Unit 4  Bonding and Structure

Section 4.1  The Nature of Forces holding Atoms together

Electrostatic interactions between electrons and nuclei

1. Metallic bonding
A metallic bond is the electrostatic attraction between neighbouring metal cations and the mobile valence electrons between them.

2. Covalent bonding
A covalent bond is the electrostatic attraction between two nuclei and the shared electrons between them.

3. Ionic bonding
An ionic bond is the electrostatic attraction between two oppositely charged ions formed as a result of electron transfer.

Section 4.2  Metallic Bonding
(1) Formation of metallic bonding

The most comprehensive definition of a metallic element is one which readily forms positive ions.

Metallic elements have the following general characteristics:

1. Metallic elements form positive ions readily. They have lower ionization enthalpies than non-metallic elements.

2. Metallic elements have vacant valence orbitals to allow delocalization of valence electrons. This results in the good electrical conductivity of metallic elements.

3. Metallic elements tend to adopt close-packed structures which minimize the amount of empty space between the atoms. In general, they have higher densities than non-metallic elements.

A metallic bonding is the electrostatic attraction between a lattice of positive metal ions and their mobile (delocalized) valence electrons. Metallic bonding thus represents the extreme case of undirected bonding.

Example:
In magnesium, each atom contributes its two 3s valence electrons to the overlapped vacant valence orbitals. The mobile valence electrons are said to be delocalized. They are free to move within the cationic lattice and provide the electrostatic attraction which binds each Mg$^{2+}$ ion to its twelve close neighbours.

(2) Strength of metallic bond
The strength of metallic bonds increases as
1. the number of valence electron(s) per atom increases,
2. the metallic radii decrease.

Example 1: Melting points of metals

The melting point of a metal is a measure of the strength of the metallic bonding that holds the atoms in a cationic lattice structure. This strength will depend largely on the number of valence electrons that each atom contributes to the delocalized ‘electron sea’.

Group I metals, which contribute one valence electron per atom, have relatively low melting points, while the melting points of Group II metals, which contribute two valence electrons per atom, are rather higher. The melting points of the metals in the first transition series are higher still, since the 3d electrons make a contribution to the bonding. The unusually low melting point of Mg is due to its distorted structure.

Example 2: Large difference between enthalpies of fusion and vaporization

When a metal melts there is only a small increase in its volume and the delocalized bonding that existed in the solid is not totally destroyed. When the metal boils, however, there is complete breakdown of the structure and the enthalpy of vaporization is much higher than the enthalpy of fusion.

<table>
<thead>
<tr>
<th>Element</th>
<th>Molar enthalpy change of fusion / kJ mol(^{-1})</th>
<th>Molar enthalpy change of vaporization / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.60</td>
<td>89.0</td>
</tr>
<tr>
<td>K</td>
<td>2.30</td>
<td>77.5</td>
</tr>
<tr>
<td>Mg</td>
<td>8.95</td>
<td>128.7</td>
</tr>
<tr>
<td>Ca</td>
<td>8.66</td>
<td>149.8</td>
</tr>
<tr>
<td>Fe</td>
<td>15.36</td>
<td>351.0</td>
</tr>
<tr>
<td>Cu</td>
<td>13.05</td>
<td>304.6</td>
</tr>
</tbody>
</table>

(3) Metallic crystals
Unit 4 - 4

In the metal crystal structure, unit cells are the smallest identical block of metal atoms which can be stacked together to fill space completely and to reproduce the whole regular arrangement.

The coordination number of a metal atom is the number of nearest equidistant atoms

1. Close-packed structures: Hexagonal and Cubic close-packed structures

The way in which the structures are built up can be investigated by considering the stacking of spheres together. Imagine a layer A of identical spheres packed together on a flat surface. Each sphere is in contact with six others (see figure a). There are spaces or holes between the spheres. Each sphere in layer B will rest in a depression between three spheres in layer A. The holes in layer B are of two kinds (see figure b). Tetrahedral holes in layer B lie over spheres in layer A, and octahedral holes in layer B lie over holes in layer A.

![Diagram of close-packed structures](image)

There are two ways in which a third layer can be laid on layer B.

The spheres of the third layer can cover the tetrahedral holes; in this case the third layer is identical with layer A. This type of structure is made up of alternating layers ABABA and is described as hexagonal close-packed (see figure c). Since every atom is contact with 12 others, it is said to have a coordination number of 12.

Alternatively, the sphere in layer C can cover the octahedral holes in layer B, so that layer C is not identical with layer A. When a fourth layer of spheres is laid on layer C, it is identical with A. This type of structure, with the sequence ABCABC, is a cubic close-packed (see figure d). The coordination number is also 12.

Unit cells of close-packed structures are shown below:
X-ray studies reveal that the metal atoms occupy 74% of the space in the hexagonal and the cubic close-packed structures.

Question: How many atoms are there in a unit cell of the close-packed structures?

<table>
<thead>
<tr>
<th>Close-packed structure</th>
<th>Hexagonal</th>
<th>Face-centred-cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of atoms in a unit cell</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Open structure: Body-centred cubic structure
The less closely packed **body-centred-cubic structure** is shown in figure a. With one atom at each of the eight corners of a cube and one in the centre touching these eight, the **coordination number** is 8.

Figure b shows an expanded view, and figure c shows the unit cell with tie-lines to show that the coordination number is 8.

X-ray studies reveal that the metal atoms occupy 68% of the total volume in the body-centred cubic structure.

**Example 1**

The figure below shows a unit cell of sodium metal. This has a body-centred-cubic structure. X-ray diffraction measurements show that the length of the unit cell is 0.429 nm.

Given that: density of Na = 0.97 g cm\(^{-3}\) and relative atomic mass of Na = 22.99, calculate the Avogadro’s constant.
Figure I above represents an ‘expanded’ view of a model of three layers of spheres on top of one another. Layer a is in contact with layer b, and layer b is in contact with layer c.

If a fourth layer is placed on layer c so that the centres of the spheres are directly above the centres of the spheres in the first layer and the model is repeated, the sequence of the layers become abcabc…….

(i) What type of packing does this model represent ?

(ii) If the sequence is changed to abab……., what type of packing would the model represent ?

(iii) What is the coordination number in both (i) and (ii) ?

A unit cell for the abcabc…… arrangement is shown in Figure II.

(iv) How many equivalent complete spheres can be considered to belong to the unit cell ?

(v) Copper has the abcabc….. arrangement and therefore each sphere in Figure II may be thought of as a Cu atom. The Cu atoms are seen to be in contact with one another along the diagonal of a face of the unit cell.

Given that : density of Cu = 8.90 g cm⁻³,
relative atomic mass of Cu = 63.5 and
Avogadro’s constant = 6.02 x 10²³ mol⁻¹,
calculate the length of one side of the cubic unit cell.

(4) Alloys

1. Properties of alloys as compared with their constituents
An alloy is a combination, either in solution or compound, of two or more elements, at least one of which is a metal, and where the resultant material has metallic properties different from those of its constituents.

Metals will readily form alloys since the metallic bond is non-specific. The presence of small quantities of a second element in the metal frequently increases its strength. Atoms of the second metal are different in size to those of the original metal. These differently sized atoms interrupt the orderly arrangement of atoms in the lattice and prevent them sliding over each other.

Alloys are usually designed to have properties that are more desirable than those of their components. For instance, steel is stronger than iron, one of its main elements, and brass is more durable than copper, but more attractive than zinc.

2. Properties and uses of some alloys

Steel is a metal alloy whose major component is iron, with carbon being the primary alloying material. Carbon acts as a hardening agent, preventing iron atoms, which are naturally arranged in a lattice, from sliding past one another. Varying the amount of carbon and its distribution in the alloy controls the qualities of the resulting steel. Steel with increased carbon content can be made harder and stronger than iron, but is also more brittle. One classical definition is that steels are iron-carbon alloys with up to 5.1 percent carbon; ironically, alloys with higher carbon content than this are known as cast iron.

Stainless steel is defined as a ferrous alloy with a minimum of 10.5% chromium content. The name originates from the fact that stainless steel stains, or rusts, less easily than ordinary steel. Stainless steel has higher resistance to oxidation (rust) and corrosion in several environments. High oxidation resistance in air is normally achieved with additions of more than 12% (by weight) chromium. The chromium forms a layer of chromium (III) oxide (Cr$_2$O$_3$) when exposed to oxygen. The layer is too thin to be visible, meaning the metal stays shiny. It is, however, impervious to water and air, protecting the metal beneath. Also, when the surface is scratched this layer quickly reforms.

Duralumin is an alloy of aluminium (about 95%), copper (about 4%), and small amounts of magnesium (0.5%–1%) and manganese (less than 1%). It is considerably stronger than elemental aluminium, and more resistant to corrosion. This alloy also adds considerable tensile strength to normal aluminium, which otherwise "rips" quite easily. With this new rip-resistant mixture, duralumin quickly spread throughout the aircraft industry in the early 1930s, where it was well suited to the new monocoque construction techniques that were being introduced at the same time. Duralumin also is popular for use in precision tools such as levels because of its light weight and strength.

Brass is an alloy of copper and zinc. Brass is a versatile manufacturing material because of its hardness and workability. Some types of brass have other metals added to modify their properties. Brass has a yellow colour, somewhat similar to gold. Because of this, and its relative resistance to tarnishing it is used as a decoration. The malleability and acoustic properties of brass have made it the metal of choice for musical instruments such as the trumpet. Instruments where the sound is produced by the vibration of the musician's lips are collectively known as brass instruments.

Bronze is the traditional name for a broad range of alloys of copper. It is usually copper with zinc and tin but it is not limited to those metals. First used during the Bronze Age, to which it gave its name, bronze made tools, weapons and armor that were either harder or more durable than their stone and copper predecessors. Bronzes are softer and weaker than steel, and more elastic. Bronzes resist corrosion (especially seawater corrosion) and metal fatigue better than steel. Bronzes also conduct heat and electricity better than most steels.

Section 4.3 Ionic Bonding

(1) Formation of ionic bonding
Ionic bonding occurs when one type of atom gives one or more electrons to another type of atom. This produces positively and negatively charged atoms called ions, and the electrostatic attraction between the ions is responsible for the bonding.

Ions are formed as a result of the transfer of one or more electrons from the valence shell of an atom of a metal to the valence shell of an atom of a non-metal.

Ions often, but not always, possess noble gas electronic configurations. The lack of chemical reactivity of the noble gases is an indication of the great stability of their electronic structure; and ions with such electronic structure.

Compounds that are composed of ions are described as ionic compound (electrovalent compound). They are usually crystalline solids of high melting temperature, in which appositively charged ions are held together by electrostatic attraction. Lattice enthalpy is a measure of the strength of this attractive force.

**Lewis structure - ‘Dot and Cross’ diagram** can be used to show the transfer of electrons from one atom to another gives ions. It should be remember when writing ‘Dot and Cross’ diagrams that the dot and cross are a means of counting electrons, and show the number present; they do not show the positions of the electrons. The electrons are distributed in space as diffuse negative charged clouds.

Example 1 : Formation of lithium oxide

Example 2 : Formation of magnesium chloride

(2) **Formation of positive ions from Group I and Group II elements**

Group I and Group II elements tend to form positive ions (cations) by losing electrons to attain electronic configurations of noble gases. The ease with which an atom loses an electron to form a positive ion is measure by its ionization enthalpy.
Group I elements (The alkali metals)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>First Ionization enthalpy / kJ mol$^{-1}$</th>
<th>Electronic configuration of M$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td></td>
<td>520</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td></td>
<td>496</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td></td>
<td>419</td>
<td></td>
</tr>
<tr>
<td>Rubidium</td>
<td></td>
<td>403</td>
<td></td>
</tr>
<tr>
<td>Caesium</td>
<td></td>
<td>376</td>
<td></td>
</tr>
</tbody>
</table>

The first ionization enthalpy of an alkali metal atom is lower than for any other atom in the same period. The ions which is formed also has the stable noble gas electronic structure. This indicates that the alkali metals form ions easily. They are the most reactive metals and powerful reducing agents.

