## Fxam skills 11

This exam-style question uses knowledge and skills you have already revised. Have a look at pages 115-117 for a reminder about reaction rates and order of reaction.

## Worked example

Hydrogen peroxide reacts with iodide ions to form iodine. If thiosulfate ions, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$, are also present, they react with the iodine formed. Once all these ions have reacted, iodine is no longer reduced. The appearance of iodine is detected by starch solution.
(a) Describe the final colour of the reaction mixture.

Blue-black.
(b) The concentration of $\mathrm{I}^{-}$ions was varied while keeping the concentrations and volumes of the other reagents the same and the time for the mixture to change colour was recorded.

| $\left[\mathbf{I}^{\mathbf{}} \mathbf{]} / \mathbf{m o l ~ d m}^{\mathbf{3}}\right.$ | time/s | $\mathbf{1 / t i m e / ~} \mathbf{s}^{\mathbf{- 1}}$ |
| :---: | :---: | :---: |
| 0.040 | 16.5 | 0.0606 |
| 0.030 | 22.4 | 0.0446 |
| 0.016 | 41.7 | 0.0239 |
| 0.008 | 85.2 | 0.0117 |

(i) Complete the table, and plot a graph of $1 /$ time on the vertical axis against $\left[\mathrm{I}^{-}\right]$. (3 marks)

$\left[l^{-}\right] / \mathrm{mol} \mathrm{dm}{ }^{-3}$
(ii) $1 /$ time is a measure of the initial rate of reaction. Deduce the order of reaction with respect to iodide ions, and justify your answer. (2 marks)
The reaction is first order with respect to iodide ions because the rate is proportional to $\left[l^{-}\right]$. The graph is a straight line (it has a constant gradient).
(iii) Describe a way in which the experiment could be improved, without changing the method, measuring apparatus or the solutions used.
(1 mark)
You could repeat the experiment.

This describes a version of the "iodine clock experiment':
l. $\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{I}^{-} \rightarrow \mathrm{I}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
2. $\mathrm{I}_{2}+2 \mathrm{~S}_{2} \mathrm{O}_{3}^{2-} \rightarrow \mathrm{S}_{4} \mathrm{O}_{6}^{2-}+2 \mathrm{I}^{-}$

Sulfuric acid is added to provide $\mathrm{H}^{+}$ions.

## 7 Practical skills

Water is usually added before the reactants are mixed together so that the total volume remains the same.
Laboratory digital stop clocks often time to $\pm 0 . \mathrm{Ol} s$, but this precision is unnecessary when you have to judge when to stop the clock.


Make sure you can recall colours and colour changes from practical activities.
'Purple' would not be correct here.

When you plot a graph, you need to make sure you:

- choose sensible scales on which the plotted points occupy at least half of the grid supplied
use linear scales
- plot points accurately
- draw a line of best fit.

You should also:

- make sure you have your axes the right way round
- label each axis with the quantity and unit.


## Command word: Deduce

If a question asks you to deduce something, it means you need to reach a conclusion from the information given.

## Command word: Justify

If a question asks you to justify something, it means you need to give evidence to prove something.


#### Abstract

\section*{Practical skills}

Since temperature is one of the factors that determines the rate of a reaction, the experiment should be repeated at the same temperature. This could be done using a thermostatic water bath.


## Topic 18

## Methods in organic chemistry 2

 skillsRefluxing and simple distillation are useful for preparing organic liquids, while fractional distillation and steam distillation are useful for purifying them.

## Refluxing

Refluxing allows you to heat a reaction mixture for a long time without losing any liquid.

You set up the condenser in a different way from when you use it for distillation (see right).


## Fractional distillation

You can use fractional distillation to separate more than one liquid from a mixture of liquids.


