02 Chemical Bonding

GUIDING QUESTIONS

- What holds particles together?
- What are the different models that describe the forces that hold particles together?
- How do these models explain the properties of matter?
- How do we determine the shapes of molecules?
- What are the trends and variations in physical properties in compounds?
- How can the trends and variations in physical properties be explained?

LEARNING OUTCOMES

Students should be able to:

2(a) show understanding that all chemical bonds are electrostatic in nature and describe:
  - **(i)** ionic bond as the electrostatic attraction between oppositely charged ions
  - **(ii)** covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
  - **(iii)** metallic bond as the electrostatic attraction between a lattice of positive ions and delocalized electrons

2(b) describe, including the use of 'dot-and-cross' diagrams:
  - **(i)** ionic bonding as in sodium chloride and magnesium oxide
  - **(ii)** covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
  - **(iii)** co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule

2(c) describe covalent bonding in terms of orbital overlap *(limited to s and p orbitals only)*, giving σ and π bonds

2(d) explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory

2(e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)

2(f) explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is not required]

2(g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d));

2(h) describe the following forces of attraction (electrostatic in nature):
  - **(i)** intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3(l)$; $Br_2(l)$ and the liquid noble gases
  - **(ii)** hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups

2(i) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water

2(j) explain the terms bond energy and bond length for covalent bonds

2(k) compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity

2(l) describe, in simple terms, the lattice structure of a crystalline solid which is:

- **(i)** ionic, as in sodium chloride, magnesium oxide
- **(ii)** simple molecular, as in iodine
- **(iii)** giant molecular, as in graphite; diamond
- **(iv)** hydrogen-bonded, as in ice
- **(v)** metallic, as in copper

[the concept of the 'unit cell' is **not** required]

2(m) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

2(n) suggest the type of structure and bonding present in a substance from given information

5(b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionization energy and electronegativity,

- **(i)** across a Period in terms of shielding and nuclear charge,
- **(ii)** down a Group in terms of increasing number of electronic shells and nuclear charge

(Refer to Topic 1 Atomic Structure & Physical Periodicity for trends and variations in atomic and ionic radii, and first ionization energy.)

5(c) interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular)

11.1(d) describe *sp*^{3} hybridisation, as in ethane molecule, *sp*^{2} hybridisation, as in ethene and benzene molecules, and *sp* hybridisation, as in ethyne molecule (Refer to Topic 12 Arenes with regards to benzene)

11.1(e) explain the shapes of, and bond angles in, the ethane, ethene, benzene and ethyne molecules in relation to σ and π carbon-carbon bonds (Refer to Topic 12 Arenes with regards to benzene)

REFERENCES

1. Peter Cann and Peter Hughes, Chemistry for Advanced Level, 1st Edition, John Murray (Publishers) Ltd, Chapters 3 & 4.
2. Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, Global Edition, Chapter 9 to 12.
3. http://www.chemguide.co.uk/index.html

1 INTRODUCTION

LOOKING BACK

The discovery of electrons by J. J. Thomson and the development of the atomic model, led to the development of the concept of a chemical bond. As you uncover the nature of the chemical bond, consider the following questions:

- Which parts of the atom is responsible for chemical bonding?
- How does the structure of the atom affect the chemical bonding it participates in?

1.1 Overview

Why is copper (and most other metals) shiny, malleable and able to conduct electricity when solid or molten? Why is table salt (or any other ionic substance) a hard, brittle, high-melting solid that conducts electricity only when molten or dissolved in water? Why do simple molecular substances, which is the main ingredient of candle wax, have a low melting point, is soft and non-conducting, while diamond (or other giant molecules like Si or SiO_2) has a high melting point and is extremely hard? The answer lies in the type of bonding in the substance.

In nature, only six elements exist as free, unbonded atoms at room temperature and pressure. These are the noble gases. All other elements exist in a form in which their atoms are said to be chemically bonded to each other – in the form of a metallic lattice, an ionic compound or a covalent molecule (simple molecules like O_2, HCl and pentane; or giant molecules like diamond).

Why do atoms bond? Bonding lowers the potential energy between positive and negative particles, which could be metal cations and delocalised valence electrons, oppositely charged ions, or atomic nuclei and the electrons between them. The natural state of most atoms, the state in which they have the lowest energy, is the bonded state. This also means that the bonded state is energetically more stable than the unbonded state. Energy is given off when atoms form bonds. On the other hand, it always requires an input of energy to break a chemical bond – bond breaking is endothermic.

When atoms bond, the electrons in one atom are attracted to the nucleus of another atom. The three major types of chemical bonding – metallic, ionic and covalent – differ only in how far this attraction to another nucleus overcomes the attraction of the electron to its own nucleus. It is the valence electrons of the atoms that are involved in bonding. These valence electrons may be transferred from one atom to another or be shared between two or more atoms. Just as the electronic configuration and the strength of the nucleus-electron attraction determine the properties of an atom, the type and strength of chemical bonds determine the properties of a substance.

In this topic, we will study how atomic properties give rise to the three major types of chemical bonding. We will practice drawing dot-and-cross diagrams to illustrate ionic and covalent bonding. In covalent bonding, the bonded atoms share electrons and that is achieved through overlapping of orbitals. A simple covalent molecule is a fine little unit of architecture – a molecule containing three or more atoms has a three-dimensional shape. Simple covalent molecules form intermolecular attractions. We will study how each model of bonding and intermolecular attractions explains physical properties of substances such as melting and boiling points, electrical conductivity and solubility in water versus organic solvents. We will be able to interpret, explain or even predict the physical properties from the type of structure and bonding present in a given substance.

1.2 Nature of a Chemical Bond

Electrostatic attraction and repulsion is the fundamental force that governs how charged particles interact. In Topic 1 Atomic Structure, the electrostatic force gives rise to the attraction that the nucleus exerts on electrons. It also determines the size of the atom, and the amount of energy needed to remove an electron from an atom.

Similarly, **all chemical bonds involve electrostatic forces of attraction between positively and negatively charged particles**, which could be metal cations and delocalised valence electrons, oppositely charged ions, or atomic nuclei and the electrons between them.

1.3 Electronegativity

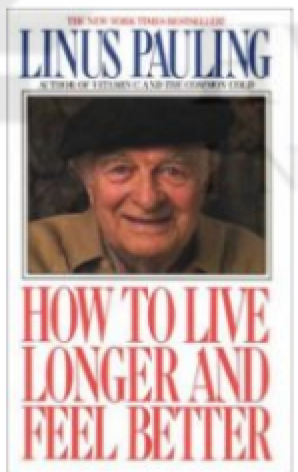
In Topic 1 Atomic Structure, you learnt about effective nuclear charge, which gives rise to a net force experienced by the outermost electrons of an atom. However, in that topic we only considered an unbonded atom. In reality, the electrostatic force of attraction due to the effective nuclear charge of the atom extends beyond the outermost electron.

When two atoms are in proximity, the nucleus of each atom exerts an attractive force on its own electrons as well as the electrons of the other atom and also a repulsive force on the nucleus of the other atom. There is a net attractive force on the electrons of the other atom. So how do we know how strongly each atom attracts the electrons of another atom?

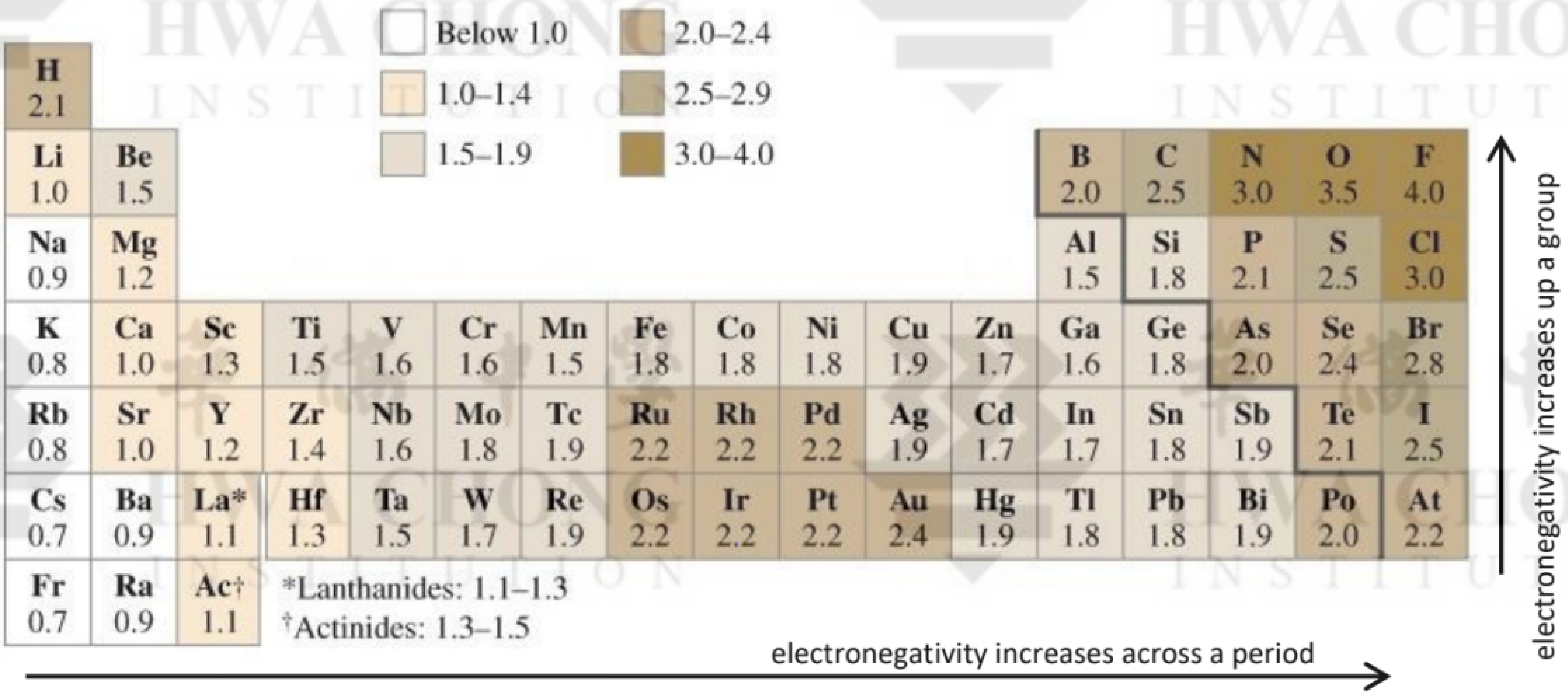
Electronegativity is a concept introduced by Linus Pauling that helps us to answer this question. It quantifies the attractive force one atom exerts on the electrons of another atom in close proximity. A larger number implies a larger force of attraction towards electrons.

Thus, the **electronegativity** of an atom is a measure of its **ability to attract the electrons** in a **covalent bond** to itself.

Using various properties of molecules such as the energy needed to break bonds and the dipole moments, Pauling devised an electronegativity scale and he assigned numerical values to the elements on a scale of 0 to 4.



Linus Carl Pauling (1901 – 1994), American chemist, biochemist, peace activist, author and educator. He was one of the most influential chemists in history. He is also the only person who won two unshared Nobel Prizes – Nobel Prize in Chemistry (for his research in the nature of the chemical bond and its application to elucidation of the structures of complex substances) and Nobel Peace Prize (for campaigning for nuclear disarmament). One of the founders of the fields of quantum chemistry and molecular biology, he was also known for creating concepts like bond order, electronegativity, orbital overlap and resonance. In 1932, he published his paper on the hybridisation of atomic orbitals and the tetravalency of carbon.



H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.7	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

☐ Below 1.0
▨ 1.0–1.4
▨ 1.5–1.9
▨ 2.0–2.4
▨ 2.5–2.9
▨ 3.0–4.0

*Lanthanides: 1.1–1.3
†Actinides: 1.3–1.5

Figure 1. Electronegativity values for the elements; to which group of elements do you think Pauling assigned an electronegativity value of zero?

You are not required to memorise any of the electronegativity values!
However, you are expected to describe and explain the following trends, bearing in mind that the electronegativity of an atom depends on its effective nuclear charge or the number of electron shells.

- **Electronegativity increases across a period**

  Reason:
  Across the period, the effective nuclear charge increases due to the increase in nuclear charge while shielding effect remains relatively constant (hence the attractive forces between the nucleus and the outermost electron are stronger) and the nucleus has a greater attraction for electrons of another nucleus. Thus, the greater the electronegativity of an atom.

- **Electronegativity decreases down a group**

  Reason:
  Down the group, the larger the atom due to the increase in the number of electron shells, (and thus the longer the distance and the weaker the attraction between the nucleus and the outermost electron), the nucleus has a weaker attraction for electrons of another nucleus. Thus, the smaller the electronegativity of an atom.

- **The most electronegative atoms are F > O > N**

1.4 Electronegativity and the Classification of the Type of Chemical Bonding formed

Previously, when exploring Chemistry at the O-Levels, you have learned that ionic bonding generally occurs in compounds formed by metals and non-metals, while covalent bonding generally occurs in compounds formed by non-metals.

In reality, it is difficult to classify all types of chemical bonding using these two simple descriptions. Instead, the difference in electronegativity between two atoms is the best predictor of the type of bond formed between them. The description of ionic and covalent bonding are simply two extremes of a continuum, between which most actual cases of bonding fall – this means that most cases of chemical bonding has characteristics of both ionic and covalent bonding, each to differing extents (see Section 6).

In general,

- Covalent bonds are formed between atoms of non-metals of similar electronegativity, resulting in electron sharing.
- Ionic bonding occurs between a metal and non-metal with a great difference in electronegativity, resulting in electron transfer.
- Metallic bonding is not part of the continuum described above, and occurs between metals, resulting in a type of electron sharing that is different from covalent bonding, i.e. a 'sea of delocalised electrons'.

While the classification of chemical bonds should be viewed as a continuum, it is nevertheless useful and convenient to define three *idealized* classes of chemical bonds with distinct properties – metallic bonding, ionic bonding and covalent bonding. In the later sections, we will discuss the nature of each of these three classes of chemical bonds, and how it gives rise to the physical properties of the substance.

2 METALLIC BONDING & PHYSICAL PROPERTIES OF METALS

2.1 Metallic bonding & the metallic lattice

Metals in the solid state have a **giant metallic lattice structure** held together by **metallic bonding**. **Metallic bonding** is the **electrostatic forces of attraction** between **a lattice of metal cations** and the **sea of delocalised electrons** in a metal.

A clue to the nature of metallic bonding comes from studying the atomic properties of metallic elements – the Group 1, 2 and 3 metals all have respectively only one, two or three electrons in the outer shell, and have low ionisation energies. The physical property that is most characteristic of metals, their electrical conductivity, increases as the number of ionisable outer shell electrons increases. Electrical conductivity depends on the presence of mobile carriers of electric charge – in this case the outer shell electrons or valence electrons.

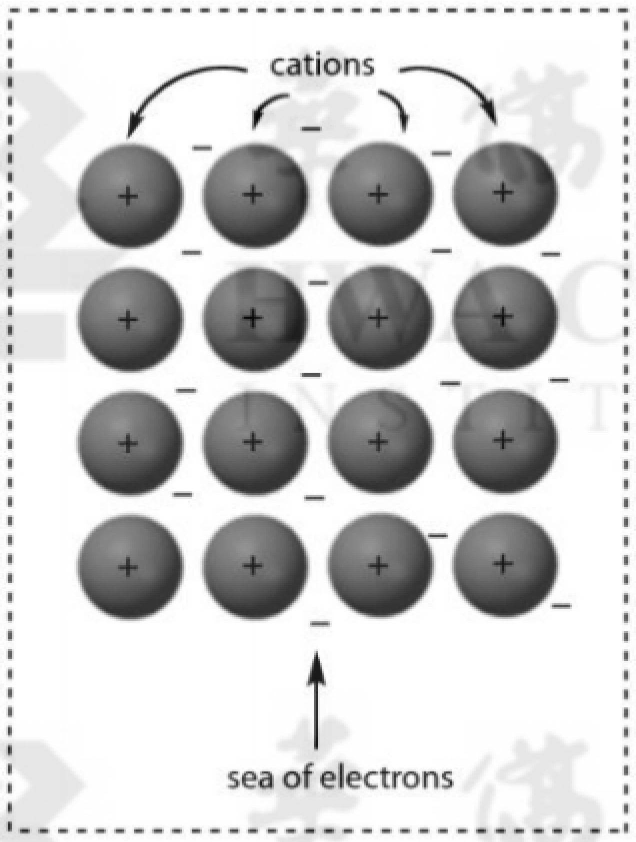


Figure 2. The metallic lattice

In this simplified model of metallic bonding, all the metal atoms in a piece of metal 'pool' their outer shell electrons into an evenly distributed 'sea' of electrons that 'flows' between and around the metal-ion cores (nucleus plus inner shell electrons, i.e. metal cations) and attracts the metal cations, thereby holding them together. The electrons in metallic bonding are said to be delocalised, moving freely throughout the piece of metal.

Note: The metal is electrically neutral as the number of positive and negative charges balance out.

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Self-Practice 2.1

Describe the structure and bonding in calcium with the aid of a labelled diagram.

[N2013/II/4(b)(i)]

2.2 Factors affecting the strength of metallic bonding

The strength of metallic bonding is determined by:

1. **Number of valence electrons contributed per metal atom** into the sea of delocalised electrons. The larger the number of valence electrons contributed per atom, the greater the number of delocalised electrons, the stronger the metallic bonding.
2. **Charge, and radius of the metal cation**. The higher the charge and the smaller the radius of the metal cation, the higher its charge density, the stronger the metallic bonding.
   (The charge density of an ion, sometimes called surface charge density, is the amount of charge per unit surface area of that ion by treating it as a sphere. For simplicity, we can compare the charge densities of two ions by determining the ratio of charge/ionic radii.)

2.3 Physical properties of metals

High melting and boiling points

The attraction between the delocalised electrons and these positive ions is strong and is responsible for the strength of the metallic lattices, and for their fairly high melting and boiling points.

Table 1. Melting and boiling points of metals are usually high

Metal	sodium	magnesium	titanium	copper	iron	silver
Melting point /°C	98	649	1668	1083	1535	962
Boiling point /°C	883	1091	3287	2562	2862	2162

In molten metal (liquid state), metallic bonding is still present, although the ordered structure has been broken down. The metallic bonding **is not completely broken until the metal boils**. This means that the boiling point is actually a better guide to the strength of metallic bonding than the melting point is. **On melting, the metallic bonding is weakened, not broken**.

Good electrical conductivity and thermal conductivity

In order for a material to conduct electricity, it must have mobile charge carriers which are typically electrons or ions. Metals are good electrical conductors because the delocalised 'sea' of electrons, which act as mobile charge carriers, are free to move about. When a piece of metal is attached to a battery, electrons flow from the negative terminal into the metal and replace electrons flowing from the metal into the positive terminal.

Metals are good conductors of heat because of the mobile delocalised electrons. Thermal energy is picked up by the electrons as additional kinetic energy which makes them move faster. The energy is transferred throughout the rest of the metal by the moving electrons. So heat flows quickly from the hotter part to the cooler part of the metal.

Hardness

Metals are usually hard e.g. iron is hard and has good mechanical strength – meaning that it does not deform easily when subjected to the stress of physical forces. However, the Group 1 and 2 metals are soft e.g. sodium can be cut easily with a pen knife.

The hardness of a solid material depends on how easily we can move the particles from their fixed position in the solid lattice. In metals, this depends on the strength of metallic bonding.

Malleable and ductile

Metals are usually malleable (can be beaten or rolled into sheets) and ductile (can be drawn out under tension into rods, wires and tubes).

When a large stress (e.g. hammering) is applied to a piece of solid metal, the layers of ions will slide over one another into new positions. The overall shape of the metal piece changes (the metal deforms) but it does not break or shatter apart because the 'sea' of delocalised electrons prevents repulsion between the cations as they move past one another, and metallic bonding remains intact.

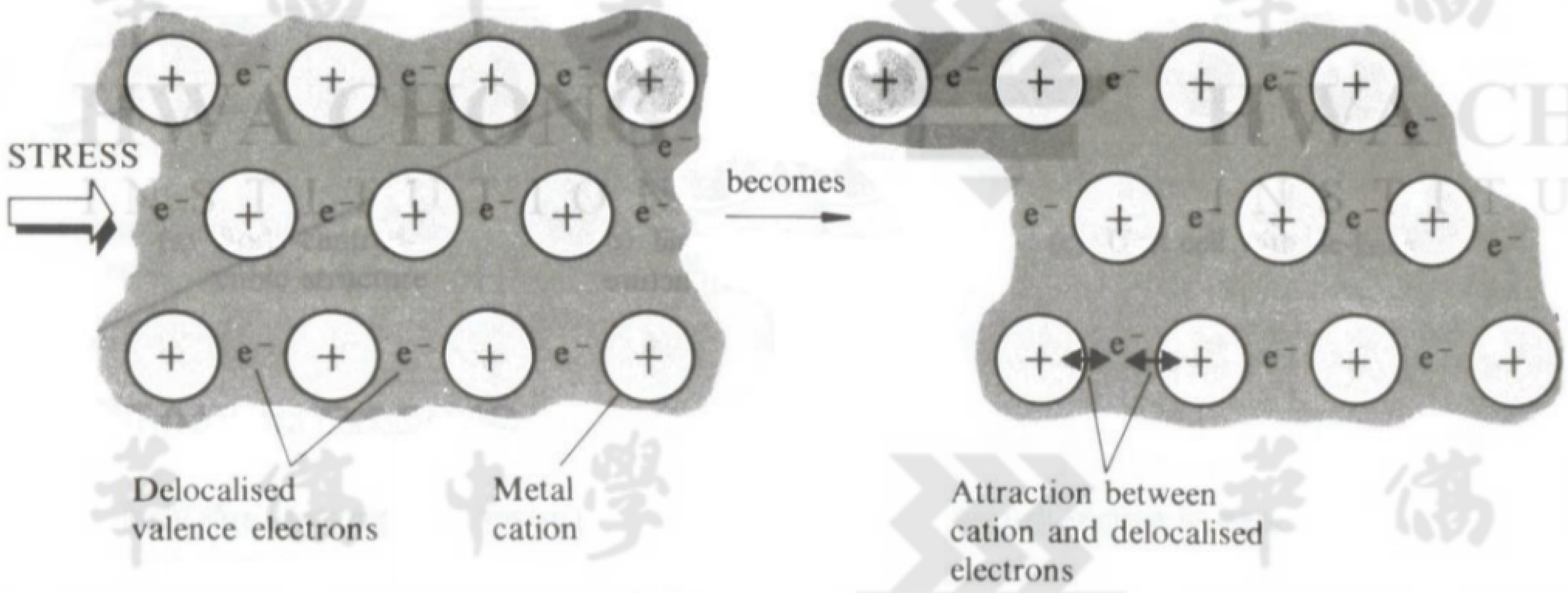

Figure 3. The metallic lattice when subjected to shear stress

Self-Practice 2.2

Explain why the melting point of Na (98 °C) is lower than that of Mg (649 °C), quoting relevant data from the *Data Booklet*.

2.4 Alloys & their uses

Most metals used in practical applications such as aluminium aircraft frames are in the form of an alloy instead of the pure metal.

Alloys are mixtures of metals involving incorporation of small quantities of other element(s) into the pure metal. Alloying makes metals harder. This is because atoms of the added element(s) have a different size. This will disrupt the orderly arrangement of the main metal atoms such that they can no longer slide over each other easily when a force is applied. This increases the hardness and strength of the alloy compared to the pure metal.

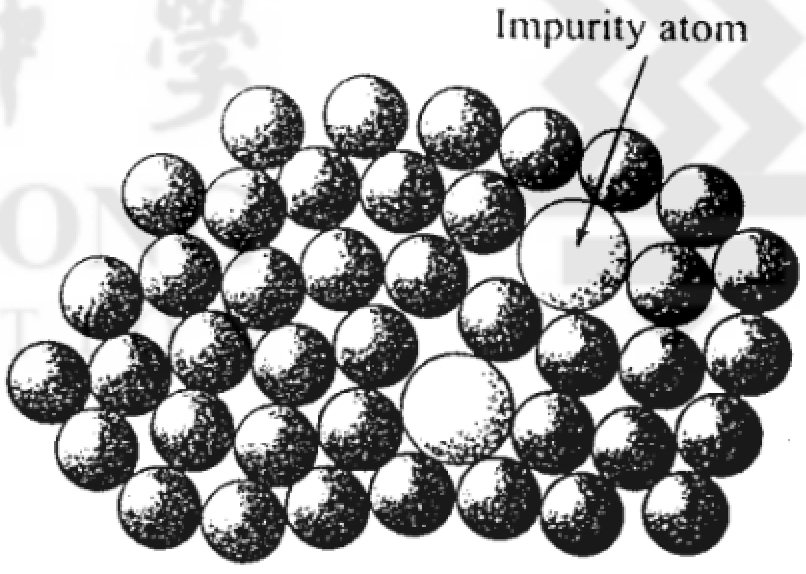

Figure 4. Arrangement of atoms in an alloy

Table 2. Common uses of some alloys

Alloy	Parent element	Alloying element(s)	Characteristics	Uses
bronze	copper (90%)	tin (10%)	hard and strong	ship propellers
brass	copper (70%)	zinc (30%)	corrosion resistant	castings, hardware items, boilers in ships
steel	iron (99.8%)	carbon (0.2%)	hard and strong	bridges, buildings
stainless steel	iron (74%)	chromium (18%) nickel (8%)	strong and corrosion resistant	hospital and chemical equipment, cutlery
pewter	tin (97%)	copper + antimony (3%)	hard and strong	ornaments

Metals are useful materials because of their malleable and ductile properties, conductivity as well as high melting points.

Most metals are produced commercially from subsurface ores (oxides, sulfides, halides, silicates, carbonates and sulfates). Hence metals are a finite resource. Recycling is not only environmentally friendly, but also cost effective. For example, recycling aluminium requires less than 1% of the energy required for the entire manufacturing process (mining, pretreating, maintaining operating conditions, electrolysing, etc) of producing the element from its ore.

Self-Practice 2.3

1. Which of the following are features of the structure of metallic copper?

1 ionic bonds
2 delocalised electrons
3 lattice of ions

A **1**, **2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

[N1988/III/32]

2. Why does copper wire conduct electricity when a potential difference is applied?

A Bonding electrons in the crystal lattice move.
B Copper(II) ions move to the cathode.
C The atoms of copper become ionised.
D The crystal lattice breaks down.

[J2002/I/5]

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3 IONIC BONDING & PHYSICAL PROPERTIES OF IONIC COMPOUNDS

3.1 Formation of ionic bonding

Ionic compounds in the solid state have a **giant ionic lattice structure** held together by **ionic bonding**. **Ionic bonding** is the **electrostatic forces of attraction** between **oppositely charged ions** in an **ionic compound**.

