), a sulfite (if sulfur dioxide is given off) or it may be an insoluble basic oxide. The colour of the resulting solution may help to identify the cation.

### Sulfuric acid

If there is no reaction with aqueous hydrochloric acid, a fresh sample of the solid may be treated with a few drops of concentrated sulfuric acid. The reaction must be carried out in a fume cupboard. The mixture may be carefully warmed if there is no reaction in the cold. Table 19.10 shows the likely gases that may be detected.

**Table 19.10** Common gases evolved when a solid is treated with concentrated sulfuric acid

Gas	Likely anion present	Typical equation
HCl	chloride, Cl <sup>-</sup>	$\text{MgCl}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Mg}(\text{HSO}_4)_2(\text{s}) + 2\text{HCl}(\text{g})$
HBr + Br <sub>2</sub> + SO <sub>2</sub>	bromide, Br <sup>-</sup>	$\text{KBr}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{KHSO}_4(\text{s}) + \text{HBr}(\text{g})$ $2\text{HBr}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Br}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
HI (very little) + I <sub>2</sub> + SO <sub>2</sub> + H <sub>2</sub> S (+ S)	iodide, I <sup>-</sup>	$\text{NaI}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HI}(\text{g})$ $2\text{HI}(\text{g}) + \text{H}_2\text{SO}_4(\text{s}) \rightarrow \text{I}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ and other reactions
HNO <sub>3</sub>	nitrate, NO <sub>3</sub> <sup>-</sup>	$\text{KNO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{KHSO}_4(\text{s}) + \text{HNO}_3(\text{g})$
CO	methanoate, HCO <sub>2</sub> <sup>-</sup>	$\text{HCO}_2\text{H}(\text{l}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
CO + CO <sub>2</sub>	ethanedioate, C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	$\text{H}_2\text{C}_2\text{O}_4(\text{s}) \rightarrow \text{CO}(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
CH <sub>3</sub> CO <sub>2</sub> H	ethanoate, CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	$\text{CH}_3\text{CO}_2\text{K}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{KHSO}_4(\text{s}) + \text{CH}_3\text{CO}_2\text{H}(\text{g})$

In these reactions, concentrated sulfuric acid acts as a strong non-volatile acid, displacing more volatile acids as gases. With bromides and iodides, it also acts as an oxidising agent. With methanoates and ethanedioates, it also acts as a dehydrating agent.

Bromine gas is red-brown and iodine vapour is purple. Nitric acid vapour is usually pale brown as it decomposes slightly to nitrogen dioxide. It condenses on the cooler part

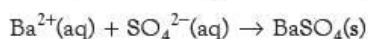


of the test tube as an oily liquid. Carbon monoxide is colourless and burns quietly with an intense blue flame. Ethanoic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , can be identified by its smell of vinegar.

## 19.9 Precipitation reactions for anions

### Aqueous barium chloride

Aqueous barium chloride (or barium nitrate) gives a precipitate with a large number of ions, including carbonate, sulfite and sulfate. In the presence of aqueous hydrochloric acid (or aqueous nitric acid), only sulfate ions give a dense white precipitate. So if the addition of aqueous hydrochloric acid and aqueous barium chloride to a solution of the unknown substance gives a dense white precipitate, sulfate ions are present.



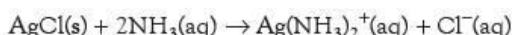
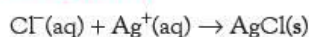
### Aqueous silver nitrate

Aqueous silver nitrate gives precipitates with a large number of ions, including carbonate, chromate(VI) ( $\text{CrO}_4^{2-}$ ), hydroxide, chloride, bromide and iodide. However, in the presence of aqueous nitric acid as well, only chlorides, bromides and iodides give precipitation (see Table 19.11). The colours of these precipitates and their solubilities in aqueous ammonia distinguish them from one another.

**Table 19.11** The action of silver ions on halide ions

Anion	Precipitate	Effect of $\text{NH}_3(\text{aq})$ on precipitate
$\text{Cl}^-$	white	soluble in dilute $\text{NH}_3(\text{aq})$
$\text{Br}^-$	cream or pale yellow	soluble in concentrated $\text{NH}_3(\text{aq})$
$\text{I}^-$	deep yellow	insoluble in concentrated $\text{NH}_3(\text{aq})$

#### Typical equations



The different colours and solubilities of the silver halides are discussed in section 11.3.