## Simple distillation

Simple distillation allows the product to leave the reaction mixture as it forms.

distilled product

## Steam distillation

You can use steam distillation to separate an insoluble liquid from an aqueous solution.
It involves:

- passing steam into the reaction mixture
- the steam bubbling through the mixture brings both liquids to the surface
- both liquids can form part of the liquid that evaporates.

The insoluble liquid is removed from the reaction mixture below its boiling temperature, reducing the chance of it decomposing. For example, the boiling temperature of phenylamine is $184^{\circ} \mathrm{C}$ but a mixture of phenylamine and water distils at $98^{\circ} \mathrm{C}$.

## Worked example

Describe how you could use boiling temperature data to determine the purity of an organic liquid.
(2 marks)
Compare the boiling temperature of the organic liquid with its known value (from a data book). The closer the two temperatures, the purer the liquid is.


You could use simple distillation apparatus set up with a thermometer instead of a dropping funnel. You may reach an incorrect conclusion about the identity and purity of the liquid if, for example:

- your thermometer is incorrectly calibrated
- the liquid shares the same boiling temperature with another liquid.


## Solvent extraction

You can use a separating funnel to separate two immiscible liquids (liquids that do not mix).
This method works because the liquids form two layers, one above the other.
You can find details about this on page 61.

## Now try this

Which of the techniques described on this page:
(a) involves continuous evaporation and condensation?
(1 mark)
(b) is suitable for separating limonene, an insoluble liquid that boils at $176^{\circ} \mathrm{C}$, from water? (1 mark)

## p階 o bases

You can calculate the pH of a strong base if you take into account the ionic product of water, $K_{w}$.

## Ionic product of water, ${ }^{\text {m }}$ w

Water reacts with itself in an acid-base reaction:

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

This can be simplified to:

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

You can write an expression for $K_{c}$ but for water this is called the ionic product of water:
$K_{w}=\left[\mathrm{H}^{+}(a q)\right]\left[\mathrm{OH}^{-}(a q)\right]-\left[\mathrm{H}_{2} \mathrm{O}(1)\right]$ is a constant For pure water at 298 K : the is not included

- $K_{w}=1.00 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$

In the same way that $p K_{a}=-\log _{10} K_{a}$ :

$$
p K_{w}=-\log _{10} K_{w}
$$

For pure water at 298 K ,

- $p K_{w}=14.0$


## Maths Neutral plil <br> skills

In pure, neutral water,
$\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$.
This means that:

- $K_{w}=\left[\mathrm{H}^{+}(a q)\right]^{2}$
- $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\sqrt{K_{w}}$

You can calculate the pH of water at 298 K :

$$
\mathrm{pH}=-\log _{10}\left(\sqrt{\left(1.00 \times 10^{-14}\right.}\right)=7.00
$$

The dissociation of water is endothermic.
This means that as the temperature increases:
(V) $K_{w}$ increases
(1) $\mathrm{PK} \mathrm{K}_{\mathrm{w}}$ decreases
(V) the pH of pure water decreases.

Neutral pH is only 7.00 at 298 K .

## Worked example

(a) Explain why sodium hydroxide, NaOH , is a strong base.
(1 mark)
It is fully dissociated in aqueous solution:

$$
\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

(b) Calculate the hydrogen ion concentration in $0.250 \mathrm{~mol} \mathrm{dm}^{-3}$ sodium hydroxide at 298 K . $\left(K_{\mathrm{w}}=1.00 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}\right)$
(1 mark)
$K_{w}=\left[H^{+}(a q)\right]\left[\mathrm{OH}^{-}(a q)\right]$
so $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{\mathrm{K}_{\mathrm{w}}}{\left[\mathrm{OH}^{-}(\mathrm{aq})\right]}$
$\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{\left(1.00 \times 10^{-14}\right)}{0.250}$

$$
=4.00 \times 10^{-14} \mathrm{~mol} \mathrm{dm}^{-3}
$$

(c) Calculate the pH of this solution at 298 K . Express your answer to 2 decimal places.
(1 mark)
$\mathrm{pH}=-\log _{10}\left(4.00 \times 10^{-14}\right)=-(-13.40)$ $=13.40$

Strong bases are fully dissociated in solution. They include KOH and $\mathrm{Ca}(\mathrm{OH})_{2}$ (a dibasic base). Weak bases are only partially dissociated in solution. Ammonia is a weak base.

