5 Equilibrium

Contents

An **equilibrium** is a steady state which can be achieved during a reversible reaction. It is reached when the rates of the forward and reverse reactions are equal. This does not mean that the reaction has stopped when equilibrium is reached. There are still changes at the microscopic level, but bulk properties such as colour and pH do not change. It is for this reason that they are often described as **dynamic equilibria** (A1.0j). In a concentration *versus* time graph the equilibrium is reached at the point where the concentrations of the reactants and products remain constant. This is because the rate of formation of product in the forward reaction exactly matches the rate of formation of reactant in the reverse reaction.
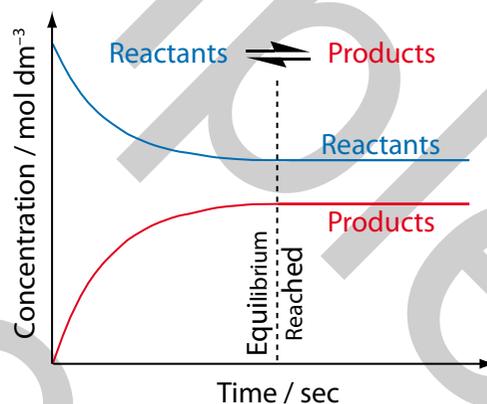
For an equilibrium to occur, there needs to be closed system so that there is no exchange of matter. A closed system in the laboratory is as simple as a conical flask with a bung in it or a syringe with a sealed end.
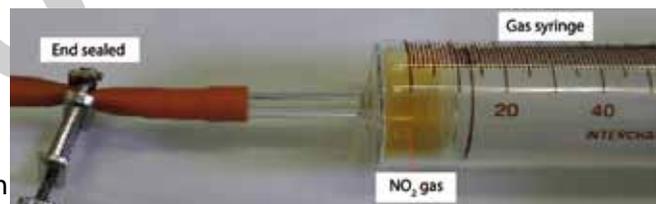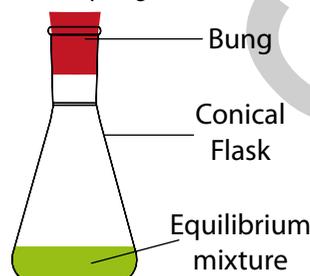
The symbol for an equilibrium (⇌) is essentially two arrows with half arrow head pointing in opposite directions. It is conventional to show the top arrow pointing to the right and the lower arrow pointing to the left. Despite the symbol representing an equilibrium, do not fall into the trap of thinking that every equilibrium mixture contains

50% reactant and 50% product. This is certainly not the case and we will return to this point again in terms of equilibrium constants (B1.5c).

One area of chemistry which is seemingly understood well by students is the pH scale. But does everyone know that the pH of the blood is 7.4 and that if it should vary by more than ± 0.5 from its usual equilibrium value, then the organism will be in trouble? Climbing to high altitudes can lead to an increase in the pH of blood which is one of the hazards climbers face on top of mountains such as Mount Kilimanjaro in Tanzania.


Climbers on top of Mount Kilimanjaro, the highest point in Africa

B1.5 (a)
Le Chatelier's principle

Le Chatelier's Principle states: "if a chemical system at equilibrium undergoes changes to the established conditions, then the chemical system will alter in such a way as to tend to restore the original conditions and therefore responds by minimising the effects of the changes."

Le Chatelier's Principle was first published in 1888 and it is very important because it allows chemists to deduce qualitatively the effects of a system in equilibrium when subjected to changes in temperature, pressure and concentration. When an equilibrium is disturbed, it can do one of three things. It can remain as it was before the disturbance or it can shift towards the forward reaction (RHS = right hand side) or it can shift towards the reverse reaction (LHS = left hand side).
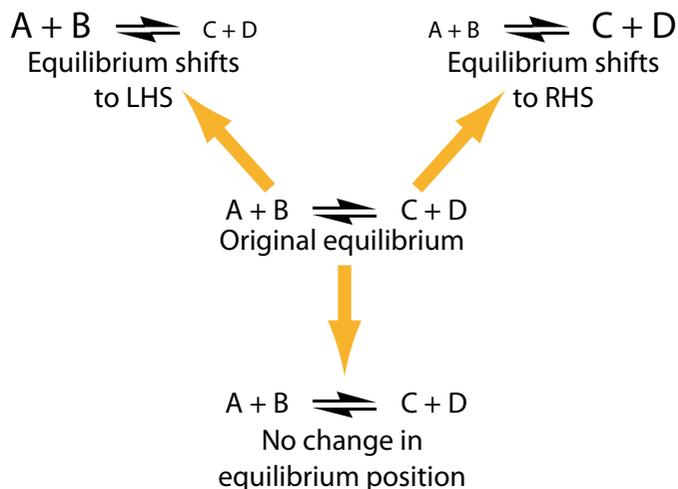
Le Chatelier's principle says that an equilibrium has a tendency to oppose every change that you make to it. A useful analogy is to view an equilibrium in much the same way that a parent views a stubborn child who does the exact opposite of what the parent asks them to do.

The three factors which do affect an equilibrium's position (temperature, pressure and concentration) will be looked at it in turn. Pressure is the only factor which is exclusive to gaseous equilibria and catalysts do not affect the equilibrium position but they do allow the equilibrium to be achieved in a quicker time.

Knowledge of Le Chatelier's Principle can help to increase the yield in an equilibrium reaction, *e.g.* esterification (B3.7b). Molecular sieves can be added to reaction mixtures to greatly increase the yield of ester as these zeolites (cavity-containing aluminosilicates) absorb the product, water.

Effect of changes in temperature

This section takes a look at the qualitative effect that changes in temperature will have on the equilibrium positions of some examples. When considering how changes in temperature affect an equilibrium, you need to establish whether the reaction is exothermic or endothermic. This is done by looking at the sign of the enthalpy change given for the reaction (A1.3a). If the forward reaction is exothermic (negative ΔH) then the reverse reaction will be endothermic (positive ΔH). The opposite is also true so if the forward reaction is endothermic (positive ΔH) then the reverse reaction will be exothermic (negative ΔH). According to Le Chatelier's principle, an increase in temperature results in the equilibrium shifting in the cooler, endothermic direction. According to Le Chatelier's principle a decrease in temperature results in the equilibrium shifting in the warmer, exothermic direction.

Worked examples for K_{sp}

Example 5.21

Calculate K_{sp} at 298 K when $CaCO_3$ has a solubility of 7.07×10^{-5} mol dm^{-3}.

Equation: $CaCO_3 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + CO_3^{2-} \text{ (aq)}$

$K_{sp} = [Ca^{2+}] [CO_3^{2-}]$

The concentration of $[Ca^{2+}] = [CO_3^{2-}] = 7.07 \times 10^{-5}$ mol dm^{-3}

$$K_{sp} = (7.07 \times 10^{-5}) \times (7.07 \times 10^{-5})$$

$$= (7.07 \times 10^{-5})^2$$

$$= 5.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

Example 5.22

Calculate K_{sp} at 298 K when $CaSO_4$ has a solubility of 0.743 g dm^{-3}.

[A_r: Ca (40.1) S (32.1) O (16.0)].

There are two concentration units; mol dm^{-3} and g dm^{-3}.

The conversion to the more usual mol dm^{-3} concentration is g dm$^{-3} \div M_r$

M_r for $CaSO_4$ = 40.1 + 32.1 + (4 × 16.0) = 136.2 g mol^{-1}.

Solubility of $CaSO_4 = \frac{0.743}{136.2} = 5.46 \times 10^{-3}$ mol dm^{-3}

Equation: $CaSO_4 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)}$

$K_{sp} = [Ca^{2+}] [SO_4^{2-}]$

The concentration of $[Ca^{2+}] = [SO_4^{2-}] = 5.46 \times 10^{-3}$ mol dm^{-3}

$$K_{sp} = (5.46 \times 10^{-3}) \times (5.46 \times 10^{-3})$$

$$= (5.46 \times 10^{-3})^2$$

$$= 2.98 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

Example 5.23

Calculate the solubility in mol dm^{-3} of AgCl at 298 K if the solubility product $K_{sp} = 2.0 \times 10^{-10}$ mol^2 dm^{-6}.

Equation: $AgCl \text{ (s)} \rightleftharpoons Ag^+ \text{ (aq)} + Cl^- \text{ (aq)}$

$K_{sp} = [Ag^+] [Cl^-]$

$2.0 \times 10^{-10} = [Ag^+] [Cl^-]$ and since $[Ag^+] = [Cl^-]$

$\sqrt{2.0 \times 10^{-10}} = [Ag^+] = 1.41 \times 10^{-5}$ mol dm^{-3}.

Example 5.24

Calculate the solubility in mol dm^{-3} of $Ca(OH)_2$ at 298 K if the solubility product $K_{sp} = 1.43 \times 10^{-8}$ mol^3 dm^{-9}.

Equation: $Ca(OH)_2 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + 2 OH^- \text{ (aq)}$

$K_{sp} = [Ca^{2+}] [OH^-]^2 = [Ca^{2+}](2[Ca^{2+}])^2$ (since $[OH^-] = 2[Ca^{2+}]$)

$1.43 \times 10^{-8} = 4[Ca^{2+}]^3$ and

$[Ca^{2+}] = \sqrt[3]{\frac{1.43 \times 10^{-8}}{4}} = 1.53 \times 10^{-3}$ mol dm^{-3}.

Questions 5.8

1. Calculate the solubility product at 298 K for $MgCO_3$ and AgBr.

   [A_r: Mg (24.3), C (12.0), O (16.0), Ag (108), Br (79.9)]

   Solubility of $MgCO_3$ is 0.267 g dm^{-3}

   Solubility of AgBr is 7.07×10^{-7} mol dm^{-3}

2. Calculate the solubility in mol dm^{-3} at 298 K of the following compounds:

   a. Ag_2S where its $K_{sp} = 6.3 \times 10^{-50}$ mol^3 dm^{-9}

   b. AgCNS where its $K_{sp} = 2.0 \times 10^{-12}$ mol^2 dm^{-6}

   c. SrF_2 where its $K_{sp} = 2.45 \times 10^{-9}$ mol^3 dm^{-9}

Worked examples for K_a

Example 5.25

The equilibrium between carbon dioxide and water helps buffer the blood.

$$CO_2 \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons HCO_3^- \text{ (aq)} + H^+ \text{ (aq)}$$

The acid dissociation constant $K_a = 4.5 \times 10^{-7}$ mol dm^{-3} at 310K.

If: $[HCO_3^-] = 1.3 \times 10^{-2}$ mol dm^{-3} and

$[CO_2] = 1.3 \times 10^{-3}$ mol dm^{-3}

calculate the $[H^+]$ and the pH of blood.