Dipositive alkali metal ions are not formed. This is because of the very high second ionization enthalpy required and the dipositive ions produced does not have the stable noble gas electronic structure.

Group II elements (The alkaline earth metals)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>First / Second Ionization enthalpy / kJ mol$^{-1}$</th>
<th>Electronic configuration of M$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td></td>
<td>899 / 1757</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td></td>
<td>738 / 1451</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td></td>
<td>590 / 1145</td>
<td></td>
</tr>
<tr>
<td>Strontium</td>
<td></td>
<td>549 / 1064</td>
<td></td>
</tr>
<tr>
<td>Barium</td>
<td></td>
<td>502 / 965</td>
<td></td>
</tr>
</tbody>
</table>

The second ionization enthalpy is much greater than the first ionization enthalpy. This indicates that the removal of the second electron is more difficult than the removal of the first, since it is being pulled away from positively charged ion. This considerable expenditure of energy only be justified if the subsequent bonding in the ionic compound causes an even greater release of energy. The ions formed from alkaline earth metals are dipositive ions which possess stable noble gas electronic structure.

Examples: There are many common cations which do not have noble gas electronic configuration. Write the electronic configurations of the following cations:

$$\text{Cu}^+, \text{Cu}^{2+}, \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Zn}^{2+}$$

(3) Formation of negative ions from Group VI and Group VII elements

Group VI and Group VII elements tend to form negative ions (anions) by gaining electrons to attain electronic configurations of noble gases. The ease with which an atom gains an electron to form a negative ion is measure by its electron affinity.
Group VII elements (The Halogens)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>First Electron Affinity / kJ mol⁻¹</th>
<th>Electronic configuration of X⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td></td>
<td>-333</td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td>-348</td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td></td>
<td>-324</td>
<td></td>
</tr>
<tr>
<td>Iodine</td>
<td></td>
<td>-295</td>
<td></td>
</tr>
</tbody>
</table>

The halogens complete their outer energy level by gaining an electron to give the halide ion (X⁻¹) with noble gas electronic configuration. The electron affinity indicates the ease of ion formation. Fluorine is anomalous in that it has a lower value than chlorine. The electron cloud of fluorine is very compact due to its small atomic size and thus requires higher electrostatic energy to force the electron into the region of outer energy level.

Group VI elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>First / Second Electron Affinity / kJ mol⁻¹</th>
<th>Electronic configuration of X²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td></td>
<td>-141 / +791</td>
<td></td>
</tr>
<tr>
<td>sulphur</td>
<td></td>
<td>-200 / +649</td>
<td></td>
</tr>
</tbody>
</table>

Oxygen and sulphur can attain the stable noble gas electronic structure by gaining two electrons to form the oxide ion and the sulphide ion:

Both formation of oxide and sulphide ions are endothermic. This considerable expenditure of energy can be justified if the subsequent bonding in the ionic compound causes an even greater release of energy.

Summary:

Ionization enthalpies and electron affinities give us information about the energy changes involved in the production of ions from neutral atoms, but this is only part of what happens when an ionic compound is formed. The story is completed by knowledge of the lattice enthalpy of the compound. This is the energy released when the ions in the gas phase come together to form one mole of solid. For sodium chloride, this is the process:

which releases 781 kJ mol⁻¹ of energy.

(4) Energetics of formation of ionic compounds: The Born-Haber cycle

The lattice enthalpy of an ionic compound is the enthalpy change for the general process:
Lattice enthalpy is the enthalpy change when one mole of an ionic compound is formed from its constituent ions in the gaseous state.

Lattice enthalpy is **exothermic** because it reflects the electrostatic attraction between cations and anions and thus the strength of ionic bonds. Lattice enthalpies cannot be determined directly and so they are found from enthalpy cycles, called Born-Haber cycles.

**Example**: The Born-Haber cycle of sodium chloride

![Born-Haber cycle diagram]

The enthalpies changes can be identified as follows:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Process</th>
<th>Enthalpy change / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The enthalpy change of atomization of sodium</td>
<td>(\Delta H^\circ_{1} = +108)</td>
</tr>
</tbody>
</table>
The enthalpy change of atomization of chlorine \( \Delta H^\circ_2 = +121 \) kJ mol\(^{-1}\)

The ionization enthalpy of sodium \( \Delta H^\circ_3 = +496 \) kJ mol\(^{-1}\)

The electron affinity of chlorine \( \Delta H^\circ_4 = -348 \) kJ mol\(^{-1}\)

The lattice enthalpy of sodium chloride \( \Delta H^\circ_5 \)

The standard enthalpy change of formation of sodium chloride \( \Delta H^\circ_6 = -411 \) kJ mol\(^{-1}\)

Applying Hess’s law,

**Example**: The Born-Haber of calcium fluoride

Draw an enthalpy diagram and calculate the lattice enthalpy of calcium fluoride using the following data:

- Standard enthalpy change of formation of calcium fluoride \(-1203\) kJ mol\(^{-1}\)
- Standard enthalpy change of sublimation of calcium metal \(+193\) kJ mol\(^{-1}\)
- First ionization enthalpy of calcium \(+590\) kJ mol\(^{-1}\)
- Second ionization enthalpy of calcium \(+1145\) kJ mol\(^{-1}\)
- Standard enthalpy change of dissociation of fluorine molecules \(+158\) kJ mol\(^{-1}\)
- Electron affinity of fluorine atoms \(-333\) kJ mol\(^{-1}\)

(5) **Stoichiometry of ionic compounds**

It would be expected that the compound which has the most negative standard enthalpy change of formation would be the most stable.

For instance, energy calculation is able to show which of the three formulae, MgCl, MgCl\(_2\), and MgCl\(_3\) would be the most likely for magnesium chloride. If it is assumed that MgCl would have a sodium chloride
lattice structure, and MgCl\textsubscript{3} a structure similar to AlCl\textsubscript{3}, then a reasonable estimate of the lattice enthalpies for the hypothetical crystals MgCl and MgCl\textsubscript{3} may be made. **Born-Haber cycles** can then be constructed, and values obtained for the standard enthalpy changes of formation of these hypothetical crystals. The quantities necessary for drawing the cycles are as follows.

- \( \Delta H^\text{f} / \text{kJ mol}^{-1} \)

<table>
<thead>
<tr>
<th>AMg, IE\textsubscript{1}, IE\textsubscript{2}, IE\textsubscript{3}, ACl, EA, LE\textsubscript{1}, LE\textsubscript{2}, LE\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMg = enthalpy change of atomization of magnesium</td>
</tr>
<tr>
<td>IE\textsubscript{1} = first ionization enthalpy of magnesium</td>
</tr>
<tr>
<td>IE\textsubscript{2} = second ionization enthalpy of magnesium</td>
</tr>
<tr>
<td>IE\textsubscript{3} = third ionization enthalpy of magnesium</td>
</tr>
<tr>
<td>ACl = enthalpy change of atomization of chlorine</td>
</tr>
<tr>
<td>EA = electron affinity of chlorine</td>
</tr>
<tr>
<td>LE\textsubscript{1} = estimated lattice enthalpy of MgCl</td>
</tr>
<tr>
<td>LE\textsubscript{2} = lattice enthalpy of MgCl\textsubscript{2}</td>
</tr>
<tr>
<td>LE\textsubscript{3} = estimated lattice enthalpy of MgCl\textsubscript{3}</td>
</tr>
</tbody>
</table>

\[ \Delta H^\text{f} [\text{MgCl(s)}] = -94 \text{ kJ mol}^{-1} \]

\[ \Delta H^\text{f} [\text{MgCl}_{2(s)}] = \]

\[ \Delta H^\text{f} [\text{MgCl}_{3(s)}] = \]

The three cycles are represented to scale in the following figure:
It can be seen that the formation of MgCl is just exothermic; the formation of MgCl₂ is much more exothermic; but the formation of MgCl₃ is highly endothermic. It therefore appears that the compound formed is the one whose formation involves the greatest transfer of energy to the surroundings.

In the scale diagram, it will be seen that the largest contributions in each cycle are made by the ionization enthalpies and the lattice enthalpy, and that these two are always opposite in sign. If it requires more energy to ionize the metal than it is returned as lattice enthalpy, then the compound will not be formed. Thus, energetic considerations help us to understand the stoichiometry of ionic compounds.

Example:
Calculate the enthalpy change for the following reactions:

(a) \[ 2 \text{MgCl}_s \rightarrow \text{MgCl}_2(s) + \text{Mg}(s) \]

(b) \[ \text{MgCl}_3(s) \rightarrow \text{MgCl}_2(s) + \frac{1}{2} \text{Cl}_2(g) \]

(6) Ionic Crystals

X-ray diffraction shows that the particles in different ionic structures can be arranged in different patterns. The model of an ionic crystal is a lattice array: a regular three-dimensional arrangement of
cations surrounded by anions and each anion by cations. This arrangement gives the maximum attractive force between oppositely charged ions while minimizing repulsion between like ions. The net attractive force in the lattice is a major source of stability of ionic compound.

In the crystal structure, unit cells are the smallest identical block of ions, atoms or molecules which can be stacked together to fill space completely and to reproduce the whole regular arrangement. The coordination number of an ion or atom is the number of nearest equidistant ions or atoms.

The sodium chloride lattice

Figure a shows a space-filling model of the structure of sodium chloride. Although figure a shows only a few Na\(^+\) and Cl\(^-\) ions, there will be millions and millions of ions in even the smallest visible crystals of sodium chloride. The positions of Na\(^+\) and Cl\(^-\) ions in the crystal lattice of sodium chloride are emphasized in figure b.

In the crystal lattice of sodium chloride, each positive sodium ion is surrounded by six Cl\(^-\) ions and each negative chloride ion is surrounded by six Na\(^+\) ions. The ions are arranged in a face-centred-cubic pattern. The structure of sodium chloride is said to have a 6:6 coordination because the Na\(^+\) ions have a coordination number of 6 and the Cl\(^-\) ions also have a co-ordination number of 6.

Question: How many sodium ions and chloride ions are there in a unit cell?

The caesium chloride lattice

Figure a shows a space-filling model of caesium chloride. The Cs\(^+\) ion is similar in size to the Cl\(^-\) ion. The general shape of the lattice is simple cubic. The positions of Cs\(^+\) and Cl\(^-\) ions in the caesium chloride lattice are shown in figure b.
In the crystal lattice of caesium chloride, there are eight Cl\(^-\) ions around each Cs\(^+\) ion, so the coordination number of Cs\(^+\) ions in the structure is eight. In the same way, the coordination number of Cl\(^-\) ions is also eight. The structure of caesium chloride is therefore said to have 8:8 coordination.

Question: How many caesium ions and chloride ions are there in a unit cell?

**The calcium fluoride lattice**

The figure below shows the unit cell of calcium fluoride:

In the crystal lattice of calcium fluoride, the calcium ions are arranged in a face-centred-cubic pattern while the fluoride ions are arranged in a simple cubic pattern. Each positive calcium ion is surrounded by eight F\(^-\) ions and each negative fluoride ion is surrounded tetrahedrally by four Ca\(^{2+}\) ions. The structure of calcium fluoride is said to have a 8:4 coordination because the Ca\(^{2+}\) ions have a coordination number of 8 and the F\(^-\) ions have a co-ordination number of 4.

Question: Work out the unit cell contents and hence deduce the empirical formula of calcium fluoride.

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**Example 1**

The following is a unit cell of oxide of titanium:
(a) What is the coordination number of titanium?

(b) State the number of titanium ions and oxygen ions per unit cell. Explain your answer.

(c) Write the formula of the compound.