The temperature is quoted because the value for $K_{w}$ varies with temperature.
When you calculate $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ :

- $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=$ [monobasic strong base]
- $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=2 \times$ [dibasic strong base]

You may have to calculate the pH of a strong base from its concentration. The steps are:
I. Calculate $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ from [base] (see above).
2. Calculate $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ from $\mathrm{K}_{\mathrm{w}}$ and $\left[\mathrm{OH}^{-}\right]$
3. Calculate pH using $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$.

## Enthalpy changes of neutralisation

Strong acids are fully dissociated in solution and have the greatest magnitude of $\Delta H_{\text {neut }}^{\Theta}$.
Weak acids are partially dissociated in solution:

- Energy is needed to dissociate them.
- The magnitudes of their $\Delta H_{\text {neut }}^{\Theta}$ are lower.


## Now try this

Calculate the pH of these strong bases at 298 K .
Express your answers to one decimal place.
(a) $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ sodium hydroxide.
(2 marks)
(b) $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ calcium hydroxide, $\mathrm{Ca}(\mathrm{OH})_{2}$.
(2 marks)

## Vanadium chemistry

Vanadium can be reduced from oxidation number +5 to +2 by zinc in acidic solution.
Colours of vanadium compounds and the oxidation number of vanadium
The table summarises the colours of solutions containing vanadium ions.

| Oxidation number | +5 | +4 | +3 | +2 |
| :---: | :---: | :---: | :---: | :---: |
| Formula | $\mathrm{VO}_{2}{ }^{+}$ | $\mathrm{VO}^{2+}$ | $\mathrm{V}^{3+}$ | $\mathrm{V}^{2+}$ |
| Name | dioxovanadium( V ) | oxovanadium(IV) | vanadium(III) | vanadium(II) |
| Colour of solution |  |  |  | purple |

Be careful! You need to know these colours. Take care not to confuse $\mathrm{VO}_{2}{ }^{+}$with $\mathrm{VO}^{2+}$.

## Reduction Prom V(V) to V(IT)

Ammonium trioxovanadate $(\mathrm{V}), \mathrm{NH}_{4} \mathrm{VO}_{3}$, is a soluble vanadium( V ) compound.
In acidic conditions, it forms the dioxovanadium(V) ion, $\mathrm{VO}_{2}{ }^{+}$.

This can be reduced to vanadium(II) using:

- zinc with sulfuric or hydrochloric acid.

You see a change in colour during the reaction:
I. yellow to blue $(+3$ to +4$)$
2. blue to green $(+4$ to +5$)$
3. green to purple $(+3$ to +2$)$

## 

The table summarises, in terms of standard electrode potentials, why these reactions happen.