We typically observe ionic bonding between elements with large differences in electronegativity. One such difference occurs between reactive metals (Group 1 and 2 metals) and non-metals (Group 16 chalcogens and Group 17 halogens). The metal atom (low ionisation energy) loses its one or two valence electron(s), whereas the non-metal atom gains the electron(s). Electron transfer from metal to non-metal occurs, and each atom forms an ion with a noble gas electronic configuration. The electrostatic attraction between these positive and negative ions draws them into a regular three-dimensional array of an ionic solid, whose **chemical formula represents the cation-to-anion ratio (empirical formula) in the ionic lattice**.

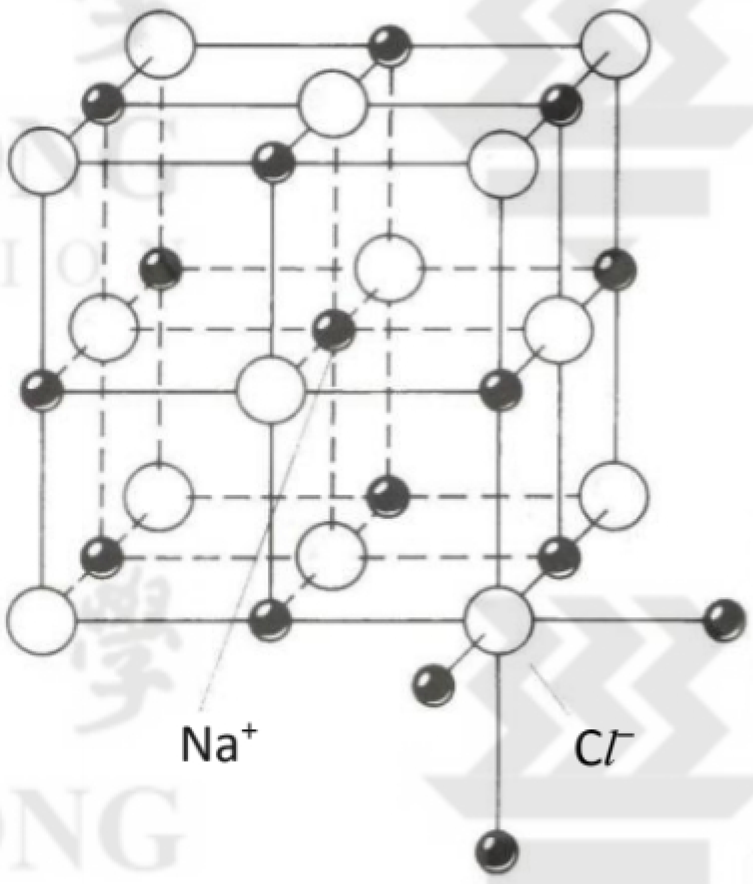

Figure 5. Model of the NaCl lattice, the ions are arranged in a regular three-dimensional structure

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Self-Practice 3.1

Sodium forms the oxide Na_2O. Explain why the oxide of sodium has this formula.

[N2006/III/4(a)]

3.1.1 Dot-and-cross diagrams for ionic compounds

The **dot-and-cross diagram** gives a method for depicting the **valence electrons** of interacting atoms as well as the type of bond (ionic or covalent) present. The **element's symbol represents the nucleus *and* the inner shell electrons**, and the **surrounding dots and crosses represent the valence electrons**.

$$Na + \tfrac{1}{2}Cl_2 \rightarrow NaCl$$

$$Mg + Cl_2 \rightarrow MgCl_2$$

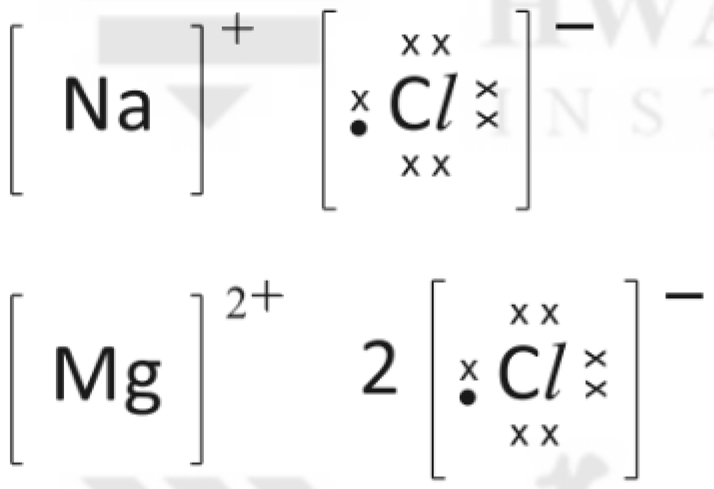

Figure 6. Balanced equation showing the formation of the ionic compounds, NaCl and $MgCl_2$. The dot-and-cross diagrams for the two compounds are also shown.

Gilbert Newton Lewis (1875 – 1946), American physical chemist known for the discovery of the covalent bond. His many contributions shaped the modern theories of chemical bonding. His 'electron-dot symbols' have become standards for representing bonding (later evolved into the 'dot-and-cross diagrams' and 'Lewis structures'). He coined the term 'photon' for the smallest unit of radiant energy. He discovered that many atoms in molecules have a valence shell of 8 electrons, which he called the 'rule of 8'; this was later refined by Irving Langmuir (American chemist and physicist) as the 'octet theory'.

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Self-Practice 3.2

Draw the dot-and-cross diagrams for the ionic compounds below.

a) potassium bromide

b) sodium oxide

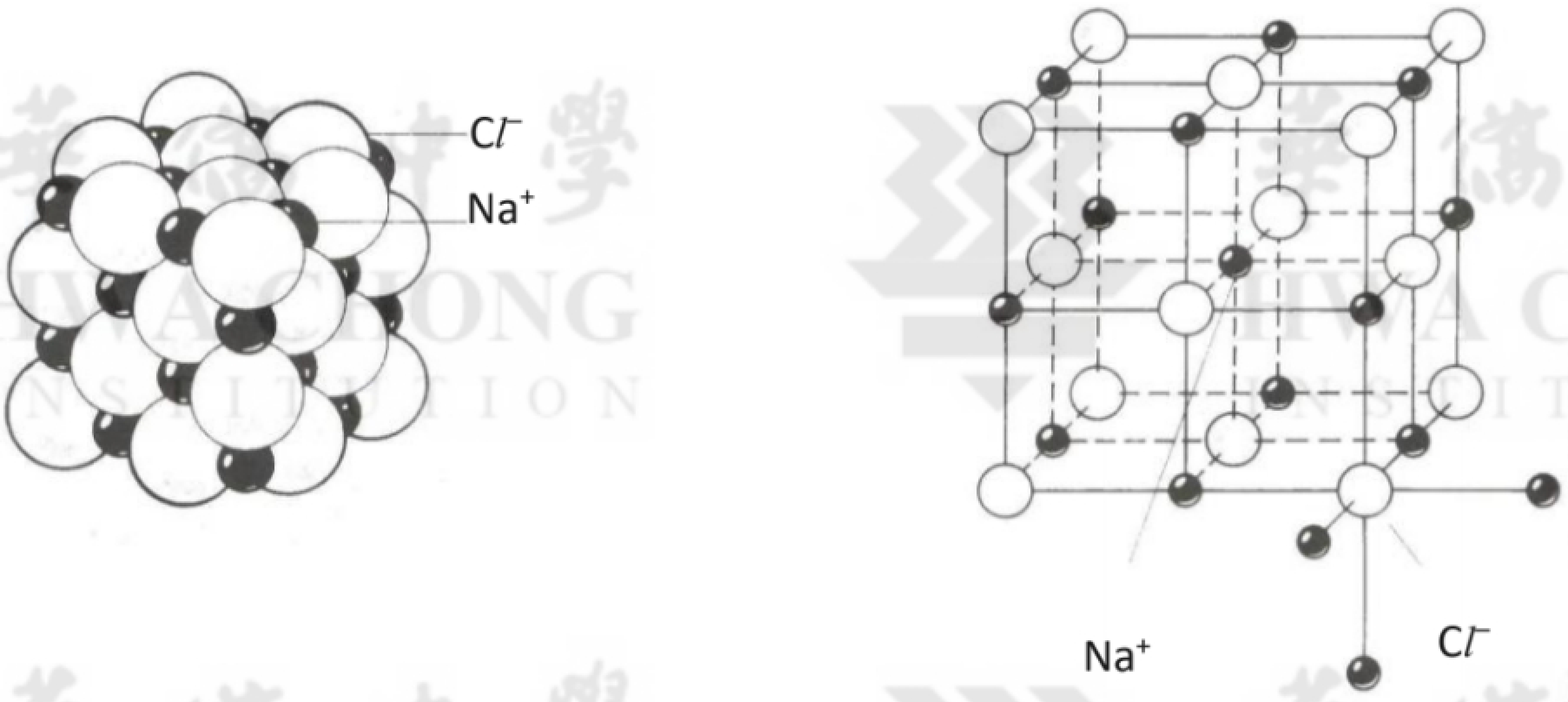
c) aluminium fluoride

d) aluminium oxide

3.2 The ionic lattice & coordination number

Now we have seen how individual ions are formed, we shall turn our attention to how they collect together in a **giant lattice**. Oppositely charged ions attract each other while ions of like charges repel each other. We therefore expect to find that each cation in an ionic lattice will be surrounded by a number of anions as its closest neighbours, and each anion will in turn be surrounded by a number of cations. We will not find two cations, or two anions, adjacent to each other.

The diagrams below are models of the sodium chloride lattice. As illustrated in the expanded version, one Na^+ cation is surrounded by six Cl^- anions and vice-versa. The force of attraction – ionic bonding – exists between *any two* adjacent ions of opposite charge. Ionic bonding is thus said to be *non-directional* (while a covalent bond is *directional* because one covalent bond can only be formed between *two specific* atoms).



Space-filling model Expanded model

Figure 7. Models of the NaCl lattice. The space-filling model illustrates the close packing of ionic solids while the expanded model shows the coordination number of each ion and the orderly arrangement within the giant ionic lattice.

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The number of ions that surround another ion of the opposite charge in an ionic lattice is called the **coordination number** of that central ion. The coordination number of an ion in an ionic lattice depends on two things – the relative sizes of the ions, and their relative charge.

If one of the ions is very small, there will not be room for many oppositely charged ions around it e.g. the maximum coordination number for Zn^{2+} is usually four as it is a smaller ion than Na^+. If the cations and anions are nearly equal in size, one ion can be surrounded by eight others. The intermediate case of six neighbours occurs when one ion is bigger than the other, but not by very much.

To gain electrical neutrality, a cation with +2 charge needs twice as many anions with –1 charge, compared to a cation with +1 charge. We therefore find that the Ca^{2+} cation in calcium chloride, $CaCl_2$, is surrounded by twice as many Cl^- anions as compared to the Li^+ cation in lithium chloride, LiC*l*.

The two factors are illustrated in the table below. This is for illustration purpose only, we are not required to memorise which type of ion has coordination number 4, 6 or 8. [See **N2009/III/1(d)**]

Table 3. Coordination number of an ion in an ionic lattice depends on relative sizes and charges of cation and anion

Compound	Cation radius /nm	Anion radius /nm	$\frac{\text{Anion radius}}{\text{Cation radius}}$	Coordination number of cation	Coordination number of anion
ZnS	0.08	0.19	2.4	4	4
NaC*l*	0.10	0.18	1.8	6	6
MgO	0.07	0.14	2.0	6	6
CsC*l*	0.17	0.18	1.1	8	8
CaF_2	0.10	0.13	1.3	8	4

3.3 Factors affecting the strength of ionic bonding

The strength of ionic bonding is determined by the **charge of the ions**, and their **radii**. The higher the charge and the smaller the radii of the ions, the stronger the ionic bonding.

We may compare the strength of ionic bonding using the term, lattice energy.

Lattice energy is defined as the heat evolved when 1 mole of a pure ionic solid is formed from its constituent gaseous ions. For example, the lattice energy of MgO is the energy released during the reaction, $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$, which has a value of –3791 kJ mol^{-1}. This is a bond forming process. For NaC*l*, its lattice energy has a value of –787 kJ mol^{-1}. Lattice energy gives an indication of the strength of ionic bonding – the larger its magnitude, the stronger the ionic bonding.

There is a simplified mathematical relationship between the magnitude of the lattice energy and the ionic radii and charge.

$$\textbf{Lattice energy} \ \alpha \ \frac{q_+ \times q_-}{r_+ + r_-}$$

where q_+ = charge on cation, q_- = charge on anion
r_+ = radius of cation, r_- = radius of anion

So the magnitude of the lattice energy of an ionic compound depends on these two factors – ionic charge and ionic radius.

Self-Practice 3.3

Using the concept of lattice energy, predict with reasoning which compound, Na*Cl* or MgO, has the higher melting point.

3.4 Physical properties of ionic compounds

High melting and boiling points

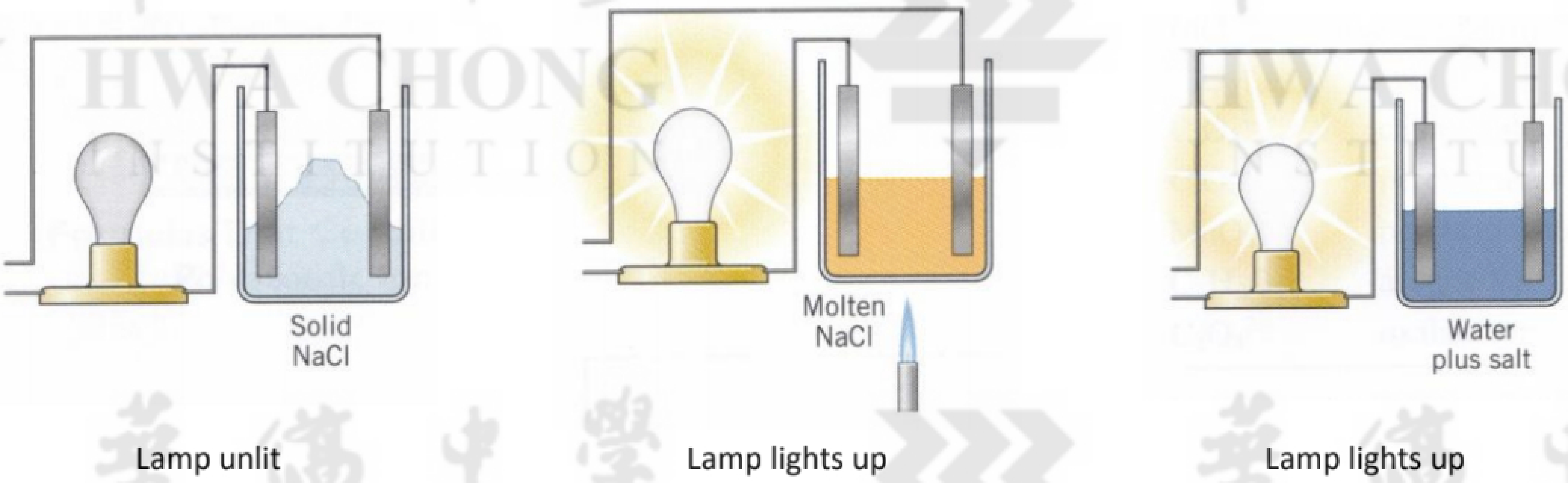
There are strong electrostatic attractions between oppositely charged ions in the giant lattice. We therefore expect that ionic solids will have high melting points. On melting, although the ordered lattice is broken down, there is still a significant level of attraction between the mobile ions in the liquid state. This will result in high boiling points. **Ionic attractions are stronger if the ions possess higher charge or are smaller**, as shown in the table below.

Table 4. Small, highly charged ions bond strongly leading to high melting points

Compound	Cation radius /nm	Anion radius /nm	Cation charge	Anion charge	m.p. /°C
Na*Cl*	0.10	0.18	+1	–1	801
NaF	0.10	0.13	+1	–1	993
MgF_2	0.07	0.13	+2	–1	1261
MgO	0.07	0.14	+2	–2	2852

Good electrical conductors when molten or dissolved in water

The conduction of electricity is the movement of electrical charge. The cation or anion that make up an ionic compound has an electrical charge. In the solid state, ionic compounds do not conduct electricity as the ions are fixed in positions and are not free to move. When an ionic solid is melted or dissolved in water, the ions are now free to move and can act as **mobile charge carriers** to conduct electricity. The mobile ions move towards the electrode that carries an opposite charge to their own.



Lamp unlit Lamp lights up Lamp lights up

Figure 8. Ionic compounds do not conduct electricity in the solid state but do so when molten or dissolved in aq. solution

The electrical conductivity of an aqueous solution of an ionic compound increases as its concentration increases, because there are more ions to carry the charge. Similarly, for the same concentration, a salt solution that contains highly charged ions such as Al^{3+}, conducts electricity better than a salt solution that contains ions of lower charge such as Na^+.

Hard and rigid but brittle

Ionic solids e.g. NaC*l* (rock salt) are hard (do not dent or deform easily), rigid (do not bend easily) but brittle (crack without deforming).

In an ionic lattice, oppositely charged ions are held in fixed positions throughout the crystal lattice by strong ionic bonding. Moving the ions out of position requires large amounts of energy to overcome these bonds. Ionic lattices are therefore quite hard and rigid.

However, if a strong enough shearing force (e.g. by cutting or knocking) is applied, it will force ions of like charges to move next to each other. Repulsion between ions of like charges will cause the lattice to shatter apart. Ionic lattices are therefore said to be brittle.

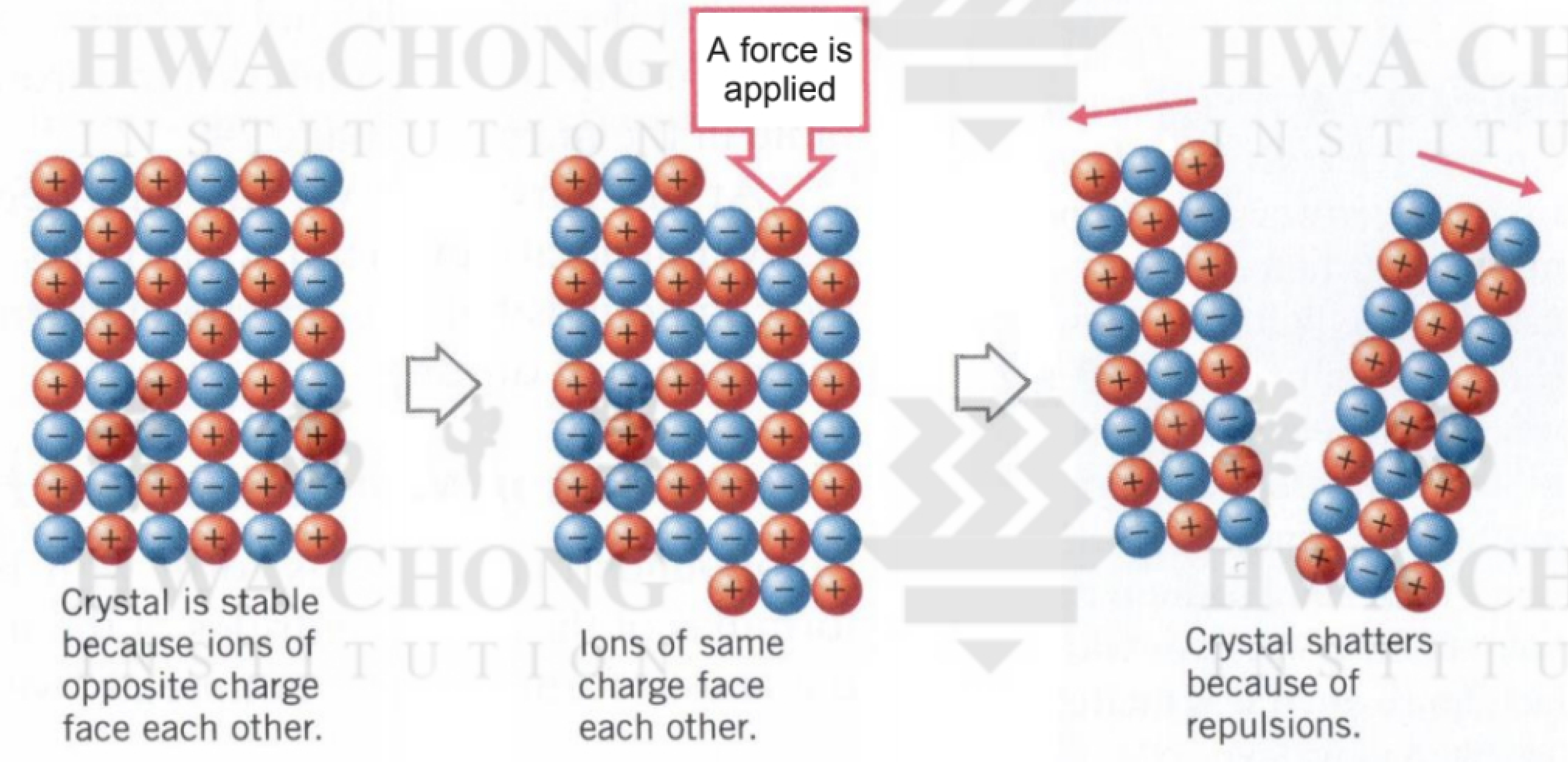


Figure 9. A shearing force will shatter an ionic crystal

Solubility

Ionic compounds are usually soluble in water, e.g. NaC*l*, KBr and BaC*l*$_2$. However, there are examples of insoluble ionic compounds as well, e.g. AgC*l*. See Section 11 for a detailed explanation on the solubility of ionic compounds.

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4 COVALENT BONDING

Covalent bonding is the **electrostatic force of attraction** between the **positively charged nucleus** of both the bonded atoms and their **shared pair of electrons**.

A covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the two nuclei, is occupied by a pair of electrons.

4.1 Formation of covalent bonds & molecular orbitals

If the two bonding atoms have similar electronegativity, we observe electron sharing and covalent bonding. This type of bonding most commonly occurs between non-metal atoms. Each non-metal atom holds onto its own electrons tightly (high ionisation energies) and tends to attract other electrons as well. The attraction of each nucleus for the valence electrons of the other atom draws the two atoms together. A shared electron pair is said to be **localised** between the two atoms because it 'spends' most of its time in the space there. The two atoms are linked in a covalent bond of a particular length and strength. In most cases, discrete or separate molecules form when covalent bonding occurs (we call these simple covalent molecules), and the chemical formula shows the actual numbers of atoms of each element in one molecule (**molecular formula**).

Let us consider the simplest covalent bond, i.e. between two hydrogen atoms in a H_2 molecule (refer to Figure 10). Imagine two hydrogen atoms, initially a large distance apart, approaching each other. As they come close to one another, the first effect is that the electron of one atom experiences repulsion from the electron of the other atom. But this is compensated by the attraction each electron experiences towards the other atom's nucleus (in addition to the attraction it always experiences from its own nucleus). As the hydrogen atoms get closer still, the two electrons encounter an attraction to the opposite nucleus that is stronger than their mutual repulsion. Eventually, when the two nuclei become very close together, they in turn start to repel each other, since they are both positively charged. The most stable situation occurs when the attractions of the two electrons to the two nuclei is just balanced by the electron-electron and nucleus-nucleus repulsions, and a H–H covalent bond forms. At this point, to separate the two H atoms to their initial unbonded state, it would require a certain amount of energy – this is the **bond energy** of that bond. In addition, the nucleus-nucleus distance, which is the measured distance between the centre of both nuclei is its **bond length**.

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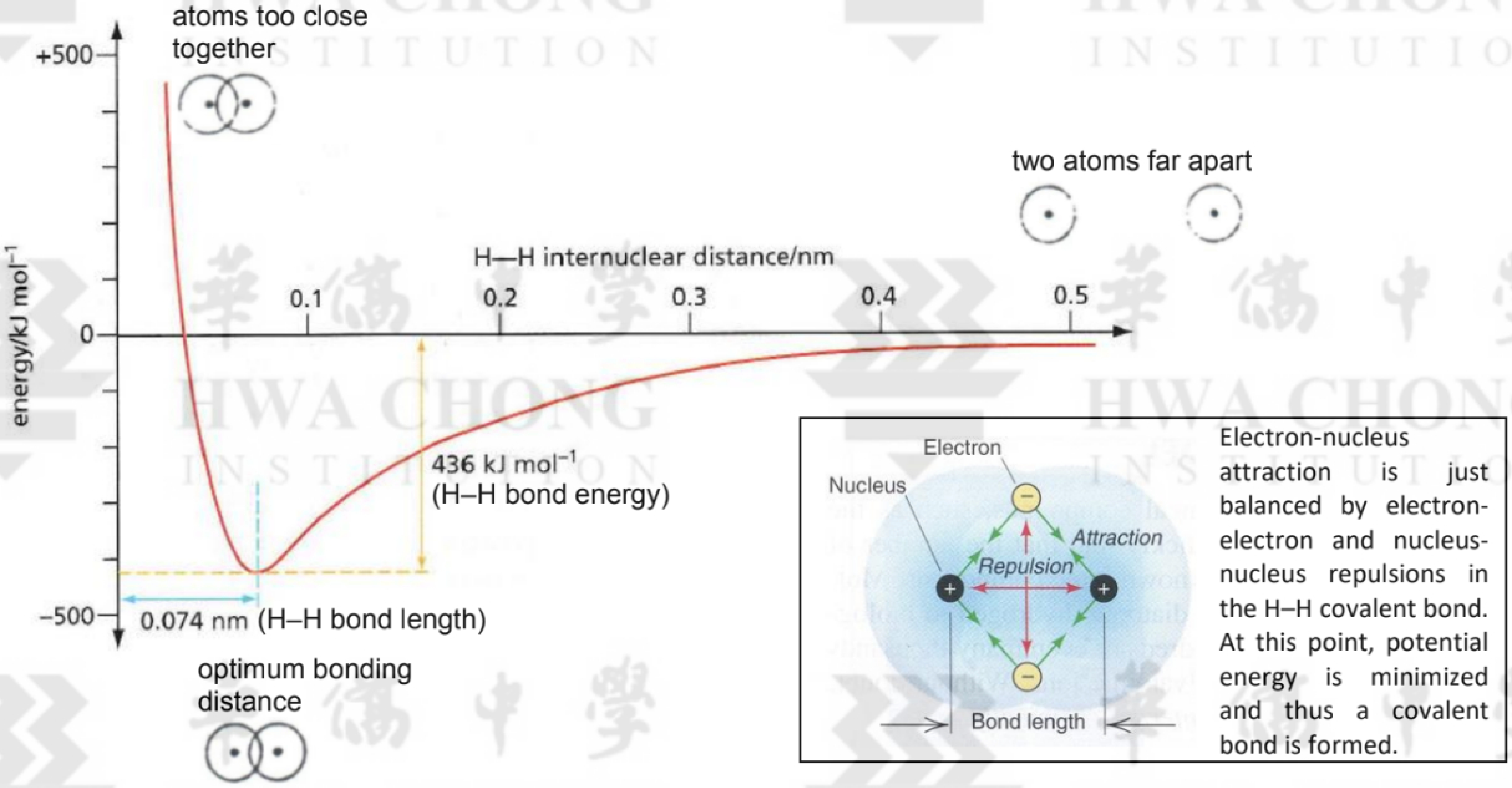


Electron-nucleus attraction is just balanced by electron-electron and nucleus-nucleus repulsions in the H–H covalent bond. At this point, potential energy is minimized and thus a covalent bond is formed.