Example 2

The crystal structure of a compound $A_xB_y$ can be described as a simple cubic lattice of $A$ atoms with $B$ atoms at the middle of all the edges. What is the empirical formula of this compound? What are the coordination numbers of an $A$ atom and a $B$ atom respectively?

(7) Ionic Radii

Comparison of sizes of ions with their parent atom

Ionic radius, like atomic radius, increases down a group because of increased occupation of electron shells.
Movement across a period is marked by a decrease in both cationic and anionic radius as number of protons and thus nuclear charge increases.

Cations have smaller radii than the corresponding atoms since their nuclear charge outweighs the electronic charge and consequently the electrons are attracted more strongly.

Anions have large radii than their atoms because the protons are exceeded by the electrons and the latter repel one another.

**Comparison of sizes of ions of isoelectronic ions**

For a series of isoelectronic ions, i.e. ions with the same number of electrons, radius decreases as charge increases, e.g.

For anions the reverse is true, the repulsion between electrons of a negative ion causes an increase in size, and the more electrons an anion possesses the larger it is, e.g.

Atomic and ionic radii in nanometres are shown below.

<table>
<thead>
<tr>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8</th>
<th>1B</th>
<th>2B</th>
<th>3B</th>
<th>4B</th>
<th>5B</th>
<th>6B</th>
<th>7B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.152</td>
<td>Be</td>
<td>0.112</td>
<td>0.050</td>
<td>Li⁺</td>
<td>0.090</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.186</td>
<td>Mg</td>
<td>0.160</td>
<td>Na⁺</td>
<td>0.095</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.231</td>
<td>Ca</td>
<td>0.197</td>
<td>Ca²⁺</td>
<td>0.099</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.244</td>
<td>Sr</td>
<td>0.215</td>
<td>Sr²⁺</td>
<td>0.113</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.262</td>
<td>Ba</td>
<td>0.217</td>
<td>Ba²⁺</td>
<td>0.135</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca⁺</td>
<td>0.169</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

(8) **Enthalpy change of solution of ionic solids**

When an ionic compound is dissolved, heat energy will be absorbed or evolved because:
1. Before a solid can dissolve, it is apparent that the crystal lattice must be broken down and that will require energy. If the ions are separated to such a distance that there is no longer any interaction between them, this energy will be numerically equal to the lattice enthalpy with the sign reversed. (Endothermic step).

2. The second step is the solvating of ions: positive ions attract the negative end of the dipole in a number of solvent molecules, whilst negative ions attract the positive end of the dipole in several solvent molecules. Energy is evolved during solvation. (Exothermic step) If water is the solvent the process of solvation is known as hydration and the energy released is the hydration energy.

The enthalpy change of solution is the enthalpy change when one mole of a substance is dissolved in so much water that further dilution produces no detectable heat change. The enthalpy level diagram involved in the dissolution of an ionic solid is shown in the following figure:

Example 1
When sodium chloride is dissolved in water, the overall changes can be represented as:

\[
\text{NaCl}_{(s)} + \text{aq.} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}
\]

The overall process of solution can be divided into two distinct stages:

1. The separation of the solid NaCl crystal into sodium ions and chloride ions in gaseous state, i.e. the reverse of the lattice enthalpy process,

2. The hydration of these gaseous ions by water molecules which is known as the hydration energy,

The first stage is always endothermic since it involves separating the ions of the NaCl. The second stage is always exothermic since it involves the attraction of ions for water molecules. In the case of NaCl, the endothermic process is marginally greater than the exothermic process so the enthalpy change of solution has a small positive value.

Example 2
When ammonium chloride dissolves in water the temperature decreases, i.e. heat is absorbed from the surroundings and the dissolving process is endothermic:
Here the hydration energy is somewhat smaller than the lattice enthalpy.

Example 3
For salt which form crystals with water of crystallization, the enthalpy change of solution depends on whether the anhydrous or hydrated form is used. The anhydrous form usually gives out heat on dissolving whilst the hydrated form may absorb heat on dissolving. This is because ions of the hydrated salt are hydrated by the water of crystallization before the salt dissolves. e.g.

Example 4
The solubility of an ionic solid is usually governed by the lattice enthalpy and hydration energy. In the case of lithium halides, the solubilities are in accord with the differences between the lattice enthalpy and hydration energy. High solubility results when the hydration energy is appreciably greater than the lattice enthalpy.

<table>
<thead>
<tr>
<th>Ionic compound</th>
<th>LiF</th>
<th>LiCl</th>
<th>LiBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>- lattice enthalpy /kJ mol(^{-1})</td>
<td>1029</td>
<td>849</td>
<td>804</td>
</tr>
<tr>
<td>hydration energy /kJ mol(^{-1})</td>
<td>-956</td>
<td>-883</td>
<td>-850</td>
</tr>
<tr>
<td>Enthalpy change of solution /kJ mol(^{-1})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility</td>
<td>very low</td>
<td>high</td>
<td>higher</td>
</tr>
</tbody>
</table>

Section 4.4  Covalent Bonding

(1) Formation of covalent bonding - Overlap of atomic orbitals
In simple molecules, electrons might be shared in pairs so that each atom could attain the stable noble gas electronic configuration.

Consider the chlorine atom which has seven electrons in its outer shell. If one electron is provided by each atom and shared equally, then each chlorine atom can acquire a share in eight electrons, i.e. they have the argon electronic structure (sometimes called a completed octet).

The sharing of two electrons, one electron being provided by each atom constitutes a single covalent bond; it is usually represented by a single line joining the two atoms together.

For example the chlorine molecule can be represented by :

When the two atoms that are bound together by covalent bonds are different the procedure is similar. For example the combination of the hydrogen atom and chlorine atom can be shown by :

Valence Bond Theory :

The valence of an atom (the number of bonds it can form) is determined by the number of unpaired electrons. Each orbital containing an unpaired electron can overlap an orbital of another atom containing an unpaired electron to form a covalent bond. The overlapping of atomic orbitals results in overlapping of electron clouds which permits the exchange of electrons between the atoms. The overlapping of electron clouds leads to a greater electron density between the two nuclei, indicating that the electrons are localized there with greater probability. The electrostatic attraction arises from the electrostatic attractive forces between bonding electrons and nuclei which outweighs the electrostatic repulsive forces between two nuclei and two electrons. The potential energy of the system thus decreases. The energy drop is called the bond dissociation enthalpy. It is the energy required to break the bond.

Example 1 : Hydrogen molecule, H₂

As the hydrogen atoms approach each other, the 1s orbitals each containing an electron begin to overlap :

Overlapping of two 1s orbitals decreases the potential energy of the hydrogen molecule system. At some internuclear distance, the stability is maximized. It is called the bond length of the hydrogen molecule.

Example 2 : Interaction between Helium atoms

Helium atom has the electronic configuration 1s². The two valence electrons of helium atom fill its valence orbital (1s orbital). The completely filled orbital of a helium atom cannot be occupied by the valence electrons of the other helium atom because each orbital can accommodate a maximum of two electrons only; otherwise, it will violate Pauli exclusion principle. Therefore, helium forms no covalent bonds and is a monoatomic molecule.

Examples : Write the structural formulae of the following molecules, showing the lone pair electron(s) of the central atom if any.

HF, H₂O, NH₃, CH₄, CHCl₃, BeCl₂, BF₃, PCl₅, SF₆
### Note:

The phosphorus atom in PCl₅ is surrounded by 10 electrons and the sulphur atom in SF₆ is surrounded by 12 electrons. P and S can violate ‘octet rule’ because their valence shell is M shell ($n = 3$) which can accommodate 18 electrons at most.

#### (2) Dative covalent bonding

In some cases, one atom will donate both the electrons involved in bond formation between two atoms. This type of bond is called dative covalent bond.
Dative covalent bond is formed by the overlapping of an empty orbital with an orbital occupied by a lone pair of electrons.

Dative covalent bond and covalent bond are identical once they have been formed. There is no real distinction between them except that in dative covalent bond only one of the bonded atoms provides the two electrons which are shared.

Dative covalent bond is sometimes designated by drawing an arrow from the donor to the acceptor atom.

Example 1: Ammonium ion

Example 2: Hydroxonium ion

In dative bonding, formal charges always arise. Formal charges may be calculated by assigning half of the electrons in a covalent bond to each atom and calculating the resulting charge on the atom. The sum of the formal charges in a molecule will be zero; the sum of the formal charges in an ion will be the same as the charge on the ion.

Example 3
Consider the stable complex \( \text{NH}_3\cdot\text{BCl}_3 \) formed between ammonia molecule and boron trichloride molecule:

(3) Multiple bonds

Some atoms can achieve a full valence shell when more than one electron pair forms a bond between two atoms. This leads to the formation of double and triple covalent bonds.
Consider the oxygen atom which has six electrons in its outer shell, and in the oxygen molecule, a stable electronic configuration can be attained by the sharing of four electrons, two being provided by each atom. The oxygen atoms are bound together by a double covalent bond and is represented by a double line:

Similarly, the nitrogen molecule contains a triple bond, which involves the sharing of six electrons, three being provided by each nitrogen atom:

Example 1
Write the structural formulae for the following covalent molecules:

\[ \text{CO}_2, \text{CO}, \text{SO}_2, \text{SO}_3, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2 \]

<table>
<thead>
<tr>
<th>CO(_2)</th>
<th>SO(_2)</th>
<th>C(_2)H(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>SO(_3)</td>
<td>C(_2)H(_2)</td>
</tr>
</tbody>
</table>

Example 2
Write the structural formulae of CH\(_3\)COOH, H\(_2\)CO\(_3\), HNO\(_3\), H\(_2\)SO\(_4\) and their corresponding anions.

<table>
<thead>
<tr>
<th>CH(_3)COOH</th>
<th>H(_2)CO(_3)</th>
<th>HNO(_3)</th>
<th>H(_2)SO(_4)</th>
</tr>
</thead>
</table>

(4) The shapes of covalent molecules and polyatomic ions

The shapes of covalent molecules and polyatomic ions can be explained in terms of valence shell electron pairs repulsion theory (V.S.E.P.R.T.):
1. The electron pairs are regarded as occupying localized orbitals which are oriented in space so that the distance between the orbitals is a maximum.

Symbols: K: central atom
X: atom(s) covalently bonded to the central atom
P: non-bonding pair(s) on the central atom

2. Number of non-bonding pair (P) =

3. Repulsive forces:

4. The repulsive forces between electron pairs at angles greater than 90° to each other are ignored.

5. The most stable structure is the one with minimum electron pairs repulsion.

**Number of electron pairs = 2**

KX₂ type: linear  Examples: BeCl₂, CO₂

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
</table>

**Number of electron pairs = 3**

KX₃ type: trigonal planar  Examples: BF₃, SO₃

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
</table>

KX₂P type: v-shaped  Example: SO₂

<table>
<thead>
<tr>
<th>Bond angle:</th>
</tr>
</thead>
</table>

**Number of electron pairs = 4**

KX₄ type: tetrahedral  Examples: CH₄, CCl₄, NH₄⁺
<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KX_3P</strong> type: trigonal pyramidal</td>
<td>Examples: NH_3, PCl_3, H_3O^+</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KX_2P_2</strong> type: v-shaped</td>
<td>Examples: H_2O, H_2S, NH_2^-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electron pairs = 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KX_5</strong> type: trigonal bipyramidal</td>
<td>Example: PCl_5</td>
<td></td>
</tr>
<tr>
<td><strong>KX_4P</strong> type: irregular tetrahedral</td>
<td>Example: SF_4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KX_3P_2</strong> type: T-shaped</td>
<td>Example: ClF_3</td>
<td></td>
</tr>
<tr>
<td><strong>KX_2P_3</strong> type: linear</td>
<td>Example: I_3^-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electron pairs = 6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle:</th>
<th>Bond angle:</th>
<th>Bond angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KX_6</strong> type: octahedral</td>
<td>Example: SF_6</td>
<td></td>
</tr>
<tr>
<td><strong>KX_5P</strong> type: square pyramidal</td>
<td>Example: IF_5</td>
<td></td>
</tr>
<tr>
<td><strong>KX_4P_2</strong> type: square planar</td>
<td>Example: XeF_4</td>
<td></td>
</tr>
</tbody>
</table>

Example 1
Draw diagrams showing the shapes of the following molecules. Indicate the lone pairs (if any) on each central atom.
(a) ICl_2
Example 2
For each of the following molecules, draw a three-dimensional structure and state the molecular geometry.
(a) SiF₄

(b) XeOF₄

Example 3
For each of the following species, draw a three-dimensional structure showing the bond electron pairs and lone electron pairs of the central atom. State the shape of the species in each case.
(a) ICl₄

(b) SCl₂

(5) Resonance Theory: The concept of delocalization of electrons

Do single bonds, double bonds and triple bonds always represent the electron distribution adequately when electrons are shared?