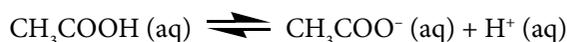$$K_a = \frac{[HCO_3^-]\,[H^+]}{[CO_2]} \text{ and rearranging gives}$$

$$[H^+] = K_a \times \frac{[CO_2]}{[HCO_3^-]}$$

$$= 4.5 \times 10^{-7} \times \frac{1.3 \times 10^{-3}}{1.3 \times 10^{-2}}$$

$$= 4.5 \times 10^{-8} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [H^+]$$

$$= -\log_{10} 4.5 \times 10^{-8}$$

$$= 7.35$$

Example 5.26

Ethanoic acid with concentration 0.01 mol dm^{-3} has a pH of 3.38 at 298 K. What is its acid dissociation constant (K_a)?

$$CH_3COOH \text{ (aq)} \rightleftharpoons CH_3COO^- \text{ (aq)} + H^+ \text{ (aq)}$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

Since $\quad [H^+] = [CH_3COO^-]$

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

$$[H^+] = 10^{-\text{pH}}$$

$$[H^+] = 10^{-3.38}$$

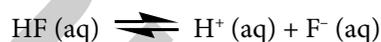$$[H^+] = 4.17 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_a = \frac{[4.17 \times 10^{-4}]^2}{[CH_3COOH]}$$

As ethanoic is a weak acid (partly ionized) and it is assumed that its concentration will be the same as that given for the acid.

$$K_a = \frac{[4.17 \times 10^{-4}]^2}{[0.01]}$$

$$= 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

Example 5.27

Hydrofluoric acid with concentration 0.0010 mol dm^{-3} has a $K_a = 1.7 \times 10^{-3}$ mol dm^{-3} at 298 K. What is its pH?

$$HF \text{ (aq)} \rightleftharpoons H^+ \text{ (aq)} + F^- \text{ (aq)}$$

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

Since $\quad [H^+] = [F^-]$

$$K_a = \frac{[H^+]^2}{[HF]}$$

rearranging this equation gives

$$[H^+] = \sqrt{K_a \times [HF]}$$

As hydrofluoric acid is a weak acid (partly ionized), it is assumed that its concentration will be the same as that given for the acid.

$$[H^+] = \sqrt{1.7 \times 10^{-3} \times 0.0010}$$

$$= 1.30 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [H^+]$$

$$= -\log_{10} (1.30 \times 10^{-3})$$

$$= 2.9$$

Questions 5.9

1. What is K_a for 0.25 mol dm^{-3} of H_3PO_4 with a pH of 1.35 at 298K?

2. What is K_a for 0.05 mol dm^{-3} of HCO_2H with a pH of 2.55 at 298K?

3. What is K_a for 0.12 mol dm^{-3} of HOCl with a pH of 4.18 at 298K?

4. What is the pH of lactic acid (0.01 mol dm^{-3}) with $K_a = 1.29 \times 10^{-4}$ mol dm^{-3}?

5. What is the pH of propanoic acid (0.02 mol dm^{-3}) with $K_a = 1.3 \times 10^{-5}$ mol dm^{-3}?

6. What is the pH of benzoic acid (0.08 mol dm^{-3}) with $K_a = 6.3 \times 10^{-5}$ mol dm^{-3}?

Worked examples for K_W

The pH at which water is neutral varies with temperature. When water ionizes, there will always be the same number of H$^+$ ions and OH$^-$ ions.

Example 5.28

What is the pH at which water is neutral at 323 K when $K_w = 5.47 \times 10^{-14}$ mol^2 dm^{-6}?

$$K_w = [OH^-] \times [H^+]$$

$$5.47 \times 10^{-14} = [OH^-] \times [H^+] \text{ and since } [H^+] = [OH^-]$$

$$= [H^+] \times [H^+]$$

$$= [H^+]^2$$

$$[H^+] = \sqrt{5.47 \times 10^{-14}}$$

$$= 2.34 \times 10^{-7} \text{ moldm}^{-3}$$

and since $\quad$ pH $= -\log_{10} [H^+]$

$$= -\log_{10} 2.34 \times 10^{-7}$$

$$= 6.6.$$

So at a pH of 6.6 at 323 K, water is neutral.

Questions 5.10

1. Calculate the pH at which water is neutral at the different temperatures using the values for K_w.

K_w / mol^2 dm^{-6}	Temperature / K
0.114×10^{-14}	273
0.293×10^{-14}	283
1.00×10^{-14}	298
2.92×10^{-14}	313
51.3×10^{-14}	373

2. Explain what happens to the pH of pure water as the temperature increases.

B1.5 (g) Acid–base titrations and indicators

A **titration** is a **volumetric analysis** used to determine the unknown concentration of a solution. In order to calculate the unknown concentration in an acid–base titration, you need to know the balanced formula equation and also the concentration of either the acid or the base.

Meniscus reading = 39.30 cm³
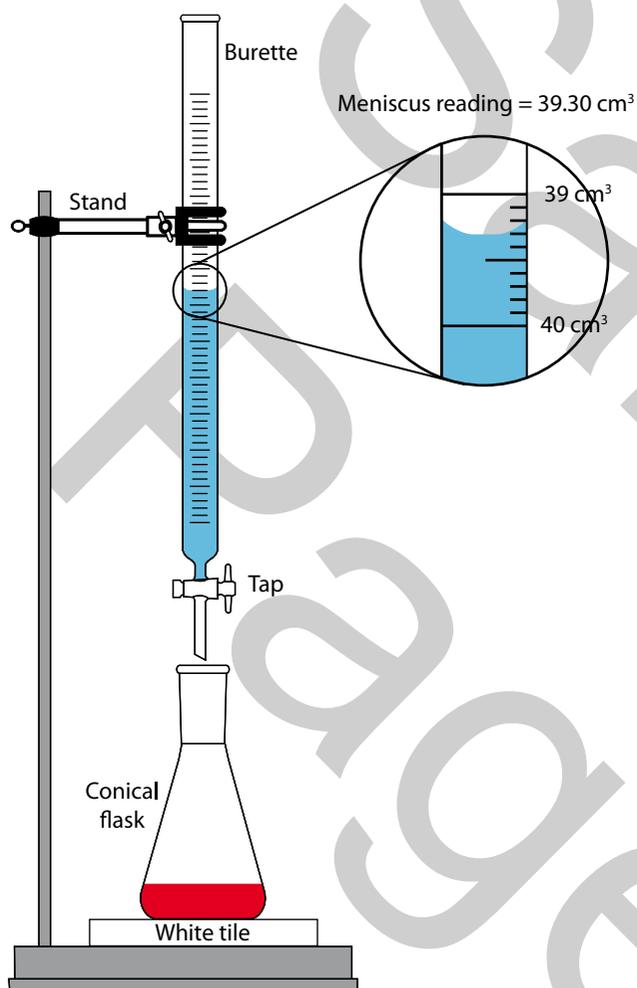
Apparatus for an acid-base titration

Volumes of acid and base are accurately known as they are measured in either a pipette or a burette. When performing a titration, the burette is held vertically in a clamp with a white tile placed beneath the conical flask. A funnel is used to load the burette but should always be removed during the titration itself. Good experimenters will ensure that there is no air bubble trapped below the burette tap and they will not allow any liquid to enter the pipette filler. When reading volume scale marks, they will get their eye level with the meniscus to avoid parallax. During a titration it is good practice near the end point to add the liquid dropwise whilst swirling the contents of the conical flask.

The pH changes during an acid-base titration can be monitored using a pH electrode. If just the end point is needed, a few drops of a suitable indicator are added to the conical flask prior to addition of liquid from the burette. When carrying out a titration, a rough value for the end point is determined followed by at least two other titrations which agree to within 0.10 cm³. The average is then taken from these results for the subsequent calculation and these results are often described as **concordant**, meaning **in agreement**. The table shows an efficient way of recording results for an acid-base titration.

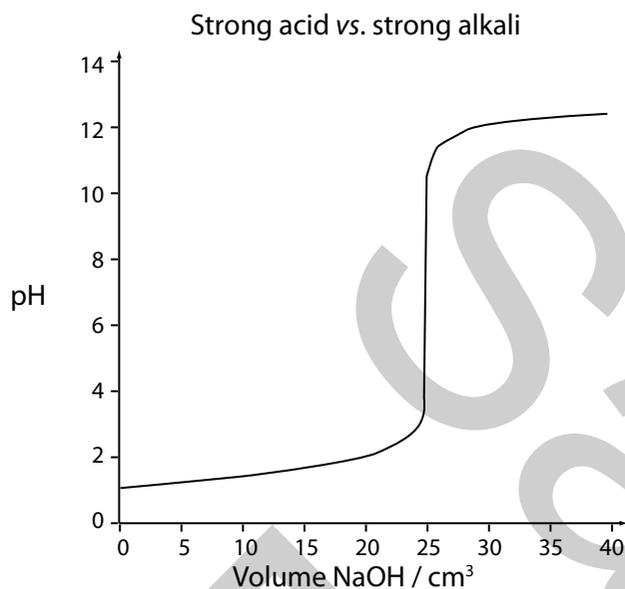| Volume added from the burette / cm³	Rough	1st	2nd	Average titres (1st & 2nd)
Final	25.20	49.80	0.20	
Initial	0.10	25.20	24.80	
Titre	25.10	24.60	24.60	24.60

Titration curves

A titration curve is a plot of pH *versus* volume of acid or alkali added from the burette. There are four types of acid-base titration which give very different changes in pH as seen by their curves. It is clear that none of the titration curves change linearly.

The titration curve of the weak acid *vs*. strong alkali starts at ~ pH = 3 with a rapid change of pH in the neutralization reaction between pH 6.5 to pH 11 as it nears its equivalence point (pH 8.8) and finishes at ~pH = 13. The equivalence point is the point at which the number of moles of H^+ = number of moles of OH^-. The equivalence point is the part of the titration curve where the almost vertical part of the graph's gradient changes direction at a point called the point of inflection.