| Change | Oxidation (left) | Reduction (right) | $E_{\text {cell }}^{\Theta}=E_{\text {right }}^{\Theta}-E_{\text {left }}^{\Theta}$ | Overall |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & +5 \\ & \text { to } \\ & +4 \\ & \hline \end{aligned}$ | $\mathrm{Zn} \rightleftharpoons \mathrm{Zn}{ }^{2+}+2 e^{-}$ | $\mathrm{VO}_{2}^{+}+2 \mathrm{H}^{+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{VO}^{2+}+\mathrm{H}_{2} \mathrm{O}$ | $\begin{gathered} +1.00-(-0.76) \\ =+1.76 \mathrm{~V} \end{gathered}$ | $\begin{gathered} 2 \mathrm{VO}_{2}^{+}+4 \mathrm{H}^{+}+\mathrm{Zn} \\ \downarrow \\ 2 \mathrm{VO}^{2+}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{Zn}^{2+} \\ \hline \end{gathered}$ |
| $\begin{aligned} & +4 \\ & \text { to } \\ & +3 \end{aligned}$ | $\mathrm{Zn} \rightleftharpoons \mathrm{Zn}{ }^{2+}+2 e^{-}$ | $\mathrm{VO}^{2+}+2 \mathrm{H}^{+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{V}^{3+}+\mathrm{H}_{2} \mathrm{O}$ | $\begin{gathered} +0.34-(-0.76) \\ =+1.10 \mathrm{~V} \end{gathered}$ | $\begin{gathered} 2 \mathrm{VO}^{2+}+4 \mathrm{H}^{+}+\mathrm{Zn} \\ \downarrow \\ 2 \mathrm{~V}^{3+}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{Zn}^{2+} \end{gathered}$ |
| $\begin{aligned} & +3 \\ & \text { to } \\ & +2 \\ & \hline \end{aligned}$ | $\mathrm{Zn} \rightleftharpoons \mathrm{Zn}{ }^{2+}+2 e^{-}$ | $\mathrm{V}^{3+}+e^{-} \rightleftharpoons \mathrm{V}^{2+}$ | $\begin{gathered} -0.26-(-0.76) \\ =+0.50 \mathrm{~V} \end{gathered}$ | $\begin{gathered} 2 \mathrm{~V}^{3+}+\mathrm{Zn} \\ \downarrow \\ 2 \mathrm{~V}^{2+}+2 \mathrm{n}^{2+} \\ \hline \end{gathered}$ |

Notice that all three $E_{c e l l}^{\theta}$ values are positive, so the reactions are feasible.

## Woxked example

Explain why $\mathrm{V}^{2+}$ ions cannot be reduced to vanadium using acidified zinc.

$$
\begin{aligned}
E_{\text {cell }}^{\Theta}=E_{\text {right }}^{\Theta}-E_{\text {left }}^{\Theta} & =-1.18-(-0.76) \\
& =-0.42 \mathrm{~V}
\end{aligned}
$$

As $E_{\text {cell }}^{\theta}$ is negative, the reaction is not feasible.

The Data Book shows you that, for the reaction:

$$
\mathrm{V}^{2+}+2 e^{-} \rightleftharpoons \mathrm{V}, E^{\theta}=-1.18 \mathrm{~V}
$$

The overall reaction required would be:

$$
\mathrm{V}^{2+}+\mathrm{Zn} \rightarrow \mathrm{~V}+\mathrm{Zn}^{2+}
$$

Since this is not feasible, the reduction reactions described above do not continue to vanadium.

## Now try this

An excess of acidified potassium manganate(VII) solution, $\mathrm{KMnO}_{4}(\mathrm{aq}) / \mathrm{H}^{+}(\mathrm{aq})$ was added to a solution containing $\mathrm{V}^{2+}(\mathrm{aq})$ ions. Identify the vanadium species present when the reaction is complete and write the half-equation for its formation.
(2 marks)
$\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightleftharpoons \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}, E^{\theta}=+1.51 \mathrm{~V}$

| Right hand electrode system | $\boldsymbol{E}^{\ominus} / \mathbf{V}$ |
| :--- | :---: |
| $\mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{Zn}$ | -0.76 |
| $\mathrm{~V}^{3+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{V}^{2+}$ | -0.26 |
| $\mathrm{VO}^{2+}+2 \mathrm{H}^{+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{V}^{3+}+\mathrm{H}_{2} \mathrm{O}$ | +0.34 |
| $\mathrm{VO}_{2}^{+}+2 \mathrm{H}^{+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{VO}^{2+}+\mathrm{H}_{2} \mathrm{O}$ | +1.00 |