Sodium methanoate has the formula HCO₂⁻Na⁺. From valence consideration, methanoate ion may be expected to have the structure:
X-ray diffraction study of sodium methanoate crystal show the methanoate ion to have the structure given below:

The two carbon-oxygen bonds have the same length and so the C=O and C-O bonds representation is not correct. Hence the ion is more correctly represented as a resonance hybrid:

It should be understood that this does not imply continual interconversion between two forms but rather the true structure cannot be represented by a single classical type structure.

In fact, both bonds have partial double bond character, the pair of electrons is delocalized between three atoms:

Example 1
The structure of the carbonate ion has been found to be as shown below. The three carbon-oxygen bonds all have the same length:

Example 2: The structure of benzene $C_6H_6$

The structure of benzene had been the subject of much controversy over the years. In 1865, Kekule suggested the structure:
Electron and X-ray diffraction studies show that the benzene molecule is planar and that all the C-C bond lengths are the same, i.e. 0.139 nm. This indicates that all the bonds are similar and intermediate in character between carbon-carbon double and single bonds which have lengths of 0.133 nm and 0.154 nm respectively. Benzene may be regarded as being a resonance hybrid of two structures:

**Evidence:**

The standard enthalpy of formation of benzene from its constituent atoms, assuming it to be a cyclic triene, may be calculated from the relevant bond enthalpies. The calculated value is +221 kJ mol\(^{-1}\). The measured value is +49 kJ mol\(^{-1}\), which suggest an extra stability of 172 kJ mol\(^{-1}\) than the hypothetical cyclic triene structure. This is known as delocalization energy, and it is the amount by which the delocalized structure is more stable than a cyclic triene.

(6) Bond enthalpy, bond length and covalent radius

1. Bond dissociation enthalpy and bond enthalpy

   The standard bond dissociation enthalpy of a certain bond is the amount of energy required to break one mole of that bond under standard conditions.

   Example 1
   
   When hydrogen chloride dissociates
The standard bond dissociation enthalpy of the H-Cl bond in HCl is 431 kJ mol\(^{-1}\).

Example 2

A methane molecule has 4 C-H bonds. The energy required to break the first C-H bond in methane is not the same as that required to remove a hydrogen atom from a CH\(_3\) radical or from CH\(_2\) or CH.

\[
\begin{align*}
\text{CH}_4(g) & \rightarrow \text{CH}_3(g) + \text{H}(g) \quad \Delta H^\circ = +425 \text{ kJ mol}^{-1} \\
\text{CH}_3(g) & \rightarrow \text{CH}_2(g) + \text{H}(g) \quad \Delta H^\circ = +470 \text{ kJ mol}^{-1} \\
\text{CH}_2(g) & \rightarrow \text{CH}(g) + \text{H}(g) \quad \Delta H^\circ = +416 \text{ kJ mol}^{-1} \\
\text{CH}(g) & \rightarrow \text{CH}(g) + \text{H}(g) \quad \Delta H^\circ = +335 \text{ kJ mol}^{-1}
\end{align*}
\]

In the complete dissociation:

\[
\text{CH}_4(g) \rightarrow \text{C}(g) + 4 \text{H}(g) \quad \Delta H^\circ = +1646 \text{ kJ mol}^{-1}
\]

Dividing the standard enthalpy change equally between four bonds gives an average value for the C-H bond of 412 kJ mol\(^{-1}\). This value is called the average standard bond enthalpy of the C-H bond.

**Average bond enthalpies**

Bond enthalpy is taken as the average energy value required to break a chemical bond. It is deduced from the energetic data of many compounds. However, the bond dissociation enthalpy refers specifically to a particular bond of a particular compound.

Example 3

Given that:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Energy to break one mole of C-Cl bond / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td></td>
<td>335</td>
</tr>
<tr>
<td>Chloroethane</td>
<td></td>
<td>342</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td></td>
<td>327</td>
</tr>
</tbody>
</table>

Calculate the average bond enthalpy of the C-Cl bond.

\[
E (\text{C-Cl}) =
\]

2. **Estimation of bond enthalpies using data from energetics**

Some bond enthalpies are shown below:

<table>
<thead>
<tr>
<th>Bond</th>
<th>(\Delta H^\circ / \text{kJ mol}^{-1})</th>
<th>Bond</th>
<th>(\Delta H^\circ / \text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>348</td>
<td>C-H</td>
<td>416</td>
</tr>
<tr>
<td>H-H</td>
<td>436</td>
<td>N-H</td>
<td>388</td>
</tr>
<tr>
<td>O-O</td>
<td>146</td>
<td>O-H</td>
<td>463</td>
</tr>
</tbody>
</table>
Note that bond enthalpies have positive value (endothermic) for bond breaking but negative values (exothermic) for bonds formation.

Bond enthalpies can be determined by thermochemical methods. Thermochemical methods involve the calorimetric determination of the enthalpy change of formation, atomization and other processes. These data from energetics are then used to calculate bond enthalpies. Notice that both the reactant(s) and product(s) involved in the bond enthalpy must be in the gaseous state.

Example 1 : Finding the average bond enthalpy of the C-H bond in methane
Given that:
- standard enthalpy change of formation of methane = - 75 kJ mol⁻¹
- standard enthalpy change of atomization of graphite = + 718 kJ mol⁻¹
- standard enthalpy change of atomization of hydrogen = + 218 kJ mol⁻¹

Construct an enthalpy cycle and determine the average bond enthalpy of the C-H bond.

Example 2 : Finding the bond enthalpy of the C-C bond in ethane
Given that:
- standard enthalpy change of formation of ethane = - 85 kJ mol⁻¹
- standard enthalpy change of atomization of graphite = + 718 kJ mol⁻¹
- standard enthalpy change of atomization of hydrogen = + 218 kJ mol⁻¹
- average bond enthalpy of the C-H bond = 416 kJ mol⁻¹

Construct an enthalpy cycle and determine the bond enthalpy of the C-C bond.

Example 3 : Finding the average bond enthalpy of C=O in CO₂
Given that:
- standard enthalpy change of formation of CO₂ = - 393 kJ mol⁻¹
- standard enthalpy change of atomization of graphite = + 718 kJ mol⁻¹
- standard enthalpy change of atomization of oxygen = + 249 kJ mol⁻¹

Construct an enthalpy cycle and determine the bond enthalpy of the C=O bond.
Example 4

Given that the standard enthalpy changes of atomization of butane and pentane are +5165 kJ mol\(^{-1}\) and +6337 kJ mol\(^{-1}\) respectively, calculate E (C-H) and E (C-C).

3. Estimation of the enthalpy changes of reactions from bond enthalpies

Any chemical reaction involves a change in bonding between atoms or ions. Some bonds in reactants are broken and new bonds are formed to give the products. Breaking of bonds is an endothermic change, since energy has to be supplied to overcome the electrostatic attractions constituting chemical bonds. On the other hand, formation of bonds release energy and is an exothermic change. The enthalpy change of reaction results from differences in overall energy of bond breaking and bond formation. If the energy released when new bonds are made is more than needed to break the old bonds, energy is evolved and the reaction is exothermic. In the reverse way, energy is absorbed and the reaction is endothermic.
Therefore, the approximate enthalpy change in a reaction can be calculated as the sum of energy used in bond breaking and the energy evolved in bond making. Small discrepancies will obviously arise since average bond enthalpies are used.

Example 1
Calculate the standard enthalpy change of formation of hydrogen chloride gas.
Given: The bond enthalpies of the Cl-Cl, H-H and H-Cl bonds are 242, 436 and 431 kJ mol\(^{-1}\) at 298 k respectively.

Example 2
Calculate standard enthalpy change of formation of ethane, using the following data.
The standard bond enthalpies are: C-C = 348, C-H = 416 kJ mol\(^{-1}\).
The standard enthalpy changes of atomization are C\(_{(s)}\) = 718, and \(\frac{1}{2}\) H\(_2\) = 218 kJ mol\(^{-1}\).

Example 3
Calculate the enthalpy change of atomization of one mole of 1-bromobutane. The relevant bond enthalpies in kJ mol\(^{-1}\) are: C-C 348, C-H 416, C-Br 284

Example 4
Calculate the approximate enthalpy change in the reaction:

$$\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_3(\text{g})$$

The relevant bond enthalpies in kJ mol\(^{-1}\) are:
- C\text{-C} 612,
- C\text{-H} 416,
- C\text{-C} 348,
- H\text{-H} 436

**Example 5**

Using the following data, calculate the enthalpy change of combustion of cyclohexane, C\(_6\)H\(_{12}\)(l).

<table>
<thead>
<tr>
<th>Enthalpy change</th>
<th>ΔH / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of vaporization of cyclohexane</td>
<td>+ 33</td>
</tr>
<tr>
<td>Enthalpy change of atomization of carbon</td>
<td>+ 718</td>
</tr>
<tr>
<td>Enthalpy change of dissociation of H(_2) molecules</td>
<td>+ 436</td>
</tr>
<tr>
<td>Enthalpy change of combustion of carbon</td>
<td>- 393</td>
</tr>
<tr>
<td>Enthalpy change of combustion of hydrogen</td>
<td>- 286</td>
</tr>
<tr>
<td>Average bond enthalpy of C\text{-C} bond</td>
<td>348</td>
</tr>
<tr>
<td>Average bond enthalpy of C\text{-H} bond</td>
<td>416</td>
</tr>
</tbody>
</table>

**4. Bond enthalpies as a comparison of the strength of covalent bonds**

The bond enthalpy is a measure of the bond strength. A greater value implies a stronger bond.

**Factors affecting bond enthalpies:**

(i) **Bond enthalpies decrease as the bond length increases.**

    The larger the atoms joined by a particular bond, the longer the bond length. Larger atoms tend to have more electrons than the smaller ones and this results in an increased screening of the nucleus, and an increase in electron cloud repulsion. Both these effects contribute to a weakening of the bond, as seen for the hydrogen halides in table:
### Hydrogen halide Bond length and Standard bond enthalpy

<table>
<thead>
<tr>
<th>Hydrogen halide</th>
<th>Bond length</th>
<th>Standard bond enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-F</td>
<td>0.109</td>
<td>565</td>
</tr>
<tr>
<td>H-Cl</td>
<td>0.135</td>
<td>431</td>
</tr>
<tr>
<td>H-Br</td>
<td>0.151</td>
<td>364</td>
</tr>
<tr>
<td>H-I</td>
<td>0.171</td>
<td>297</td>
</tr>
</tbody>
</table>

Example: Consider the halogen-halogen bond length and bond enthalpy:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length</th>
<th>Standard bond enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-F</td>
<td>0.142</td>
<td>158</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>0.198</td>
<td>242</td>
</tr>
<tr>
<td>Br-Br</td>
<td>0.228</td>
<td>193</td>
</tr>
<tr>
<td>I-I</td>
<td>0.267</td>
<td>151</td>
</tr>
</tbody>
</table>

From the bond length values given, one would predict a value for the F-F bond enthalpy in the region of about 300 kJ mol\(^{-1}\), in fact the measured value is surprisingly low. This can be attributed to the high degree of non-bonding repulsion between lone pair electrons in a bond of such short length.

