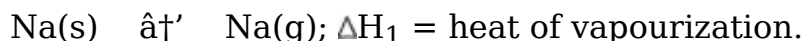# 2.   Chemical Bonding
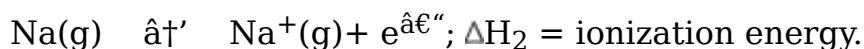
2.1   Ionic Bonding

The formation of sodium chloride from solid sodium and gaseous chlorine illustrates the factors which determine ionic bond formation. The formation of sodium chloride NaCl, involves the following processes:
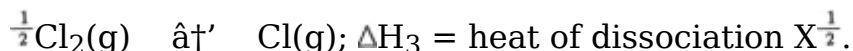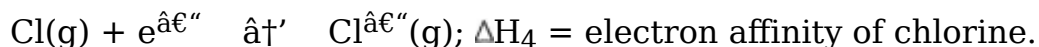
(i)   vapourization of sodium:

$Na(s) \rightarrow Na(g); \Delta H_1$ = heat of vapourization.

(ii)   ionization of sodium:

$Na(g) \rightarrow Na^+(g) + e^-; \Delta H_2$ = ionization energy.

(iii) dissociation of chlorine;

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g); \Delta H_3$ = heat of dissociation $X\frac{1}{2}$.

(iv)   electron affinity of chlorine;

$Cl(g) + e^- \rightarrow Cl^-(g); \Delta H_4$ = electron affinity of chlorine.

(v)   the sodium and chloride ions are then joined together by electrostatic attraction, releasing energy known as the lattice energy, U, of the compound.

$Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s) ; \Delta H_5$ = lattice energy.
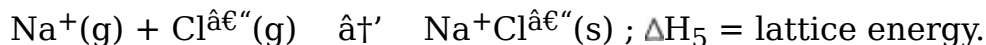
The heat of formation of sodium chloride, ΔH_f, is the algebraic sum of these different heats of reactions.

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5.$$

The formation of the compounds of the alkali and alkaline earth metals with the group 6 and 7 elements follows the same steps. The vapourization and dissociation energies, ΔH_1 and ΔH_3, are positive. That is, energy is absorbed for these processes. The ionization energies of the alkali and alkaline earth metals are also positive. The electron affinities of some groups 6 and 7 elements are positive too. Since the alkali and alkaline earth metals are able to form ionic compounds with the groups 6 and 7 elements, the lattice energies of the resulting compounds must be very high numerically and negative. That is, a lot of heat is evolved when the ions unite, giving an overall

negative heat of formation. These figures, for a number of alkali and alkaline earth metal compounds with groups 6 and 7 elements, are shown in Table 2.1.

TABLE 2.1: Heats of formation of some ionic compounds

Compound	ΔH_1	ΔH_2 (I.E)	ΔH_3	ΔH_4 (E.A)	ΔH_5 (U)	ΔH_f^*
NaCl	+ 109	+ 500	+ 121	− 370	− 711	− 411
KCl	+ 90	+ 424	+ 121	− 370	− 701	− 411
MgO	+ 150	+2198	+ 248	+ 691	− 3889	− 602
CaO	+ 193	+1752	+ 248	+ 685	− 3513	− 635
MgS	+ 150	+2198	+213	+ 330	− 3238	− 347
CaS	+ 193	+ 1752	+ 213	+ 325	− 2966	− 483

* units of ΔH = kJ mol^{-1}.

Elements with very high positive ionization energies cannot form ionic compounds with those with very high positive electron affinities. This is because the lattice energies of the products might not be high and negative enough to compensate for these two highly positive heats of reaction. Therefore, only the Groups 1, and 2 elements form truly ionic compounds with groups 6 and 7 elements.

EXERCISE 2.1

The heat of vapourization of carbon (graphite) is +715 kJ mol^{-1}. Its fourth ionization energy is +6220 kJ mol^{-1}. The heat of dissociation of chlorine is +121 kJ mol^{-1}, and its electron affinity -370 kJ mol^{-1}. What value of lattice energy is needed for carbon and chlorine to form an ionic compound with a heat of formation of at least - 1.0kJ mol^{-1}?
   Answer: -6687 kJ mol^{-1}

Properties of Ionic Compounds

(a)   Ionic compounds exist as aggregates of positively and negatively charged ions held together in regularly shaped crystals by electrostatic forces. The shape of the sodium chloride crystal is a cube.