## Data booklet

## Physical constants

Avogadro constant ( $L$ )
Elementary charge (e)
Gas constant ( $R$ )
Molar volume of ideal gas:
at s.t.p.
at r.t.p.
Specific heat capacity of water
Ionic product of water ( $K_{w}$ )
$1 \mathrm{dm}^{3}=1000 \mathrm{~cm}^{3}=0.001 \mathrm{~m}^{3}$
$6.02 \times 10^{23} \mathrm{~mol}^{-1}$
$1.60 \times 10^{-19} \mathrm{C}$
$8.31 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
$22.4 \mathrm{dm}^{3} \mathrm{~mol}^{-1}$
$24.0 \mathrm{dm}^{3} \mathrm{~mol}^{-1}$
$4.18 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}$
$1.00 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$

## Correlation of infrared absorption wavenumbers with molecular structure

| Group | Wavenumber range/cm ${ }^{-1}$ |
| :---: | :---: |
| $\mathrm{C}-\mathrm{H}$ stretching vibrations <br> Alkane <br> Alkene <br> Alkyne <br> Arene <br> Aldehyde | $\begin{aligned} & 2962-2853 \\ & 3095-3010 \\ & 3300 \\ & 3030 \\ & 2900-2820 \text { and } 2775-2700 \end{aligned}$ |
| $\mathrm{C}-\mathrm{H}$ bending variations <br> Alkane <br> Arene 5 adjacent hydrogen atoms <br> 4 adjacent hydrogen atoms <br> 3 adjacent hydrogen atoms <br> 2 adjacent hydrogen atoms <br> 1 adjacent hydrogen atom | $\begin{aligned} & 1485-1365 \\ & 750 \text { and } 700 \\ & 750 \\ & 780 \\ & 830 \\ & 880 \end{aligned}$ |
| $\mathrm{N}-\mathrm{H}$ stretching vibrations <br> Amine <br> Amide | $\begin{aligned} & 3500-3300 \\ & 3500-3140 \end{aligned}$ |
| $\mathrm{O}-\mathrm{H}$ stretching vibrations Alcohols and phenols Carboxylic acids | $\begin{aligned} & 3750-3200 \\ & 3300-2500 \end{aligned}$ |
| $\mathrm{C}=\mathrm{C}$ stretching vibrations <br> Isolated alkene <br> Arene | $\begin{aligned} & 1669-1645 \\ & 1600,1580,1500,1450 \end{aligned}$ |
| $\mathrm{C}=\mathrm{O}$ stretching vibrations <br> Aldehydes, saturated alkyl <br> Ketones alkyl <br> Ketones aryl <br> Carboxylic acids alkyl <br> aryl <br> Carboxylic acid anhydrides <br> Acyl halides chlorides <br> bromides <br> Esters, saturated <br> Amides | $\begin{aligned} & 1740-1720 \\ & 1720-1700 \\ & 1700-1680 \\ & 1725-1700 \\ & 1700-1680 \\ & 1850-1800 \text { and } 1790-1740 \\ & 1795 \\ & 1810 \\ & 1750-1735 \\ & 1700-1630 \end{aligned}$ |
| Triple bond stretching vibrations CN CC | $\begin{aligned} & 2260-2215 \\ & 2260-2100 \end{aligned}$ |

## Exam skills 6

This exam-style question uses knowledge and skills you have already revised. Have a look at pages 60 and 61 for a reminder about oxidation of alcohols and halogenoalkanes from alcohols.