#### Worked example

Substance **A** is a white amorphous powder. It is insoluble in water. **A** dissolves in aqueous hydrochloric acid, with effervescence, to give a colourless solution **B**. The gas evolved, **C**, turns limewater milky. When aqueous sodium hydroxide was added to solution **B**, a faint white precipitate was formed that did not dissolve in excess. On addition of aqueous ammonia to solution **B**, no precipitate was formed. Substance **A** coloured a Bunsen burner flame green. Explain all these observations, identify **A**, **B** and **C**, and give equations for the reactions that take place.

#### Answer

The inferences that can be drawn from the observations are summarised in Table 19.12. (It is relatively easy to identify the substance as barium carbonate. However, to answer the question fully, it is important to explain all the observations.)

**Table 19.12**

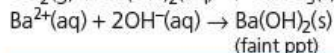
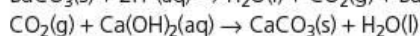
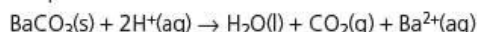
Observation	Inference
white, amorphous powder	not a transition metal
insoluble in water	not Group 1; not $\text{NO}_3^-$
dissolves in $\text{HCl}$ with effervescence	suggests $\text{CO}_3^{2-}$ (or $\text{HCO}_3^-$ )
gas turns limewater milky	$\text{CO}_2$ produced from $\text{CO}_3^{2-}$ (or $\text{HCO}_3^-$ )
solution <b>B</b> + $\text{NaOH}(\text{aq})$ gives a faint ppt	$\text{Sr}^{2+}$ or $\text{Ba}^{2+}$ present
solution <b>B</b> + $\text{NH}_3(\text{aq})$ gives no ppt	$\text{Sr}^{2+}$ or $\text{Ba}^{2+}$ present
flame test green	$\text{Ba}^{2+}$

**A** is barium carbonate,  $\text{BaCO}_3(\text{s})$ . (It is not  $\text{Ba}(\text{HCO}_3)_2$ , because it is insoluble.)

**B** is barium chloride solution,  $\text{BaCl}_2(\text{aq})$ .

**C** is carbon dioxide,  $\text{CO}_2(\text{g})$ .

The equation for the reactions are as follows:



### Now try this

**1** **D** is a hygroscopic brown solid. It is readily soluble in water to give a green solution. With aqueous sodium hydroxide, this solution gives a dark green precipitate, **E**, that does not dissolve in an excess of the reagent. **E** turns brown on exposure to air. **D** shows no reaction with aqueous hydrochloric acid, but with concentrated sulfuric acid it frothed and gave off an acidic gas, **F**, as well as a red-brown gas, **G**. When moist air is blown over the mouth of the test tube, **F** gives steamy fumes, and it also gives dense white fumes when a drop of ammonia on a glass rod is brought near. The addition of aqueous nitric acid and silver nitrate to a solution of **D** produced a precipitate that turned green when aqueous ammonia was added.

Explain all these observations, identify **D**, **E**, **F** and **G**, and write equations for the reactions that take place.

**2** **H** is a white amorphous powder. It is insoluble in water but dissolves readily in aqueous hydrochloric acid, with no evolution of gas, to give a colourless solution **I**. To a portion of **H**, aqueous sodium hydroxide is added. A white precipitate forms that dissolves in an excess of the reagent. To a separate portion of **H**, aqueous ammonia is added. This also gives a white precipitate that dissolves in an excess of the reagent. A flame test on a sample of **I** is negative.

Explain all these observations, identify **H** and **I**, and write equations for the reactions that take place.

## 19.10 Organic tests

The solubility of an organic substance in water gives an indication of what group it contains (see section 19.4). Further specific tests can then be used to provide more evidence (see Table 19.13).