Figure 10. Potential energy vs. distance between nuclei for the H_2 molecule

Being attracted to two nuclei, the two electrons in a H_2 molecule 'spend' most of their time in the region half-way between the two nuclei. This is where the highest electron density, or highest probability of locating an electron, occurs in a single covalent bond.

We use the term **atomic orbital** to describe the region of space around the nucleus of an atom where an electron can be found. Similarly, we use the term **molecular orbital** to describe the region of space within a molecule where the pair of bonding electrons or shared electrons can be found.

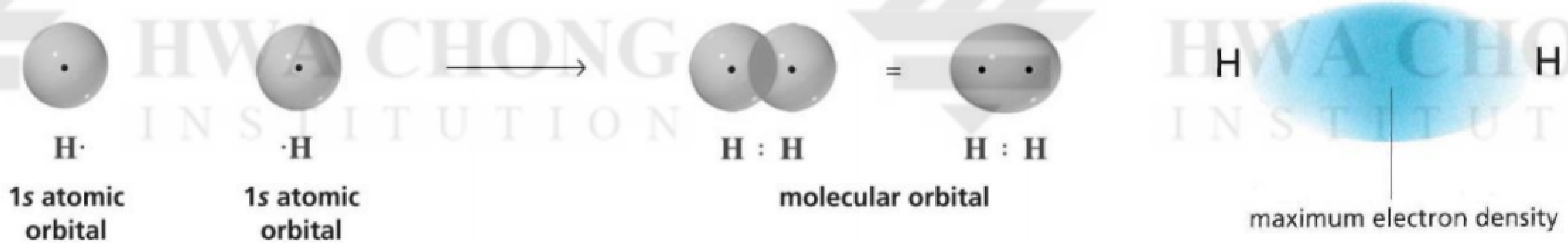


Figure 11. Bonding between two H atoms, their 1s orbitals overlap to form a molecular orbital

4.2 Covalent bonding in terms of orbital overlap

There are two types of orbital overlap:

1. **Sigma (σ) bond** formed by **'head-on' overlap** of two orbitals:

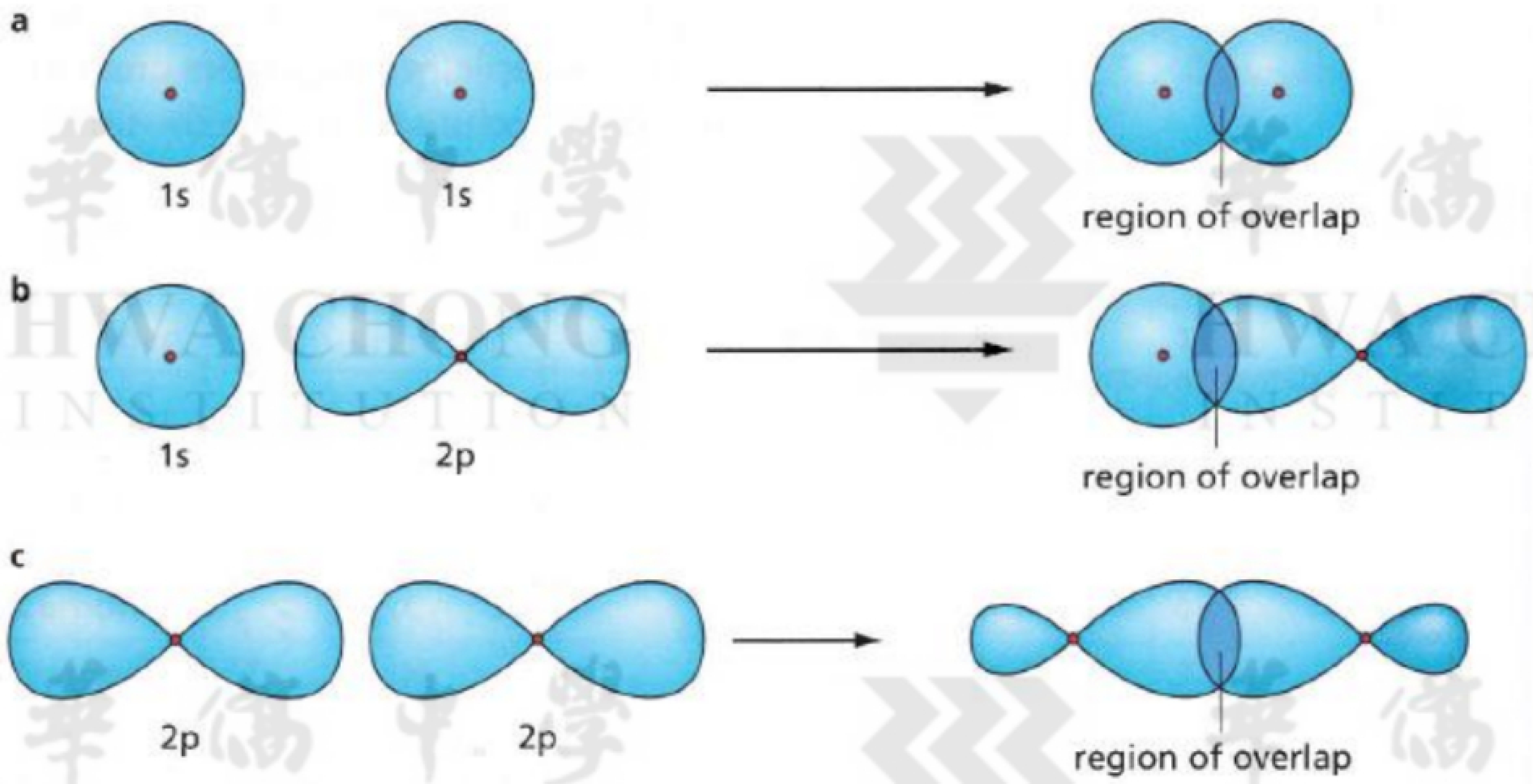


Figure 12. Examples of σ bond: ***(a)*** *σ bond formed by s-s overlap (i.e., σ bond in H_2);* ***(b)*** *σ bond formed by s-p overlap (e.g. H–F bond);* ***(c)*** *σ bond formed by p-p overlap (e.g. F–F bond)*

σ bond formed through s-p overlap can also be found in other hydrogen halides like HC*l* and HBr.
σ bond formed through p-p overlap can also be found in other halogen molecules like Cl_2 and Br_2.

When two atoms share only one electron pair, they form a single bond.
A single bond consists of a σ bond, as shown in the examples above.

Sharing two electron pairs produces a **double bond** e.g. O=O in O_2, C=O in CO_2 and C=C in alkenes. Sharing three electron pairs produces a **triple bond** e.g. N≡N in N_2, C≡C in organic compounds, C≡O in carbon monoxide, and C≡N in HCN. But there can only be one σ bond between two atoms as it is not possible for a second pair of orbitals to overlap head-on as well. Thus, the second type of orbital overlap is described in Figure 13.

2. **Pi (π) bond** formed by **'side-on' overlap** of two orbitals:

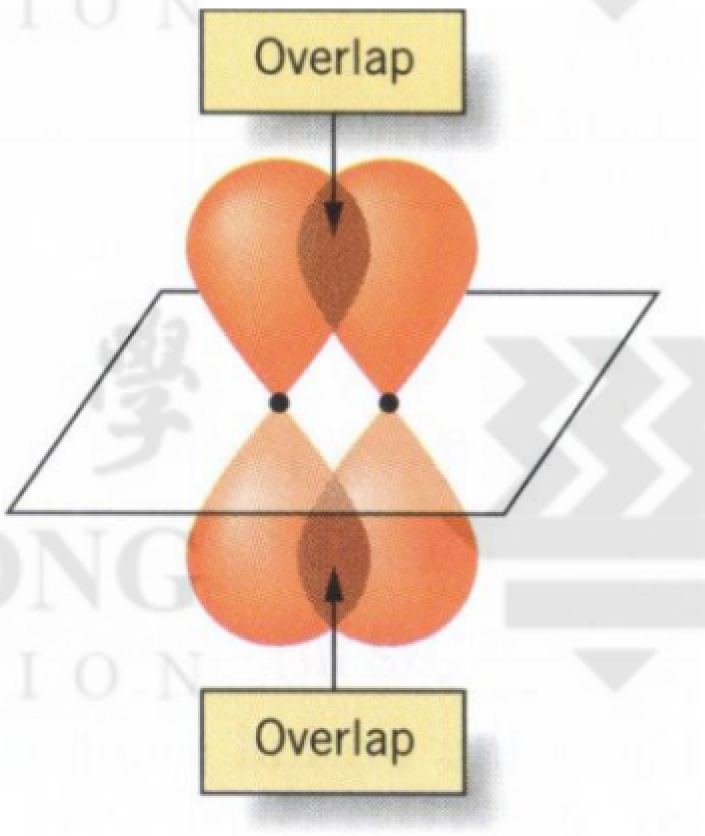


Figure 13. Example of π bond formed by side-on overlap between two sets of p orbitals (found in O_2, CO_2, C=C, N_2, C≡C, C≡N, C≡O etc).

For a π bond to exist, a σ bond must first be present.
Therefore, **a double bond consists of one σ bond and one π bond**.
And **a triple bond consists of one σ bond and two π bonds**.

Self-Practice 4.1

a) Draw a simple diagram to illustrate how the atomic orbitals overlap for each of the following situations. Label your diagrams clearly.

i) σ bond in the H_2 molecule **ii)** π bond in the ethene molecule

b) Suggest in terms of orbital overlap, why a π bond is weaker than a σ bond.

4.3 Factors affecting the strength of covalent bonding

The strength of a covalent bond is measured by the **bond energy** of that covalent bond. The bond energy of a covalent bond is the average energy required to break 1 mole of that covalent bond in the gaseous state. The bond energy is dependent on how strongly the two positively charged nuclei attracts the shared electrons. This in turn is affected by the bond length and the bond order.

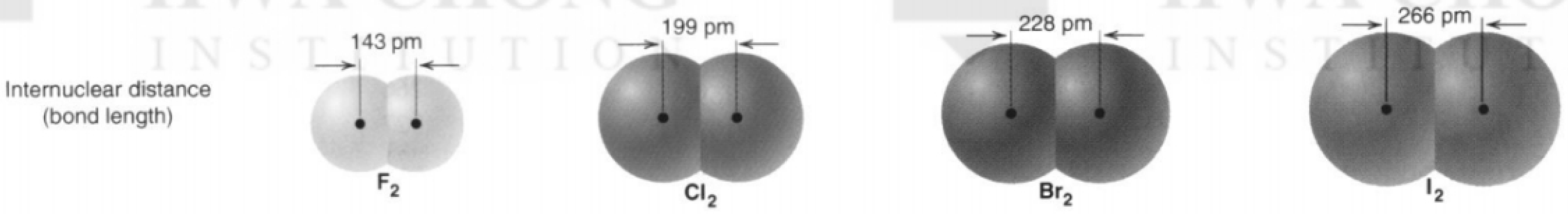
The **bond length** of a covalent bond is the distance between the nuclei of the two bonded atoms.
The **bond order** is the number of covalent bonds between a pair of atoms.

Two generalisations can be made:

1. **Smaller atoms form shorter and stronger bonds**

   For small atoms, overlap between the valence orbitals is more effective and the valence orbitals are close to the nucleus. Electrons in overlapping orbitals experience a strong attraction to the bonding nucleus.

   Exceptions: The O–O (148 pm, +204 kJ mol^{-1}) and F–F bonds are shorter *but* weaker than S–S (204 pm, +266 kJ mol^{-1}) and C*l*–C*l* bonds respectively. This is possibly due to the repulsion between the lone pairs on the adjacent atoms, which are very close.



Covalent Radius	72 pm	100 pm	114 pm	133 pm
Bond energy /kJ mol^{-1}	+158	+244	+193	+151

Figure 14. Bond length, covalent radius and bond energy in the diatomic halogen molecules

2. **Multiple bonds are stronger and shorter than single bonds**

   The more valence orbitals that overlap, the more electrons being shared, the stronger the attraction between the two positively charged nuclei and the shared electrons.

   Since a triple bond has six shared electrons, there will be a much stronger attraction between the shared electrons and the two positively charged nuclei as compared to a double bond which has four shared electrons; or a single bond which has only two shared electrons.

Table 5. Multiple bonds are stronger and shorter than single bonds

Bond	Bond length /pm	Bond energy /kJ mol^{-1}	Bond	Bond length /pm	Bond energy /kJ mol^{-1}
C–C	154	+350	C–O	143	+360
C=C	134	+610	C=O	123	+740
C≡C	121	+840	C≡O	113	+1080

How is bond energy or bond length related to the reactivity of covalent bonds?

A longer, hence, weaker bond is usually broken more easily and reacts more readily. We will study more about this in the organic chemistry reactions.

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4.4 Using dot-and-cross diagrams to represent covalent bonding

The dot-and-cross diagram is a method for depicting the valence electrons of interacting atoms as well as the type of bond (ionic or covalent) present.

For the drawing of dot-and-cross diagrams, the syllabus specified a number of substances (refer to learning outcomes on pg.32). Other than these simple examples, you will need to be able to draw the dot-and-cross diagrams for analogous situations as well as more complicated situations.

To do well in A-level chemistry, you must first master the basic content, then develop skills and exam strategies. For example, if you are tested on the dot-and-cross diagrams for substances stated in the syllabus or substances analogous to them, you must be able to simply recall the answers. Next, you must develop some general rules for drawing dot-and-cross diagrams to handle the more complicated situations.

General rules for drawing dot-and-cross diagrams

When drawing dot-and-cross diagrams for covalent compounds, note the following.

- Show *all* the valence electrons, including those valence electrons not involved in bonding.
- The element's symbol represents the nucleus *and* the inner shell electrons.
- Use *only* dots (•) and crosses (×) to represent valence electrons. Do not use other symbols like circles, triangles or squares, unless otherwise stated.
- Between any two bonded atoms, use different electron symbols (but • and × only). By doing so, a legend for the electrons is not necessary.
- Following the octet rule, compounds should be bonded such that each atom has eight elections in its valence shell.

Let us look at the simple examples first.

Lecture Exercise 4.1

Draw the dot-and-cross diagrams for the following molecules.

a) H_2 **b)** O_2 **c)** N_2

d) CO_2 **e)** CH_4

4.5 Co-ordinate bonding (also called dative bonding)

So far, we have looked at covalent bonds in which each of the two bonding atoms provides one electron to form the bond. It is possible for just one of the atoms to provide both bonding electrons. This atom is called the **donor atom**, and it must have a **lone pair**. The other atom in the bond is called the **acceptor atom**, and it must contain an **empty orbital in its valence shell**. This kind of bonding is called **dative bonding** or **co-ordinate bonding**.

You should also know that **donor atoms**, containing a lone pair of electrons, is also known as a ***Lewis base***. While an **acceptor atom**, which has an empty orbital in its valence shell, is known as a ***Lewis acid***. This definition of acids and bases is very general, very useful, and will recur in later topics. For each of the following three examples, can you identify which molecule is acting as the Lewis acid, and which molecule is acting as the Lewis base?

Example 1: NH_3BF_3

When gaseous NH_3 and gaseous BF_3 react together, white solid NH_3BF_3 forms. The nitrogen atom in NH_3 has a lone pair. As a Period 2 element, the boron atom can accommodate a maximum of 8 electrons. However, in BF_3, the boron atom has only 6 electrons in its outermost shell and is electron deficient. It has an empty 2p orbital, which can overlap with nitrogen's orbital containing the lone pair.

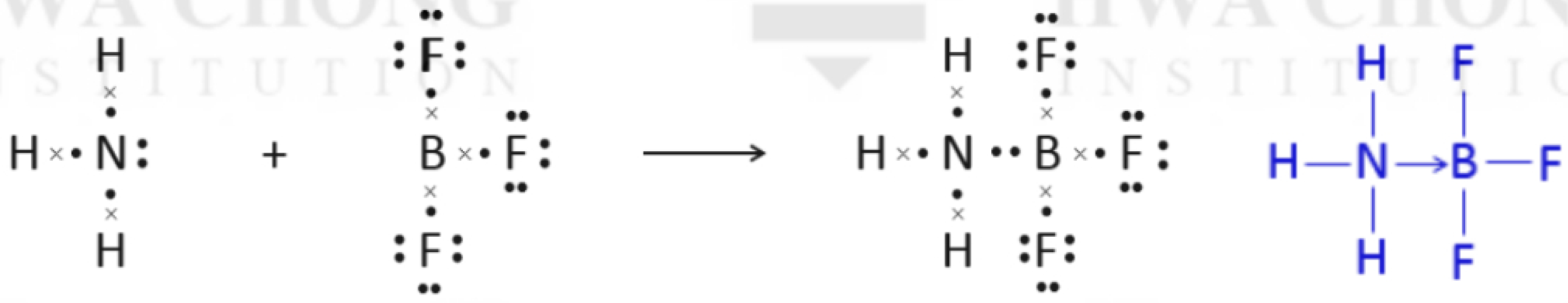

Figure 15. Dot-and-cross diagrams for NH_3, BF_3, and NH_3BF_3 which contains a dative bond

Example 2: Al_2Cl_6

Just below its melting point, aluminium chloride exists as covalent Al_2Cl_6 molecules. This is because aluminium, like boron, has only 6 electrons in its outermost shell in the monomer $AlCl_3$ and is electron deficient. It has an empty 3p orbital which can accept a lone pair of electrons from the chlorine atom of another $AlCl_3$ monomer, to form a dimer as shown in Figure 16. This persists in the gas phase but if the temperature is raised to 800 °C, the dimer breaks down to monomeric $AlCl_3$.

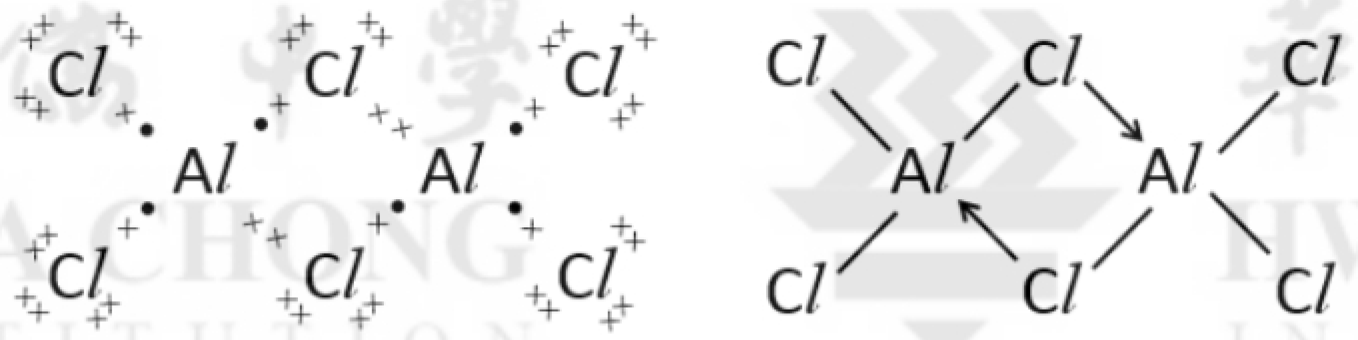

Figure 16. Dot-and-cross diagrams and drawings of Al_2Cl_6 dimer

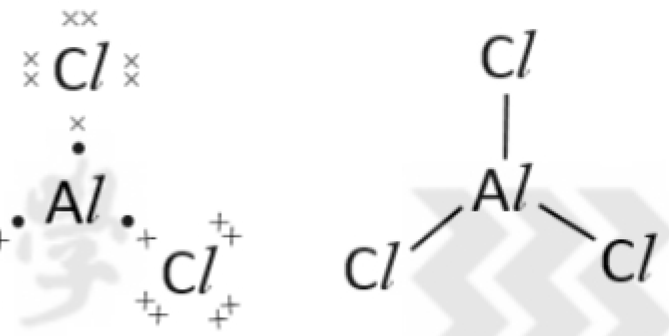

Figure 17. Dot-and-cross diagrams and drawings of $AlCl_3$ monomer

Example 3: The ammonium cation, NH_4^+

When gaseous NH_3 and gaseous HCl react together, the H–C*l* bond breaks to give H^+ and Cl^-. The lone pair of electrons on the nitrogen atom forms a dative bond with the H^+, which has an empty 1s orbital, to form NH_4^+. The resultant NH_4Cl is a white ionic solid which contains NH_4^+ and Cl^- ions.

Figure 18. Using dot-and-cross diagrams to represent formation of the ionic compound NH_4Cl from NH_3 and HCl; there is a dative bond in the resultant NH_4^+ cation

A dative bond, once formed, is no different from an ordinary covalent bond.
For example, in the NH_4^+ cation, all four N–H bonds are exactly the same.
A dative bond can be a σ bond or a π bond.

4.6 Exceptions to the octet rule

In his studies of chemical bonding, Lewis generalised much of bonding behavior into the **octet rule**: when atoms bond, they lose, gain or share electrons to attain a filled outer electron shell of eight electrons. So the atom attains the noble gas electronic configuration, $ns^2\ np^6$. The octet rule is obeyed by nearly all of the compounds of Period 2 elements and also for a large number of compounds of elements in other periods as well.

However, the octet rule is based on empirical observation. It could be used to identify structures which are likely to be stable but it **cannot** be used to explain the stability of chemical bonds.

Hence we will cite several exceptions to the octet rule.

Electron deficient species (usually the central atom)

BF_3 and $AlCl_3$ molecules, given in the earlier examples, can exist even though the central atom has yet to achieve octet and is electron deficient. Two more examples are given below.

Self-Practice 4.2

Draw the dot-and-cross diagrams for the following covalent molecules.

a) beryllium chloride, $BeCl_2$ **b)** BH_3

Expansion of octet (usually the central atom)

Period 2 elements have only four orbitals in their valence shells (2s, $2p_x$, $2p_y$ and $2p_z$) and thus cannot accommodate more than four pairs of electrons. The number of covalent bonds formed is restricted by this overall maximum of eight electrons, since every new bond brings another electron into the valence shell.

Elements **from period 3 onwards** can utilize their d orbitals in covalent bonding, in addition to their s and p orbitals. We say that their **d orbitals are energetically accessible**. They can therefore form more than four covalent bonds to other atoms. We say that they can expand the octet.

Like nitrogen ($1s^2\ 2s^2\ 2p^3$), phosphorus ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$) has five electrons in its valence shell. But unlike nitrogen, phosphorus can utilize all five of its valence electrons in covalent bonding by making use of five orbitals (one 3s + three 3p + one 3d). For nitrogen, we say that its 3d orbitals are not energetically accessible, because they are in a different outer quantum shell which is at a much higher energy level than its valence shell. Thus, nitrogen forms only NF_3 with fluorine, while phosphorus can form PF_3 as well as PF_5.

In a similar way, sulfur can use each of its six valence electrons to form six single covalent bonds to form SF_6. It does so by utilizing six valence orbitals (one 3s + three 3p + two 3d).

The chlorine atom can also expand its octet to form ClF_3 and ClF_5 but not ClF_4 and ClF_6 because it will result in an unpaired valence electron. It is not able to form ClF_7 because the Cl atom is too small to accommodate seven fluorine atoms around it.

Lecture Exercise 4.2

a) Draw the dot-and-cross diagrams for the following molecules.

i) phosphorus pentachloride, PCl_5 **ii)** sulfur hexafluoride, SF_6

b) Oxygen and sulfur are both Group 16 elements. Oxygen forms OF_2 with fluorine but not OF_4 or OF_6. Sulfur forms SF_2, SF_4 as well as SF_6. Give reasoning for this observation.

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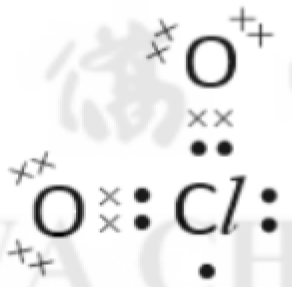
Radicals

In some molecules, there are unpaired electrons in the outermost shell. Such species are called **radicals**, and they are usually very reactive. Most radical molecules have a central atom that has an unpaired electron, and that central atom is usually a Group 15 or Group 17 element. So certainly, that central atom does not have an octet structure.

e.g. ClO_2 in which the Cl atom has a total of 11 electrons in its outermost shell

Another example is nitrogen monoxide, NO.



What about cations?

There are far more cations which do not have noble gas electronic configuration than those which do!

e.g.
Fe^{3+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Cu^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$
Zn^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$
Ag^+ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$
Pb^{2+} $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2$
H^+ $1s^0$

The only elements that form cations with noble gas electronic configuration are those in Group 1, Group 2, scandium, and aluminium in Group 13.

What about anions?

Anions are tidier. The non-metal elements in Groups 15, 16 and 17, and hydrogen which form simple anions all attain noble gas electronic configuration $ns^2\ np^6$, and $1s^2$ for the H^- anion.

4.7 Dot-and-cross diagrams for covalent molecules or polyatomic ions

In Section 4.4, you have learnt to draw dot-and-cross diagrams for simple covalent molecules, many of which you may have encountered in O Level Chemistry. In this section, you will be dealing with covalent molecules or polyatomic ions where the situation may be more complex and requires practice before you master this skill.

Now let us develop some skills and strategies for drawing such dot-and-cross diagrams.

General guidelines for drawing dot-and-cross diagrams for covalent molecules or polyatomic ions

1. Decide on the central atom, and the terminal atoms. The central atom is usually the one with lowest electronegativity (carbon in CO_2) or the one that can form more covalent bonds (carbon in CH_4). The notion of 'central' and 'terminal' atoms is only of concern if the molecule or ion has three or more atoms. If there are only two atoms, e.g. CO and OH^-, one atom is just *next* to the other!

2. When dealing with polyatomic anions or cations:
   If it is an anion, for each (–) charge, add one electron to the more electronegative atom. E.g. fluorine is assigned the extra electron, not chlorine, in ClF_4^-.
   If it is a cation, for each (+) charge, remove one electron from the less electronegative atom. E.g. the electron is removed from hydrogen, not nitrogen, in NH_4^+.
   Remember to draw square brackets around the ion and label its charge.

3. Draw dot-cross pairs to make terminal atoms achieve octet by assigning single, double or triple bonds accordingly.
   Do this by using the periodic table to locate the group number, and hence determine the number of valence electrons of the element. By considering the number of outer shell electrons already present for each surrounding atom, we will know how many covalent bonds it must form to achieve octet. Draw in the remaining valence electrons of the atom in pairs.

4. Finally, check the central atom:
   (i) Are there any valence electrons yet to be accounted? These are non-bonding valence electrons and should be drawn as pairs. These are termed 'lone pairs' (see Section 5.2).
   (ii) Count the total number of outer shell electrons. Only elements from period 3 onwards can expand octet. If a central atom cannot expand octet, change a double bond to a dative bond (see Lecture Exercise 4.3 (iv)).
   Sometimes, the central atom may be electron deficient or turn out to be a radical.