## Worked example

(a) Ethanal can be made from ethanol.
(i) State the names or formulae of the two substances needed to make ethanal from ethanol.
(2 marks)
Potassium dichromate(VI), acidified with dilute sulfuric acid.
(ii) Draw a diagram to show the laboratory apparatus needed to make ethanal from ethanol and to collect the ethanal. ( $\mathbf{2}$ marks)

(iii) Describe what would be seen when ethanol and ethanal are warmed separately with Tollens' reagent.
(1 mark)
There would be no visible change with ethanol but a silver mirror would form with ethanal.
(b) Phosphorus(V) chloride, $\mathrm{PCl}_{5}$, reacts with ethanol.
(i) Describe what would be seen during the reaction.
(1 mark)
Steamy fumes are produced.
(ii) Write an equation for the reaction. (1 mark)
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{PCl}_{5} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Cl}+\mathrm{POCl}_{3}+\mathrm{HCl}$
(c) A mixture of ethanol and water can be distilled to separate some of the ethanol. Name a suitable drying agent to absorb remaining water in the distilled ethanol and describe how you would produce dry ethanol using it. (2 marks)

Use anhydrous calcium oxide. Mix it with the distilled ethanol, then filter the mixture to remove the solid.
'Potassium dichromate' would not be enough - you need to include the oxidation number of chromium in $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$. Similarly, 'acid' would not be enough for $\mathrm{H}_{2} \mathrm{SO}_{4}$ - you need to state its name or formula.
Practical skills

You need to draw apparatus for heating under distillation conditions. If you showed apparatus for reflux instead, further oxidation to ethanoic acid would occur if this apparatus was used.

Make sure you show that heat is needed (a labelled arrow is enough). Take care that your drawing shows:

- the still head sealed so that the vapours could not escape without entering the condenser
- the condenser open at one end so that the apparatus would not explode.

Make sure you can recall the expected observations when experiments are carried out.

## The answer describes the expected observations for both compounds.

## Command word: Describe

If a question asks you to describe something, it means you need to:

- give an account of something
- link statements if necessary.

You do not need to:

- include a justification or reason.

The organic reactant and product are shown using structural formulae rather than molecular formulae.

Ethanol and water can be separated from each other by distillation because they have different boiling points.

[^0]
## Topic 2

## Shapes of molecules and ions

Valence shell electron pair repulsion (VSEPR) theory lets you predict shapes of molecules and ions.

## Predicting a shape

Use a dot and cross diagram to find the number of pairs of electrons around the central atom.
This gives you the basic shape (see table below).

## Multiple bonds

Treat these as single bonds.
For example, $\mathrm{O}=\mathrm{C}=\mathrm{O}$ and $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H}$ are linear molecules with a bond angle of $180^{\circ}$.

## Maths skiths

Make sure you can visualise the angles and shapes in regular 2D and
3D shapes and can draw them.

## The effect of lone pairs

The arrangement of electron pairs around the central atom keeps repulsion to a minimum.

$$
\begin{array}{lc}
\text { lone pair-lone pair } & \text { most repulsion } \\
\text { lone pair-bond pair } & \downarrow \\
\text { bond pair-bond pair } & \text { least repulsion }
\end{array}
$$

Each lone pair of electrons reduces the bond angle by about $2.5^{\circ}$. For example, $\mathrm{NH}_{3}$ is trigonal pyramidal, bond angle $107^{\circ}$ (compared with $109.5^{\circ}$ if it were tetrahedral).

## Shapes and angles



| Bond <br> pairs | Lone <br> pairs | Shape | Example |  |
| :--- | :---: | :---: | :---: | :---: |
| 5 | 0 | trigonal <br> bipyramidal | A dashed line <br> shows a bond <br> going into the <br> plane of the |  |
| paper. |  |  |  |  |

## Worked example

Draw the shape of a water molecule, including its bond angle.


There are two bonding pairs and two lone pairs around the O atom, so the basic shape is tetrahedral.
Repulsion by the two lone pairs reduces the bond angle by about $5^{\circ}$, producing a V -shaped (or bent line) molecule.