Weak acid *vs*. strong alkali

pH

Volume NaOH / cm³
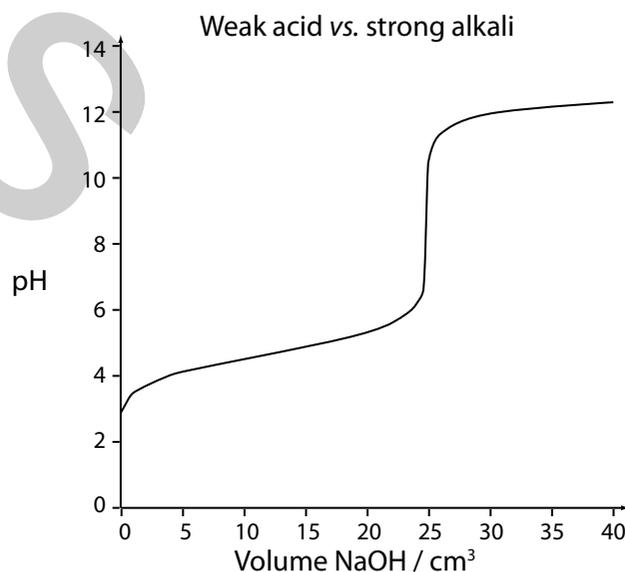
The titration curve of the strong acid *vs.* strong alkali starts at ~ pH = 1 with a rapid change of pH in the neutralization reaction between pH 3 to pH 11 as it nears its equivalence point (pH 7) and finishes at ~pH = 13.

The titration curve of the weak acid *vs.* weak alkali starts at ~pH = 3 and there is no rapid change of pH in the neutralization reaction and it finishes at ~pH = 9.

Strong acid *vs.* strong alkali

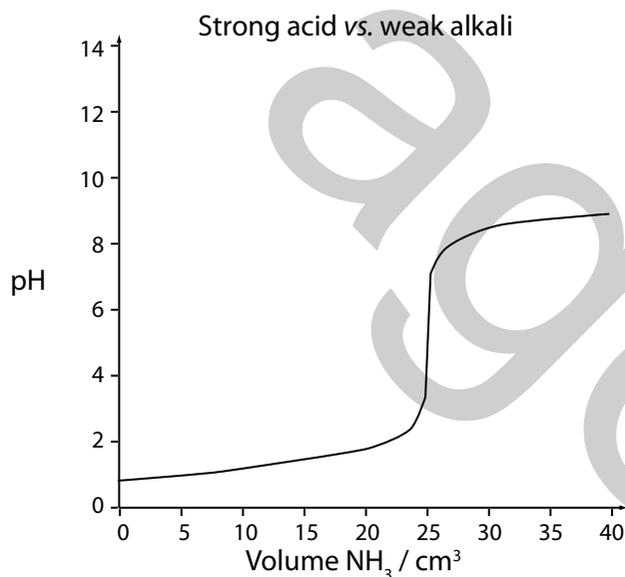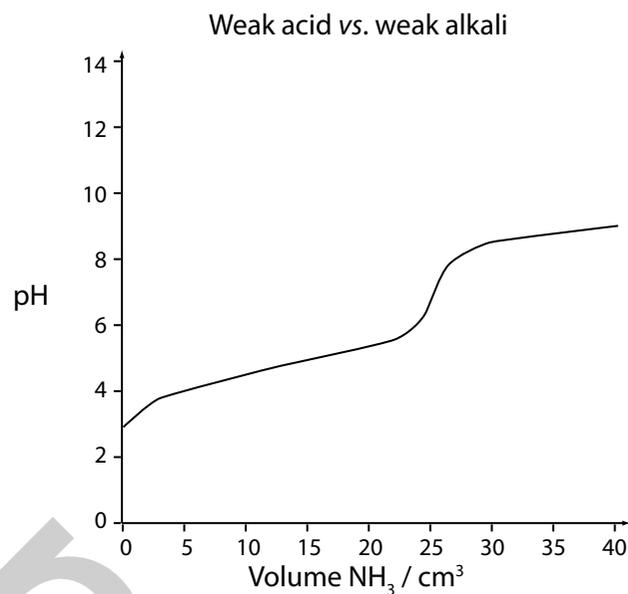pH vs Volume NaOH / cm³

Weak acid *vs.* weak alkali

pH vs Volume NH₃ / cm³

The titration curve of the strong acid *vs.* weak alkali starts at ~ pH = 1 with a rapid change of pH in the neutralization reaction between pH 3 to pH 7 as it nears its equivalence point (pH 5.2) and finishes at ~pH = 9.

When drawing titration curves, start and finish in the right pH region and ensure that the vertical part is at the volume corresponding to the equivalence point. If 25 cm³ of 1.0 mol dm⁻³ hydrochloric acid is titrated against 1.0 mol dm⁻³ sodium hydroxide, the equivalence point will come at 25 cm³. But if 10 cm³ of 1.0 mol dm⁻³ sulfuric acid is titrated against 1.0 mol dm⁻³ sodium hydroxide, the equivalence point will come at 20 cm³.

Strong acid *vs.* weak alkali

pH vs Volume NH₃ / cm³

Indicators

Indicators are water soluble dyes which are weak acids which have distinct and sharp colour changes over a narrow range of ~2 pH units. There are lots of examples of indicators and the two most useful for acid-base titrations are methyl orange and phenolphthalein.

Indicator	colour in acid (HIn)	pK_{in}	colour in alkali (In⁻)	Colour change pH range
Methyl orange	Red	3.7	Yellow	3.2–4.4
Methyl red	Red	5.1	Yellow	4.2–6.3
Aaolitmin (litmus)	Red	7.0	Blue	5.0–8.0
Bromothymol blue	Yellow	7.0	Blue	6.0–7.6
Phenol red	Yellow	7.9	Red	6.8–8.4
Phenolphthalein*	Colourless	9.3	Pink	8.2–10.0

* phenolphthalein is dissolved in ethanol.

The undissociated form of an indicator HIn (weak acid) will have a different colour from its dissociated conjugate base form (In⁻). The indicator phenolphthalein has two different structures corresponding to HIn (colourless) and In⁻ (pink).

Phenolphthalein (colourless)

Phenolphthalein (pink)
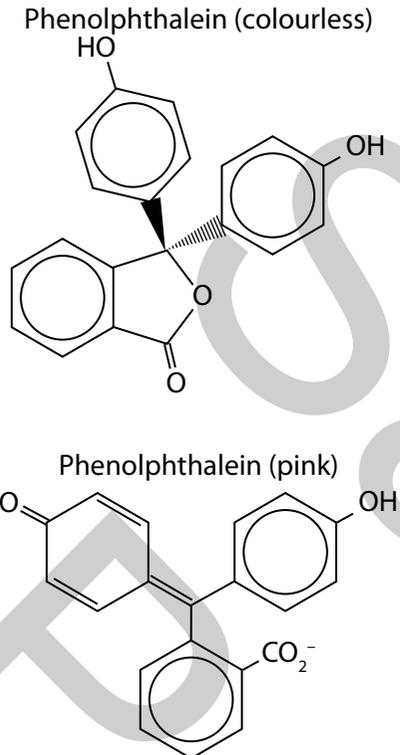
Colours of indicators in acid and alkali

Indicator	Colour in acid	Colour in alkali
Phenolphthalein		
Litmus		
Methyl orange		
Bromophenol blue		
Bromothymol blue		

The choice of indicator for a titration depends on which type of acid-base pair is under investigation. The indicator chosen for a titration needs to change from one of its colours to the other where there is a large change in pH, *i.e.* the almost vertical part of the titration curve. The end point of a titration is when [HIn] = [In⁻], which is the same as the pK_{in} value.

If the value of pK_{in} and the colour change range for an indicator match the vertical part of titration curve, then it is a suitable indicator for the titration. This is why phenolphthalein is a suitable indicator but methyl orange is not for the titration of a weak acid with a strong alkali. In the titration of a strong acid with a weak alkali, methyl orange is a suitable indicator but phenolphthalein is not.

Weak acid *vs.* strong alkali

Strong acid *vs.* weak alkali
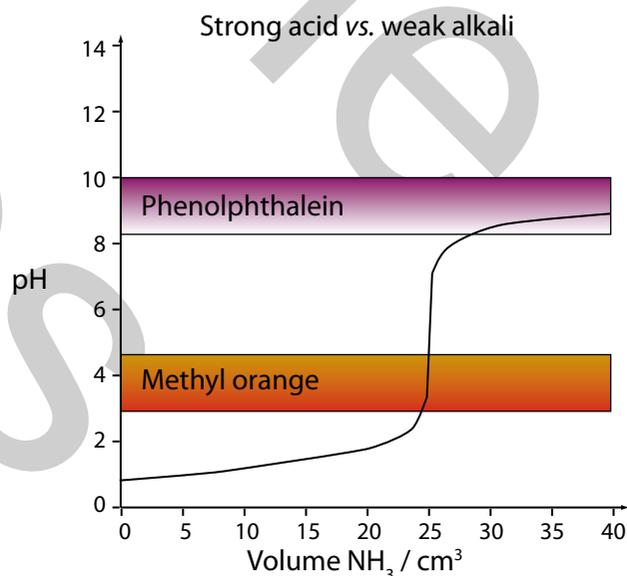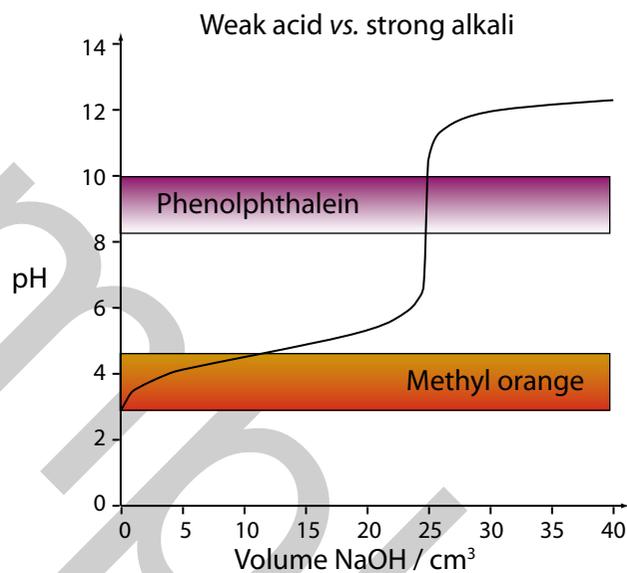
Can you work out what a suitable indicator will be for the titration of a strong acid *vs.* strong alkali and the titration of a weak acid *vs.* weak alkali? Find an indictor whose colour change coincides with the near vertical section of the titration curve. There is no sharp change in pH for the titration between a weak acid and a weak alkali.

	Weak acid	Strong acid
Weak alkali	No suitable indicator	Methyl orange
Strong alkali	Phenolphthalein	Methyl orange or Phenolphthalein

Questions 5.12

1. Which option shows a titration which will not show a sharp end point with either methyl orange or phenolphthalein?

   A   Strong acid *vs* weak alkali

   B   Strong acid *vs* strong alkali

   C   Weak acid *vs* strong alkali

   D   Weak acid *vs* weak alkali

2. What is a titration curve?

3. Complete the following table, which is helpful when drawing titration curves.

	Start the curve
Strong acid	pH = ?
Weak acid	pH = ?
	Finish the curve
Strong base	pH = ?
Weak base	pH = ?