Let us practice.

Lecture Exercise 4.3

Draw the dot-and-cross diagrams for the following substances. Some are covalent molecules, some are ionic compounds containing polyatomic ions.

i) F_2O

ii) NO_2

iii) Na_2CO_3

iv) O_3

Self-Practice 4.3

Draw the dot-and-cross diagrams for the following substances. Some are covalent molecules, some are ionic compounds containing polyatomic ions.

i) ClF_4^-

ii) PCl_4^+

iii) $Mg(NO_3)_2$

iv) PCl_3

v) CaH_2

vi) SO_4^{2-}

vii) BaO_2 (it contains one cation and one anion)

viiii) NaC*l*O (it contains one cation and one anion)

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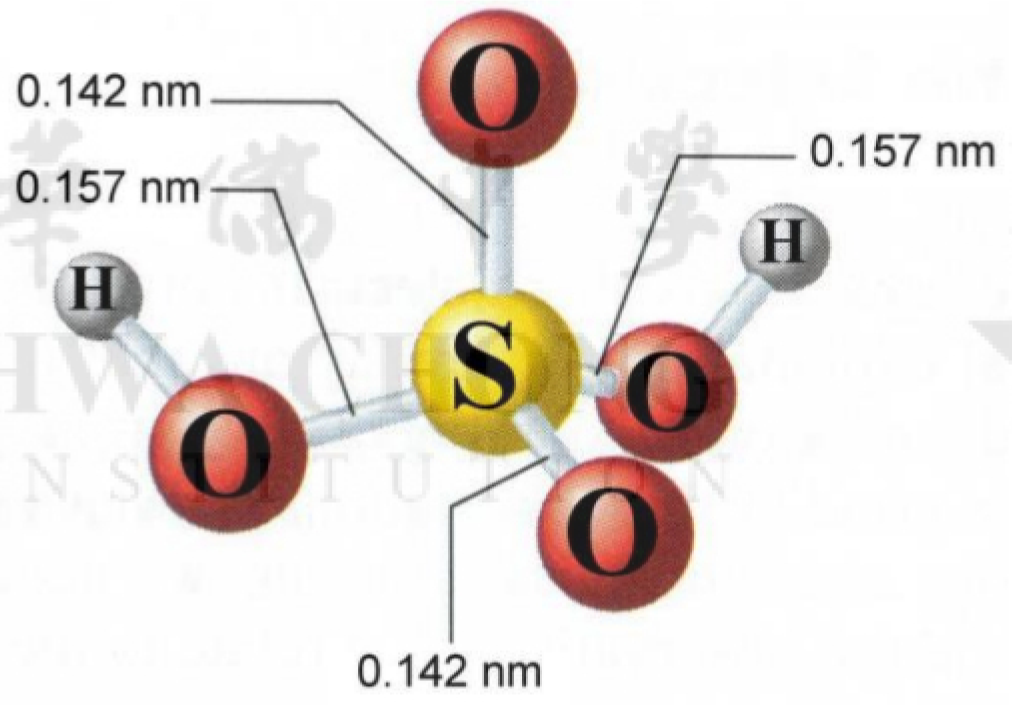
5 SHAPES OF MOLECULES & POLYATOMIC IONS

5.1 Introduction to molecular geometry

Jacobus Henricus van't Hoff, Jr. (1852 – 1911), Dutch physical and organic chemist and the first winner of the Nobel Prize in Chemistry. He is best known for his discoveries in chemical kinetics, chemical equilibrium, osmotic pressure and stereochemistry. His work in these subjects helped found the discipline of physical chemistry as it is today. In 1874, van't Hoff suggested for the first time that molecules possessed three-dimensional shapes. The shapes are determined by the angles between the bonds which are in turn determined by the arrangement of electrons around each central atom.

Why study the shapes of molecules (molecular geometry)? In any molecule, each atom and electron pair has its own position in space relative to one another, determined by attractive and repulsive forces. With definite angles between bonds (bond angles) and distances between any two nuclei (bond length), a molecule is a fine little unit of architecture.



angle H–O–S ≈ 104.5°,
the molecule is bent about this O atom

angle O–S–O ≈ 109.5°,
the molecule is tetrahedral about the S atom

Figure 19. 'Ball-and-stick' model of the sulfuric acid (H_2SO_4) molecule

Whether we consider the details of simple reactions, the properties of synthetic materials, or the intricate life-sustaining processes of living cells, molecular geometry is a crucial factor.

Geometry is a branch of Mathematics that deals with the measurement, properties, and relationships of points, lines, angles and shapes. Transferring these concepts to Chemistry – 'points' would be the atoms, 'lines' would be the covalent bonds, 'angle' would be the bond angle (an angle between two covalent bonds around a central atom) and 'shapes' would refer to the three-dimensional shapes of molecules and polyatomic ions about the central atom.

Dot-and-cross diagrams are not used to represent the shapes of molecules and ions. We may use them to count the number of electron pairs around a central atom, and hence deduce the shape and bond angles using the **Valence Shell Electron Pair Repulsion (VSEPR) theory**.

Nevil Vincent Sidgwick (1873 – 1952), English theoretical chemist. He explained the bonding in coordination compounds (complexes), with a convincing account of the significance of the dative bond. Together with his students, he demonstrated the existence and wide-ranging importance of the hydrogen bonding. In 1940, Sidgwick and Herbert Marcus Powell (Oxford crystallographer) correlated molecular geometry with the number of valence electrons on a central atom. These ideas were later developed into the VSEPR theory by Ronald James Gillespie and Sir Ronald Sydney Nyholm.

5.2 Valence shell electron pair repulsion (VSEPR) theory

There are two main principles of the VSEPR theory:

1. The electron pairs (or electron groups) around the central atom of a molecule (or ion) arrange themselves as far apart as possible so as to minimise their mutual repulsion.
2. The repulsion between electron pairs decreases in strength in the following order:
   lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion

An electron pair that is shared between bonded atoms is called a **bond pair**. An electron pair that is part of an atom's valence shell but not shared with another atom is called a **lone pair**.

The five arrangements of electron pairs

We mainly deal with molecules or ions containing 2, 3, 4, 5 or 6 electron pairs (bond pairs and lone pairs) around the central atom. Using VSEPR main principle no. 1, these total numbers of electron pairs give the following five types of electron-pair arrangements:

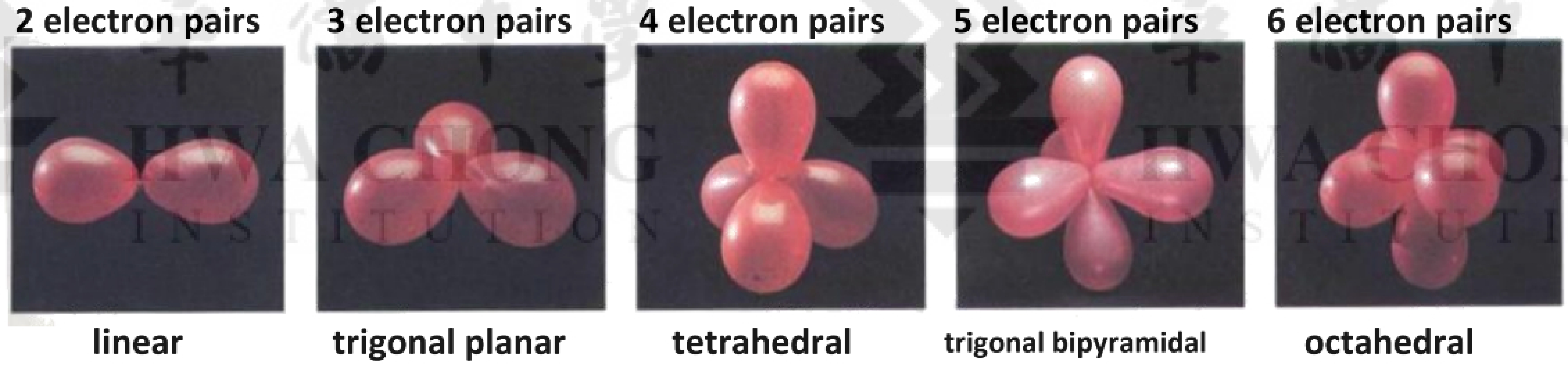


Figure 20. Five types of electron-pair arrangements depending on the total no. of electron pairs present, the balloons represent electron clouds (of the electron pairs); where do you think is the location of the nucleus of the central atom?

The five basic shapes of molecules (or polyatomic ions) without lone pairs

If there are only bond pairs and no lone pairs around the central atom, the name given to the shape of the molecule (or ion) is the same as that given to the arrangement of the electron pairs. So we have the five basic shapes of molecules (or ions) without lone pairs:

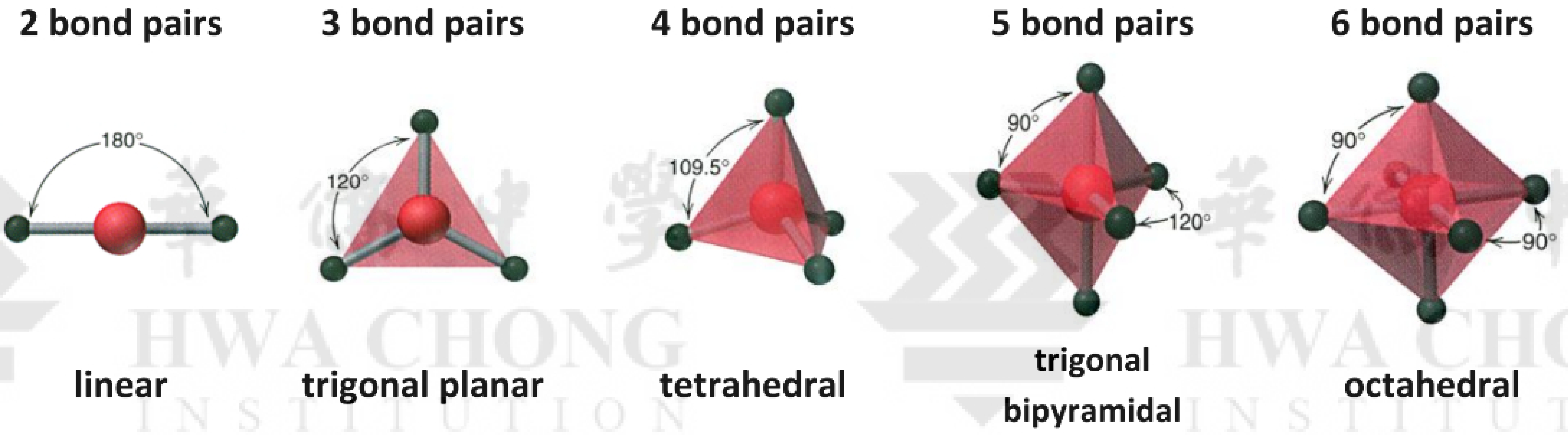
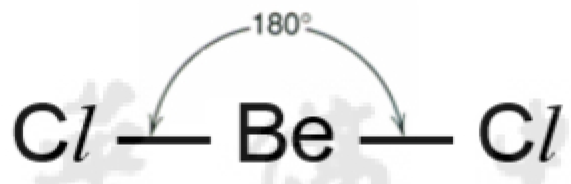
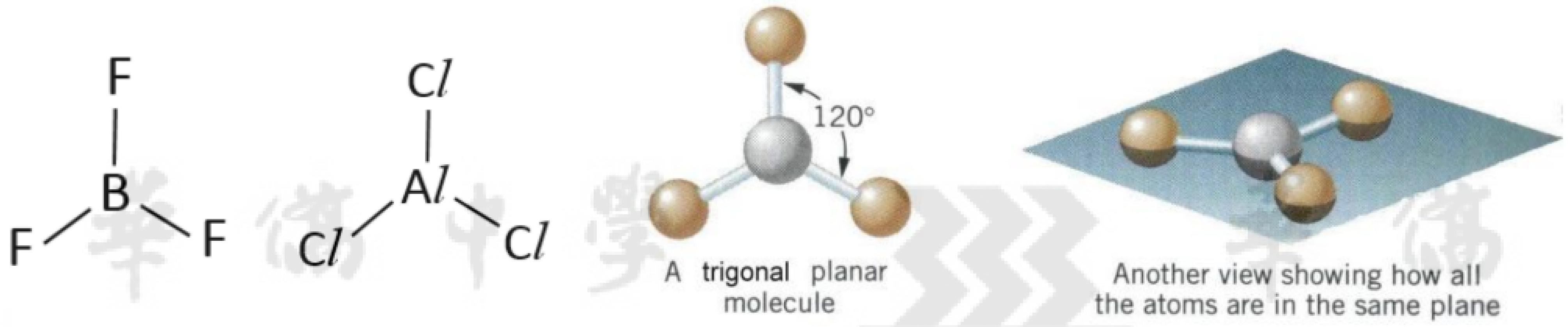


Figure 21. The five basic shapes of molecules (or ions) in which there are only bond pairs and no lone pairs around the central atom; and their bond angles

e.g. $BeCl_2$ contains two bond pairs and no lone pair around the central atom. The two bond pairs arrange themselves as far apart as possible so as to minimise their mutual repulsion, thus giving a linear molecular shape with a bond angle of 180°.



BF_3 and gaseous $AlCl_3$ are examples of trigonal planar molecules. The word 'planar' means that all the atoms of that molecule lie on the same plane. And since the three surrounding atoms occupy the corners of a triangle, we have the name 'trigonal planar'.

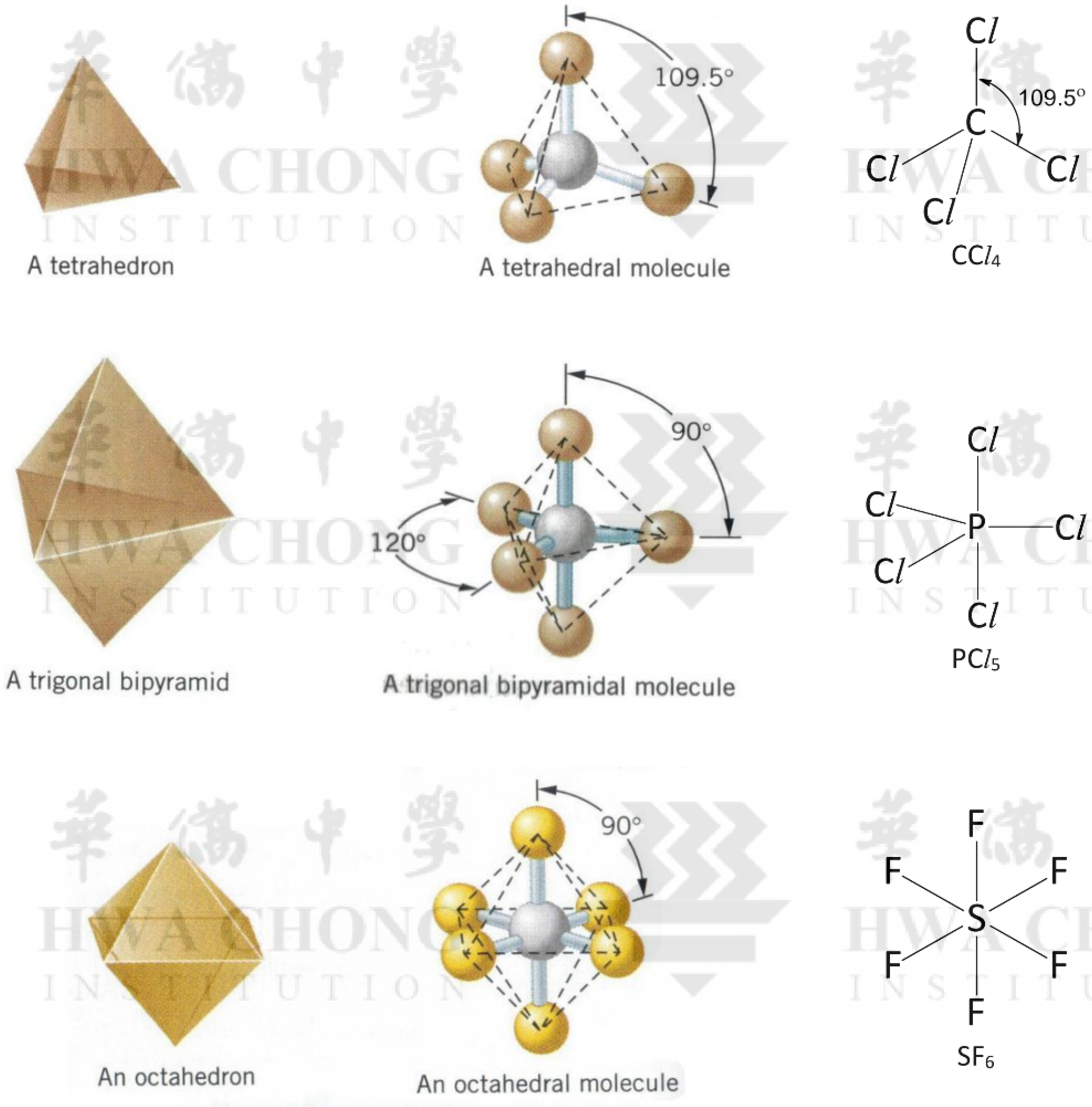


A trigonal planar molecule

Another view showing how all the atoms are in the same plane

Figure 22. Structures of the trigonal planar BF_3 and $AlCl_3$ molecules, and their molecular model

'Tetrahedral', 'trigonal bipyramidal', 'octahedral' – these names are derived from the names of the geometrical figures obtained if the surrounding atoms were the vertices of a solid figure:



A tetrahedron

A tetrahedral molecule

CCl_4

A trigonal bipyramid

A trigonal bipyramidal molecule

PCl_5

An octahedron

An octahedral molecule

SF_6

Figure 23. Models of tetrahedral, trigonal bipyramidal and octahedral molecules, bond angles and examples

To master molecular geometry, you need to use your imagination – close your eyes and visualise these three-dimensional shapes in your mind

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Axial and equatorial bonds for trigonal bipyramidal molecules

Notice there are two bond angle values for this shape, 90° and 120°. We call the corresponding bonds, axial bonds and equatorial bonds.

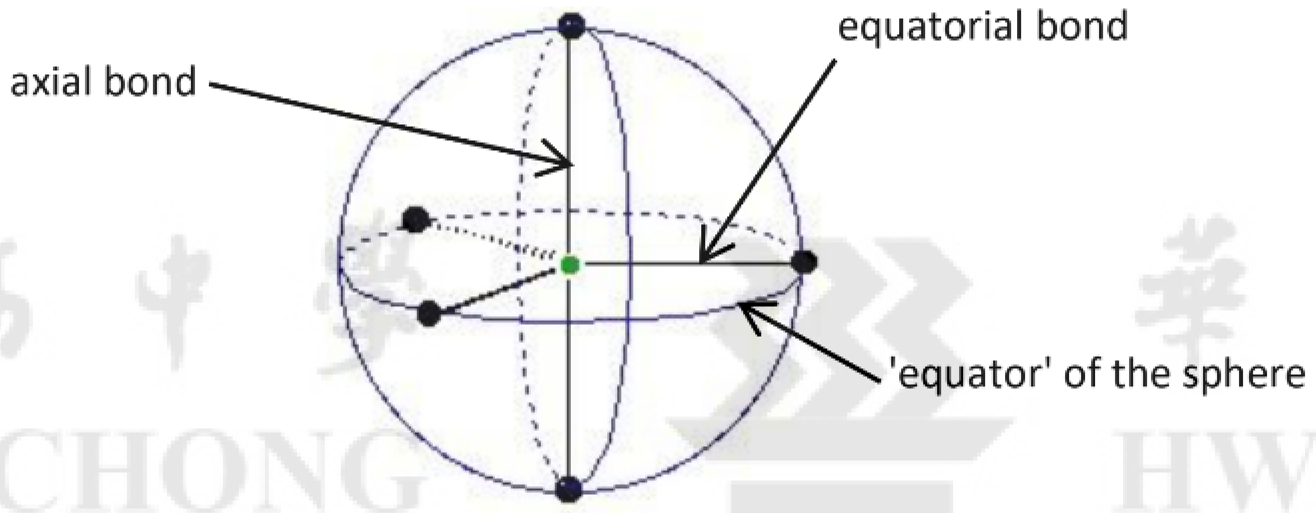


Figure 24. Axial and equatorial bonds for trigonal bipyramidal shape

What happens to the molecular shape if there are lone pairs?

Although lone pairs are important in determining the shape of a molecule, they are 'ignored' when the molecule's shape is described. The shape is named based on relative positions of atoms. And so we have another eight shapes if there are lone pairs. See Table 6.

What happens to the bond angle if there are lone pairs?

Let us refer to VSEPR main principle no. 2:

The repulsion between electron pairs decreases in strength in the following order,

lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion

A lone pair is attracted by only one nucleus while a bond pair is attracted by two nuclei. So a lone pair electron cloud is less 'elongated' than a bond pair. A lone pair takes up more space around the central atom and its electrons are, on average, closer to the nucleus of the central atom. Thus, a lone pair repels other electron pairs around it more than a bond pair would.

Consider CH_4, NH_3 and H_2O. All three molecules have four electron pairs around the central atom, which arrange themselves in a tetrahedral fashion. The tetrahedral 109.5° bond angle is found in CH_4. NH_3 and H_2O contain one and two lone pairs respectively, which give stronger repulsion than the bond pairs. The bond pairs in NH_3 and H_2O are pushed more closely together resulting in slightly smaller bond angles, 107° and 104.5° respectively.

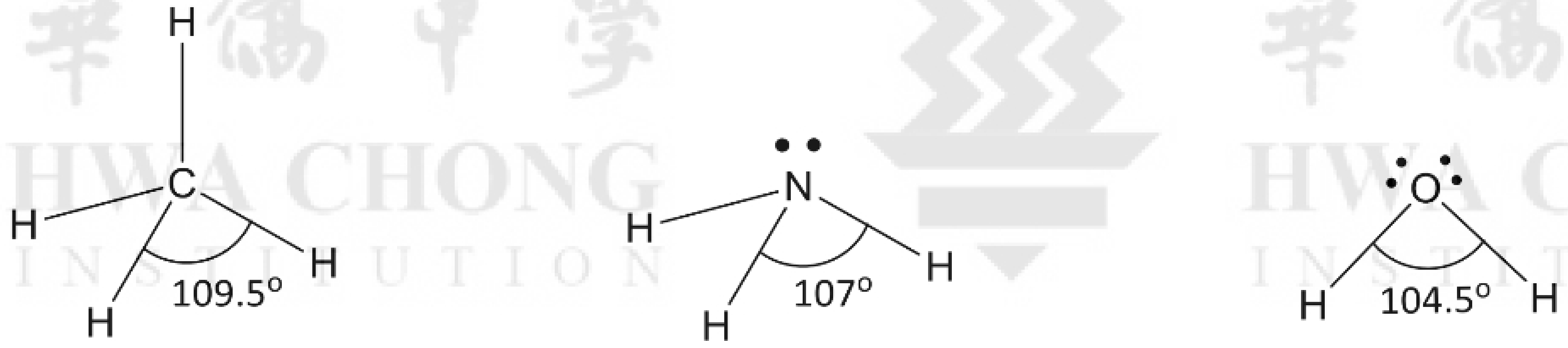
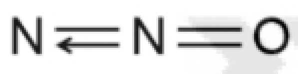


Figure 25. Drawings of the shapes of CH_4 (tetrahedral), NH_3 (trigonal pyramidal) and H_2O (bent) with lone pairs on the central atom indicated (may be drawn like an 'electron cloud' or simply indicated as two dots)

What happens if the molecule or ion contains double or triple bonds?

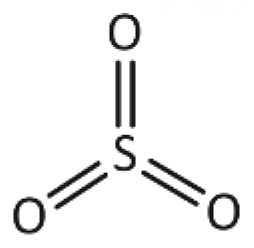
As far as the VSEPR theory is concerned, the four electrons in a double bond count as <u>one</u> *group* of electrons. Similarly, the six electrons in a triple bond count as <u>one</u> *group* of electrons.

Examples:

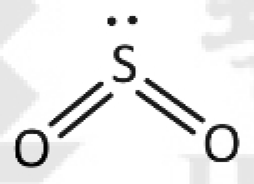


(one possible structure of N_2O)

CO_2, HCN and N_2O are linear molecules as there are two 'bond pairs' or two groups of shared electrons and no lone pair around the central atom. The bond angle is 180°.



SO_3 is a trigonal planar molecule because there are three 'bond pairs' or three groups of shared electrons and no lone pair around the central atom.
The bond angle is 120°.

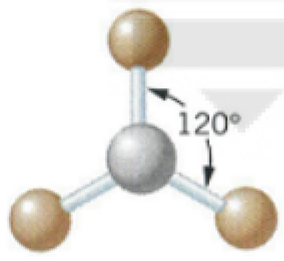
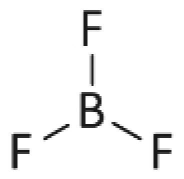
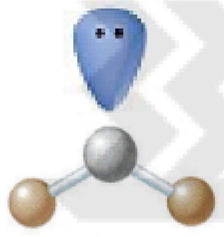
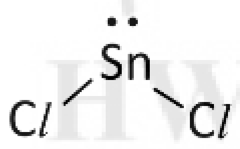
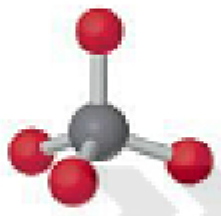
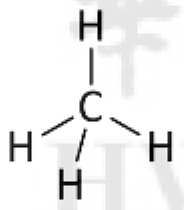
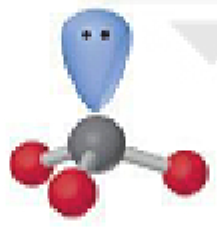
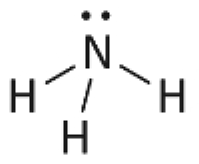
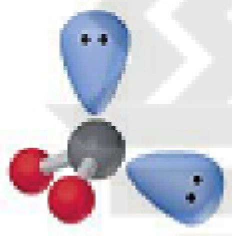


SO_2 is a bent molecule as there are two 'bond pairs' or two groups of shared electrons and one lone pair around the central atom.
Since the lone pair gives stronger repulsion than any one group of shared electrons, the two S=O bonds are pushed more closely together, so the bond angle is expected to be smaller than the basic value of 120°, we may predict it as 118°.
(actual value is 119°, found from X-ray studies)

Since a double bond or a triple bond doesn't contain a *pair* of electrons, it is better to use terms like 'groups of shared electrons' rather than 'bond pairs', and 'electron groups' rather than 'electron pairs' in our descriptions for such situations.