## Now try this

1 Predict the bond angles in the following molecules and ions.
(a) $\mathrm{CHCl}_{3}$
(b) $\mathrm{NH}_{4}^{+}$
(c) $\mathrm{NH}_{2}^{-}$
(d) $\mathrm{BeF}_{2}$
(e) $\mathrm{PF}_{5}$
(5 marks)

2 Predict the bond angles in $\mathrm{BH}_{3}$ and $\mathrm{PH}_{3}$. Explain the difference between them.
(3 marks)
3 Sulfur trioxide, $\mathrm{SO}_{3}$, has three triple bonds around the central atom and no lone pairs. Name the shape of the $\mathrm{SO}_{3}$ molecule and suggest its bond angle.
(2 marks)

## Shells，sub－shells and crbitals

Electrons surround the nucleus of an atom and are arranged in orbitals，sub－shells and shells．

## Quantum shells

Electrons in atoms exist in energy levels called quantum shells．


## Sub－shells and orbitals

Each shell contains one or more sub－shells，which have the letters $s, p$ or $d$ ．
Each sub－shell contains different numbers of orbitals．

| Sub－shell | $s$ | $p$ | $d$ | $f$ |
| :--- | :---: | :---: | :---: | :---: |
| Number of orbitals | 1 | 3 | 5 | 7 |
| Number of electrons | 2 | 6 | 10 | 14 |

An orbital is a region around the nucleus where there is a high probability of finding an electron．
（V）An orbital can hold up to two electrons with opposite spins．

## Worked example

Draw diagrams to show the shape of an s－orbital and of a p－orbital．
（2 marks）


## Flectrons in shells

You need to know the maximum number of electrons in the first four quantum shells．

| Shell | Sub－shell（s） | Maximum number of <br> electrons |
| :---: | :--- | ---: |
| 4 | $4 s 4 p 4 d 4 f$ | $2+6+10+14=32$ |
| 3 | $3 s 3 p 3 d$ | $2+6+10=18$ |
| 2 | $2 s 2 p$ | $2+6=8$ |
| 1 | $1 s$ | 2 |

The $4 d$ and $4 f$ sub－shells are included here only so you can see why the fourth shell can contain up to 32 electrons．

## rlectrons in orbitals

Electrons have a property called spin．
The electrons in an orbital have opposite spins．

| $4 p$ Tl $\uparrow \downarrow \uparrow \downarrow$ |  |
| :---: | :---: |
| 3d 个】 T】 T】 ¢ $\downarrow \uparrow \downarrow$ | 3d is higher |
| 4 T 个 $\downarrow$ | in energy than 4s |
| $3 p$ T】 ¢】 $\uparrow \downarrow$ |  |
| $3 s$ TV |  |
| $2 p$ T $\uparrow \downarrow \uparrow \downarrow<$ | $2 p_{x} 2 p_{y} 2 p_{z}$ <br> orbitals |
| 2s TV | arrows represent |
| Is $\uparrow \downarrow<$ | electrons with |

## Now try this

1 （a）Explain what is meant by the term orbital．
（2 marks）
（b）Draw the shapes of an s－orbital and a p－orbital．
（2 marks）

2 State the maximum number of electrons that can occupy：
（a）an s－，a p－and a d－sub－shell
（1 mark）
（b）each of the first four quantum shells．
（1 mark）

3 Explain why electrons may be represented as arrows in boxes．
（2 marks）
$\square$

## Stability ol carbonates and nitrates

Group 1 and 2 carbonates and nitrates may undergo thermal decomposition, reactions in which heat is used to break down a reactant into two or more products.