(ii) **Bond enthalpies increase as the number of electrons making up the bond increases.**

A double bond consists of two pairs of shared electrons, and therefore there is a greater electron density between the nuclei than the corresponding single bond. It would cause a greater forces of attraction between the nuclei, and be reflected in a shorter bond length and a greater bond enthalpy.

It can be generalized that the more electrons that constitute a bond, the greater the strength of the bond. Triple bonds would be expected to be stronger than double bonds which, in turn, should be stronger than single bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length</th>
<th>Standard bond enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>0.154</td>
<td>+348</td>
</tr>
<tr>
<td>C=C</td>
<td>0.134</td>
<td>+612</td>
</tr>
<tr>
<td>C≡C</td>
<td>0.121</td>
<td>+837</td>
</tr>
<tr>
<td>C-O</td>
<td>0.143</td>
<td>+358</td>
</tr>
<tr>
<td>C=O</td>
<td>0.122</td>
<td>+745</td>
</tr>
<tr>
<td>C≡O</td>
<td>0.113</td>
<td>+1070</td>
</tr>
</tbody>
</table>

### 5. Bond lengths and covalent radii

Covalent radius is defined as half the internuclear distance between two identical atoms joined by a single covalent bond.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Internuclear distance /nm</th>
<th>Covalent radius /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(_2)</td>
<td>0.198</td>
<td>0.099</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>0.228</td>
<td>0.114</td>
</tr>
<tr>
<td>I(_2)</td>
<td>0.267</td>
<td>0.133</td>
</tr>
<tr>
<td>P(_4)</td>
<td>0.220</td>
<td>0.110</td>
</tr>
</tbody>
</table>
Some covalent radii (in nm) are shown below:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Covalent Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.037</td>
</tr>
<tr>
<td>B</td>
<td>0.080</td>
</tr>
<tr>
<td>C</td>
<td>0.077</td>
</tr>
<tr>
<td>N</td>
<td>0.074</td>
</tr>
<tr>
<td>O</td>
<td>0.073</td>
</tr>
<tr>
<td>F</td>
<td>0.072</td>
</tr>
<tr>
<td>Si</td>
<td>0.117</td>
</tr>
<tr>
<td>P</td>
<td>0.110</td>
</tr>
<tr>
<td>S</td>
<td>0.104</td>
</tr>
<tr>
<td>Cl</td>
<td>0.099</td>
</tr>
<tr>
<td>Br</td>
<td>0.114</td>
</tr>
<tr>
<td>I</td>
<td>0.133</td>
</tr>
</tbody>
</table>

The covalent radius shows the following general trends:

(i) It increases down a group as the number of completed electron shells in the atoms increases.
(ii) It decreases across a period as the increase in nuclear charge decreases atomic size.

Covalent radii are roughly additive:

Bond length = covalent radius of element A + covalent radius of element B

Example 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Calculated bond length /nm</th>
<th>Experimentally determined bond length /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-Cl</td>
<td>0.214</td>
<td></td>
</tr>
<tr>
<td>I-Cl</td>
<td>0.232</td>
<td></td>
</tr>
<tr>
<td>C-H</td>
<td>0.109</td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>0.143</td>
<td></td>
</tr>
<tr>
<td>C-F</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>0.154</td>
<td></td>
</tr>
</tbody>
</table>

Note that:

When atoms with a great electronegativity difference are joined by a covalent bond, the actual bond length is different from the sum of the corresponding covalent radii. This is because the bond between atoms of different electronegativities is not purely covalent but carries some ionic character.

Example 2: Compare O2 with H2O2:

<table>
<thead>
<tr>
<th>Bond</th>
<th>O-O in H2O2</th>
<th>O=O in O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length</td>
<td>0.148 nm</td>
<td>0.121 nm</td>
</tr>
<tr>
<td>Bond energy</td>
<td>147 kJ mol⁻¹</td>
<td>500 kJ mol⁻¹</td>
</tr>
</tbody>
</table>

(7) Covalent crystals: Giant covalent structures

Giant covalent structure consists of millions of atoms covalently bonded together in a structural network and there is no simple molecule present. Examples are diamond, graphite and quartz.

1. Diamond

A crystal of diamond contains millions of carbon atoms. Each carbon atom is bonded tetrahedrally to four neighbouring carbon atoms by identical and directional strong C-C covalent bonds. This gives a three dimensional covalent network structure. The C-C bonding pattern accounts for the stability, extreme hardness and very high melting point of diamond. For a diamond to melt or undergo a chemical change,
many strong C-C bonds within the crystalline structure must be broken. Because of the incredible hardness and high melting point (3827 °C), applications of diamond are endless: scratch proof cookware, watch crystal, lifetime drill bits and razor blade.

Furthermore, the localization of the electrons within C-C bonds prevents their moving freely in an applied electric field and thus diamond does not conduct electricity.

2. Graphite

Graphite is made up of hexagonal arrays of carbon atoms arranged in layers. Within each layer, each carbon atom forms bonds with three other carbon atoms. A network of coplanar hexagons is formed, with a C-C bond distance of 0.142 nm. Weak van der Waals’ forces hold the layers together and distance between adjacent layers is 0.335 nm. The weak van der Waals’ forces of attraction between the layers allow one layer to slide easily over another layer. This explains why graphite is soft and slippery and can be used as a lubricant.

Moreover, each carbon atom in graphite forms three bonds only and has one electron left. The non-bonding electrons of the carbon atoms are delocalized among the layers, so graphite is a conductor of electricity.

Note that:

The C-C bond in graphite has some double bond character due to the delocalized electrons. Hence, the C-C bond length (0.142 nm) is smaller than that in diamond (0.154 nm).

Therefore, the C-C bond in graphite is stronger than that in diamond.

<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density / g cm⁻³</td>
<td>3.51</td>
<td>2.27</td>
</tr>
<tr>
<td>Hardness (Mohs scale)</td>
<td>10</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Melting point / °</td>
<td>3827</td>
<td>3827</td>
</tr>
<tr>
<td>Electricity conductivity</td>
<td>None</td>
<td>High (along layer)</td>
</tr>
</tbody>
</table>

3. Quartz

Quartz is a three-dimensional lattice of silicon(IV) oxide, SiO₂. In the quartz lattice, each silicon atom is bonded tetrahedrally to four neighbouring oxygen atoms by identical and directional strong Si-O
covalent bonds. Thus, the coordination number of Si is 4. Each oxygen atom is bonded to 2 silicon atoms. Thus, the coordination number of O is 2. The formula of silicon(IV) oxide is SiO₂.

It is very difficult to distort a covalent crystal of quartz, because this would involve breaking many Si-O covalent bonds. Consequently, quartz is hard (Mohs scale : 7) with high melting points (1700 °C). Furthermore, the localization of the electrons within Si-O bonds prevents their moving freely in an applied electric field and hence quartz does not conduct electricity. Quartz is one of the basic raw materials of the glass and ceramics industry.

Questions:
1. Why is graphite sometimes more suitable than oil for lubricating the moving parts of machinery ?

2. How do you think the proportion of graphite to clay affects the hardness of the ‘lead’ in pencils ?

3. Explain why quartz can exist in nature for ages.

Section 4.5  Bonding Intermediate between Ionic and Covalent

(1) Polarization of ions : Incomplete electron transfer in ionic compounds

Lattice enthalpy is the energy involved in bringing well separated ions together to form a lattice. It should therefore be possible to make an estimation of the magnitude of this energy change, using the principles of electrostatics. The calculations are done on the basis of ions being charged spheres in contact. It is assumed that the ions are spherical, separate entities, each with its charged distributed uniformly around it (pure ionic model).

The theoretical lattice enthalpies of some ionic compounds are compared with the corresponding experimental values in table :
Notice the similarity between the theoretical and experimental lattice enthalpies for the three alkali metal halides. The calculated values are only one or two per cent less than the experimental values. This close agreement provides evidence that the simple model of an ionic lattice composed of discrete spherical ions with evenly distributed charge is a satisfactory one in the case of alkali metal halides.

For silver halides the theoretical values are approximately 130 kJ mol\(^{-1}\) (i.e. about 15\%) less than the experimental values. This suggests that the bonding in silver halides is stronger than the ionic model predicts. The explanation of this anomaly is that the bonding in silver halides is not pure ionic but is intermediate in character between ionic and covalent. The partly covalent nature of the ionic bonds can be interpreted by the idea that electrons are incompletely transferred in forming the ions. The ionic bonds in silver halides have been polarized and the electronic clouds of the ions have been distorted. This effect may be represented diagrammatically as in the following figure:

```
increasing polarization in ionic compound
```

The polarization of ion represents the start of transition from ionic bonding to covalent bonding.

**Fajan’s Rules of polarization of ions:**

The positive charge on the cation in an ionic compound can attract electrons toward it from the anion. This results in distortion of the anion. This distortion is called polarization. The ability of a cation to attract electrons and distort an anion is called its **polarizing power**.

**Polarizing power of a cation =**

Example a polarizing power:

The ease with which an electron cloud of the anion is distorted is called **polarizability**. Anion with large polarizability is due to its large size and highly negatively charged. The electrons are far from the nucleus and so less under control.
Fajan’s rules state that:
(i) An ionic compound will have appreciable covalent character if the cation is highly charged.

Example 1 polarizing power:

Thus, LiCl is predominantly ionic, BeCl₂ is covalent and BCl₃ is also covalent.

(ii) An ionic compound will have appreciable covalent character if the cation is small.

Example 2 polarizing power:

melting point of chloride: BeCl₂(405 °C), MgCl₂(714 °C), CaCl₂(772 °C), SrCl₂(872 °C), BaCl₂(960 °C)

In this series, beryllium ion is the smallest cation with the greatest polarizing power, so BeCl₂ has the greatest covalent character as indicated by its melting point.

(iii) An ionic compound will have appreciable covalent character if the anion is large.

Example 3 polarizability:

solubility in water:

Increasing polarization of silver halides as increasing size of anions is reflected by the decreasing solubilities in water.

(iv) Transition metal ions such as Zn²⁺ and Ag⁺ appear to have higher polarizing power than similarly sized ions having the same net charge. This is because the d electrons that are added to the atom as the transition series is crossed do not completely shield the nuclear charge, which has also increased. As a result, these cations have higher charge density and thus higher polarizing power.

Examples 4 melting points of chlorides:

NaCl (808 °C) AgCl (455 °C)
MgCl₂ (714 °C) ZnCl₂ (246 °C)

(2) Polarity of covalent bond

1. Electronegativity and the formation of a polar covalent bond

In polar covalent bonds, the unequal sharing of the bonded electron pairs is caused by a difference in electron attracting ability of the bonded atoms. This electron attracting ability of the atom is described as electronegativity of the element.
Electronegativity (Pauling Scale) is an arbitrary measure of an atom’s tendency in a molecule to attract electrons.

In Pauling’s scale a value of 4.0 is assigned to the most electronegative element, fluorine. All other elements having a lower electron attracting ability than fluorine are assigned lower electronegativity values.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td>Ca</td>
<td>1.5</td>
<td>1.8</td>
<td>2.1</td>
<td>2.5</td>
<td>3.0</td>
<td>Br</td>
</tr>
<tr>
<td>Rb</td>
<td>0.8</td>
<td>Sr</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td>I</td>
<td>2.5</td>
</tr>
<tr>
<td>Cs</td>
<td>0.7</td>
<td>Ba</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Trends: Electronegativity increases on going from left to right across the period and decreases down a group.