The 13 shapes of molecules or polyatomic ions

Table 6. The 13 shapes as determined by the numbers and types of electron pairs (bond pairs and lone pairs) present around the central atom

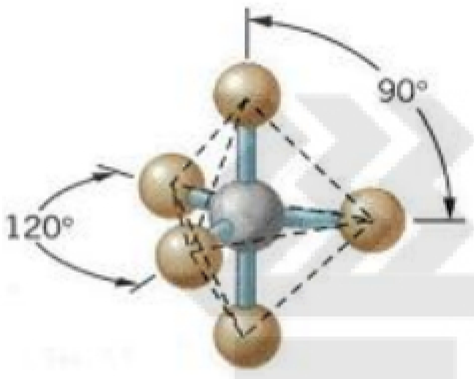
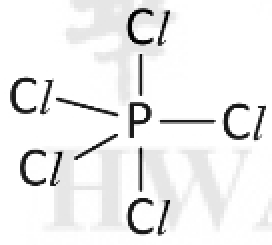
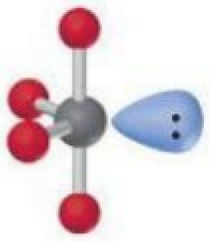
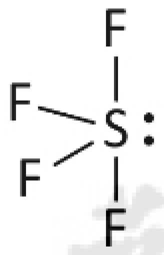
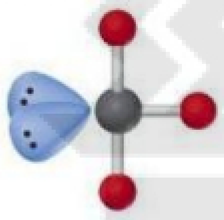
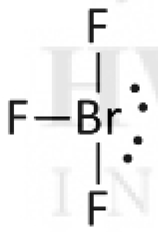
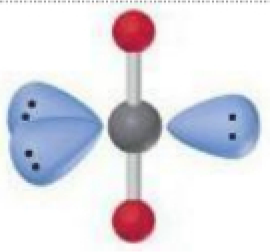
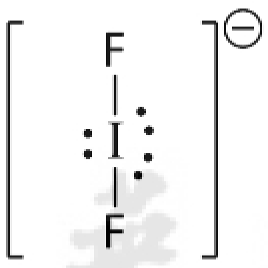
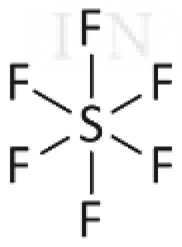
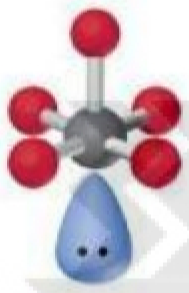
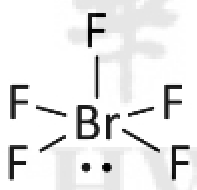
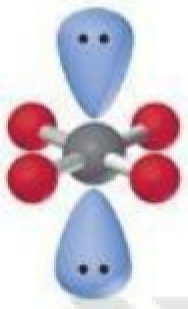
Total no. of electron pairs	No. of bond pairs	No. of lone pairs	Molecular model, name of shape & bond angle	Examples
2	2	0	 linear 180°	$BeCl_2$, CO_2, CS_2, HCN Cl–Be–Cl
3	3	0	 trigonal planar 120°	BF_3, BCl_3, SO_3, NO_3^-, CO_3^{2-}, HCHO (methanal) 
	2	1	 bent e.g. 118°	SO_2, $SnCl_2$, $PbCl_2$, NO_2^-, O_3  (a lone pair on the central atom may be indicated as two dots or drawn like an 'electron cloud')
4	4	0	 tetrahedral 109.5°	CH_4, CCl_4, $SiCl_4$, NH_4^+, SO_4^{2-}, ClO_4^- 
	3	1	 trigonal pyramidal 107°	NH_3, NF_3, PH_3, PCl_3, PF_3, ClO_3^-, H_3O^+ 
	2	2	 bent 104.5°	H_2O, H_2S, OF_2, SF_2, SCl_2 

(continue next page)

Lewis structure

In Lewis structures, lines instead of dots and crosses are drawn between bonded atoms ('–', '=' and '≡' to represent single, double and triple bonds respectively). An arrow → can be used to represent a dative bond. A lone pair on the central atom is indicated as two dots. When drawing structures to illustrate the shapes of molecules, we need not indicate the lone pairs of terminal atoms since these are not considered in the determination of the shapes.

Table 6 (continued)

Total no. of electron pairs	No. of bond pairs	No. of lone pairs	Molecular model, name of shape & bond angle	Examples
5	5	0	 trigonal bipyramidal	PCl_5, AsF_5, SF_5^+ 
	4	1	 see saw	SF_4 
	3	2	 T-shape	BrF_3, ClF_3, ICl_3 
	2	3	 linear 180°	IF_2^-, I_3^-, XeF_2 
6	6	0	 octahedral 90°	SF_6, PCl_6^-, IF_6^+ 
	5	1	 square pyramidal	BrF_5, IF_5, SF_5^-, $SbCl_5^{2-}$ 
	4	2	 square planar 90°	XeF_4, ICl_4^-, ClF_4^- 

General considerations for predicting molecular shapes and bond angles using VSEPR theory

1. Determine the total number of electron pairs (or electron groups) around the central atom.
   To do this, we use the dot-and-cross diagram. With experience, you may not need to draw the dot-and-cross diagram to determine the number of pairs of electrons around the central atom.

2. Use VSEPR main principle no. 1 to determine the electron-pair arrangement.
   - The number of bond pairs equals the number of terminal atoms.
   - If there are only bond pairs, no lone pairs, the name of the molecule's shape is the same as that given to the electron-pair arrangement.
   - If there are lone pairs, the molecule's shape is named based only on the relative positions of the atoms.

3. After deducing the shape of the molecule or ion, bond angles 180°, 120° and 90° are easily recognised by visualising the molecule in three-dimensions. Bond angles 109.5°, 107° and 104.5° -- for tetrahedral, trigonal pyramidal and bent -- we memorise them, and we must be able to explain why the angles for trigonal pyramidal and bent are smaller than that for tetrahedral using VSEPR main principle no. 2.

The shape is only of concern if the molecule or ion has three or more atoms. If there are only two atoms e.g. CO, O_2, N_2, the halogens and OH^-, one atom is just *next* to the other! Also, the notion of 'bond angle' will not be relevant.

If there is more than one central atom e.g. H_2SO_4 (Figure 19), H_2O_2, N_2H_4, propane, CH_3CO_2H etc, state the shape with respect to each central atom.

With experience gained from lots of conscientious practice, plus organised memory work and some imagination, we can easily deduce the shape after counting the numbers of bond pairs and lone pairs. Develop your own skills so that you can work quickly when solving MCQs during an exam.

Let us practice.
Remember to draw square brackets around an ion and label its charge.

Lecture Exercise 5.1

For each of the following species, draw its structure showing the shape and indicate the lone pairs (if any) on the central atom. State the shape about the central atom and suggest the bond angle.

i) ClO_4^-

ii) H_2O_2

Self-Practice 5.1

For each of the following species, draw its structure showing the shape and indicate the lone pairs (if any) on the central atom. State the shape about the central atom and suggest the bond angle.

i) BCl_3

ii) PCl_3

iii) ClF_4^-

iv) $PbCl_2$ (a covalent molecule)

v) PCl_6^-

vi) PCl_5

vii) XeF_2

viii) CS_2

Self-Practice 5.2

For each of the following molecules, draw its structure showing the shape and indicate the lone pairs (if any) on the central atom. State the name of the shape.

i) ClF_3

ii) IF_5

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5.3 Hybridisation of Atomic Orbitals

To account for the bonding in diatomic molecules like HF, we picture the direct overlap of s and p orbitals of isolated H and F atoms. But how can we account for the shapes of so many molecules and polyatomic ions through the overlap of spherical s orbitals, dumbbell-shaped p orbitals and cloverleaf-shaped d orbitals? After all, the s, p or d orbitals aren't oriented toward the corners of a tetrahedron or a trigonal bipyramid!

For example consider the methane molecule, CH_4. As accounted by the VSEPR model and measured by an X-ray study of the molecule, CH_4 has a tetrahedral shape and a bond angle of 109.5°. Its tetrahedral shape suggests that its C atom should 'provide' four orbitals oriented in a tetrahedral geometry, each containing one electron, and each orbital forms a σ bond with the 1s orbital of a H atom (Figure 26).

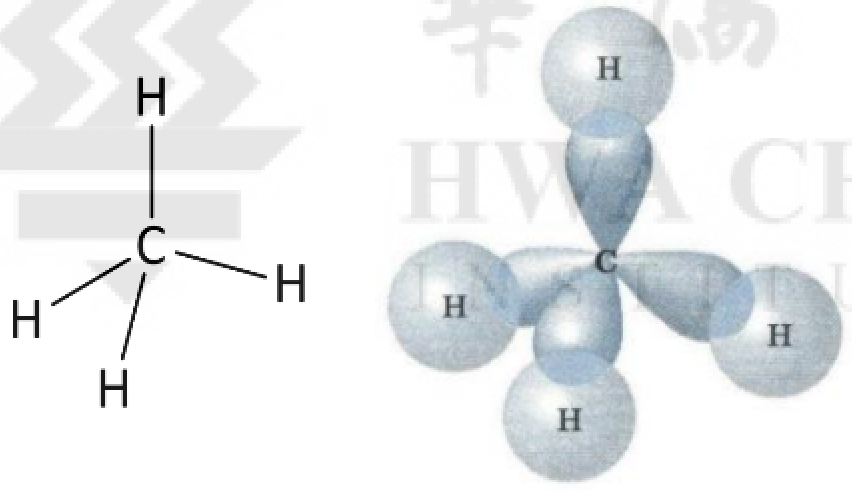


Figure 26. CH_4 molecule and expected shapes of orbitals around the C atom (each orbital forms a σ bond with the 1s orbital of a H atom)

Now look at an isolated ground-state carbon atom's valence shell electronic configuration ($2s^2\ 2p^2$), and the shapes of its 2s and 2p orbitals:

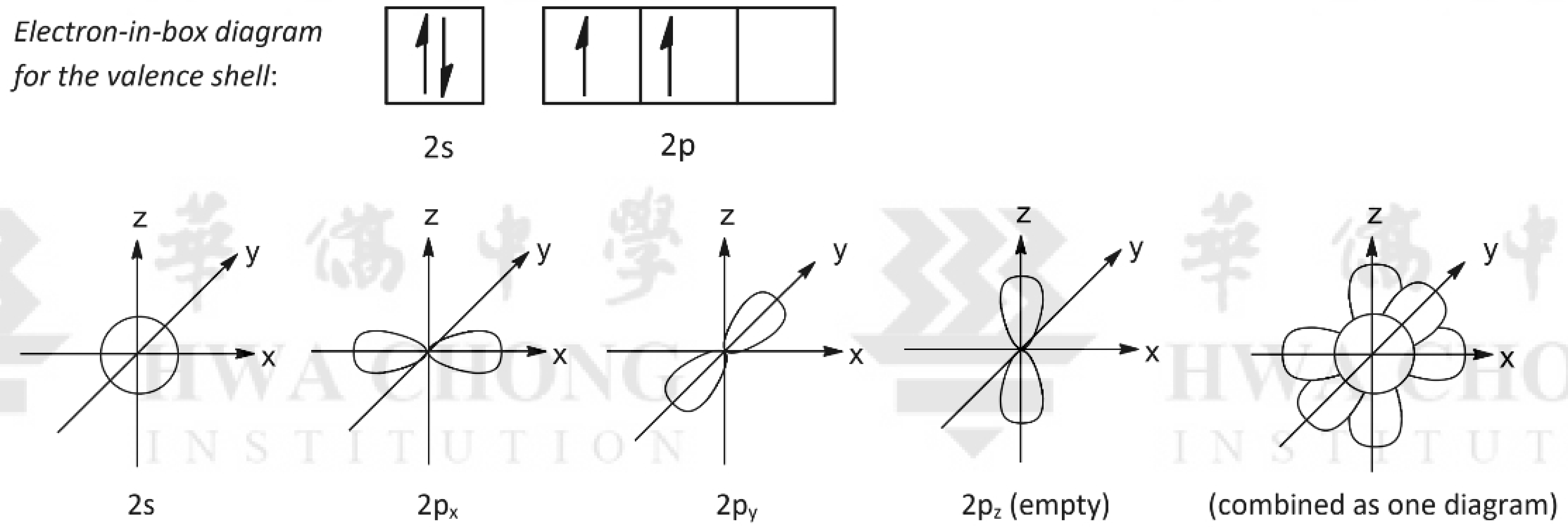


Figure 27. Electron-in-box diagram and shapes of valence atomic orbitals of an isolated ground-state C atom

There is a mismatch between the expected orientation of the orbitals involved in bonding for the C atom in CH_4, compared to those of an isolated C atom; and also in terms of the numbers of single unpaired electrons that can be used for σ bonding.

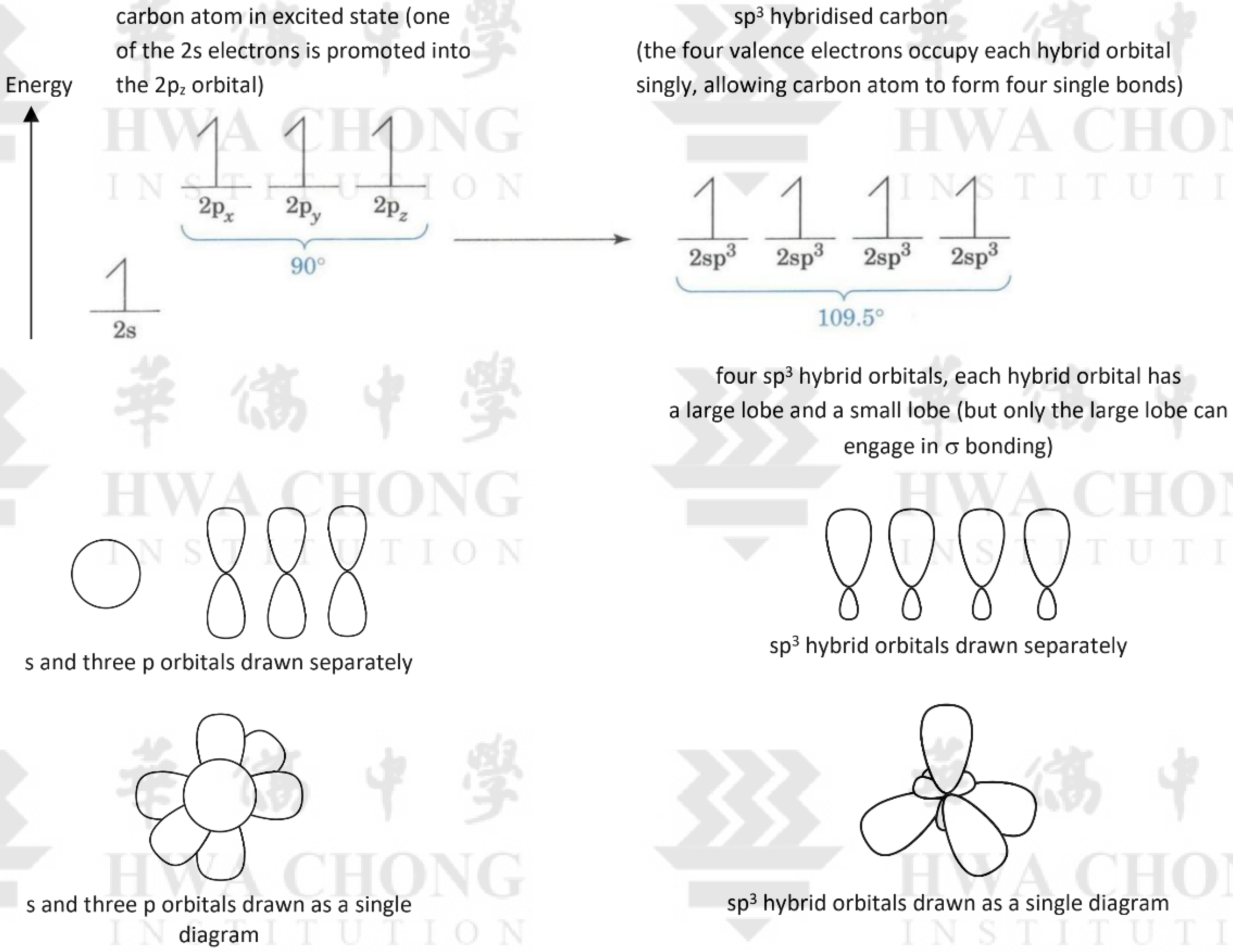
Linus Pauling proposed that valence atomic orbitals of atoms in a molecule are *different* from those of isolated atoms. In his **hybridisation theory**, **atomic orbitals (s and p, and sometimes d) mix to form new orbitals called hybrid orbitals** which may then involve in σ bonding. Using this theory, we can explain **how molecular shapes arise from interactions of atomic hybrid orbitals**. For the A-levels, we focus on the learning of sp^3, sp^2 and sp hybridisation of carbon. In the following pages, we will study these concepts with reference to the examples of methane (CH_4), ethene ($CH_2{=}CH_2$) and ethyne ($H{-}C{\equiv}C{-}H$).

The VSEPR and orbital hybridisation theories are different models to account for molecular shapes. Well, don't be concerned if we need more than one model to explain a complex phenomenon like bonding. All scientific models have limitations because they are simplifications of reality. In every science, one model or theory often accounts for some aspect of a topic better than another. Scientific theories are based on evidence, scientific knowledge is reliable and durable but never absolute.

5.3.1 sp^3 hybridisation of carbon

Mixing **one s orbital and three p orbitals** gives four **sp^3 hybrid orbitals**. These four hybrid orbitals point towards the corners of a regular tetrahedron and are directed at 109.5° to each other so as to minimize repulsion with one another. All four hybrid orbitals are identical in shape. They are also identical in energy which is intermediate between the energies of the s and p orbitals. (The naming of the new hybrid orbitals follows the original numbers of s and p orbitals that made them.)

The carbon atom in methane, CH_4, is sp^3 hybridised.



carbon atom in excited state (one of the 2s electrons is promoted into the $2p_z$ orbital)

sp^3 hybridised carbon (the four valence electrons occupy each hybrid orbital singly, allowing carbon atom to form four single bonds)

four sp^3 hybrid orbitals, each hybrid orbital has a large lobe and a small lobe (but only the large lobe can engage in σ bonding)

s and three p orbitals drawn separately

sp^3 hybrid orbitals drawn separately

s and three p orbitals drawn as a single diagram

sp^3 hybrid orbitals drawn as a single diagram

Figure 28. Mixing of an s orbital and three p orbitals to form four sp^3 hybrid orbitals for a carbon atom

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The bonding in methane, CH_4, is shown in the figure below.
There are four C–H bonds, each is an s-sp^3 σ bond, formed from head-on overlap between the 1s orbital of a H atom and one sp^3 hybrid orbital of the C atom.

Indeed, the hybridisation theory helps to explain in terms of orbitals, why methane is tetrahedral in shape with a bond angle of 109.5°. It also explains why the four C–H bonds are equal in length and strength. It is important to understand, however, that hybridization is not a physical process which consists of electron promotion, orbital hybridization, and then bonding. Rather, it is a mathematical model which combines atomic orbitals in a way which is consistent with the observed shape and bond angle of the molecule.

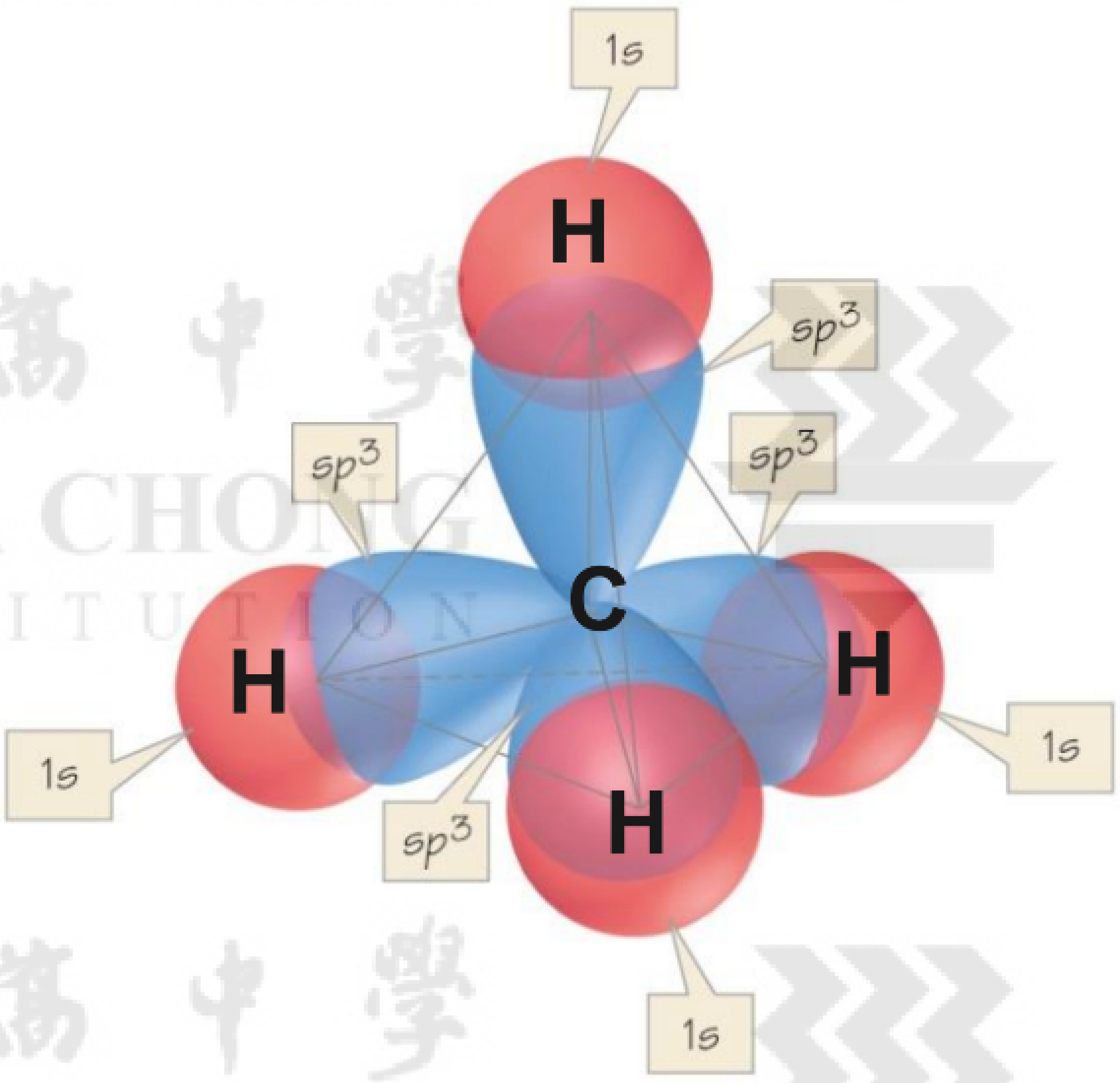
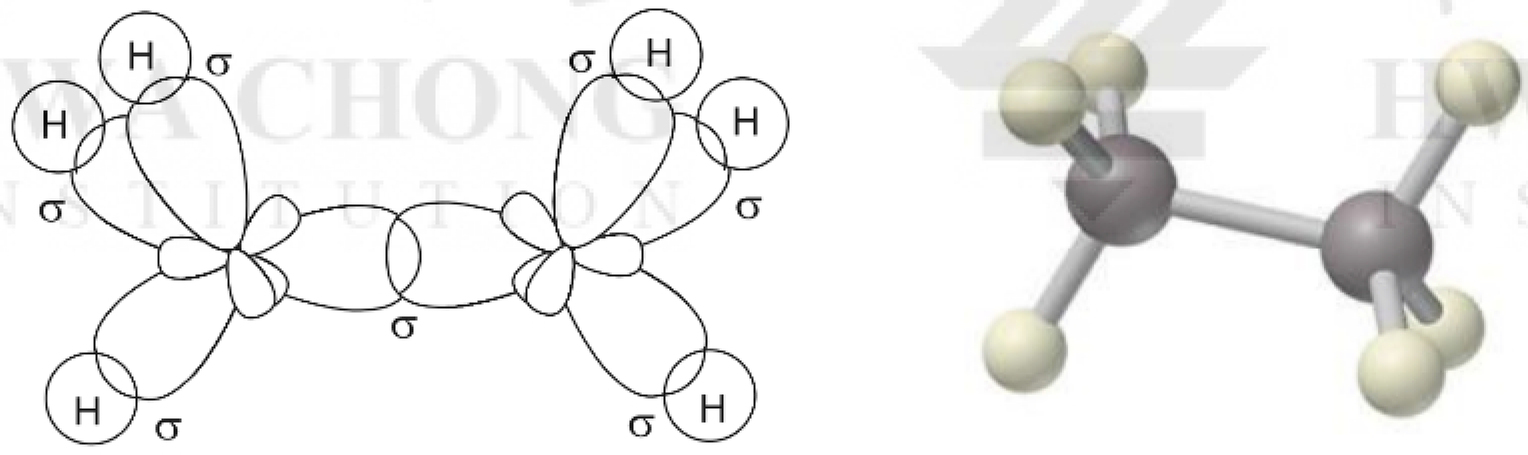


Figure 29. Overlapping of orbitals in methane, CH_4 (small lobes of the hybrid orbitals are omitted)

How about ethane, CH_3CH_3?
In ethane, both carbon atoms are sp^3 hybridised.
The C–C bond is an sp3-sp^3 σ bond, formed from a head-on overlap of orbitals.
There are six C–H bonds, each bond is s-sp^3 σ bond, formed from a head-on overlap of orbitals.
Ethane is tetrahedral around each C atom and the bond angle around each C atom is 109.5°.



overlapping of orbitals ball & stick model

Figure 30. Bonding in ethane, CH_3CH_3

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5.3.3 sp hybridisation of carbon

Mixing **one s orbital and one p orbital** gives two **sp hybrid orbitals**, directed at 180° to each other to minimize repulsion with one another.

Both carbon atoms in ethyne, H–C≡C–H, are sp hybridised.