## Carbonates

Many, but not all, Group 1 and 2 carbonates decompose to form metal oxides and carbon dioxide.

| $\mathrm{CO}_{3}$ | decomposes | $\mathrm{BeCO}_{3}$ | decompose with |
| :---: | :---: | :---: | :---: |
| $\mathrm{Na}_{2} \mathrm{CO}_{3}$ | do not decompose | $\mathrm{MgCO}_{3}$ |  |
| $\mathrm{K}_{2} \mathrm{CO}_{3}$ |  | $\mathrm{CaCO}_{3}$ |  |
| $\mathrm{Rb}_{2} \mathrm{CO}_{3}$ |  | $\mathrm{SrCO}_{3}$ | difficulty |
| $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ |  | $\mathrm{BaCO}_{3}$ |  |

In Group I, only lithium carbonate decomposes at Bunsen burner temperatures:

$$
\mathrm{Li}_{2} \mathrm{CO}_{3}(\mathrm{~s}) \rightarrow \mathrm{Li}_{2} \mathrm{O}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

Going down Group 2, the carbonates become more stable and need higher temperatures to decompose them. In general:
$\mathrm{MCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{MO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$

## Nitrates

Group 1 and 2 nitrates decompose to form different products, depending on their stability.

| $\mathrm{LiNO}_{3}$ | $\mathrm{Li}_{2} \mathrm{O} \mathrm{NO} \mathrm{O}_{2}$ | $\mathrm{Be}\left(\mathrm{NO}_{3}\right)_{2}$ | $\begin{gathered} \mathrm{MO} \mathrm{NO} \\ \mathrm{O}_{2} \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{NaNO}_{3}$ | $\mathrm{MNO}_{2}$ | $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ |  |
| $\mathrm{KNO}_{3}$ |  | $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ |  |
| $\mathrm{RbNO}_{3}$ | $\mathrm{O}_{2}$ | $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ |  |
| $\mathrm{CsNO}_{3}$ |  | $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$ |  |

Here are three example equations:

- $4 \mathrm{LiNO}_{3}(\mathrm{~s}) \rightarrow 2 \mathrm{Li}_{2} \mathrm{O}(\mathrm{s})+4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
- $2 \mathrm{RbNO}_{3}(\mathrm{~s}) \rightarrow 2 \mathrm{RbNO}_{2}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g})$
- $2 \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2} \rightarrow 2 \mathrm{MgO}(\mathrm{s})+4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$

Going down Groups 1 and 2, nitrates become more stable. Higher temperatures are needed to decompose them.

## Woxked example

The diagram shows apparatus that can be used to investigate the thermal stability of Group 2 carbonates. The time taken for the limewater to turn cloudy is measured for each carbonate.


State three factors to control so a fair comparison can be made.
(3 marks)

The same number of moles of carbonate should be used each time. The size of the flame and its distance to the boiling tube should be the same.


Other factors include the volume of limewater and the particle size of the carbonates. There should also be a way to standardise the measurement of cloudiness, such as a black cross drawn on the opposite side of the tube.


You need to understand experimental procedures to show patterns in the thermal decomposition of Group 1 and 2 nitrates and carbonates.

## Explaining trends

Cations (positively charged ions) can affect anions such as $\mathrm{CO}_{3}{ }^{2-}$ and $\mathrm{NO}_{3}{ }^{-}$.
They can lower the energy needed to break a
$\mathrm{C}-\mathrm{O}$ bond or $\mathrm{N}-\mathrm{O}$ bond.
This effect increases:

- the smaller the cation
- the greater the cation's charge.
$\mathrm{Li}^{+}$ions and Group 2 ions can cause:
- $\mathrm{CO}_{3}{ }^{2-}$ ions to decompose to $\mathrm{O}^{2-}$ and $\mathrm{CO}_{2}$.
- $\mathrm{NO}_{3}{ }^{-}$ions to decompose to $\mathrm{O}^{2-}, \mathrm{NO}_{2}$ and $\mathrm{O}_{2}$.


## Now try this

Lithium nitrate behaves differently from other Group 1 nitrates.
(a) Describe, with the help of equations, the differences in the thermal decomposition of lithium nitrate and potassium nitrate. (4 marks)
(b) Explain the difference in observed thermal stability of these two nitrates.
(2 marks)


[^0]:    Anhydrous sodium sulfate or anhydrous magnesium sulfate could be used instead. You could decant the mixture instead of filtering it (the solid would stay behind).