Example 1

If two atoms of same element are joined by a covalent bond, the electrons in the bond will be shared equally between them. A pure covalent bond is formed:

Example 2

When two atoms with different electronegativity values form a covalent bond, the one with higher electronegativity attracts the bonded electron pair more, and this results in a polar bond.

2. Electronegativity difference and polarity of covalent bond

It is apparent that bonds between elements with a large difference in electronegativity will be highly polarized, i.e. predominantly ionic, whilst bonds between elements with similar electronegativity will be only slightly polarized, i.e. predominantly covalent. It should be noted that pure ionic or covalent bonds are extreme cases; there are very many compounds with intermediate types of bonding. The relation of ionic character and electronegativity difference for compound A-B is shown in the following table:

| EnA - EnB | Ionic character of | EnA - EnB | Ionic character of |
Since a difference of 1.7 corresponds to 51% ionic character, therefore, a difference greater than 1.7 represents a bond that is effectively ionic.

To summarize:

<table>
<thead>
<tr>
<th>bond A-B (%)</th>
<th>bond A-B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>0.6</td>
<td>9</td>
</tr>
<tr>
<td>0.8</td>
<td>15</td>
</tr>
<tr>
<td>1.0</td>
<td>22</td>
</tr>
<tr>
<td>1.2</td>
<td>30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bond A-B (%)</th>
<th>bond A-B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>39</td>
</tr>
<tr>
<td>1.6</td>
<td>47</td>
</tr>
<tr>
<td>1.7</td>
<td>51</td>
</tr>
<tr>
<td>1.8</td>
<td>55</td>
</tr>
<tr>
<td>2.1</td>
<td>67</td>
</tr>
<tr>
<td>2.4</td>
<td>76</td>
</tr>
<tr>
<td>2.6</td>
<td>82</td>
</tr>
</tbody>
</table>

To summarize:

- **Non-polar bond** (pure covalent bond)
  - $En_A = En_B$
  - $En_A - En_B < 1.7$

- **Polar covalent bond**
  - $En_A - En_B > 1.7$

The extent of polarity in a bond depends on the electronegativity difference of the two bonded atoms. The following table shows some examples.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>EnA - EnB</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>F-F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OF₂</td>
<td>O-F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF₃</td>
<td>N-F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₄</td>
<td>C-F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BeF₂</td>
<td>Be-F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>Li-F</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When the electronegativity difference between the bonded atoms is large, such as in the case for F and Li, the bond formed will predominantly be ionic.

### 3. Polar covalent bond and dipole moment

In a covalent bond where the bonded electron pair is not shared equally between the bonded atoms, there will be a displacement of the electron cloud. This results in the formation of a dipole with two equal opposite charges (+q and −q) separated by a distance $d$.

This bond is said to be polarized and described as a **polar covalent bond**. The extent of bond polarization can be measured in terms of **dipole moment**, $\mu$, which is given by:

Dipole moments are usually expressed in **Debye (D)** unit.
Dipole moments are vector quantities. For a molecule with more than one polar bond, the dipole moment is given by the vector sum of the dipole moments of various polar bonds. If the vector sum is zero, the dipole moment of the molecule is zero, and the molecule is described as non-polar. The greater the resultant dipole moment, the more polar the molecule is.

The dipole moment of a molecule is determined by three factors:
(i) The difference in electronegativity and thus the degree of ionic character of individual bonds.

Example 1

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye</td>
<td>1.91</td>
<td>1.05</td>
<td>0.80</td>
<td>0.42</td>
</tr>
</tbody>
</table>

(ii) The shape of the molecule.
Dipole moments can provide important structural information about a molecule. As an example, the zero dipole moment of CO₂ shows that the molecule must be linear such that the dipole moment of each C=O bond cancels each other in the vector sum. On the other hand, existence of a dipole moment for SO₂ molecule indicates that the molecule contained polar bonds which are not linearly.

Example 2: The following molecules are non-polar:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>BF₃</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Example 3: The following molecules are polar:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>H₂O</th>
<th>NH₃</th>
<th>SO₂</th>
<th>C₆H₅Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye</td>
<td>1.84</td>
<td>1.48</td>
<td>1.63</td>
<td>1.67</td>
</tr>
</tbody>
</table>

(iii) Bond length
Example 4: CH₃Cl 1.87D  CH₃F 1.81D

4. Experiment: Investigation of the effect of a non-uniform electrostatic field on a jet of liquid

The phenomenon of polarization of covalent bonds may be readily demonstrated with the apparatus show in the following figure.
Unit 4 - 45

The glass rod acquires a positive charge by rubbing it with polythene sheet. The results obtained with a series of liquids are given below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>CHCl₃</th>
<th>CCl₄</th>
<th>CH₂CH₂OH</th>
<th>CH₃COCH₃</th>
<th>C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No deflection occurs with tetrachloromethane because the molecule is symmetrical and the four dipoles cancel each other. Benzene does not possess a permanent dipole but its π electrons are readily displaced and so, in an electric field, it has temporary induced dipole which subsequently causes some deflection.

Section 4.6  Intermolecular Forces

(1) Van der Waals forces
**Van der Waals forces** are weak short-range forces between molecules arising from the attraction between dipoles. The origins of van der Waals forces include dipole-dipole interactions, dipole-induced dipole interactions and instantaneous dipole-induced dipole interactions.

### 1. Dipole - dipole interaction

Polar molecules are molecules with permanent dipoles. Dipole - dipole interaction occurs between the negative end of the dipole moment of one polar molecule and the positive end of the dipole moment of the next polar molecule.

**Example 1**

Propanone is a polar molecule which possesses a permanent dipole. Dipole - dipole interactions exist between propanone molecules:

\[
\text{CH}_3\text{COCH}_3 \quad \text{b.p. 50°C} \quad \text{CH}_3\text{CH}_2\text{CH}_3 \quad \text{b.p. 0°C}
\]

**Example 2**

The existence of dipole - dipole interactions will explain the forces holding together polar molecules in liquids such as trichloromethane, ethoxyethane and nitrobenzene.

### 2. Dipole - induced dipole interaction

Dipole - induced dipole interactions are the intermolecular attractions between polar and non-polar molecules. For instance, a polar water molecule would induce a temporary dipole on a neighbouring non-polar iodine molecule in iodine solution:

### 3. Instantaneous dipole - induced dipole interaction

Molecular elements and even the atomic noble gases can be liquefied and then solidified by cooling. This implies that there are forces of attraction even between non-polar molecules that possess no charge separation.
Examples:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Number of electrons in the molecule</th>
<th>Boiling point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2</td>
<td>- 253</td>
</tr>
<tr>
<td>N₂</td>
<td>14</td>
<td>- 196</td>
</tr>
<tr>
<td>O₂</td>
<td>16</td>
<td>- 183</td>
</tr>
<tr>
<td>Cl₂</td>
<td>34</td>
<td>- 35</td>
</tr>
<tr>
<td>I₂</td>
<td>126</td>
<td>+ 185</td>
</tr>
</tbody>
</table>

The number of electrons in each molecule appears to affect the force of attraction of one molecule for the next. The stronger the attractive force, the higher is the liquid’s boiling point.

Consider a picture of the electron cloud of a diatomic molecule:

![Diagram showing electron cloud of a diatomic molecule](image)

It is quite possible at any moment for the distribution of the electrons to be uneven through the molecule. By chance there may be momentarily a greater electron density at one end of the molecule than the other. This produces an **instantaneous dipole** in the molecule. The instantaneous dipole has the effect of inducing a second dipole on a neighbouring molecule:

![Diagram showing instantaneous dipole and induced dipole](image)

The weak force of attraction between the neighbouring oppositely charged ends of an instantaneous dipole and an induced dipole is called a **van der Waals force**.

### 4. The strength of van der Waals forces

As the **number of electrons** in a molecule increases, the electron cloud will be more diffuse and polarizable. There is more displacement in the electron cloud and unequal distribution of charge. This results in stronger van der Waals forces.
Example 1: Larger alkane members have higher boiling points and densities

In the alkane series, as the length of the carbon chain increases, the molecular size and electron cloud of the alkane molecule increases. Larger molecular electron clouds are more easily displaced and polarized. As a result, van der Waals forces between the alkane molecules then increases. More energy is required to separate neighbouring molecules. This gives rise in the progressively higher boiling points.

Example 2: The melting points and boiling points of halogens increase down the group

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Number of electrons</th>
<th>Bond length nm</th>
<th>Melting point K</th>
<th>Boiling point K</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>18</td>
<td>0.148</td>
<td>53</td>
<td>85</td>
</tr>
<tr>
<td>Cl₂</td>
<td>34</td>
<td>0.198</td>
<td>172</td>
<td>239</td>
</tr>
<tr>
<td>Br₂</td>
<td>70</td>
<td>0.228</td>
<td>266</td>
<td>331</td>
</tr>
<tr>
<td>I₂</td>
<td>106</td>
<td>0.266</td>
<td>387</td>
<td>456</td>
</tr>
</tbody>
</table>

The rise in melting points and boiling points down Group VII is due to the increase in electrons present in the halogen molecules and the consequent increase in van der Waals forces.

Example 3: The boiling points of two structural isomers of C₅H₁₂

In the case of pentane, the ‘linear’ molecules can line up beside each other and the van der Waals forces are likely to be comparatively strong, as they can act over the whole of the molecule.

In the case of 2,2-dimethylpropane, the ‘spherical’ molecules can only become close to one another at one point, so the van der Waals forces are likely to be comparatively weak. The isomer with the linear molecules thus has the higher boiling point.

5. Van der Waals radii

In molecular crystals the van der Waals forces draw molecules together until their electron clouds repel each other to the extent of balancing the attraction.
The atomic distances within simple molecules and between simple molecules are not the same. The **covalent radius** is one half of the distance between two atoms in the same molecule. The **van der Waals radius** is one half of the distance between the nuclei of two atoms in adjacent molecules.

Example 1: Covalent radius and van der Waals radius for molecules of I\(_2\) in an iodine crystal.

Example 2: Comparative values for covalent and van der Waals radii.

<table>
<thead>
<tr>
<th>Element</th>
<th>Covalent radius / nm</th>
<th>Van der Waals radius / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>0.037</td>
<td>0.12</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.075</td>
<td>0.15</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.073</td>
<td>0.15</td>
</tr>
<tr>
<td>P(_4)</td>
<td>0.110</td>
<td>0.19</td>
</tr>
<tr>
<td>S(_8)</td>
<td>0.102</td>
<td>0.18</td>
</tr>
</tbody>
</table>

(2) **Hydrogen bonding**

1. Nature of hydrogen bonding
A **hydrogen bond** is the electrostatic force of attraction between the poorly shielded proton of a hydrogen atom bonded to a small highly electronegative atom such as nitrogen, oxygen or fluorine, and the lone pair electrons of a neighbouring molecule.

Bond enthalpies of typical hydrogen bonds are around 5 - 25 kJ mol\(^{-1}\). Those of typical single covalent bonds are about 150 – 400 kJ mol\(^{-1}\).

**Example 1: Water**

The poorly shielded proton in water molecule is attracted to a lone pair of electrons in a neighbouring water molecule producing a particularly strong type of dipole-dipole interactions. This strong intermolecular force is called hydrogen bonding.

In water, however, there are two O-H bonds and two lone pairs of electrons per H\(_2\)O molecule. This means that each water molecule can form two hydrogen bonds. As a result, water has extremely high boiling point.

**Example 2: Ammonia**

In the NH\(_3\) molecules, there are three N-H bonds and one lone pair electrons. This means that there can be an average of one hydrogen bond per molecule.

**Example 3: Hydrogen fluoride**

How many lone pairs of electrons are there in each HF molecule?

What is the maximum number of hydrogen bonds per HF molecule?

**Intermolecular and intramolecular hydrogen bonding**

Hydrogen bonds may be formed between two molecules (**intermolecular**) or between atoms within the same molecule (**intramolecular**).