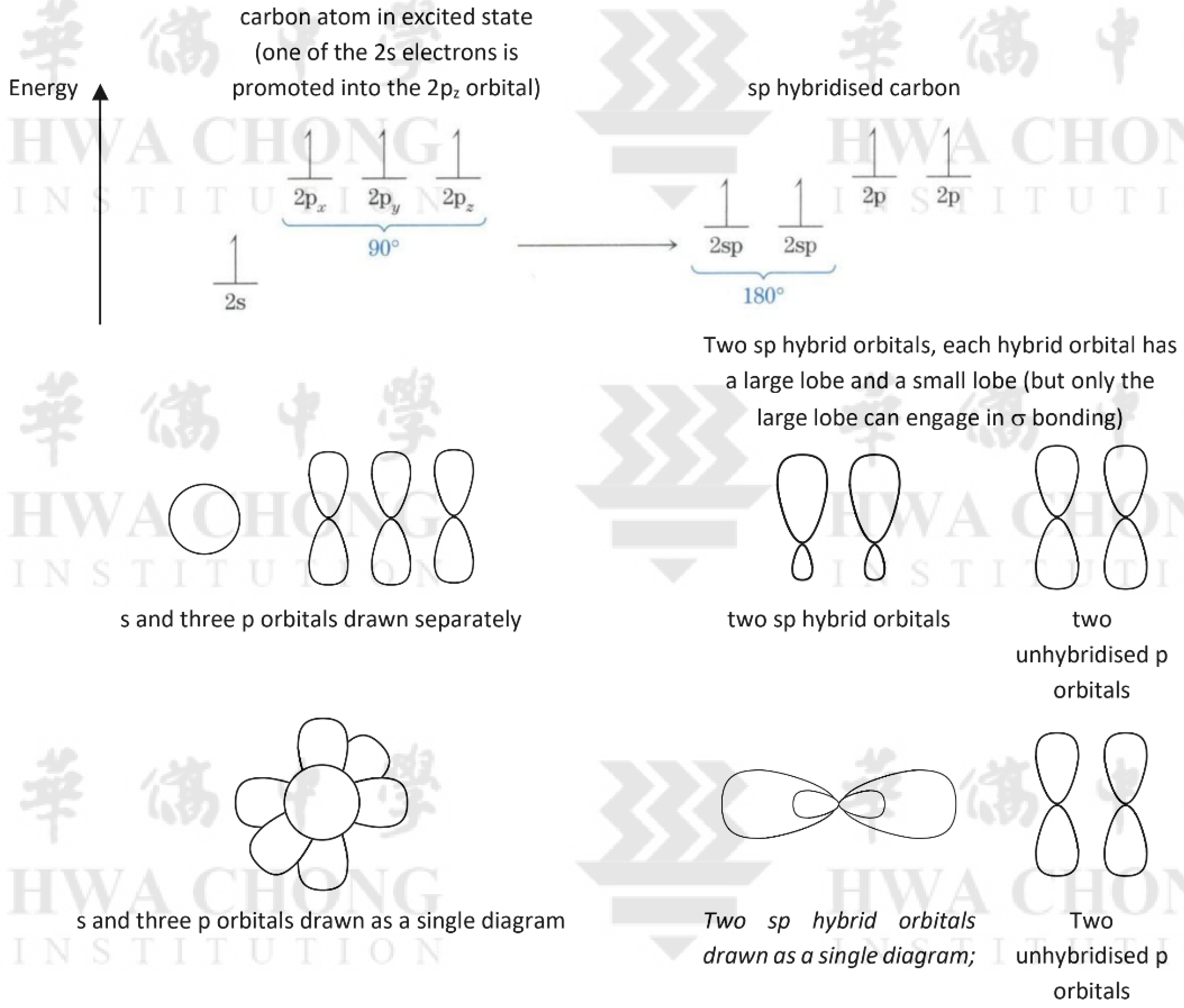


Figure 35. Mixing of an s orbital and a p orbital to form two sp hybrid orbitals for a carbon atom, two sets of p orbitals remain unhybridised

6 BONDING AS A CONTINUUM – POLAR COVALENT BONDS & IONIC BONDING WITH COVALENT CHARACTER

We have discussed typical examples of ionic bonding, e.g. $NaCl$, and covalent bonding, H_2. But there are exceptions to these *idealised* bonding models in the world of real substances. You have already seen two examples, $BeCl_2$ and gaseous $AlCl_3$, they are typical examples of covalent molecules formed by a metal and a non-metal.

Ionic bonding arises from electron transfer, while covalent bonding involves electron sharing. As mentioned in Section 1.4, *complete* electron transfer and *equal* sharing of electrons are the *extremes*, between which most actual cases of bonding fall. The electronegativity difference between two atoms is the best predictor of the degree of ionic or covalent character.

The term *ionic bonding* is used for bonding which is *predominantly* ionic.
The term *covalent bond* is used for non-polar covalent bonds *as well as* polar covalent bonds.

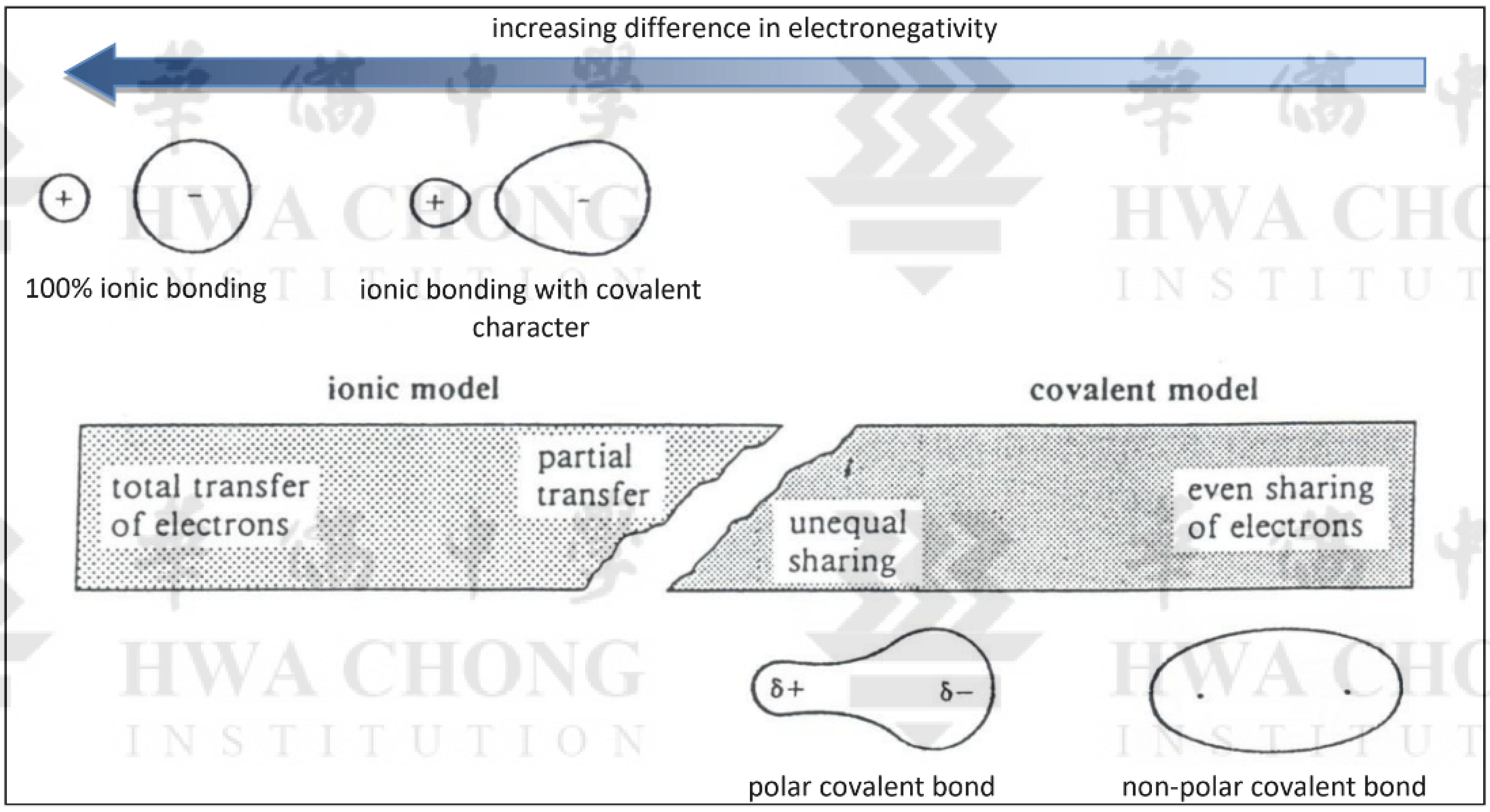
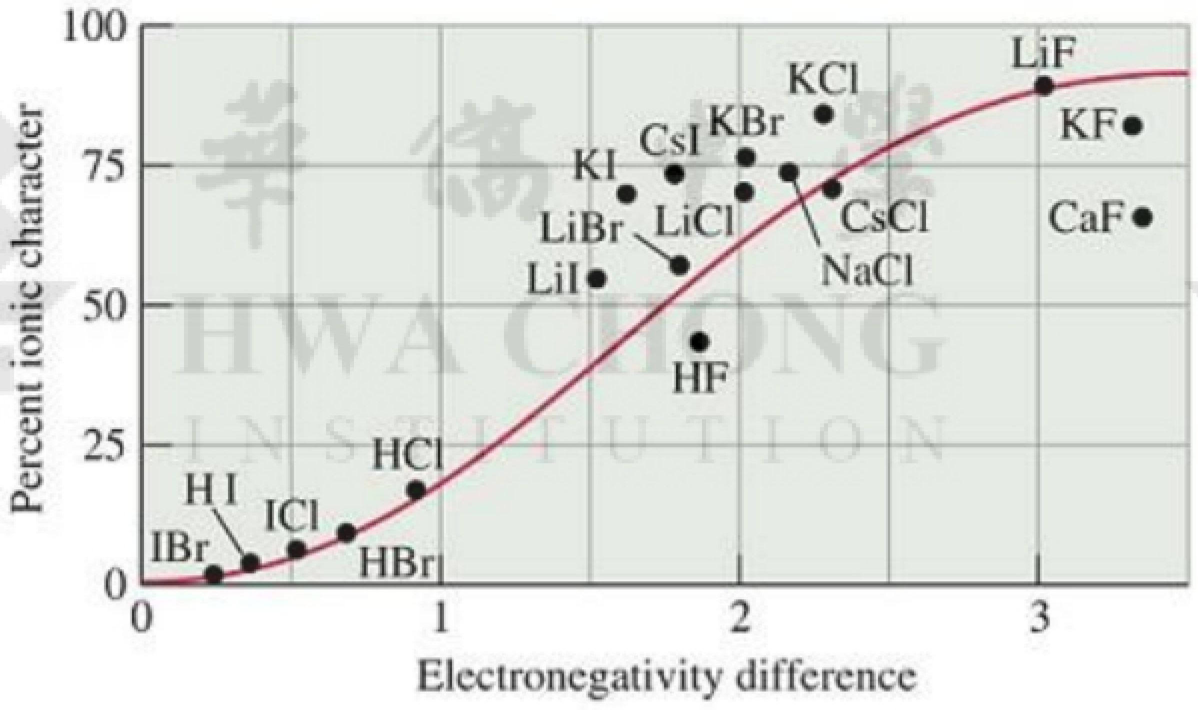


Figure 38. The classification of ionic and covalent bonds is on a continuum, rather than discrete descriptions



General guidelines (not required to memorise):

Electronegativity difference	0 – 0.5	0.5 – 2.0	> 2.0
Nature of bond	non-polar covalent	polar covalent	ionic
Examples	H–H Cl–Cl C–H	H–Cl	Na^+ Cl^-

Figure 39. The electronegativity difference suggests whether a covalent or ionic bonding forms between two atoms

In this section, we will examine other segments of the continuum of chemical bonding – the polar covalent bond and ionic bonding with covalent character.

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a simple covalent molecule in which there's a difference in electronegativity between bonded atoms
↓
unequal sharing of bonding electrons in covalent bond(s)
↓
polar covalent bond(s) in this molecule
↓
any net dipole moment? (shape of molecule must be considered)
↓*yes* ↓*no*
polar molecule non-polar molecule

Figure 46. Summary of the concepts of 'polar covalent bonds' and 'polar vs. non-polar simple covalent molecules'

The concept of molecular polarity only applies to simple covalent molecules. Polyatomic ions like NH_4^+, SO_4^{2-}, CO_3^{2-} and NO_3^- have a full net charge, so the terms 'polar' or 'non-polar' are not applicable to them.

Lecture Exercise 7.1

Deduce whether $CHCl_3$ is polar or non-polar. Draw the structure of the molecule showing the shape. Use δ+ and δ– symbols to identify any individual bond dipoles and deduce if the molecule has a net dipole moment.

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Factors affecting the strength of dispersion forces

1. **The number of electrons or size of electron cloud**. The electron cloud of the molecule or atom is distorted when an instantaneous dipole or induced dipole is set up. The ease with which the electron cloud of a particle can be distorted is called its **polarisability**.

   The larger the number of electrons in a molecule or atom, the larger the size of the electron cloud and the more polarisable it is, as the electrons are further from the nucleus and are therefore held less tightly. So instantaneous dipoles and induced dipoles can form more easily, resulting in stronger dispersion forces.

   Dispersion forces are very weak for small particles like H_2 and He, but much stronger for larger particles like I_2 (thus it is a solid at room temperature).

   In Figure 50, the strength of dispersion forces increases with number of electrons when we go down Group 17 and down Group 18. As a result, boiling point increases.

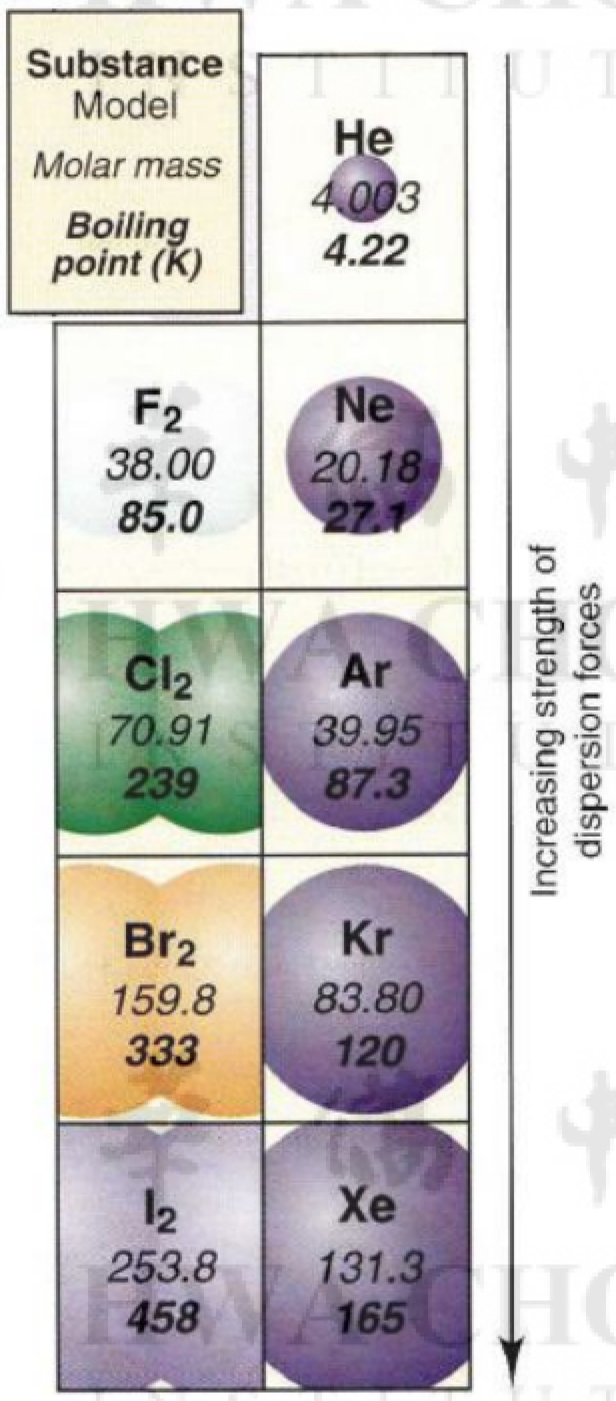


Figure 50. Strength of dispersion forces increases with number of electrons

2. **The molecular shape – surface area of contact between adjacent molecules**. For **non-polar substances with similar number of electrons**, the strength of dispersion forces is influenced by molecular shapes. Shapes that allow more points of contact have more surface area over which electron clouds can be distorted, so induced dipoles can form more easily, resulting in stronger dispersion forces.

   This factor is usually considered when we compare two structural isomers, usually a straight-chain isomer vs. a branched-chain isomer, e.g. pentane vs. 2,2-dimethylpropane (Figure 51). They have the same molecular formula (C_5H_{12}) and therefore the same number of electrons, but different shapes. The straight-chain pentane molecule has a cylindrical shape whereas the branched-chain 2,2-dimethylpropane has a more spherical shape. A cylindrical shape has a larger surface area than a sphere, thus, the surface area of contact between adjacent molecules is greater for pentane than for 2,2-dimethylpropane. Greater contact means induced dipoles can form more easily and dispersion forces can act at more points. Hence, more energy is needed to overcome stronger dispersion forces between pentane molecules and pentane has the higher boiling point.

8.3 Hydrogen bonding

The name 'hydrogen bond' is somewhat a misnomer as it is not a true *bond* but **a stronger type of permanent dipole-permanent dipole attraction**, and must not be confused with a covalent *bond*.

When a hydrogen atom bonds to another atom, its sole electron is used up in the covalent bonding. In the F–H, O–H and N–H bonds, the bonding electrons are pulled strongly towards the highly electronegative fluorine, oxygen and nitrogen atoms. This gives the hydrogen atom a δ+ charge. In fact, the hydrogen atom which has no inner electrons, is practically left with its nucleus which contains only one proton, and so it carries a really significant δ+ charge.

The highly electron deficient hydrogen atom (with a δ+) experiences a particularly strong attraction from the lone pair of electrons on the highly electronegative fluorine, oxygen or nitrogen atom of an adjacent molecule. This force of attraction is called **hydrogen bonding**.

Formation of hydrogen bonding

There are two requirements for hydrogen bonding to occur between two molecules:

- One molecule must contain a hydrogen atom bonded to a highly electronegative fluorine or oxygen or nitrogen atom.
- The other molecule must contain an atom with a lone pair of electrons, on a fluorine or oxygen or nitrogen atom.

[See **N2007/III/5(a)(i)**]

HF, H_2O and NH_3 are typical examples of molecules which form intermolecular hydrogen bonding.

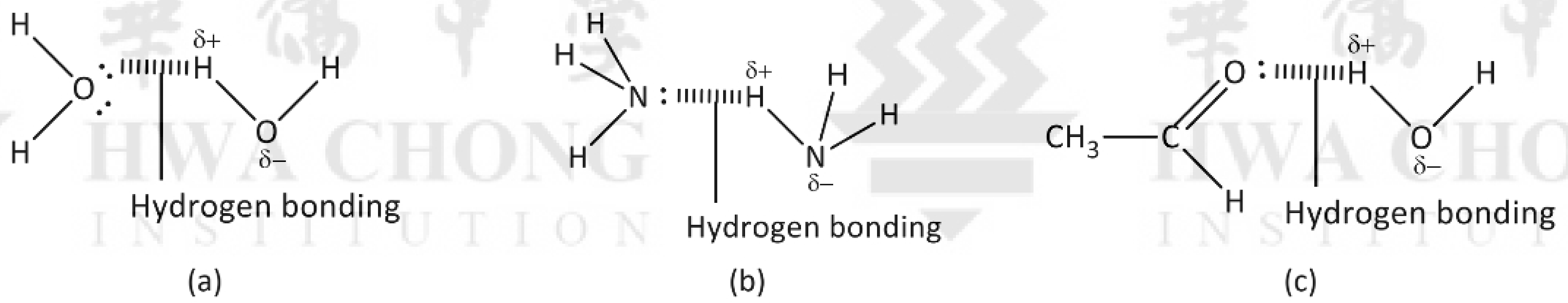


Figure 53. Intermolecular hydrogen bonding

When asked to draw a diagram to illustrate hydrogen bonding, note the following:

- label the dipole for the covalent bond (F–H, O–H or N–H) carrying the acceptor hydrogen atom with 'δ+' and 'δ–' symbols
- draw in the lone pair of electrons for the fluorine, oxygen or nitrogen atom involved in the hydrogen bonding
- Indicate the hydrogen bonding using a dotted/dashed line together with a label

Intermolecular vs. intramolecular hydrogen bonding

An intermolecular hydrogen bond forms between two molecules.

An intramolecular hydrogen bond forms between two different parts of the same molecule. This can occur if the hydrogen bonding 'sites' are near each other in the same molecule. An example is salicylic acid, present in the bark of willow trees.

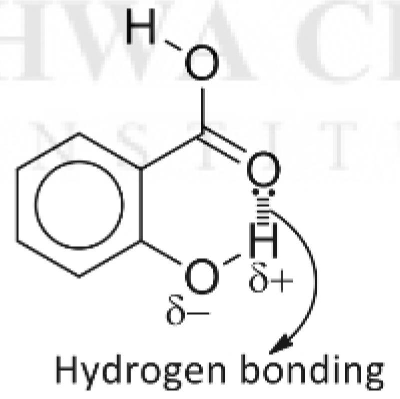
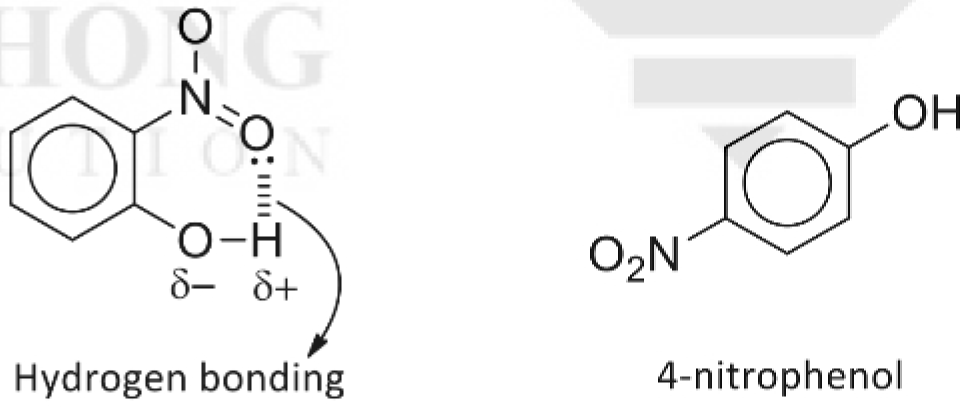


Figure 54. Intramolecular hydrogen bonding in salicyclic acid

The structures of two molecules, *A* and *B*, are shown below (they are structural isomers). In molecule *A*, the –OH and $–NO_2$ groups can form intramolecular hydrogen bonding, so there is less extensive intermolecular hydrogen bonding in a sample of *A* compared to a sample of *B*. Therefore, less energy is needed to overcome the intermolecular hydrogen bonding when *A* boils, hence its lower boiling point. (You may treat the words 'less extensive' as referring to lower average number of hydrogen bonds present in the same mass of molecules *A* vs. *B*.)



molecule *A*, b.p. 214 °C

2-nitrophenol

molecule *B*, b.p. 290 °C

4-nitrophenol

Figure 55. The proximity of the two functional groups in A allows intramolecular hydrogen bonding, and that has an effect on its boiling point compared to its structural isomer B

Many molecules in biological systems, like proteins and nucleic acids, contain polar $^{\delta-}$N–H$^{\delta+}$ and $^{\delta-}$O–H$^{\delta+}$ bonds. Hydrogen bonding in these substances is one factor that determines their overall structures and biological functions. For example, intermolecular hydrogen bonding gives the double helix structure of DNA; intramolecular hydrogen bonding gives the secondary structures of proteins.

Effect of hydrogen bonding on the boiling points of NH_3, H_2O and HF compared to other hydrides

The boiling points of NH_3, H_2O and HF are considerably higher than that of CH_4; and considerably higher than those of other hydrides in their respective groups.

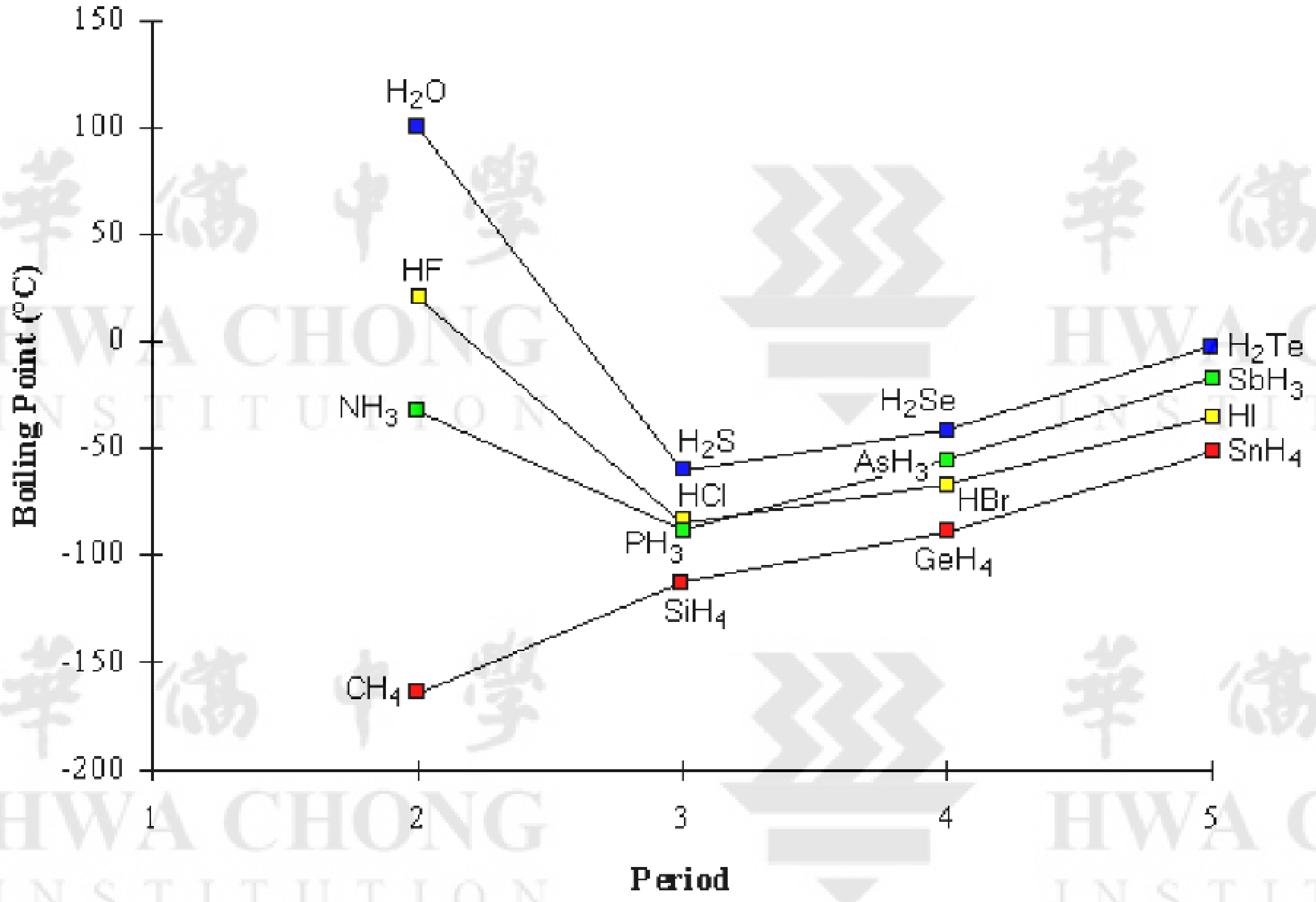


Figure 56(a). Boiling points of simple covalent hydrides of Periods 2-5 and Groups 14 – 17 (including NH_3, H_2O and HF)

Let us examine the boiling point data down each Group.