4. What are the colours of these indicators in 1.0 mol dm^{-3} of hydrochloric acid?

   a.   Methyl orange

   b.   Phenolphthalein

   c.   Bromothymol blue

5. Sketch a titration curve for the addition of NaOH (0.1 mol dm^{-3}) to 10 cm^3 of 0.1 mol dm^{-3} of oxalic acid $(CO_2H)_2$ and explain any near vertical sections.

B1.5 (h) Buffer solutions

A buffer solution is one that resists changes in its pH on the addition of small amounts of acid or the addition of small amounts of alkali. There are two types of buffer:

- acidic buffers (pH < 7) and

- alkaline buffers (pH > 7).

The two types of buffer are compared and contrasted in the following table.

Acidic buffer	Alkaline buffer
Weak acid and its sodium salt (Weak acid and its conjugate base)	Weak alkali and its chloride salt (Weak alkali and its conjugate acid)
pH < 7	pH > 7
Ethanoic acid and sodium ethanoate	Ammonia solution and ammonium chloride
$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$ (Equilibrium lies well over to the left hand side)	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (Equilibrium lies well over to the left hand side)
High [CH_3CO_2H]	High [NH_3]
$CH_3CO_2Na + H_2O \rightarrow CH_3CO_2^- + Na^+$ (Sodium ethanoate fully ionizes)	$NH_4Cl + H_2O \rightarrow NH_4^+ + Cl^-$ (Ammonium chloride fully ionizes)

So how does an acidic buffer help to resist changes in its pH if small amounts of acid are added? If the [H_3O^+] is increased, the equilibrium will shift to the left hand side to minimise the applied change by removing the added acid, *i.e.* the added acid will combine with the ethanoate ion. So how does an acidic buffer help to resist changes in its pH if small amounts of alkali are added? If the [OH^-] is increased, the equilibrium will shift to the right hand side to minimise the applied change by replacing the H_3O^+ which is lost in its neutralization reaction with OH^-.

So how does an alkaline buffer help to resist changes in its pH if small amounts of acid are added? If the [H_3O^+] is increased, the equilibrium will shift to the right hand side to minimise the applied change by replacing the removed hydroxide which reacted with the additional acid to form water. So how does an alkaline buffer help to resist changes in its pH if small amounts

B2.5 (c) Lattices (geometry and coordination number)

Shapes and geometry were discussed for simple molecules and hypervalent species in A1.2g. In terms of lattices, we will only consider the geometry for tetrahedral and octahedral atoms/ions. A particle with four nearest neighbours is said to have a coordination number of four and is described as having a **tetrahedral geometry**. A particle with six nearest neighbours is said to have a coordination number of six and is described as having an **octahedral geometry**. Coordination number is defined as the number of nearest neighbouring atoms or ions touching or surrounding a central atom or ions within a three dimensional lattice structure. It is sometimes overlooked that the ratio of coordination numbers is the same as the stoichiometric ratio found in the formula for the compound.

(NaCl) (●) = chloride and (●) = sodium ion

CN = 6
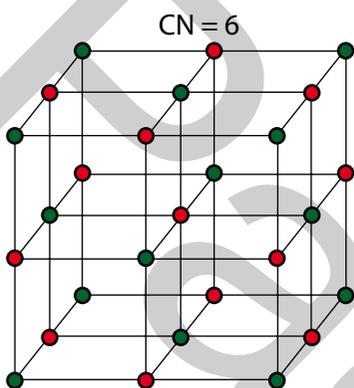
Ball-and-stick model of sodium chloride

CN = 6

Octahedral geometry

Octahedron

Sodium chloride

In the diagram ● represents a sodium ion and ● represents a chloride ion. It should be easy to spot that the central sodium ion has a coordination number of six in this cubic-close packed arrangement. If this is not apparent, then there is no substitute for holding a plastic model of the sodium chloride crystal lattice in your hand and looking at it more closely. The next three diagrams show the coordination number, geometry and shape by focussing on the central sodium ion of the unit cell. The blue lines show how the coordination number (CN) of six is arrived at for the central sodium ion. This coordination number gives rise to an octahedral geometry.
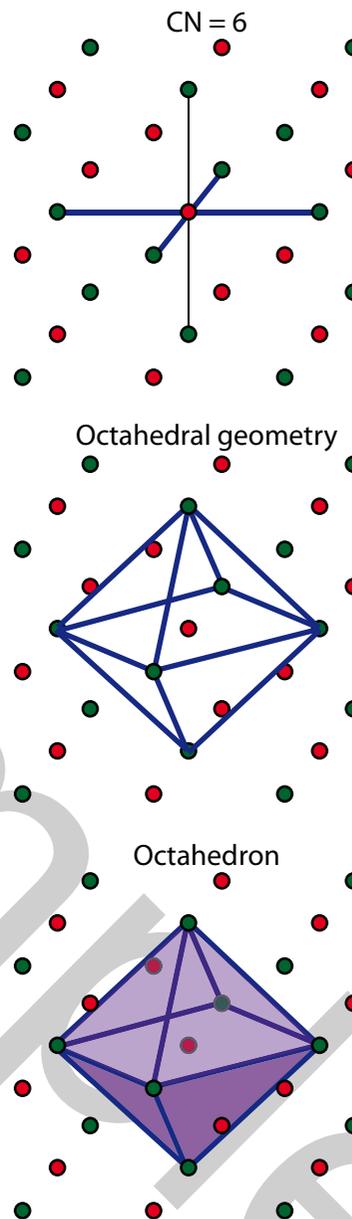
You can see that the six nearest neighbours of the sodium in the body centre of the unit cell are the chloride ions in the centre of the six faces of the cube. It is important to realise that the nearest neighbours of an ion can only be the counter ions of opposite charge. This is how the structure maximises the attractive ionic forces between ions of opposite charge. The coordination number of chloride is also six. This is less easy to observe in the unit cell drawing but, using the same arguments and making ● represent a chloride ion and ● represent a sodium ion would work.

Calcium fluoride

Calcium fluoride has twice as many fluoride ions as calcium ions because it has a 1:2 stoichiometry. The calcium ions are found in the corners and the centres of the faces of the unit cell whilst the fluoride ions occupy the tetrahedral sites.

By stitching together two unit cells, it is possible to see that calcium has a coordination number of eight. By looking at a calcium ion that is on the centre of a face, it is apparent that there are four fluoride ions above the edge of the unit cell and four fluoride ions below the edge of the unit cell.
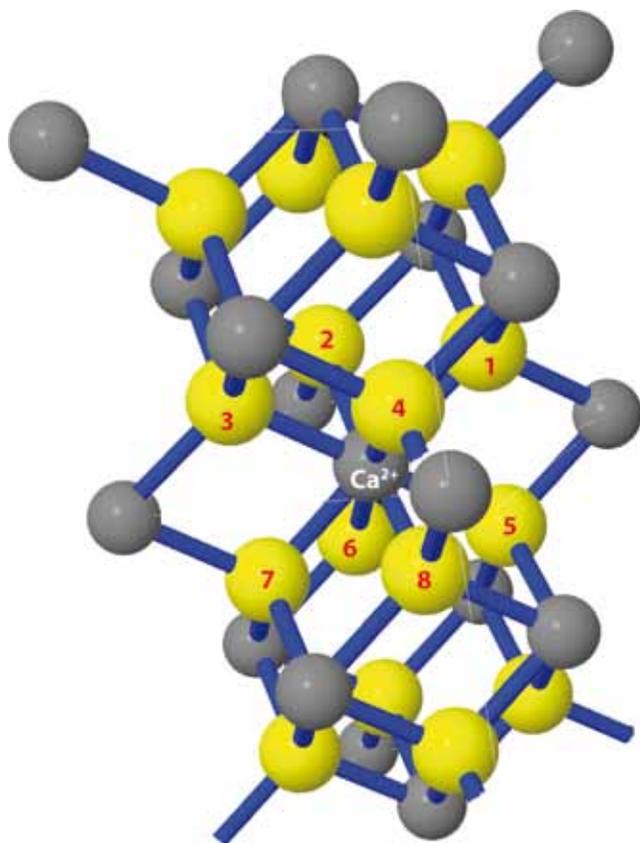

Diagram to show that calcium has a CN = 8 in CaF_2

It is a little easier to look at a diagram of a calcium fluoride lattice and spot that each fluoride ion has a coordination number of four and therefore a tetrahedral geometry. A simplified diagram to show that the fluoride ions have tetrahedral geometry can be drawn by placing a calcium ion at four alternate corners of a cube and placing a fluoride ion at the centre of the cube. What is worth remembering here is that, for CaF_2, it is the ion with the smallest number in the formula that has the largest coordination number and, by inference, it is the ion with the largest number in the formula that has the smallest coordination number.

The coordination number for an ion depends on the relative sizes of the ions contained within the lattice. It is common sense to realise that a larger ion can accommodate more counter ions around it than a smaller ion. The coordination number has been found to relate to the ratio of the radii of the cations and anions. When the cation radius is divided by the anion radius, the number arrived at is called the **radius ratio**.

Ion	Ionic radius / nm
Na^+	0.102
Cl^-	0.180
Ca^{2+}	0.100
F^-	0.133

For sodium chloride:

the radius ratio $= \dfrac{0.102 \text{ nm}}{0.180 \text{ nm}} = 0.57$

and for calcium fluoride:

the radius ratio $= \dfrac{0.100 \text{ nm}}{0.133 \text{ nm}} = 0.75$

The larger radius ratio for calcium fluoride compared with sodium chloride offers an explanation as to why Ca^{2+} ions have a larger coordination number of eight compared with that for Na^+, which is six. It has been found that ionic substances with radius ratios between 0.41 and 0.73 and 1:1 stoichiometry tend to have the sodium chloride type structure.