**Example 4: 2-nitrophenol and 4-nitrophenol**

2-nitrophenol boils at 489 K and the 4-isomer boils at 532 K.

2-nitrophenol possesses an intramolecular hydrogen bonds, whereas 4-nitrophenol forms intermolecular hydrogen bonds. The intramolecular hydrogen bonds within 2-nitrophenol molecules reduce the chance of intermolecular hydrogen bonds between molecules. Thus less energy is required to separate neighbouring molecules. As a result, 2-nitrophenol boils at lower temperature.

**2. Relative strength of hydrogen bonding and van der Waals’ forces**

Hydrogen bonding is stronger than van der Waals forces and permanent dipole-dipole interactions but weaker than covalent bonding.
**Example 1 : Determination of the approximate strength of hydrogen bonds in water**

The energy which vaporizes water is needed to overcome the forces holding the water molecules in the liquid state. Thus, the enthalpy change of vaporization of water will give a rough idea of the strength of hydrogen bonds between H₂O molecules. The following graph shows the molar enthalpy change of vaporization for the hydrides of Group VI elements. If we assume that H₂S, H₂Se and H₂Te have intermolecular forces due only to van der Waals forces, a value for the strength of van der Waals force in water can be found by extrapolating the curve.

\[
\Delta H_{vap}^\circ \text{kJ mol}^{-1}
\]

<table>
<thead>
<tr>
<th>Relative molecular mass</th>
<th>Estimated strength of van der Waals’ forces in water = 18.5 kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total strength of intermolecular forces in water = 40.7 kJ mol(^{-1})</td>
</tr>
<tr>
<td>Approximate strength of hydrogen bonds in water =</td>
<td></td>
</tr>
</tbody>
</table>

**Example 2 : Determination of the strength of the hydrogen bond formed between CHCl₃ and ethyl ethanoate**

Trichloromethane and ethyl ethanoate do not form hydrogen bonds with themselves. In trichloromethane, three electronegative chlorine atoms are bonded to a carbon atom, their combined electron-withdrawing effect will leave the hydrogen atoms a partial positive charge. As the size of chlorine atom is so large that the approach of hydrogen atoms is made difficult.

However, trichloromethane and ethyl ethanoate can interact through hydrogen bonding:

\[
\text{When 17.7 cm}^3 (0.1 \text{ mole}) \text{ of trichloromethane were mixed with 7.9 cm}^3 (0.1 \text{ mole}) \text{ of ethyl ethanoate in an insulated boiling tube, there was a temperature rise of 17 } \degree \text{C. Given the following data:}
\]

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Relative molecular mass</th>
<th>Density / g cm(^{-3})</th>
<th>Specific heat capacity / J g(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane</td>
<td>119.5</td>
<td>1.48</td>
<td>0.98</td>
</tr>
<tr>
<td>Ethyl ethanoate</td>
<td>88</td>
<td>0.90</td>
<td>1.92</td>
</tr>
</tbody>
</table>

(i) Determine the strength of the hydrogen bond formed between CHCl₃ and ethyl ethanoate.

(ii) Suggest two sources of errors in the determination of the hydrogen bond strength.

**3. Boiling points of the hydrides of Group IV, V, VI and VII**

The graph below shows the variations in the boiling points of Group IV, V, VI and VII hydrides.
Observation 1:
Except NH₃, H₂O and HF, the boiling points of the hydrides of the same group increase as relative molecular masses of the hydrides increase.

Explanation:
As relative molecular mass increases, the electron cloud increases in size and becomes more polarizable. Van der Waals’ forces increase. Therefore, hydrides in any particular group would be expected to have gradually increasing boiling points.

Observation 2:
The three hydrides NH₃, H₂O and HF have much higher boiling points than expected.

Explanation:
The high electronegativities of N (3.0), O (3.5) and F (4.0) and the availability of lone pairs of electrons on these atoms enable hydrogen bonds to form between the molecules. Energy is needed to break the strong hydrogen bonds in ammonia, water and hydrogen fluoride before boiling occurs. Higher boiling points result.

4. Hydrogen bonding in alcohols and carboxylic acids
Hydrogen bonding occurs in any compound containing hydroxyl ( -OH ) groups, such as alcohols and carboxylic acids.

**Alcohols**

Hydrogen bonding occurs between the alcohols molecules:

*Boiling point*: Energy is required to break the hydrogen bonds before the alcohol molecules can escape as vapour. The boiling points of alcohols are therefore higher than expected from relative molecular mass.

*Liquid flow*: Hydrogen bonding affects liquid flow, as well as boiling point. As the number of hydroxyl groups increases, there is a greater degree of hydrogen bonding. The effect on liquid flow and boiling point of increasing the number of hydroxyl groups in alcohols is illustrated by the following data:

<table>
<thead>
<tr>
<th></th>
<th>Propane</th>
<th>Propan-1-ol</th>
<th>Propane-1,2-diol</th>
<th>Propane-1,2,3-triol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point / ℃</td>
<td>- 42</td>
<td>97</td>
<td>189</td>
<td>290</td>
</tr>
<tr>
<td>Liquid flow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Viscosity)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Solubility in water**: hydrogen bond is also formed between water molecules and alcohols. Therefore, alcohols can dissolve in water (especially those of low molecular mass).

**Carboxylic acid**

*Dimer formation*: When carboxylic acid is dissolved in non-polar solvent or exists in vapour state, its relative molecular mass is found to be doubled. It can be deduced that association of carboxylic acid molecules occurs:

For instance, ethanoic acid molecules exist as *dimers* in benzene, its relative molecular mass is found to be 120, instead of the expected 60.

**Solubility in water**: Hydrogen bonds can form between water and the carboxylic acid molecules. Therefore, carboxylic acid (of low molecular mass) can dissolve in water

5. **Hydrogen bonding in ice**
A water molecule has two hydrogen atoms and two lone pairs of electrons on the oxygen atom. Each water molecule can form 2 hydrogen bonds. In ice lattice, each water molecule is hydrogen bonded with four water molecules in the tetrahedral positions. This results in an open lattice of hexagonal network with very inefficient packing of molecules. Therefore, ice has a low density and floats on water.

On melting, the hydrogen bonds in the ice lattice break down. Water molecules can become more closely packed, so that water has a higher density.

At 4 °C, water molecules pack most compactly, and the density of water reaches a maximum.

The fact that ice is less dense than water at 0 °C means that ponds and lakes freeze from the surface downwards and the layer of ice insulates the water below, preventing complete solidification, if ice were more dense than water, water would freeze from the bottom upwards and ponds would freeze completely killing fish, aquatic plants and other water-living creatures.

6. Hydrogen bonding in proteins and DNA
Hydrogen bonding plays a crucial role in the structure of many biochemical substances such as proteins and deoxyribonucleic acids (DNA).

**Proteins**
Proteins consist of long chains of formula

\[
\text{Where } R \text{ can be a number of groups. Protein chains are held in close proximity to one another by hydrogen bonds formed between the N-H and C=O groups of the neighbouring chains.}
\]

**DNA**
In DNA, the two helical nucleic acid chains are held together by hydrogen bonds. These hydrogen bonds are formed between specific pairs of bases on the DNA chains, such as between an adenine unit an one chain and a thymine unit in the other; or between a guanine unit in one chain and a cytosine unit in the other.

![DNA molecule diagram](image)

**Pairs of bases forming hydrogen bonds in DNA**

\[\cdots \text{hydrogen-bonding system} \cdots\]

\[\text{adenine} \quad \text{thymine}\]

\[\text{cytosine} \quad \text{guanine}\]

\[\text{(- - represents hydrogen bond)}\]

The double helix structure maintained by hydrogen bonds between base pairs in helical chains is very important for life.

(3) **Molecular crystals**
Molecular crystals consist of molecules held in lattice sites by weak intermolecular forces such as van der Waals forces or hydrogen bonds. The structures of molecular crystals are determined by the shape of the basic molecular units which tend to pack together as efficiently as possible.

Example 1: Molecular crystal structure of iodine

By X-ray diffraction measurements, the arrangement of \( I_2 \) molecule in solid iodine is shown below:

The arrangement of iodine molecules in the crystal lattice is described as face-centred-cubic. The molecules are arranged in a cube with a molecule at each corner and a molecule at the centre of each face. The coordination number is 12.

Iodine molecules are non-polar. Individual molecules are attracted through van der Waals’ forces.

Example 2: Molecular crystal structure of carbon dioxide

The arrangement of \( \text{CO}_2 \) molecules in the crystal lattice is also face-centred-cubic. The \( \text{CO}_2 \) molecules are arranged in a cube with a molecule at each corner and a molecule at the centre of each face. The coordination number is 12.

By simple van der Waals forces considerations carbon dioxide might be expected to boil at a temperature of about -120 \( ^\circ \text{C} \). The \( \text{CO}_2 \) molecule has 22 electrons and this number lies between that of \( \text{O}_2 \) (16) and \( \text{Cl}_2 \) (34) whose boiling points are -183 \( ^\circ \text{C} \) and -35 \( ^\circ \text{C} \) respectively. In fact, carbon dioxide boils at -80 \( ^\circ \text{C} \), a temperature some 40 \( ^\circ \text{C} \) higher than that predicted by electron number. The carbon dioxide molecular crystal lattice is held together by more than just simple van der Waals forces: there are attractive forces between the opposing dipoles.

Example 3: Buckminsterfullerene (C\(_{60}\))
**Fullerenes** are one of the three types of naturally occurring forms of carbon. They are molecules composed entirely of carbon, taking the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are sometimes called **buckyballs**, while cylindrical fullerenes are called **buckytubes** or **nanotubes**.

Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar.

The smallest fullerene in which no two pentagons share an edge is $C_{60}$ (**buckminsterfullerene**), and as such it is also the most common.

The structure of $C_{60}$ is that of a truncated icosahedron, which resembles a round soccer ball of the type made of hexagons and pentagons, with a carbon atom at the corners of each hexagon and a bond along each edge.

---

1. **Properties of fullerenes**

   In April, 2003, fullerenes were under study for potential medicinal use — binding specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma.

   Fullerenes are not very reactive due to the stability of the graphite-like bonds, and are also sparingly soluble in many solvents. Common solvents for the fullerenes include toluene and carbon disulfide. Solutions of pure Buckminsterfullerene have a deep purple color. Fullerenes are the only known allotrope of carbon that can be dissolved. Researchers have been able to increase the reactivity by attaching active groups to the surfaces of fullerenes. Other atoms can be trapped inside fullerenes, and indeed recent evidence for a meteor impact at the end of the Permian period was found by analysing noble gases so preserved. In the field of nanotechnology, heat resistance and superconductivity are some of the more heavily studied properties.

2. **Fullerenes in mathematics**

   In mathematics, a **fullerene** is a trivalent convex polyhedron with pentagonal and hexagonal faces. Using Euler formula, one can easily prove that there are exactly 12 pentagons in a fullerene. The smallest fullerene is $C_{20}$, the dodecahedron. There are no fullerenes with 22 vertices. The number of fullerenes $C_{2n}$ grows rapidly with increasing $n = 12, 13, \ldots$. But $C_{60}$, the buckminsterfullerene, is the only one has no pair of adjacent pentagons.

---

(4) **The pressure-temperature diagram of water**
(a) The region bounded by the curves represent conditions where a single phase is stable. At any temperature and pressure enclosed by the curves BT and TC, water exists in the **liquid state**. At any temperature and pressure below the curves AT and TC water exists in the **vapour state**.

(b) The curves represent conditions under which two phases are in equilibrium. Curve TC is the vapour pressure curve of water. Along the curve TC water and water vapour are in equilibrium. At point X on this curve, liquid water and water vapour are in equilibrium at a temperature of 373 K (100 °C) and a vapour pressure of one atmosphere (101.325 kPa). 373 K is the **boiling point** of water at one atmosphere.