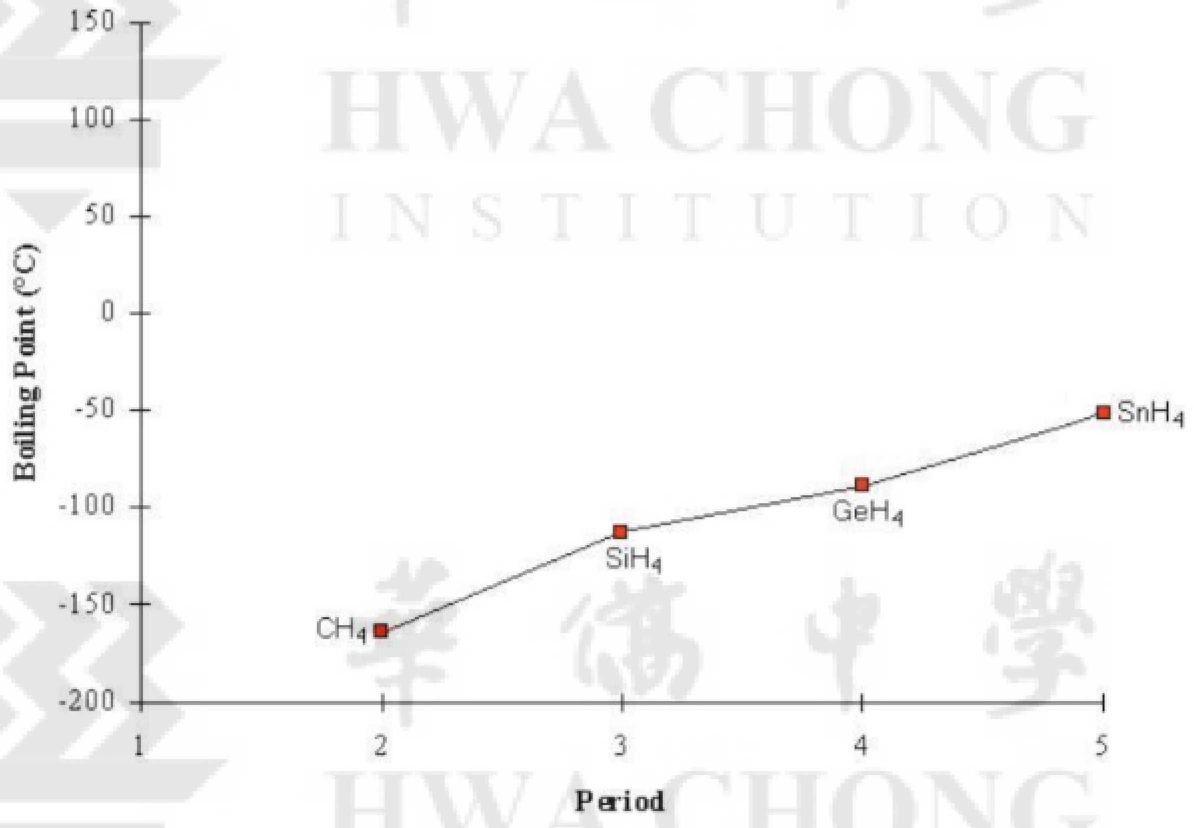


Figure 56(b). Boiling points of hydrides of Group 14

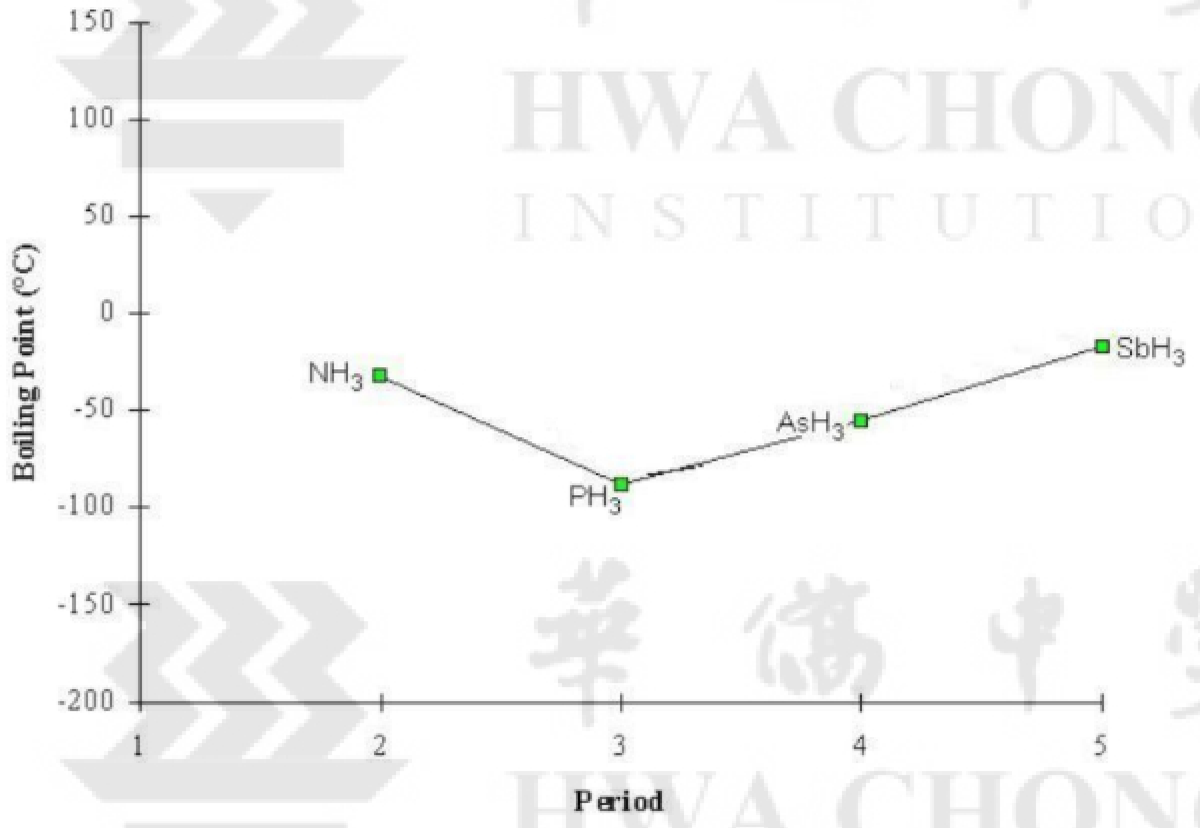


Figure 56(c). Boiling points of hydrides of Group 15

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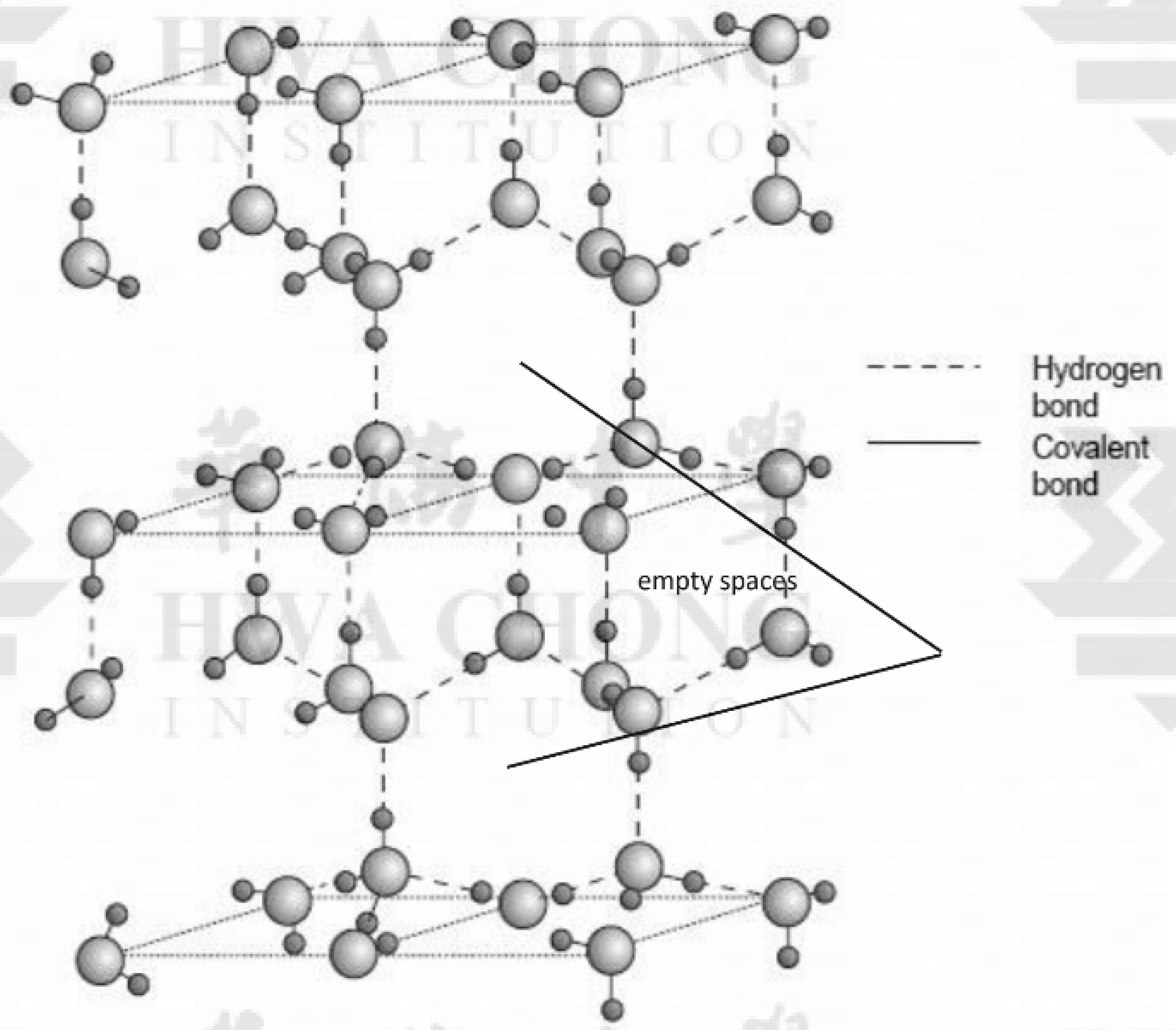
Unusual properties of water due to hydrogen bonding

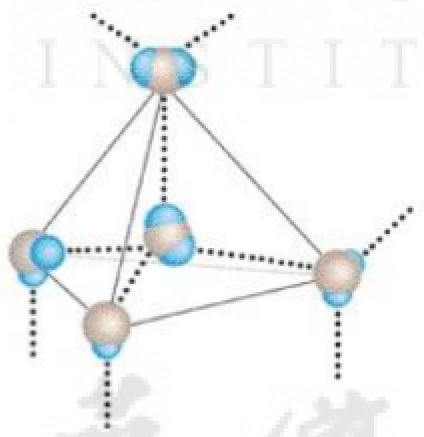
Apart from its higher-than-expected boiling point, water shows the following anomalous properties.

1. Liquid water has high surface tension (defined as the amount of force required to break the layer of water molecules on its surface). The hydrogen-bonded H_2O molecules form an array across the surface of water, allowing objects which you might expect to sink in water, such as pond skaters and even small coins (if you are careful), to 'float' on water.
2. Most substances have a higher density in the solid state than in the liquid state. However, ice (solid state) is less dense than liquid water. In the solid state, H_2O molecules are held at fixed positions and arranged in an orderly manner to form a regular lattice such that hydrogen bonding is maximised to *four* per molecule. The hydrogen bonding between water molecules in ice are positioned in a roughly tetrahedral shape around each O atom. This produces an open lattice, with empty spaces between the H_2O molecules. The more random arrangement of hydrogen bonding in liquid water results in H_2O molecules packing much more closely and, together, take up less space. So the lattice structure of ice occupies a larger volume for the same mass of liquid water, hence ice has a lower density than liquid water.

(a) lattice structure of ice



(b) tetrahedral arrangement of other H_2O molecules around each H_2O molecule in ice



(c) random arrangement of H_2O molecules in liquid water

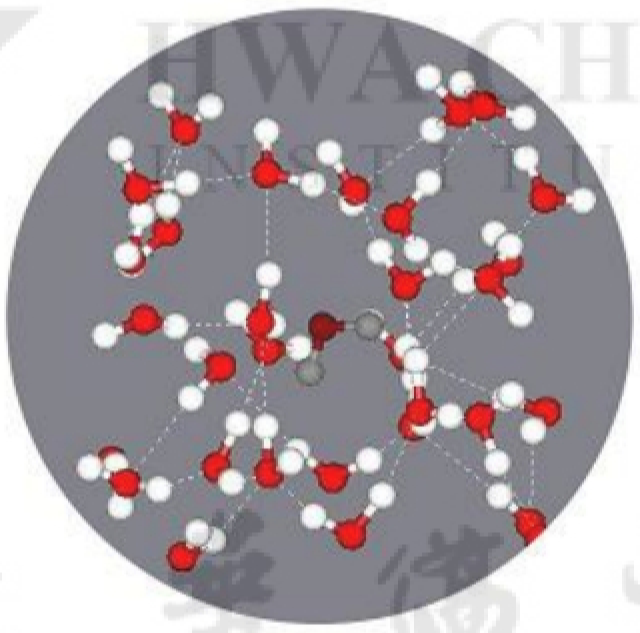
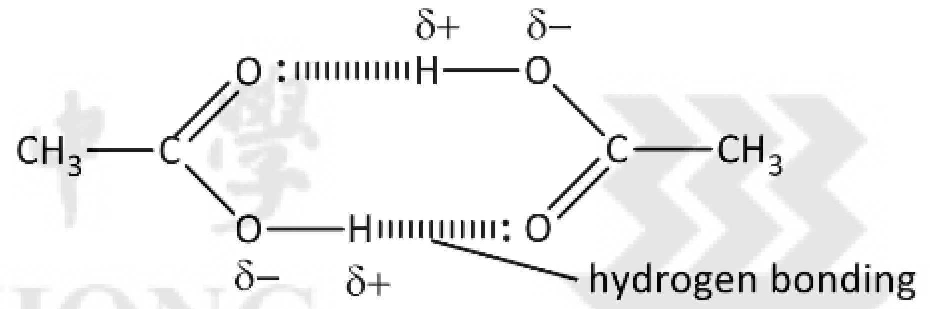


Figure 57. Tetrahedral arrangement in ice vs random arrangement in liquid water

Dimerisation of carboxylic acids due to hydrogen bonding

An example of this occurs in ethanoic acid, CH_3CO_2H. The relative molecular mass, M_r, of ethanoic acid is 60. If the M_r of a sample of ethanoic acid, measured in the gas phase or when it is dissolved in a non-polar solvent, is found to be 120, the molecules must have formed dimers.



9 PHYSICAL PROPERTIES OF COVALENT COMPOUNDS

9.1 Physical properties of simple covalent compounds

Melting and boiling points

The melting and boiling points of simple covalent compounds are usually lower than those of metals, ionic compounds or giant molecular compounds. This is because less energy is needed to overcome the weaker intermolecular attractions between the discrete molecules (dispersion forces, permanent dipole-permanent dipole attractions or hydrogen bonding), compared to the stronger metallic bonding, ionic bonding or covalent bonds.

Electrical conductivity

Simple covalent compounds are unable to conduct electricity in the solid or liquid state as there are no mobile charge carriers. This is because in the molecules, all electrons are either held in the covalent bonds or held by the nuclei and are not free to move throughout a sample of that substance. Also, no mobile ions are present. Simple covalent molecules are electrically neutral and cannot act as charge carriers.

However, some simple covalent substances are able to react with water to give aqueous ions. This allows the resulting solution to conduct electricity. Example: $HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$

Solubility

Many simple covalent compounds are soluble in organic solvents like propanone (CH_3COCH_3), tetrachloromethane (CCl_4) and benzene (C_6H_6). Some are soluble in water (e.g. ethanol, ethanoic acid, glucose). See Section 11 for a detailed explanation on the solubility of covalent compounds.

9.2 Physical properties of giant molecular compounds

Giant molecular compounds are also known as network covalent solids. They do not consist of separate or discrete molecules. Instead, the atoms in the compounds are held together by covalent bonds that extend in three dimensions throughout the sample. This type of covalent compound is said to have a giant molecular lattice structure. Their physical properties reflect the strength of covalent bonds.

Diamond and quartz

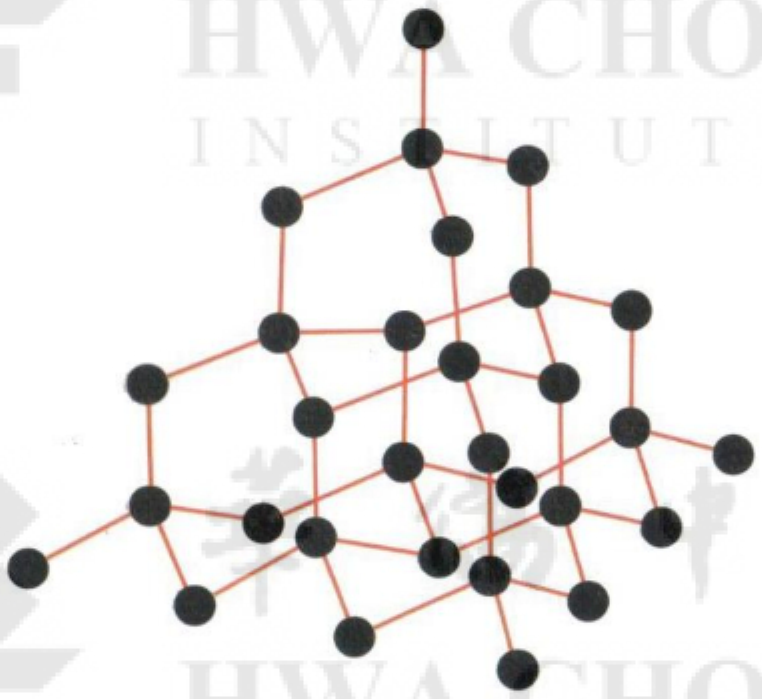


Figure 58. Structure of diamond

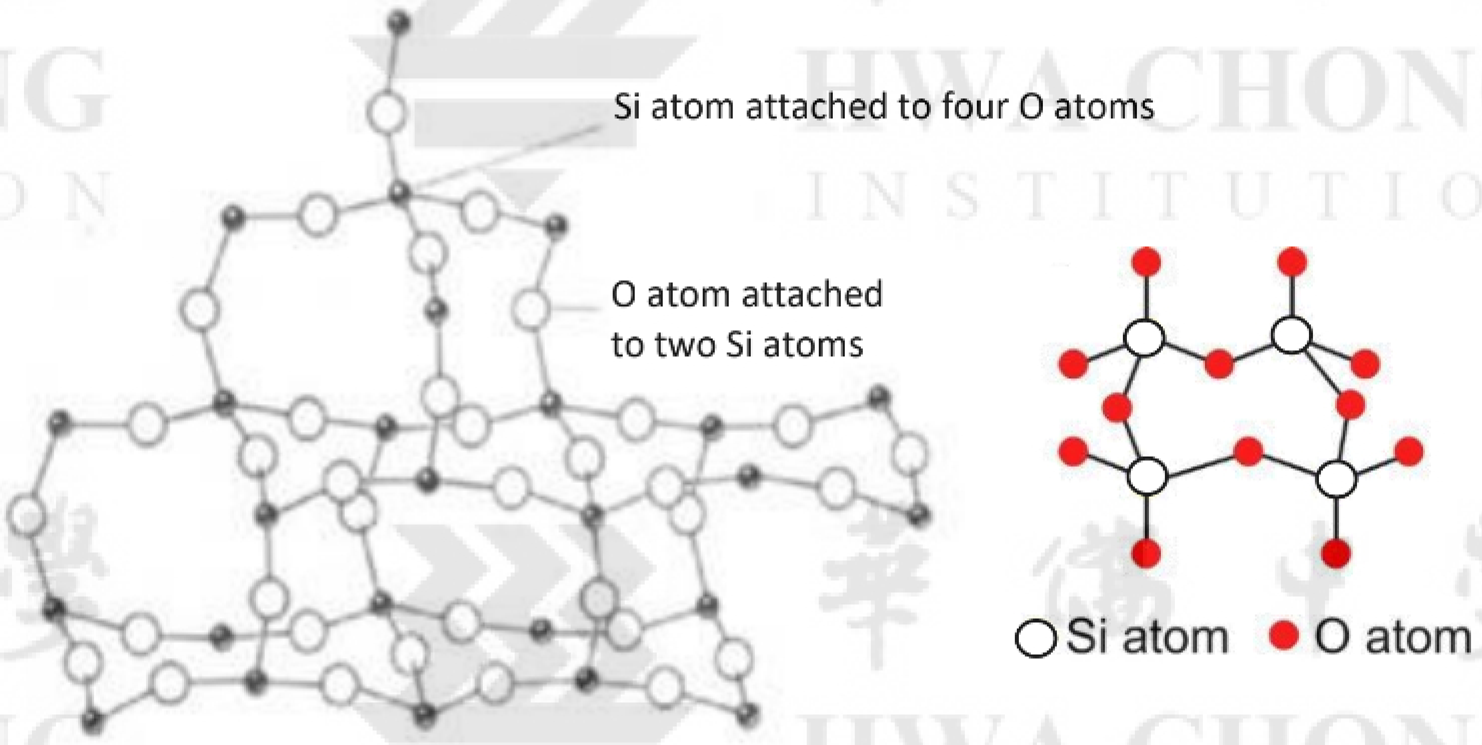


Figure 59. Structure of quartz (SiO_2)

In diamond, each C atom is tetrahedrally bonded to four other C atoms, an arrangement that extends throughout the giant lattice. With its giant lattice and strong covalent bonds connecting all the C atoms, diamond is very hard (the hardest natural substance known), has an extremely high melting point (3550 °C) and is insoluble in any solvent. (A single crystal of diamond or quartz is in fact a *single* molecule containing maybe 1×10^{23} atoms.)

The diamond molecule is electrically neutral, no ions are present. All electrons are either held in the covalent bonds or held by the nuclei and are not free to move. Without mobile charge carriers, diamond is a non-conductor of electricity.

In quartz (SiO_2), each Si atom is covalently bonded to four O atoms, and each O atom is bonded to two Si atoms in a pattern that extends throughout the giant lattice. No separate SiO_2 molecules exist. Hence the formula SiO_2 is an empirical formula, not a molecular formula. Quartz is also very hard and has a very high melting point (1610 °C).

Graphite

Graphite is also considered as having a giant molecular structure. Graphite and diamond are allotropes of carbon. (Allotropes are different forms of the same element, in which the atoms or molecules are arranged in different ways.)

Table 8. The physical properties of diamond and graphite are very different

Property	Diamond	Graphite
Colour	colourless and transparent	black and opaque
Hardness	very hard – the hardest naturally occurring solid	very soft and slippery – over 500 times softer than diamond
Electrical conductivity	very poor – a good insulator	very good along the layers
Density	3.51 g cm^{-3}	2.27 g cm^{-3}

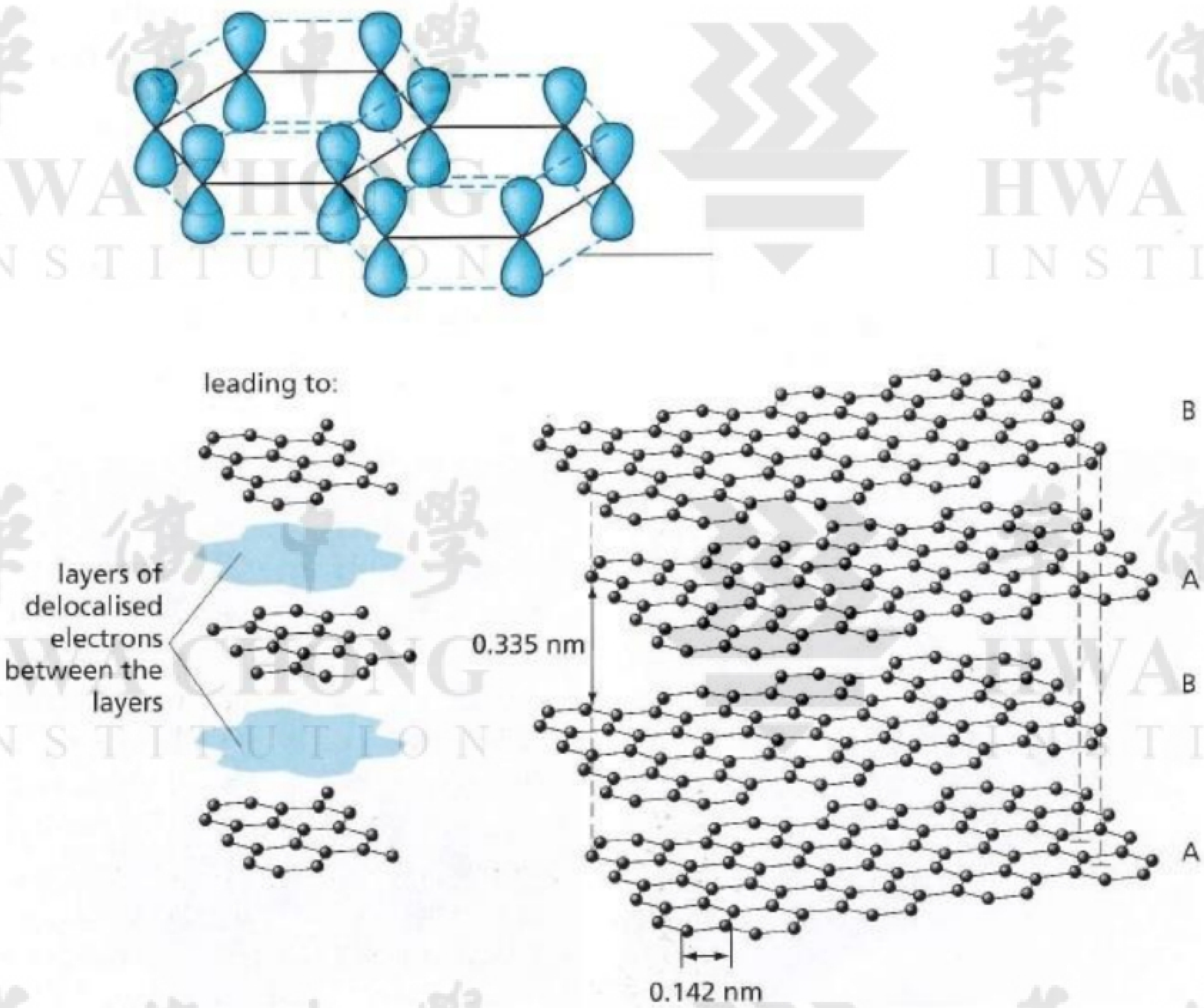


Figure 60. Structure of graphite

In graphite, all the C atoms are sp^2 hybridized and each C atom is covalently bonded to three other C atoms. A two-dimensional sheet of C atoms is formed (unlike diamond's three-dimensional network). Each C atom has a 2p orbital containing one electron that is not used in the formation of C–C bonds. The 2p orbitals can overlap with each other to form a two-dimensional delocalised π bonding system spreading throughout the whole sheet of atoms. A graphite crystal is composed of many sheets or layers of atoms, stacked one on top of another. Each sheet is actually a single molecule.