**Table 19.13** Some common tests used in organic chemistry

Test	Observation	Possible functional group present
shake with bromine water (see page 256)	bromine water decolorised	alkene
add small piece of sodium metal (see pages 284 and 308)	$\text{H}_2(\text{g})$ evolved	alcohol, carboxylic acid
add solid $\text{PCl}_5$ (see pages 286 and 309)	$\text{HCl}$ evolved	alcohol, carboxylic acid
warm with acidified potassium dichromate (see pages 287–289)	goes from orange to green	primary or secondary alcohol, aldehyde
add sodium carbonate (see page 308)	$\text{CO}_2$ evolved	carboxylic acid
add a few drops of cold acidified $\text{KMnO}_4$ (see page 260)	goes from purple to brown to colourless	alkene
add 2,4-DNPH (see page 300)	orange ppt	aldehyde, ketone
warm with Fehling's solution (see page 301)	red ppt	aldehyde
gently warm with Tollens' reagent (see page 301)	silver mirror	aldehyde
boil under reflux with $\text{NaOH}(\text{aq})$ and test with $\text{HNO}_3/\text{AgNO}_3$ (see page 273)	ppt forms	chloride, bromide, iodide
warm with $\text{NaOH}(\text{aq})$ and $\text{I}_2(\text{aq})$	yellow ppt forms	methyl ketone or $\text{CH}_3\text{CH}(\text{OH})^-$

All these functional group tests are described in detail in section 30.5.

## Worked example

A colourless liquid **J** dissolves easily in water. Liquid **J** gives steamy fumes when treated with  $\text{PCl}_5$ . It does not react with sodium carbonate. When warmed with acidified potassium dichromate, the solution turns green. When this green solution is distilled, the distillate **K** gives a precipitate with 2,4-DNPH but does not give a silver mirror with Tollens' reagent. Explain all these observations, identify **J** and **K**, and write equations for the reactions that take place.

## Answer

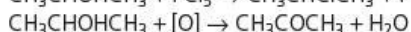
The inferences that can be drawn from the observations are summarised in Table 19.14.

Table 19.14

Observation	Inference
soluble in water	lower alcohol, carboxylic acid, aldehyde or ketone
gives fumes with $\text{PCl}_5$	alcohol or carboxylic acid
no reaction with $\text{Na}_2\text{CO}_3$	not acid, therefore alcohol
potassium dichromate goes green	primary or secondary alcohol
distillate reacts with 2,4-DNPH	aldehyde or ketone
no reaction with Tollens' reagent	not aldehyde

Therefore **J** is a secondary alcohol. It is probably propan-2-ol,  $\text{CH}_3\text{CHOHCH}_3$ , as higher secondary alcohols are only slightly soluble in water. **K** would then be propanone  $\text{CH}_3\text{COCH}_3$ .

The equations for the reactions are as follows:



## Now try this

- 1 A colourless liquid **L** was insoluble in water and had a density greater than 1. It did not decolorise bromine water. When boiled under reflux with sodium hydroxide, some of the liquid dissolved. When the aqueous layer was treated with an excess of nitric acid and silver nitrate, a pale yellow precipitate **M** was formed that was soluble in concentrated ammonia.

Suggest the group present in **L** and write an equation for the action of concentrated ammonia on **M**.

- 2 A colourless liquid **O** was soluble in water. It gave fumes when treated with  $\text{PCl}_5$ . When warmed with acidified potassium dichromate, there was no change in colour. With sodium carbonate it effervesced and gave off a gas.

Suggest the group present in **O** and write equations for its reactions with  $\text{PCl}_5$  and sodium carbonate.

## Summary

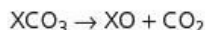
- Enthalpy changes can be measured with a calorimeter, either directly or indirectly.
- The three most common types of titration are acid–base, redox with potassium manganate(VII) and iodine–thiosulfate.
- Cations can be identified by:
  - the colour of the salt
  - flame tests
  - the action of aqueous sodium hydroxide and aqueous ammonia on a solution.
- Anions can be identified by:
  - the action of heat on the solid
  - the action of  $\text{HCl}(\text{aq})$  and  $\text{H}_2\text{SO}_4(\text{l})$  on the solid
  - the action of  $\text{Ag}^+(\text{aq})$  ions or  $\text{Ba}^{2+}(\text{aq})$  ions on solutions.
- Organic substances can be identified by their solubility in water and by a range of specific tests.



## Examination practice questions

Please see the data section of the CD for any  $A_r$  values you may need.

- 1 The carbonates of Group 2 in the Periodic Table decompose on heating forming an oxide and carbon dioxide.  
X is any Group 2 cation (e.g.  $\text{Mg}^{2+}$ ).



This decomposition occurs because the positively charged cations polarise (distort) the C—O bond in the carbonate ion causing the ion to break up. The charge density of the Group 2 cations decreases down the group. This affects the decomposition rate.

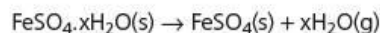
You are to plan an experiment to investigate how the rate of decomposition of a Group 2 carbonate varies as the group is descended. The rate can be conveniently measured by finding the time taken to produce the same volume of carbon dioxide from each carbonate.