Questions 12.4

1. What is the ratio of coordination numbers in NaCl and CaF_2 and how do they relate to their formulae?

2. Which option shows the correct coordination numbers for the cations in CaF_2 and NaCl?

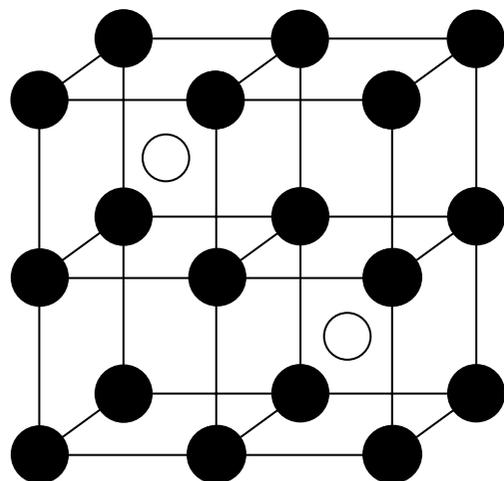|	Coordination number of Ca^{2+}	Coordination number of Na^+
A	6	8
B	8	6
C	6	4
D	4	6

3. Which option shows the correct coordination numbers for the anions in CaF_2 and NaCl?

	Coordination number of Cl^-	Coordination number of F^-
A	4	6
B	6	8
C	6	4
D	8	6

4. Label the diagram which shows one chloride ion in place for part of a sodium chloride crystal.
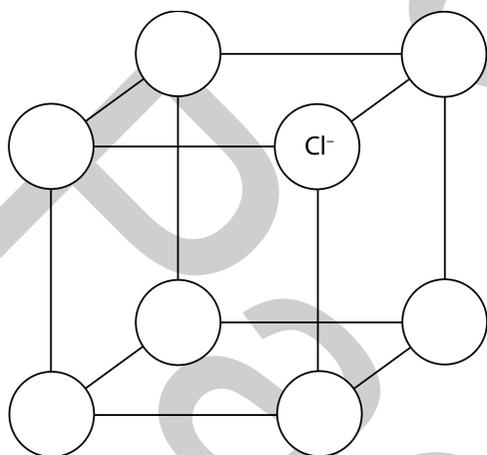
5. What information is obtained from the coordination numbers for the ions in fluorite?

6. A student drew a diagram to represent part of a lattice and later could not remember whether it was for NaCl or CaF_2. Describe their lattice and assign the ions in this lattice.

**7.** What affects the geometry in a crystal lattice?

8. Complete the following table by giving the coordination numbers of the ions in the crystals of sodium chloride and calcium fluoride, where C.N. = coordination number.

| Crystal	C.N. of Cation	C.N. of Anion
NaCl		
CaF_2		

B2.5 (d) Holes in close-packed structures

In close-packed structures, there are two types of hole (octahedral and tetrahedral) that counter ions can occupy within the three dimensional lattice. Ions occupying octahedral holes will have a coordination number of six. Ions occupying tetrahedral holes will have a coordination number of four. With a little experience, you should be able to locate and identify the different types of holes in close-packed structures. The diagrams show how a tetrahedral site fits into a cube and how an octahedral site cuts into eight different cubes. A particle set in a tetrahedral hole will have four nearest neighbours and a particle set in an octahedral hole will have six nearest neighbours.
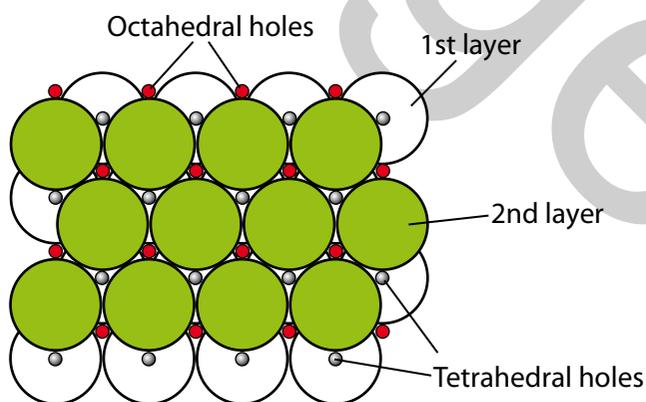
Tetrahedral site
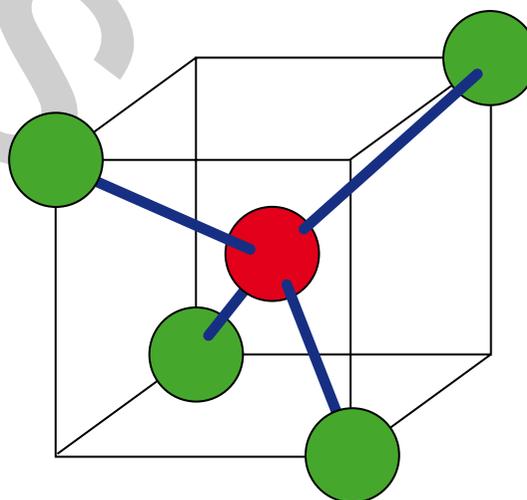
Part of an octahedral site
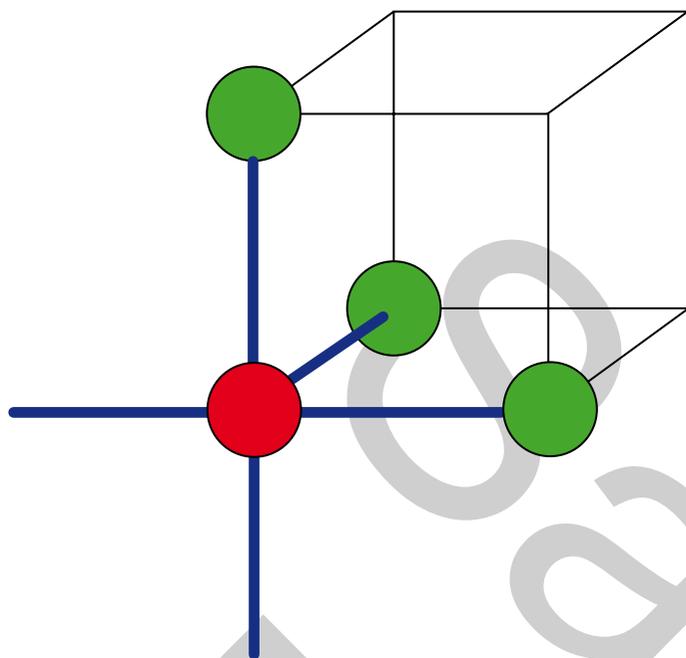
By examining crystal structures, it has been found that both structures have three times as many holes as atoms/ions. They each have one octahedral hole per atom, and two tetrahedral holes per atom. It has also been shown that octahedral holes are larger than tetrahedral holes. In close-packed structures, the 3rd layer of particles fit above the tetrahedral holes (⊘) in HCP crystals and above the octahedral holes (⊙) in CCP crystals. The tetrahedral holes are directly above the centre of the spheres in the first layer, which is why you get an ABAB arrangement with HCP crystals. The octahedral holes are above the hollows in the first layer, which is why you get an ABC arrangement with CCP crystals.

The position of octahedral and tetrahedral holes in the second layer of close packed spheres

Questions 12.5

1. Which option shows the correct ratio of holes to ions in close-packed structures?

	Ratio of holes : ions	
	CCP	HCP
A	1:3	3:1
B	1:1	2:1
C	1:1	1:2
D	2:1	1:1

2. Explain in words how you can distinguish between the two types of hole in a crystal lattice.

3. The diagram shows the arrangement of close-packed spheres. If a second layer of close-packed spheres rests directly on top of **B**, which holes will be tetrahedral and which octahedral in this second layer?
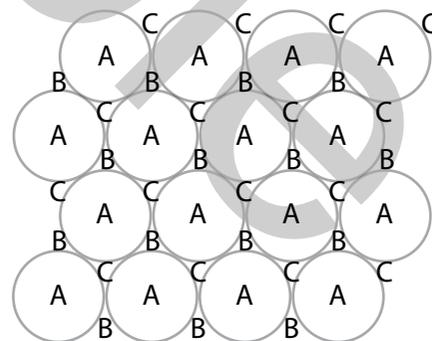
# B2.5 (e) Lattice structures of sodium chloride and calcium fluoride

In crystal lattices of compounds such as sodium chloride and calcium fluoride a cation is always surrounded by anions and an anion is always surrounded by cations. Oppositely charged ions are sometimes described as counter ions. The counter ion to an anion is a cation and the counter ion to an anion is a cation. How ionic substances are held together by electrostatic forces results from the arrangement of their constituent ions.

Another way to describe the lattice of sodium chloride is that it is two interlocking cubic-close packed lattices one of Na^+ ions and the other of Cl^- ions. The Na^+ ions rest in all the octahedral holes in the Cl^- lattice. The Cl^- ions rest in all the octahedral holes in the Na^+ lattice.

Another way to describe the lattice of calcium fluoride is that it consists of cubic close-packed Ca^{2+} ions with F^- ions in the tetrahedral holes in the Ca^{2+} lattice. The calcium ions are situated at alternate corners of a cube with the fluoride ion in its centre. The diagram has red lines joining the calcium ions to show how the fluoride ion is at the centre of a tetrahedron. The size of the fluoride ions keeps the calcium ions further apart than in CCP, but in the same geometric arrangement. There are twice as many tetrahedral holes as octahedral holes which also fits with the stoichiometry for CaF_2 and NaCl.
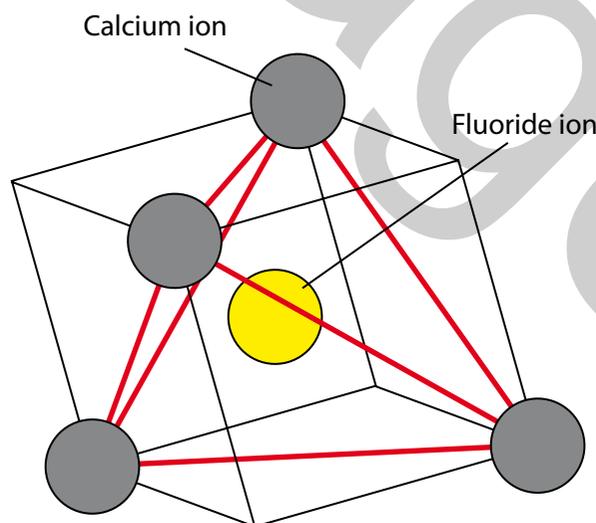
How to draw a tetrahedral fluoride ion in calcium fluoride

Questions 12.6

1. Complete the following table to show which factors are maximised and which factors are minimised when ions arrange themselves as a crystal grows in a saturated solution of a salt.

Property	Minimised	Maximized
Contact between oppositely charged ions		
Contact between ions of the same charge		
Repulsive forces		
Attractive forces		
Stability in terms of energy		
Lattice enthalpies		
Lattice entropies		

2. Complete the table for the two minerals: fluorite and halite.

Mineral	Formula	Crystal type	Position of six consecutive layers	Geometry of occupied holes
Fluorite				
Halite				

3. Why does the fluoride ion adopt its geometry in the fluorite lattice?

28

Infra-red Spectroscopy

Contents

Humans can detect only a small range of wavelengths in the visible spectrum (from 300 nm to 800 nm). The infra-red part of the electromagnetic spectrum is at longer wavelength than visible light. Infra-red spectroscopy is a particularly important technique routinely used by organic chemists to confirm the presence of functional groups. Infra-red spectroscopy is colloquially referred to as IR. It provides structural information about the presence or absence of particular functional groups as well as providing evidence for both intermolecular and intramolecular hydrogen bonding. It is a non-destructive method (unlike mass spectrometry A4.2) where the sample under investigation is exposed to infra-red radiation which causes bonds to vibrate (resonate) at particular frequencies.