(b)   Most ionic compounds have high melting points because the ions are held together by strong forces stretching out in all directions.

(c)   In the molten state or solution, the ions are free to move towards the poles of an applied potential difference. Ionic compounds therefore conduct electricity in these states. Their ability to conduct electricity when dissolved in water means that there is an

interaction between the water molecules and the ions, strong enough to break the stable crystal arrangements. This interaction is due to the dipole nature of water. Each sodium ion in solution is surrounded by the negative end of water molecules and each chloride ion by the positive end of water molecules.
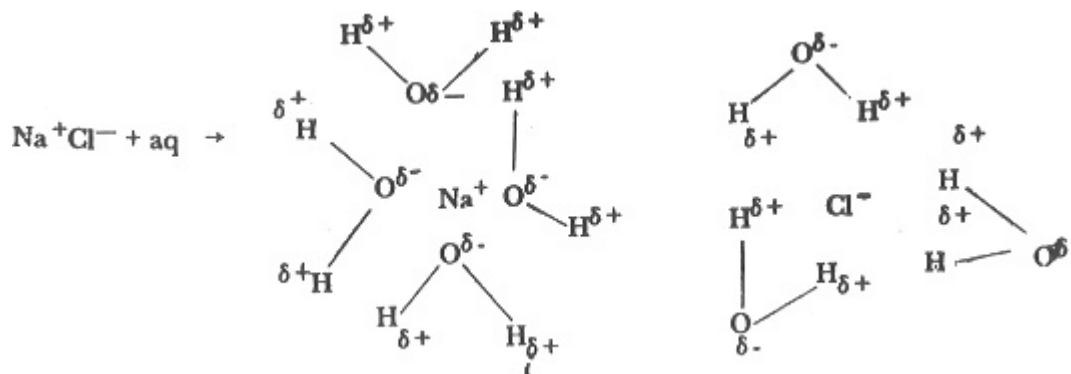

2.2 Covalent Bonding

Covalent bond has been described as a link between two atoms resulting from the sharing of equal number of valence electrons contributed by each atom. Only electrons in unpaired atomic orbitals may be contributed for sharing. Sharing involves the overlap of two atomic orbitals, each of which contains an unpaired electron. Such an overlap results in the formation of a molecular orbital from the two atomic orbitals. The electrons in the overlapping atomic orbitals spin in opposite directions in the resulting molecular orbital.

Two conditions necessary for the overlap of atomic orbitals are:

(i)   the overlapping atomic orbitals must be of similar energy levels; and

(ii) the orbitals must be in the same plane.

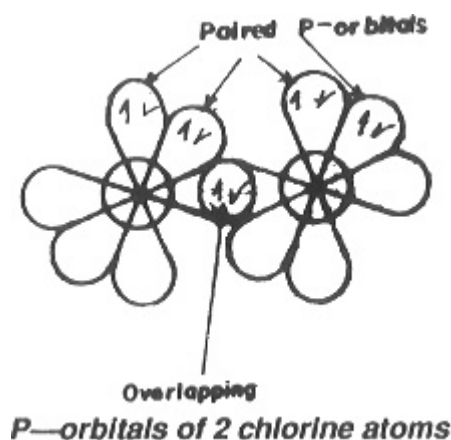The overlap of the s– atomic orbitals of two hydrogen atoms is shown in Figure 2.1.
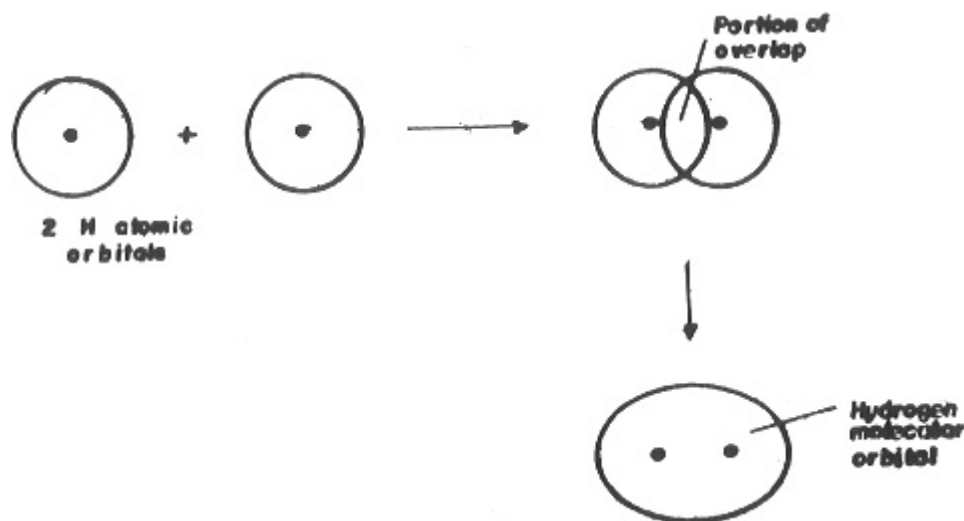
The electronic configuration of the resulting molecular orbital is $1s^2$, which is the configuration of a helium atom. So, the driving force for the overlap is the attainment of a stable, noble gas electronic configuration.