The dispersion forces between one sheet and the next are quite substantial because of the large surface area involved. But they are still weak enough to allow the layers to slide over each other easily. Thus, graphite is soft and slippery. It is used as a component of lubricating greases. As the layers of C atoms can easily be rubbed off a lump of graphite leaving a black trace on paper, graphite is used in pencils (that is one of its first uses).

Graphite is a good conductor of electricity and is used as electrodes for electrolysis and brushes in electric motors. Each C atom only uses three valence electrons in covalent bonding, its fourth electron is delocalised over each layer. These delocalised electrons can act as mobile charge carriers. But the delocalised electrons cannot 'jump' from one layer to the next. So graphite is a good conductor only along the layers but a poor conductor in the direction at right angles to the layers. The same is true of the conduction of heat. Therefore, graphite is used in large crucibles (e.g. containing a molten metal) where the conduction of heat along the walls needs to be encouraged, but the transfer of heat directly through the bottom is not wanted.

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10 LATTICE STRUCTURES OF CRYSTALLINE SOLIDS

10.1 Types of lattice structures

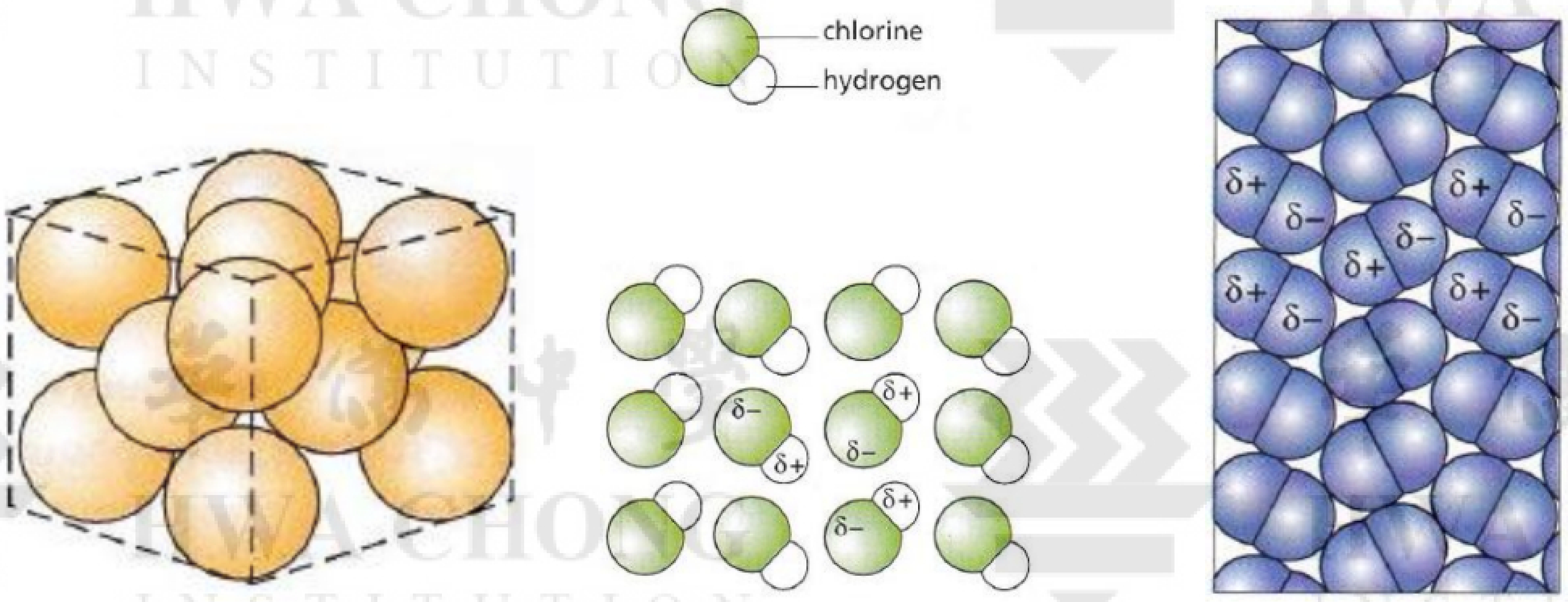
In **crystalline solids**, particles are arranged in a **regular** three-dimensional pattern or array. This is called a **lattice**.

There are a few types of lattice:

- giant metallic lattice e.g. in copper, iron and all other solid metals
- giant ionic lattice e.g. in $NaCl$, MgO, $CaCO_3$
- simple atomic lattice e.g. in solid argon and the other noble gases
- simple molecular lattice e.g. in ice, solid HCl, solid iodine
- giant molecular lattice e.g. in diamond, Si, SiO_2, boron nitride

Each type confers different physical properties upon the substance that contains it. The features of each lattice structure and its associated physical properties have already been explained in earlier sections, with the exception of the simple atomic and simple molecular lattices, which is illustrated in Figure 61.

Simple atomic and simple molecular lattices



(a) In solid argon, a simple atomic lattice, the Ar atoms are held together by weak dispersion forces

(b) Solid hydrogen chloride, a simple molecular lattice. What intermolecular attraction hold the HCl molecules together?

(c) Solid iodine, a simple molecular lattice. What intermolecular attraction hold the I_2 molecules together?

Figure 61. Lattice structures of solid Ar, solid HCl, solid I_2

In this course, we are required to know how to describe in simple terms, the different types of lattice structures of the following crystalline solids:

• metallic, as in copper	(see Section 2.1)
• ionic, as in $NaCl$, MgO	(see Section 3.3)
• simple molecular, as in iodine	(see above)
• hydrogen-bonded, as in ice	(see section on 'Unusual properties of water')
• giant molecular, as in graphite; diamond	(see Section 9.2)

10.2 Covalent radius and van der Waals radius (Refer to the *Data Booklet*)

Consider the example of solid iodine, which has a simple molecular lattice structure. When we measure the distances between two iodine nuclei in a sample of solid I_2, we obtain two different values.

The shorter distance is between two bonded iodine atoms in the same molecule. That is the I–I **bond length** and half of this distance is called the **covalent radius**, and is listed in the *Data Booklet* under the label 'single covalent'.

The longer distance is between two non-bonded iodine atoms in adjacent molecules. It is called the van der Waals distance. Half of this distance is called the **van der Waals radius**, and is listed in the *Data Booklet* under the label 'van der Waals'.

The van der Waals radius of an atom is always larger than its covalent radius, but the van der Waals radii decreases across a period and increases down a group, just as the covalent radii does.

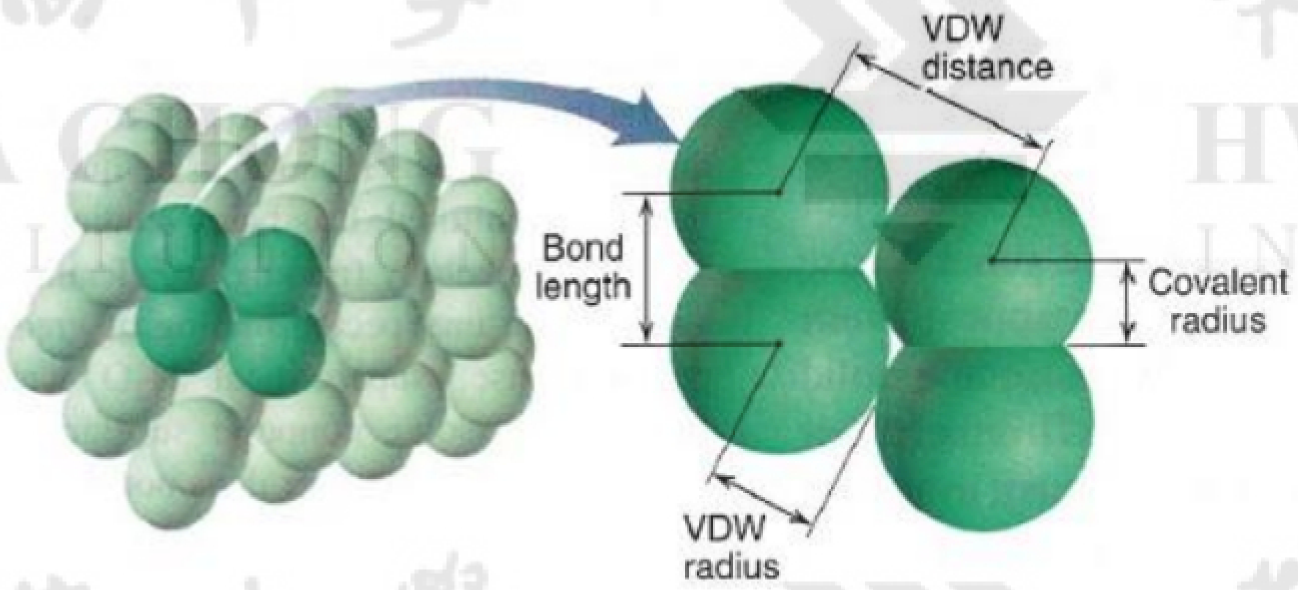
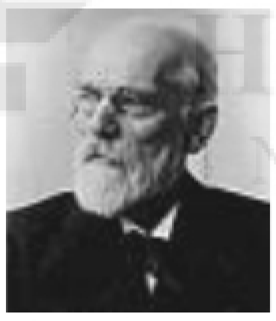


Figure 62. Covalent radius and van der Waals radius shown for solid iodine

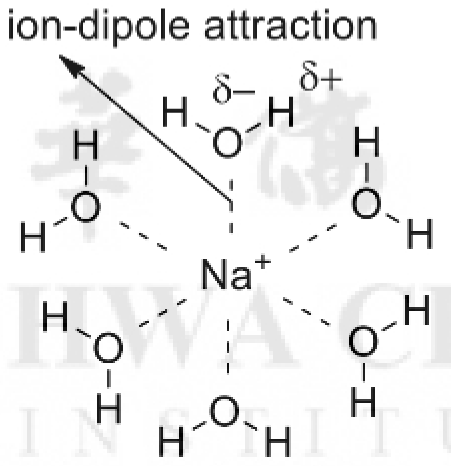


Johannes Diderik van der Waals (1837 – 1923), winner of the Nobel Prize in physics. Dutch theoretical physicist and thermodynamicist famous for his work on an equation of state for gases and liquids. He was one of the first to postulate the existence of 'intermolecular force'. His name is associated with van der Waals forces (forces between molecules), van der Waals molecules (small molecular clusters bound by van der Waals forces) and van der Waals radius.

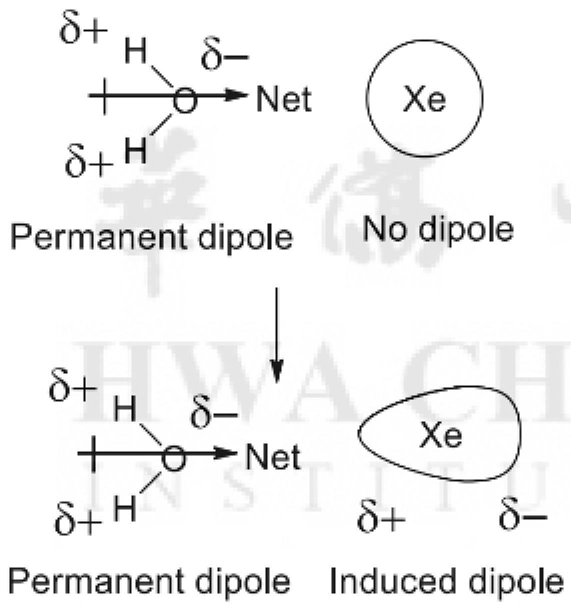
11 EXPLAINING THE SOLUBILITY/MISCIBILITY OF A SUBSTANCE IN A GIVEN SOLVENT

All intermolecular forces of attraction discussed in Section 8 for pure substances can be used to explain the solubility or miscibility of a substance in a given solvent. We also need to define several other intermolecular forces of attraction that was not discussed in Section 8.

1. **Ion-dipole attractions** occur between an ion and the oppositely charged end of a dipole. This attraction is weaker than ionic bonding but stronger than hydrogen bonding, permanent dipole-permanent dipole interactions and dispersion forces. However, because it is very extensive, it releases a lot of heat when formed.



2. **Permanent dipole-induced dipole interactions** occur when a polar molecule distorts the electron cloud of a nearby atom or non-polar molecule. This form of attraction is generally weak and releases little heat when formed. This form of interaction is very similar to dispersion forces, and is comparable to dispersion forces in terms of strength.



Previously, you have learnt that energy is released during bond forming and energy is required for bond breaking. Similarly, when intermolecular attractions are formed, energy is released, while energy is required to overcome intermolecular attractions.

The process of dissolution

When a solute dissolves in a solvent, the particles of the solute mix freely with the particles of the solvent. For this to happen, the interaction between the particles of the solute must be overcome and the same must occur for the solvent particles. Then, the particles of the solute need to form favourable interactions with the particles of the solvent.

The energetic aspect of dissolution

In terms of energy changes, a solute is soluble in a solvent if the energy released from solute-solvent interactions is greater than or comparable to the energy needed to overcome solute-solute interactions and solvent-solvent interactions.

Explaining the solubility/miscibility of two substances

When explaining the solubility/miscibility of two substances, it is helpful to:

- identify the type of interactions holding solute particles together
- identify the type of interactions holding solvent particles together
- identify the type of interaction that can occur between the solute and the solvent particles
- compare the relative strength of the new interactions (solute-solvent) against the existing interactions (solute-solute and solvent-solvent)

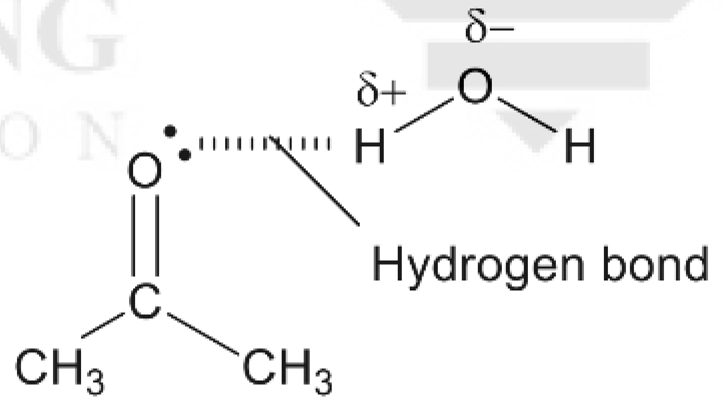


Figure 64. Hydrogen bonding between CH_3COCH_3 and water molecules

- **Hexane is immiscible with water**

The polar water molecules induces a dipole in hexane molecules, thus **permanent dipole-induced dipole interactions** occur between hexane and water. Permanent dipole-induced dipole interactions are rather weak, thus the energy released when hexane mixes with water is insufficient to compensate for the energy needed to overcome the dispersion forces between hexane molecules, and the relatively stronger hydrogen bonding in water. Thus, hexane is immiscible with water.

- **$\mathrm{NaC}l(s)$ is soluble in water**

$\mathrm{NaC}l(s)$ dissolves readily in water, i.e. $\mathrm{NaC}l(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Na^+}(aq) + \mathrm{C}l^-(aq)$, because the ions form **ion-dipole attractions** with water molecules. Ion-dipole interactions are relatively strong and very extensive, thus the energy released when $\mathrm{NaC}l$ dissolves in water is able to compensate for the energy required to overcome the hydrogen bonding in water and ionic bonding between $\mathrm{NaC}l$.

Figure 65 illustrates the 'microscopic' processes that occur when an ionic solid such as $\mathrm{NaC}l$ dissolves in water.

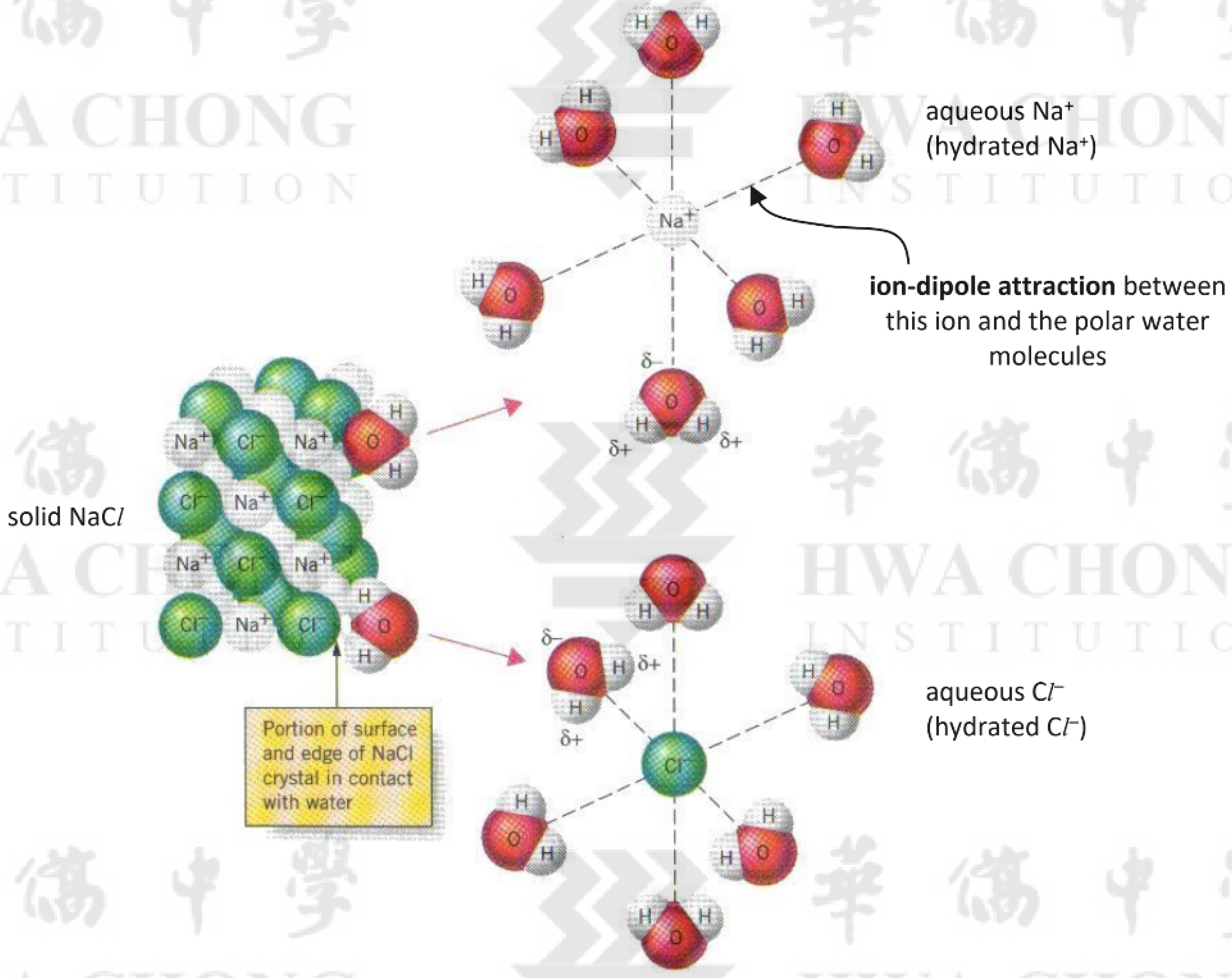


Figure 65. Water molecules form ion-dipole attractions with ions on the crystal's surface, forming solvated aqueous ions

Each ion forms **ion-dipole attractions** with the surrounding water molecules and the ion becomes detached from the crystal's surface. The detached ion which is surrounded by water molecules and is said to be **hydrated**. As more ions detach from the crystal at its surface, the ionic crystal structure breaks down and the solid dissolves.

Not all ionic compounds are soluble in water e.g. silver chloride is practically insoluble in water. We may explain in this manner: The energy released from the ion-dipole attractions is not large enough to compensate the energy required to overcome the ionic bonding and break up the ionic lattice. This is because the Ag^+ cation is much larger than the Na^+ cation. Thus, the Ag^+ cation has a much lower charge density and is unable to form ion-dipole interactions to the same extent as Na^+. In Topic 5 Energetics, you will learn how we can quantify the heat evolved when ions are hydrated, or when ionic bonding occurs, which can then be used to account for the solubility of ionic compounds.

Lecture Exercise 11.1

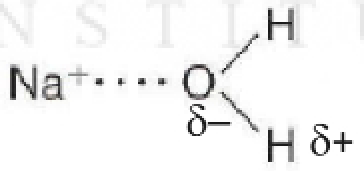
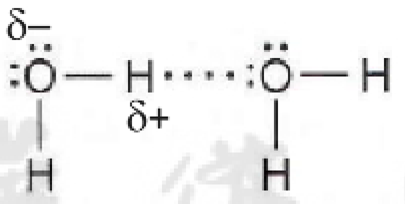
Explain why solid iodine is soluble in an organic solvent such as CCl_4 but insoluble in water.

12 SUMMARY OF THE DIFFERENT TYPES OF CHEMICAL BONDING

Chemical bonding are forces of attraction that arise from electrostatic attractions between opposite charges. These forces of attraction are due to the attraction between metal cations and delocalised valence electrons (metallic bonding), cations and anions (ionic bonding), or nuclei and electron pairs (covalent bonding). It also includes forces of attraction are due to the attraction between molecules as a result of partial charges, or the attraction between ions and molecules.

These forces of attraction differ in strength – some forces of attraction are stronger because they involve larger charges that are closer together, i.e. covalent bonding, whereas other forces of attraction are weaker because they typically involve smaller charges that are farther apart, i.e. dispersion forces.

Table 9. Comparison of the different types of chemical bonding

Types of chemical bonding	Basis of attraction	Energy /kJ mol^{-1}	Example
ionic	cation – anion	400 – 4000	$NaCl$
covalent	nuclei – shared electrons	150 – 1100	H–H
metallic	cations – delocalised electrons	75 – 1000	Fe
ion-dipole attraction	ion charge – dipole charge	40 – 600	
hydrogen bonding	δ+ H – lone pair on F or O or N	10 – 40	
permanent dipole-permanent dipole attraction	dipole charges	5 – 25	 $\overset{\delta+}{I}-\overset{\delta-}{Cl}\cdots\overset{\delta+}{I}-\overset{\delta-}{Cl}$
permanent dipole-induced dipole attraction	dipole charge – polarisable electron cloud	2 – 10	$H-Cl\cdots Cl-Cl$
dispersion forces, also called instantaneous dipole-induced dipole attraction	polarisable electron clouds	0.05 – 40	$F-F\cdots F-F$

13.2 Electrical conductivity of elements across Period 3

Figure 69 shows the variation in electrical conductivity for the Period 3 elements, sodium to argon.

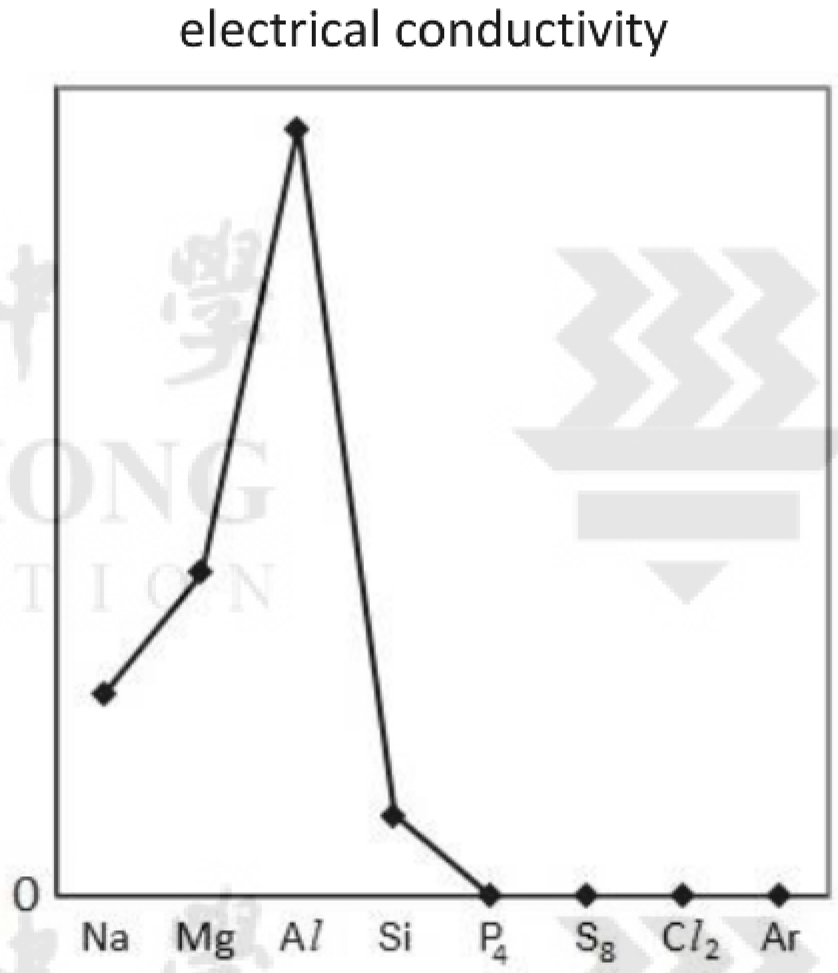


Figure 69. Variation in electrical conductivity for period 3 elements

Similarly, we can explain the variation in electrical conductivity by considering the structure and bonding present in each element:

Na, Mg and A*l* are metals. Metals are good electrical conductors because the metallic lattice contains a sea of delocalised valence electrons which are free to move and carry charge.
From Na to Al, the number of valence electrons that can be contributed per atom increases. Therefore, electrical conductivity increases.

Si is a metalloid (an element with properties of metals and non-metals).
It is a semiconductor.

P_4, S_8, Cl_2 and Ar are non-metals.
In the neutral simple covalent molecules P_4, S_8 and Cl_2, outer electrons are held strongly in covalent bonds and are not free to move about.

For Ar, it exists as individual neutral atoms.
All four do not contain mobile charge carriers and therefore do not conduct electricity.

Self-Practice 13.1

Using the data provided below, describe the various forces responsible for keeping the particles together in the element or compound. Account for the melting point of each substance in terms of its structure and bonding.

substance	*formula*	*molar mass /g mol^{-1}*	*m.p. / °C*
neon	Ne	20	–248
argon	Ar	40	–189
water	H_2O	18	0
sodium fluoride	NaF	42	993
graphite	C	12	3948

Remark: Molar mass or M_r data are often included in questions like the above. This is because the number of electrons in an atom or molecule somewhat correlates with molar mass or M_r. However, you need not discuss molar mass or M_r when comparing the strength of the various types of chemical bonding.

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LOOKING AHEAD

The study of chemical bonding, the structure of elements and compounds, as well as the interactions present explains their physical properties. These ideas will be pertinent when discussing the properties of aqueous and gaseous systems, as well as the concept of chemical changes or reactions. In preparation for the coming topics, consider the following questions:

- How does chemical bonding influence the movement of gaseous particles?
- How does chemical bonding influence chemical changes?
- How is energy related to chemical bonding?
- How can we measure the strength of a chemical bond?

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