Picture of Infra-red spectrometer (Warwick University, UK)

Samples prepared for infra-red spectroscopy can be prepared in several ways. They can be dissolved in solvents, *e.g.* chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), carbon disulfide (CS_2).

Alternatively, they can be made into a KBr disc or they can have a drop of the liquid hydrocarbon nujol added. Nujol has a characteristic C-H stretch at 2924 cm^{-1} and other identifiable and sharp troughs at 1603 cm^{-1}, 1028 cm^{-1} and 906 cm^{-1}.

Questions 28.1

1. Which option correctly shows the only information that is uniquely provided by infra-red spectroscopy?

    A   Relative molecular mass.

    B   Number of protons.

    C   Number of carbons.

    D   Functional groups.

2. Which of these spectroscopic techniques involves the absorption of the longest wavelength electromagnetic radiation?

    A   Infra-red spectroscopy.

    B   X-ray diffraction.

    C   X-ray crystallography.

    D   Ultra-violet spectroscopy.

3. Explain which of the following analytical techniques is the odd one out: infra-red spectroscopy, mass spectrometry, nmr spectroscopy and electronic spectroscopy.

A4.4 (a)
Resonant bond vibrations

Even at absolute zero (0K), atoms in molecules which are joined by covalent bonds are continually vibrating. This is because covalent bonds are not rigid and they can stretch and bend. To picture what is happening at the molecular level it can be quite useful to think of atoms as being like small spheres held together by springs which represent the bonds. Atoms and groups of atoms have increased vibrations called **resonant bond vibrations** when infra-red radiation is absorbed at certain frequencies in the electromagnetic spectrum. The frequency of the vibration depends on the nature of the bonding atoms. It has been shown that the greater the mass of the atoms the slower the vibration (A4.4b). Each type of bond

(hence functional group) vibrates at its own characteristic frequency. This is why infra-red spectroscopy is routinely used to give information about molecular structure and the presence of functional groups. The major types of molecular vibrations are **stretching** and **bending** and these are shown (in the following diagram) for carbon dioxide. Carbon atoms are black whilst oxygen atoms are red. Motion is shown as yellow coloured arrows adjacent to the oxygen atoms. When infra-red radiation is absorbed at certain frequencies the associated energy is converted into bending and stretching bond vibrations. The symmetric stretching of carbon dioxide is the only vibration that does not lead to a change in dipole moment and is therefore not detected in the infra-red spectrum.

Infra-red molecular vibrations of CO_2
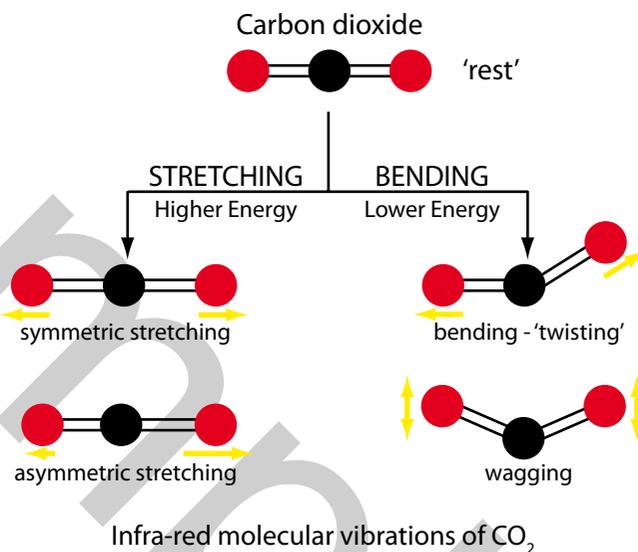
Not all vibrations of molecules will absorb infra-red radiation. It has been found that only modes of vibration that produce a net change in the dipole moment (A3.2a) of a molecule result in IR activity. Chlorine, nitrogen and hydrogen have no dipole so they will not absorb infra-red radiation. Carbon monoxide and hydrogen fluoride are gases with a dipole so these molecules do absorb infra-red radiation.

The source of the infra-red radiation is an electrically heated filament. In infra-red spectroscopy a compound is exposed to infra-red radiation from 400 cm^{-1} to 4000 cm^{-1}. The units of frequency have historically been given as **wavenumber** (cm^{-1}) which is the reciprocal of the infra-red radiation wavelength in centimetres (cm). Modern infra-red spectra are obtained using **Fourier Transform Infra-red (FTIR) spectrometers**. An infra-red beam is shone through the sample under investigation and this is compared with an infra-red reference beam. All the wavelengths that correspond to frequencies in the range 400 cm^{-1} to 4000 cm^{-1} are shone through the sample. The infra-red spectrum (A4.4c) is produced by a computer after analysis of the differences between the two beams.

Fixed Mirror

Half-silvered mirror

Moveable Mirror

Coherent light source

Sample

Detector
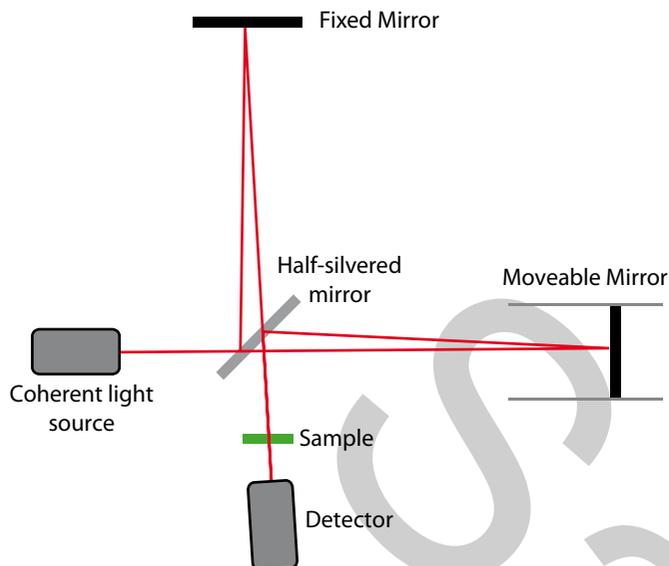
Schematic diagram of a Fourier Transform Infra-red (FTIR) spectrometer

Questions 28.2

1. Will sulfur dioxide absorb infra-red radiation when its bonds stretch and/or bend?

2. Which option best describes infra-red spectroscopy?

	Process	Principle
A	non-destructive	bond fission
B	destructive	bond vibrations
C	non-destructive	bond vibrations
D	destructive	bond fission

3. Which of the following options cannot be considered an absorption spectroscopy?

   A Mass spectrometry.

   B Nuclear magnetic resonance spectroscopy.

   C Infra-red spectroscopy.

   D Ultra-violet spectroscopy.

4. Which region of the electromagnetic spectrum corresponds to the energy of most molecular vibrations?

   A Radiowaves

   B Ultra-violet

   C Visible

   D Infra-red

5. Complete the table by placing a tick (√) in each box where infra-red radiation is absorbed by the named vibration.

Carbon dioxide	Vibration	IR absorbed?
CO_2	asymmetrical stretching	
CO_2	bending	
CO_2	symmetrical stretching	

A4.4 (b)
Stretching frequencies (bond strength and atomic masses)

The energy involved in any bond vibration depends on variables such as bond length, bond strength and the mass of the atoms at either end of the bond. This means that each different bond will vibrate in a different way, involving different amounts of energy. The IR stretching frequency increases in the order: single bonds (except those to hydrogen), double bonds, triple bonds, single bonds to hydrogen. Stronger bonds need more energy to make them vibrate, so consequently they absorb a higher frequency of infra-red radiation (higher wavenumber).

Infra-red spectrum

In an infra-red spectrum such as the one shown for ethanal (CH_3CHO), **transmittance** (%) or **absorbance** (%) is on the *y*-axis and the frequency expressed as wavenumber (cm^{-1}) is on the *x-axis*. The horizontal scale reads from right to left like chemical shift in nmr (A4.5). An individual absorption in an infra-red spectrum will be referred to as a trough (coloured blue to make it easier to spot on first meeting) which rather confusingly in many textbooks is still referred to as a 'peak'. When the transmittance is over 90%, little or no energy is absorbed at this frequency. Troughs in the graph show where energy is absorbed. In the specific case of ethanal there is a very large trough (dip in the graph) at about 1720 cm^{-1}. It is important to realise that the scale on the *x*-axis is not linear and the change in scale occurs at 2000 cm^{-1}. This means that there is more detail in this lower frequency region.
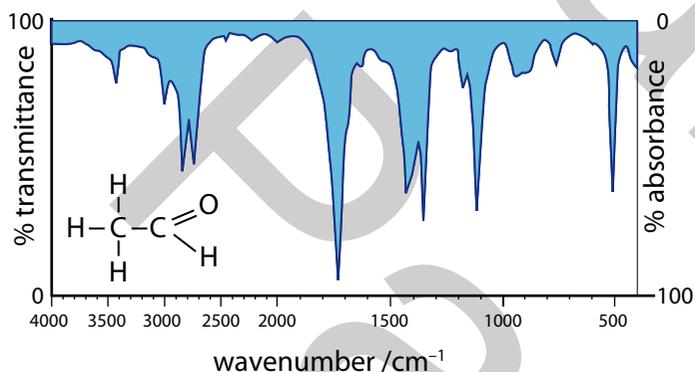

IR spectrum of ethanal (CH₃CHO)

An infra-red spectrum can be sub-divided into two regions; the band region 1500-4000 cm^{-1} where functional groups are found and the **'fingerprint region'** where the frequency is less than 1500 cm^{-1}. The fingerprint region is to the right-hand side of an IR spectrum (from about 1500 cm^{-1} to 400 cm^{-1}). It usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. The importance of the fingerprint region is that each compound produces a different pattern of troughs in this part of the spectrum.