(c) Curve AT is the vapour pressure curve for ice. Along the curve AT ice and water vapour are in equilibrium. This is often called the **sublimation curve**.

(d) Curve BT is the melting temperature curve. Along the curve BT ice and water are in equilibrium. This curve also shows the effect of pressure on the **melting point** of ice: as pressure increases the melting point of ice decreases slightly. This is unusual because increase of pressure usually favours the formation of solid. In the case of water, higher pressures result in breaking down of the hydrogen bonds which bind the water molecules in ice together in an open structure. As the hydrogen bonds break down, the denser liquid phase of water is thus formed.

(e) At point Y on curve BT ice is in equilibrium with water at a temperature of 273 K (0 °C) and a pressure of one atmosphere. This is the melting point of water at one atmosphere.

(f) The curve ST represents the vapour pressure of water below its freezing point. Since water does not normally exist as a liquid below its freezing point, any point on this curve represents water in a **metastable** condition. This means that water is not in its most stable state at this temperature and pressure. The phenomenon represented by points on this curve is known as **supercooling**.

(g) The vapour pressure curve terminates at point C, this is called the **critical point** of water. At temperatures and pressures above this point water vapour cannot be converted into liquid water no matter how great the applied pressure. In other words, the vapour and liquid forms of water are indistinguishable above this point. The critical temperature of water is 647 K and critical pressure 220 atmospheres.

(h) Point T is known as the **triple point**. At this point, ice, water and water vapour are in equilibrium. It occurs at 273.16 K and 6.03 x 10⁻³ atmospheres. These are the only temperature and pressure values at which all three phases can exist together in equilibrium. Note that the triple point of water is not the same as its normal melting point 273 K. This difference comes about because the normal melting point is the temperature at which ice melts when it is under an atmospheric pressure of 1 atm whereas at the triple point the only pressure exerted is the vapour pressure of water.

**Example 1**

Consider the following phase diagram of a compound X.

![Phase Diagram](image)
State the conditions under which
(i) the solid sublimes.
(ii) the liquid boils below its normal boiling point.
(iii) the solid melts above its normal melting point.

Example 2

The solid-liquid phase boundary of most substances has a positive slope, i.e. m.p. increases as the pressure increases. On the contrary, the solid-liquid phase boundary of water is negative indicating that the m.p. of water decreases as the pressure increases.

(i) Draw a phase diagram for water. Use a vertical arrow to indicate the phase change that occurred if sufficient pressure is applied on ice.

(ii) Ice skaters sometimes find it more difficult to skate when the weather is extremely cold (−30°C or colder) than when it is close to the m.p. of water. Explain by using the phase diagram of water.

As shown by the negative slope of the solid-liquid phase boundary, higher pressure is required to melt ice when it is colder. Under extremely cold weather, it may not be possible to melt ice by applying pressure to provide water on which the skater glides.

(5) The pressure-temperature diagram of carbon dioxide
First of all, the triple point occurs well above one atmosphere at 5.11 atm. Thus, at all pressures below this point, carbon dioxide cannot exist as a liquid. If solid carbon dioxide (dry ice) is warmed at one atm it sublimes at 195 K (-78 °C). This means that it passes directly into the gas phase without becoming a liquid.

The other notable difference is the curve BT which slopes to the right. Molecules of carbon dioxide in the solid phase are packed more closely than in the liquid phase. Thus, unlike water, the solid carbon dioxide is denser than the liquid. This is typical for most substances. An increased of applied pressure thus favours formation of solid carbon dioxide. Consequently, as pressure increases the melting point also increases.

Example 1
A lump of dry ice is placed on a metal spoon. Using the phase diagram of carbon dioxide, explain why does the lump of dry ice appear to shiver? Why does it eventually stop vibrating?

The line between the solid and gaseous phases in the phase diagram represents the conditions that the two phases can coexist. At atmospheric pressure, dry ice sublimes to carbon dioxide gas at -78 °C. As the metal spoon is a conductor of heat and initially at room temperature, it causes carbon dioxide to sublime. As the gas is produced rapidly, the gas pressure pushes against the spoon, and lifts up the lump of dry ice. The dry ice then falls back on the spoon due to its weight. The process is repeated. The dry ice stops vibrating when the spoon is cooled to a temperature that no longer causes rapid sublimation of the solid carbon dioxide.

Example 2
A lump of dry ice is placed in a beaker half-filled with water. Why does dry ice sublime more rapidly when placed in water at room temperature than in air at the same temperature?

As water is a better conductor of heat than air, sublimation of carbon dioxide will take place more rapidly than when exposed to air alone.

Section 4.7  Structures and properties of substances
(1) Physical properties of metals

The solid structure of metals is giant metallic structure. The properties of a metal depend on its crystal structure (closed-packed or open structures) and also on the size of its crystals (grains). Metals usually have high densities, high melting points, high boiling points and high molar enthalpy of fusion and vaporization. In addition, they are good conductors of heat and electricity, and they are malleable and ductile.

Metallic bonding

The valence electrons in metal atoms move about freely within the lattice. Thus, the metal consists of positive ions surrounded by a ‘sea’ of moving electrons. The valence electrons are said to be delocalized as they move from one place to another in the cationic crystal lattice. The negatively charged electrons attract all the positively charged ions and bind them together.

Malleable and ductile

There are no rigid, directed bonds in a metal, so that layers of atoms can slide over each other when a force is applied to it. This relative movement of layers in the metal lattice is called ‘slip’. After ‘slipping’ the metal atoms settle into new positions and the crystal structure is restored. Thus, a metal can be hammered into different shapes or drawn out into a wire, i.e. it is malleable and ductile.

Strength of metals

If the surface of a metal plate is examined closely, it is possible to see small irregularly shaped areas clearly separately from each other by distinct boundaries. These irregularly shaped areas are known as grains. X-ray analysis shows that the metal atoms are packed regularly within the grains.

Metallurgists can increase the strength of metals by inserting barriers in the metal lattice which prevent ‘slip’ occurring. Two important methods of strengthening metals are:
1. reducing the size of the crystals grains,
2. alloying.

Slip does not readily take place across grain boundaries. Thus metals with small grain size and more grain boundaries per unit volume are harder to deform, less malleable and less ductile than metals with larger grains.

Metals will readily form alloys since the metallic bond is non-specific. The presence of small quantities of second element in the metal frequently increases its strength. For example, brass – an alloy of zinc and copper – is much stronger than either pure copper or pure zinc. Atoms of the second metal are different in size to those of the original metal. These differently sized atoms interrupt the orderly arrangement of atoms in the lattice and prevent them sliding over each other.

(2) Physical properties of ionic compounds
The solid structure of ionic compounds is giant ionic structure. Crystals of ionic solids are:
1. hard and brittle,
2. involatile with high melting point and high boiling point,
3. good conductor of electricity when molten, but non-conductor when solid,
4. soluble in polar solvents such as water, but soluble in non-polar solvents such as tetrachloromethane.

**Hardness**

In an ionic solid, every ion is held in the crystal by strong attractions from the oppositely charged ions around it. Consequently, ionic solids are hard and difficult to cut. However, they are also very brittle and may be cleaved using a sharp-edged razor. When the crystal is tapped sharply along a particular plane it is possible to displace one layer of ions relative to the next. As a result of this displacement, ions of similar charge come together. Repulsion then occurs, forcing apart the two portions of the crystal.

**Solubility in water**

When ionic solid dissolves in water, the positive ends of polar water molecules are attracted to negative ions in the crystal and negative ends of the water molecules are attracted to positive ions. The formation of ion-water attractions results in a release of energy. This is sufficient to cause the detachment of ions from the crystal lattice. Thus, ionic crystals will often dissolve in polar solvents such as water, ethanol and propanone.

**Solubility in non-polar solvents**

Non-polar liquids such as tetrachloromethane, benzene and hexane will not solvate ionic solids. Non-polar molecules are held together by weak intermolecular forces (van der Waals’ forces). These are much smaller in magnitude than the forces between ions in an ionic crystal. The ion-ion attractions are in fact much stronger than either the solvent-solvent interactions or the ion-solvent interactions. So the non-polar solvent molecules cannot penetrate the ionic lattice. Thus, ionic solids are virtually insoluble in non-polar solvents such as tetrachloromethane and benzene.
(3) **Physical properties of covalent substances**

1. **Giant covalent structure**

   In covalent crystals such as diamond and quartz, the atoms are bonded together by strong covalent bonds and all the valence electrons are highly localized as bonding electron pairs. Such covalent compounds therefore possess the following characteristic properties:

   (i) They are extremely hard because each atom is held firmly in position by strong covalent bonds.
   (ii) They have very high melting points and boiling points because many covalent bonds must be broken to destroy the giant covalent structure.
   (iii) Since there are no free electrons they are poor conductors of heat and of electricity.
   (iv) Incident light is not absorbed and so they are often transparent.

2. **Simple molecular structure**

   Molecular crystals such as iodine, dry ice and ice have the following properties:

   (i) They are usually soft.
   (ii) They have low melting points and boiling points.
   (iii) They do not conduct electricity when molten or in aqueous solution.

   The properties of molecular crystals can be explained in terms of their structure which consists of simple molecules. Although the atoms within these molecules are joined by strong covalent bonds, the separate molecules are held together by very weak intermolecular forces such as van der Waals forces. These weak intermolecular forces permit the molecules to be separately easily. Hence molecular crystals of simple molecular structures are usually soft with low melting points and low boiling points.

   Molecular crystals contain neither delocalized electrons nor ions. Thus, they cannot conduct electricity when molten or when dissolved in water.

**Solubility in water**

In liquids of high polarity such as water, there are strong water-water attractions (hydrogen bonding). These are considerably stronger than either solute-solute attractions or solute-water attractions. Consequently, molecules of molecular crystals cannot penetrate the water molecules and there is little tendency for water molecules to solvate them. Molecular crystals is therefore almost insoluble in water

Example: Iodine is only slightly soluble in water

**Solubility in non-polar solvents**

In non-polar liquids, such as benzene and tetrachloromethane, there are weak intermolecular forces (van der Waals forces). The solvent-solvent attractions are similar in strength to solute-solute and solute-solvent attractions. Thus, it is easy for solvent molecules to penetrate into the molecular crystal and solvate the solute molecules.

Example: Iodine is soluble in benzene

(4) **Differences in physical properties between metals, ionic compounds and**
## Covalent Substances

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ionic Compound</th>
<th>Covalent Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td>Giant metallic</td>
<td>Giant ionic</td>
</tr>
<tr>
<td><strong>Constituents</strong></td>
<td>Atoms</td>
<td>Ions</td>
</tr>
<tr>
<td><strong>Type of Substance</strong></td>
<td>Metal element with low ionization enthalpy</td>
<td>Metal/non-metal compound with large difference in electronegativity between elements</td>
</tr>
<tr>
<td><strong>Nature of Bonding</strong></td>
<td>Electrostatic attraction of mobile valence electrons for positive metal ions binds metal atoms together through metallic bonds</td>
<td>Electrostatic attraction between positive ions and negative ions form strong ionic bond</td>
</tr>
<tr>
<td><strong>Examples</strong></td>
<td>Copper, iron, sodium</td>
<td>Sodium chloride, caesium chloride</td>
</tr>
<tr>
<td><strong>Melting Point</strong></td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td><strong>Boiling Point</strong></td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>Hard but malleable and ductile</td>
<td>Hard and brittle</td>
</tr>
<tr>
<td><strong>Electrical Conductivity</strong></td>
<td>Good conductor when solid or liquid</td>
<td>Non-conductor when solid, good conductor when molten or in aqueous solution</td>
</tr>
<tr>
<td><strong>Solubility in Polar Solvent</strong></td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td><strong>Solubility in Non-Polar Solvent</strong></td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>