This is the electronic configuration of Fluorine, Atomic No. = 9.


That is, there is a p‑orbital with an unpaired electron. The overlap of this orbital with a similar orbital in a second fluorine atom results in a molecular orbital of fluorine.


Figure 2.2: Molecular orbital of fluorine.

An oxygen atom has two unpaired-electron orbitals. Its electronic configuration is: $1s^2\ 2s^2\ 2p_x^2.\ 2p_y^1\ 2p_z^1$. The orbitals are shown in Figure 2.3 (a). The overlap of the two unpaired-electron atomic orbitals of one oxygen atom with two similar orbitals in a second oxygen atom forms a molecular orbital. A double bond is thereby formed between the two oxygen atoms.
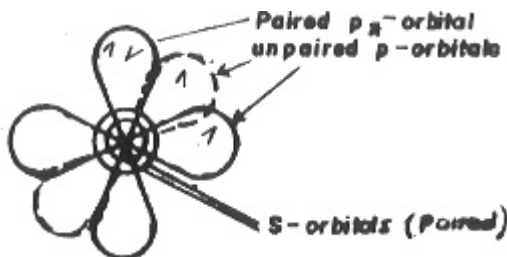
(a) A tomic orbitals of oxygen
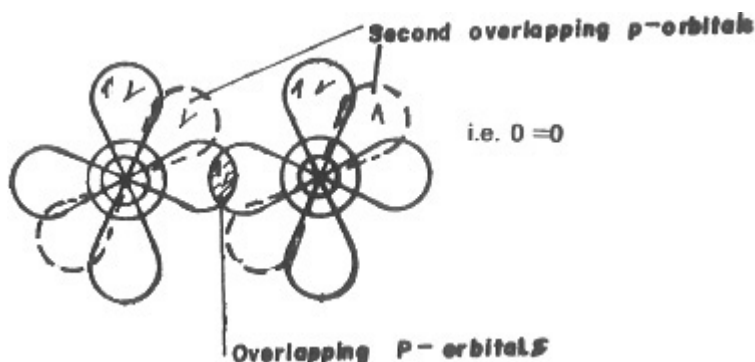
(b) Molecular orbitals of oxygen.

Figure 2.3: Atomic and molecular orbitals of oxygen.

Hybridization

Carbon has two unpaired electrons and an electronic configuration of $1s^3\ 2s^3\ 2p_x^1\ 2p_Y^1\ 2p_z^0$. But it shows a covalency of four rather than two suggested by this electronic configuration. To account for its tetravalence it is proposed that the ground state carbon first absorbs energy to become excited before bonding takes place. The energy absorbed is used to promote a 2s–electron into the vacant 2p–orbital. An excited carbon atom thus has the electronic configuration of $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