Fingerprints are sometimes used by airlines to identify passengers before boarding

A detailed look at the infra-red spectrum of ethanal shows a C-H stretch at 2900 cm^{-1} and a strong C=O (carbonyl) stretch at 1720 cm^{-1}. These troughs, shaded green, in the fingerprint region, are characteristic of ethanal.
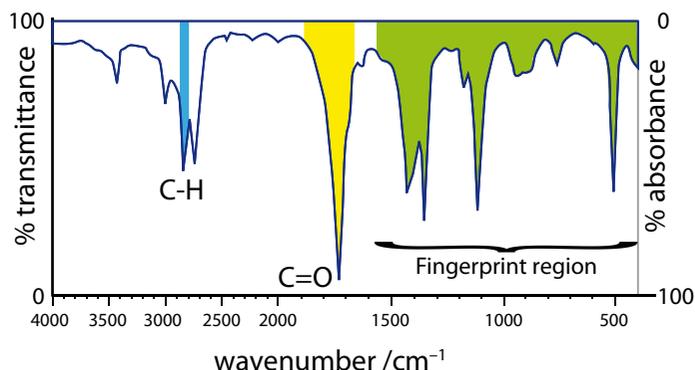
In an infra-red spectrum there are four regions to look at in turn:

- 1000 cm^{-1} to 1500 cm^{-1} (single bonds; C-O, C-Cl),

- 1500 cm^{-1} to 2000 cm^{-1} (double bonds; C=O, C=C),

- 2000 cm^{-1} to 3000 cm^{-1} (triple bonds; C≡N, C≡C), and

- 3000 cm^{-1} to 4000 cm^{-1} (single bonds to hydrogen; C-H, N-H & O-H).

As the frequency increases (cm^{-1}) so does the energy being supplied to vibrate the bonds since both quantities are proportional according to the equation $E = hf$ (A4.3b) which is equation 9 in the data booklet. As the bond order (A1.2f) increases, so does the frequency at which resonant vibrations occur because multiple bonds are 'stiffer' than single bonds. Shorter, and therefore stronger, bonds vibrate faster. The relationship between the frequency of the bond vibration, atomic mass and bond enthalpy (A1.3d) is similar to **Hooke's Law** for a simple harmonic oscillator. Without going into the details, frequency is proportional to the square root of bond strength and inversely proportional to the square root of the atomic mass.

Table to show characteristic absorbance frequencies for covalent bonds

Bond	Type	Functional group	Frequency / cm^{-1}
C-O	single	Alcohol /ether	1000-1300
C=O	double	Aldehydes / ketones / carboxylic acids / esters	1680-1750

Bond	Type	Functional group	Frequency / cm⁻¹
C≡N	triple	nitrile	2220-2260
C-H	single	alkane	2850-2960
=C-H	single	alkene	3075-3095
≡C-H	single	alkyne	2100-2260
O-H	single	carboxylic acids*	2500-3300
N-H	single	amine	3300-3500
O-H	single	alcohols* / phenols*	3590-3650

broad troughs due to hydrogen bonding.

It is possible to use infra-red spectroscopy to distinguish between intermolecular hydrogen bonding (A1.2k) and intramolecular hydrogen bonding. This is because, at increased concentrations, troughs for intermolecular hydrogen bonds increase in intensity but those troughs arising from intramolecular hydrogen bonds do not increase.

The greater the mass (A_r) of the atoms in a covalent bond the slower will be the vibration. Comparison of the frequencies for a carbon covalently bonded to hydrogen and deuterium illustrates this idea. The C-H stretch is at 3000 cm⁻¹ compared with the C-D stretch which occurs at 2200 cm⁻¹. The heavier deuterium isotope (^{2}H) resonates at a lower frequency than the much lighter ^{1}H isotope.

Questions 28.3

1. Which option gives the correct order of frequency of vibration in ascending order for the H-Cl bond and the two most abundant isotopes for hydrogen and carbon?

   A ^{1}H-^{35}Cl < ^{2}H-^{35}Cl < ^{1}H-^{37}Cl < ^{2}H-^{37}Cl

   B ^{1}H-^{35}Cl > ^{2}H-^{35}Cl > ^{1}H-^{37}Cl > ^{2}H-^{37}Cl

   C ^{2}H-^{37}Cl > ^{1}H-^{37}Cl > ^{2}H-^{35}Cl > ^{1}H-^{35}Cl

   D ^{1}H-^{35}Cl > ^{1}H-^{37}Cl > ^{2}H-^{35}Cl > ^{2}H-^{37}Cl

2. What is an infra-red spectrum?

3. What is wavenumber and what is its unit?

4. Calculate the frequency in cm⁻¹ for infra-red light of wavelengths; i) 15×10^{-6} m, ii) 26×10^{-6} m.

5. Calculate the wavelengths of electromagnetic radiation having wavenumbers;

   i)   1020 cm⁻¹

   ii)   1748 cm⁻¹

   iii)   2300 cm⁻¹

   iv)   3420 cm⁻¹

   and suggest which bonds might resonate at these frequencies.

6. What is the relationship between bond order and infra-red frequency for carbon-oxygen bonds?

   C≡O (2143 cm⁻¹), C=O (1715 cm⁻¹) & C-O (1100 cm⁻¹).

A4.4 (c) Stretching frequencies (bonds to H)

As infra-red frequency data are not given in exams, it is important to be able to recall the approximate stretching frequencies observed in IR spectra. The more infra-red spectra you assign, the easier it will become to recognise the frequencies characteristic of particular functional groups.

Order	bonds to H	triple bonds	double bonds	single bonds (except to H)
Frequencies / cm⁻¹	3700-2500	2300-1900	1900-1500	< 1500
Examples	O-H N-H C-H	C≡C C≡N	C=C C=O	C-O C-N

The order in terms of decreasing frequency is: bonds to H, triple bonds, double bonds, single bonds (except to H). Learning this pattern will make assigning infra-red spectra more straightforward.

In addition to considering the mass of atoms, one also needs to consider the strength of bonds. The three adjacent Period 2 elements in Groups 14-16 have similar masses, *i.e.* ^{12}C, ^{14}N & ^{16}O. A look at their frequencies of vibration when joined by a single covalent bond to a hydrogen atom shows how the bond enthalpy is the deciding factor on infra-red frequency of vibration. The relationship is 'the stronger the bond the higher the frequency'.
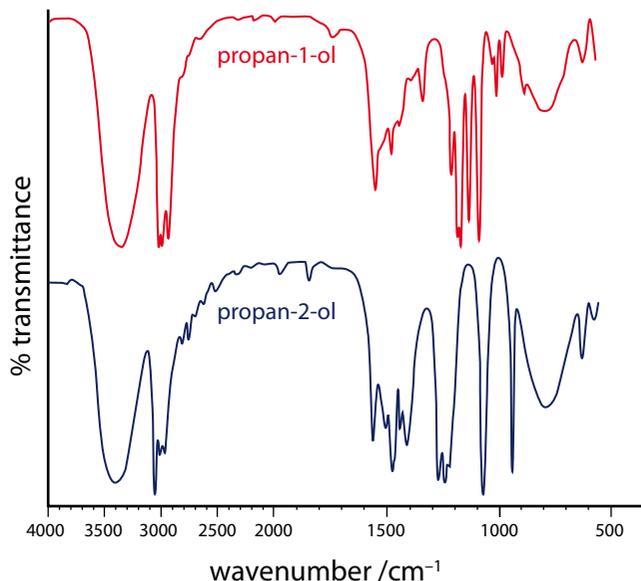
Substance	Bond	Bond enthalpy / kJ mol^{-1}	IR frequency / cm^{-1}
methane	C-H	440	2900-3200
ammonia	N-H	450	3300-3400
water	O-H	464	3500-3600

Interestingly the aromatic amine, aniline ($C_6H_5NH_2$) has two NH stretches, a symmetric N-H stretch (lower frequency) and an asymmetric N-H stretch (higher frequency).
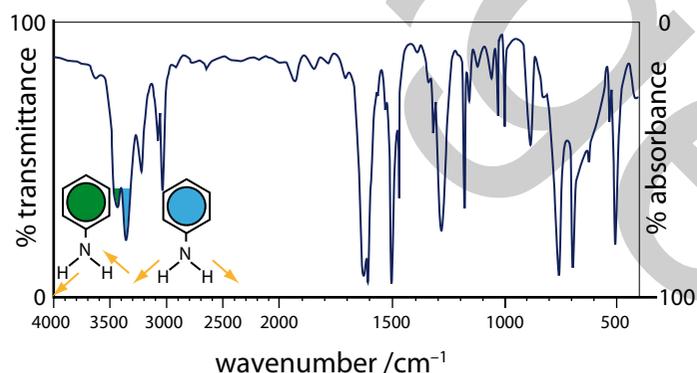
The infra-red spectrum of aniline ($C_6H_5NH_2$)

The three important bonds in ethanol are seen in its infra-red spectrum:

- 3200-3500 cm^{-1} broad trough for hydrogen bonded O-H

- sharp trough at ~3000 cm^{-1} for C-H

- and at 1030 cm^{-1} there is a large trough (low % transmittance) which is the C-O stretching vibration.

O-H is at higher frequency than C-H as the bond is more polarised and therefore stronger and more resistant to vibration.
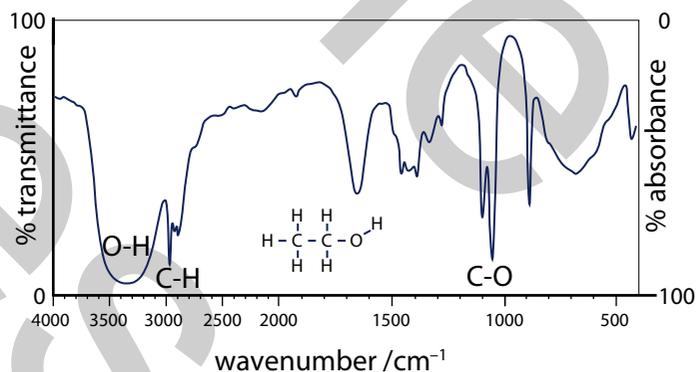

The infra-red spectrum of ethanol

The importance of differences in the fingerprint region of an infra-red spectrum is highlighted by comparing the infra-red spectra of the structural isomers propan-2-ol and propan-1-ol. Both isomers have the characteristically broad and strong trough at ~3500 cm^{-1} for their hydrogen bonded alcohol functional group (O-H).

Question 28.4

1. Which option gives the usual range for an infra-red spectrum?

    A   625 cm^{-1} to 4000 cm^{-1}

    B   400 cm^{-1} to 625 cm^{-1}

    C   625 nm to 4000 nm

    D   625 nm to 400 nm

A4.4 (d)
Interpreting simple spectra (alcohols & carboxylic acids)

If tables of data are not provided in your chemistry examinations, it becomes really important to have a handle on the figures for the main groups and to go through a series of logical steps in order to 'solve' infra-red spectra successfully. Other analytical data will usually be available to help solve structures. It should be remembered that as an analytical technique it is only an infra-red spectrum which will always positively identify the functional group. One method for interpreting an infra-red spectrum is a logical stepwise approach which involves asking a series of key questions.

Step 1:

Is there a strong carbonyl (C=O) absorbance at around 1700 cm^{-1}? If YES go to STEP 2 if NO go to STEP 3.