- a i Predict how the rate of decomposition of the Group 2 carbonates will change as the group is descended.  
Explain this prediction in terms of the charge density of the cation as the group is descended. [3]
- ii Display your prediction in the form of a sketch graph, clearly labelling the axes. [3]
- b In the experiment you are about to plan, identify the following:
  - i the independent variable
  - ii the dependent variable. [2]
- c Draw a diagram of the apparatus and experimental set up you would use to carry out this experiment.  
Your apparatus should use only standard items found in a school or college laboratory and show clearly the following:
  - i the apparatus used to heat the carbonate
  - ii how the carbon dioxide will be collected.
 Label each piece of apparatus used, indicating its size or capacity. [2]
- d Using the apparatus shown in c design a laboratory experiment to test your prediction in a.  
In addition to the standard apparatus present in a laboratory you are provided with the following materials: samples of the carbonates of magnesium, calcium, strontium and barium, a stop-watch/clock with second hand.  
Give a step-by-step description of how you would carry out the experiment by stating
  - i the gas volume you would collect from each carbonate
  - ii how you would calculate the mass of each carbonate to ensure that this volume of carbon dioxide is produced

iii how you would control the factors in the heating so that different carbonates can be compared. [4]

- e State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum. [2]
- f Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in a. The headings **must** include the appropriate units. [2]
- g This simple experiment is likely to produce only approximate results.  
Suggest an improvement to your apparatus or an alternative apparatus that may improve the reliability of the results. [1]  
*[Cambridge International AS & A Level Chemistry 9701, Paper 51 Q1 June 2011]*

- 2 Hydrated iron(II) sulfate can be represented as  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  where x is the number of molecules of  $\text{H}_2\text{O}$  for each  $\text{FeSO}_4$ . When the compound is heated, it loses the molecules of water leaving anhydrous iron(II) sulfate.  
A suggested equation is:



An experiment is carried out to attempt to determine the value of x.

- An open crucible is weighed and the mass recorded.
  - A sample of hydrated iron(II) sulfate is added to the crucible and the new mass recorded.
  - The crucible with hydrated iron(II) sulfate is heated strongly for five minutes and allowed to cool back to room temperature.
  - The crucible with the contents is reweighed and the mass recorded.
- a Calculate the relative formula masses,  $M_r$ , of  $\text{FeSO}_4$  and  $\text{H}_2\text{O}$ .  
[ $A_r$ : H, 1.0; O, 16.0; S, 32.1; Fe, 55.8] [1]
  - b The results of several of these experiments are recorded on the following page. Copy the table and process the results to calculate both the number of moles of anhydrous iron(II) sulfate and the number of moles of water.  
Record these values in the additional columns of the table. You may use some or all of the columns. Masses should be recorded to **two decimal places**, while the numbers of moles should be recorded to **three significant figures**. Label the columns you use. For each column you use include units where appropriate and an expression to show how your values are calculated. You may use the column headings A to G for these expressions (e.g. A–B).

A	B	C	D	E	F	G
mass of crucible /g	mass of crucible + $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ /g	mass of crucible + $\text{FeSO}_4$ /g				
15.20	17.03	16.20				
15.10	17.41	16.41				
14.95	17.33	16.25				
15.15	17.70	16.54				
15.05	17.79	16.55				
14.90	17.88	16.53				
14.92	18.18	16.70				
15.30	18.67	17.14				
15.07	18.64	17.02				
15.01	18.80	17.04				

[2]

- c Plot a graph to show the relationship between the number of moles of anhydrous iron(II) sulfate,  $\text{FeSO}_4$  (x-axis), and the number of moles of water (y-axis). Draw the line of best fit. It is recommended that you do not include the origin in your choice of scaling. [3]
- d Circle and label on the graph any point(s) you consider to be anomalous. For each anomalous point give a different reason why it is anomalous clearly indicating which point you are describing. [3]
- e Determine the slope of the graph. You must mark clearly on the graph any construction lines and show clearly in your calculation how the intercepts were used in the calculation of the slope. [3]

- f Comment on the reliability of the data provided in b. [1]

- g i Use the value of the slope of your graph calculated in (e) to suggest the correct formula for hydrated iron(II) sulfate.

- ii Explain your answer to i. [2]

[Cambridge International AS & A Level Chemistry 9701, Paper 51 Q2 June 2013]

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