Step 2:

It could be **aldehyde, ketone, carboxylic acid** or an **ester.** Identifying the presence of the other bonds present will confirm the identity of the FG

| wavenumber / cm^{-1}	C=O	O-H	C-O	C-H
Carboxylic acid	~1700-1725	~2500-3300	~1100-1300	
Ester	~1715-1750		~1050-1300	
Aldehyde	~1720-1740			~2750 & 2850
ketone	~1705-1720			

Step 3:

Is there a broad OH band ~3300-3600 cm^{-1} and C-O band ~1000-1300 cm^{-1}? If YES it is an **alcohol** if NO go to STEP 4.

Step 4:

If there is a weak absorbance at 1650 cm^{-1} it is due to C=C of an **alkene**. If there are strong absorptions at 1450-1650 cm^{-1} it is **aromatic**. If there is a C-H stretch ~3000 cm^{-1} and a band near 1450cm^{-1} it is an **alkane**. If it is a simple spectrum with an absorption <667 cm^{-1} it might be a **halogenoalkane**.

Example 28.1 (Phenol)
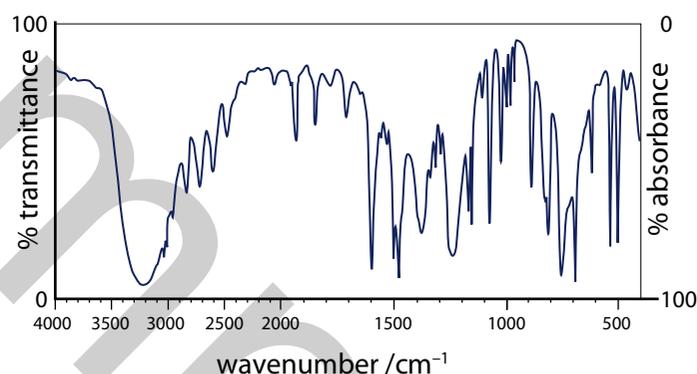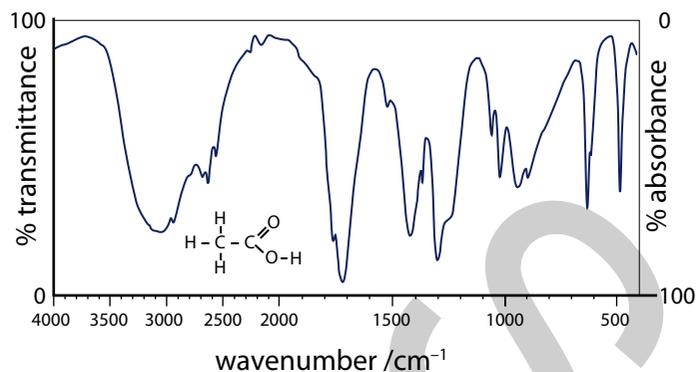

The infra-red spectrum of phenol (C_6H_5OH)

There is a broad trough at 3250 cm^{-1} corresponding to the O-H stretch.

There is a sharp moderate sized trough at 2750 cm^{-1} corresponding to a C-H stretch.

There are three strong absorptions at 1470, 1500 & 1600 cm^{-1} showing it is aromatic.

The C-O stretch is ~1050 cm^{-1}.

Example 28.2 (Ethanoic acid)

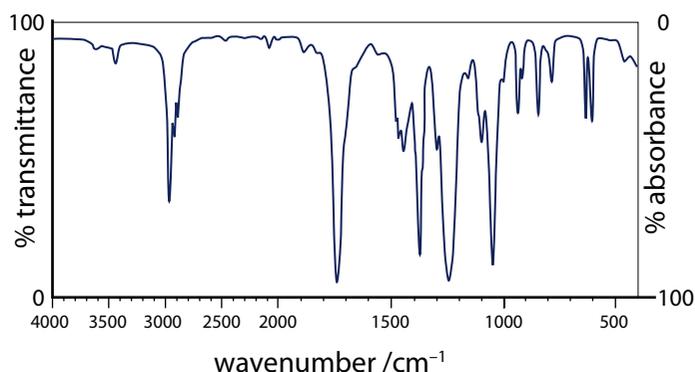The infra-red spectrum of ethanoic acid

There is a very broad trough from 2500 cm^{-1} to 3300 cm^{-1} corresponding to the O-H stretch.

There is a moderate sized trough at 2700 cm^{-1} corresponding to a C-H stretch.

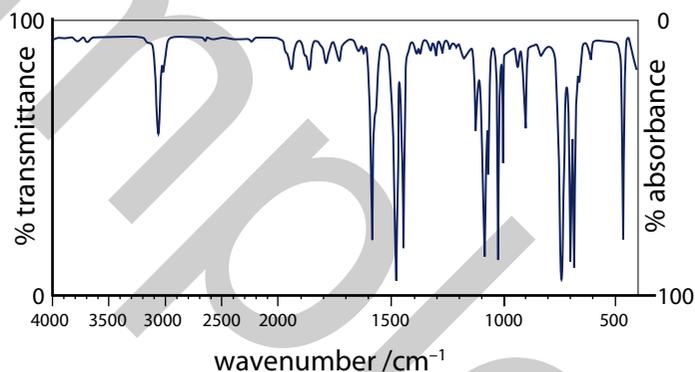There is a strong absorption at 1710 cm^{-1} showing it contains a carbonyl C=O group.

The C-O stretch is the one at ~1300 cm^{-1}.

Questions 28.5

1. Identify the major absorbances in the infra-red spectrum of benzaldeyde.

The infra-red spectrum of benzaldeyde (C$_6$H$_5$CHO)

2. Identify the major absorbances in the infra-red spectrum of ethyl ethanoate.

The infra-red spectrum of ethyl ethanoate

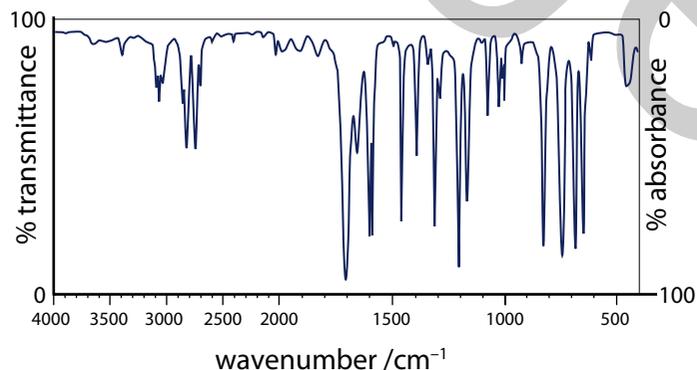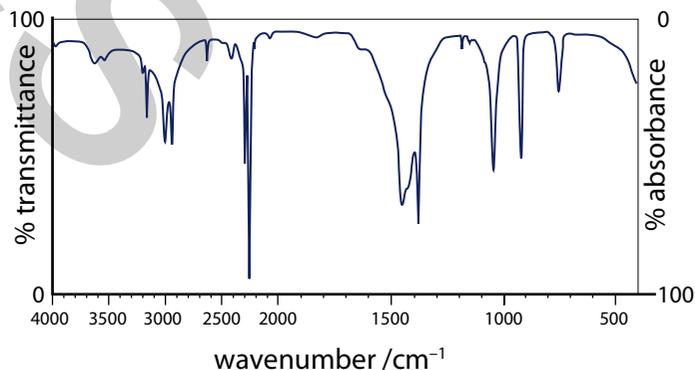3. Identify the major absorbances in the infra-red spectrum of chlorobenzene.

The infra-red spectrum of chlorobenzene

4. Identify the major absorbances in the infra-red spectrum of acetonitrile (ethanenitrile).

The infra-red spectrum of acetonitrile

5. What is the wavenumber for a trough in an infra-red spectrum for a frequency that absorbs at 2.3×10^{13} Hz? [where $c = 3.00 \times 10^8$ m s^{-1}]

6. Use the table of data to help explain the different IR absorptions for three hydrogen halides.

Hydrogen halide	Bond enthalpy / kJ mol^{-1}	Infra-red absorption / cm^{-1}
HCl	432	2886
HBr	366	2559
HI	298	2230

7. From the infra-red spectrum of propanone what structural information can be determined?
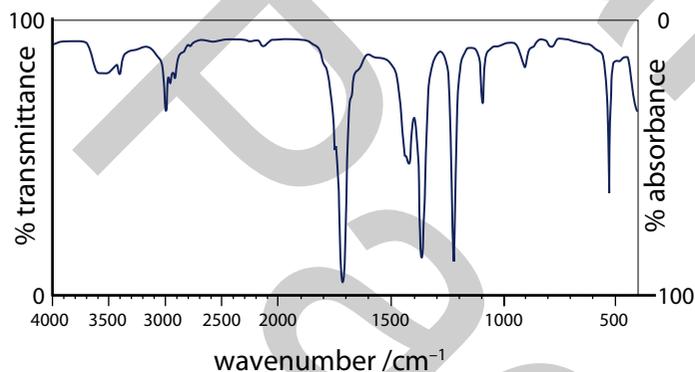
8. Explain why two different carboxylic acid derivatives have quite different infra-red stretching of their carbonyls (C=O). For example acid chlorides (1815 cm^{-1}) and esters (1745 cm^{-1}).

9. Which of the following statements about absorption in infra-red spectra is **false**?

A Large dipole moments give stronger absorptions than small dipoles.

B Strong bonds absorb at higher frequencies than weaker bonds.

C Hydrogen bonding always moves troughs to higher frequencies.

D Bonds joining light atoms absorb at high frequency than bonds joining heavier atoms.

10. Which option gives the correct relationships between the effect of the relative mass of atoms and their bond strengths on frequencies of infra-red vibrations?

	Low frequency	High frequency
A	Lighter atoms	Stronger bonds
B	Heavier atoms	Stronger bonds
C	Lighter atoms	Weaker bonds
D	Heavier atoms	Weaker bonds

11. Which option gives the correct order for descending wavenumber (cm^{-1}) for infra-red absorptions?

A N-H > C≡N > C-H > C=O

B C-H > C=O > C≡C > C-O

C N-H > C≡N > C-O > C=O

D O-H > C≡C > C=O > C-O

12. Calculate the stretching frequency of the C-H bond in wavenumbers which is 9.3×10^{13} Hz.

Additional uses of infra-red spectroscopy

Levels of atmospheric pollutants such as nitrogen dioxide (NO_2) formed in car engines can be detected by infra-red spectroscopy. The brewing industry uses infra-red spectroscopy to determine the alcohol content at various stages of the brewing process. The police use roadside infra-red spectrometers (intoximeters - pictured) to determine the concentration of alcohol in a breath which is proportional to the blood alcohol concentration.

Customs and excise can quickly identify smuggled drugs from the infra-red spectra by comparison with known samples held in databases.