Recall that the 2s–orbital is spherical and of lower energy than the 2p–orbitals. Also recall that the three 2p–orbitals are at right angles to one another. The tetrahedral structure of methane, tetrachloremethane, etc, is accounted for by assuming that before the overlap of the orbitals of the excited carbon atom by four hydrogen or four chlorine atoms to form methane or tetrachloromethane, there is a rearrangement of the unpaired orbitals. This rearrangement involves an equalization in energy of the four unpaired orbitals, and their spreading out. This is termed hybridization. In the case leading to the formation of methane or tetrachloromethane, hybridization involves one s–orbital and three p–orbitals. It is thus called Sp^3 (reads sp-three) hybridization. After spreading out, the unpaired orbitals are alligned at 109° 28′ away from each other. They point to the corners of a regular tetrahedron, with the carbon atom at the centre of the tetrahedron. The overlap of each hybrid orbital with the orbital of a hydrogen atom results in a methane molecule which is tetrahedral. Similarly, the overlap of each hybrid orbital with an unpaired p–orbital of a chlorine atom results in a molecule of tetrachloromethane, which is also tetrahedral in shape.
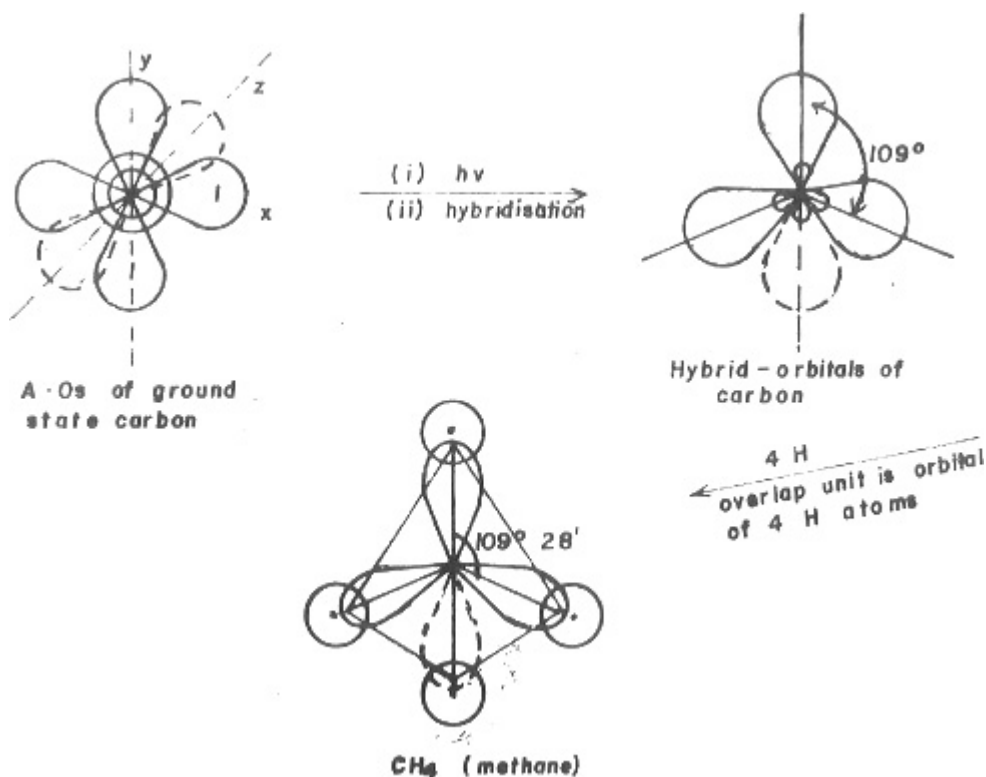
Figure 2.4: Formation of Tetrahedral methane molecule

If only two of the three unpaired p–orbitals in an excited carbon atom hybridize with the unpaired 2s–orbital, sp^2 hybridization is said to have taken place. It results in three hybrid orbitals directed 120° away from each other on the same plane. The third p–orbital which does not take part in hybridization remains at right angles to the plane of the hybrid orbitals (Figure 2.5).
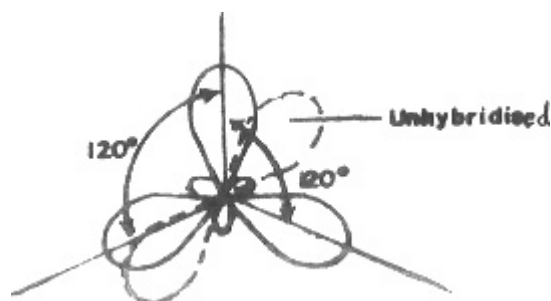

Figure 2.5: Sp^2 hybridization of a carbon atom

The linear overlap of an sp^2 hybridized orbital of one carbon atom with a similar orbital of a second carbon atom results in a strong bond, called sigma (σ) bond. At the same time, the unhybridized p–orbitals of the two carbon atoms also overlap laterally but to a small extent A weaker bond, called pi (x) bond is formed. Thus there is a double bond between the two carbon atoms, one of which is a σ–bond *mi* the other a π–bond (Figure 2.6).

Linear overlap of
sp²_ hybrid orbitals
σ - bond.

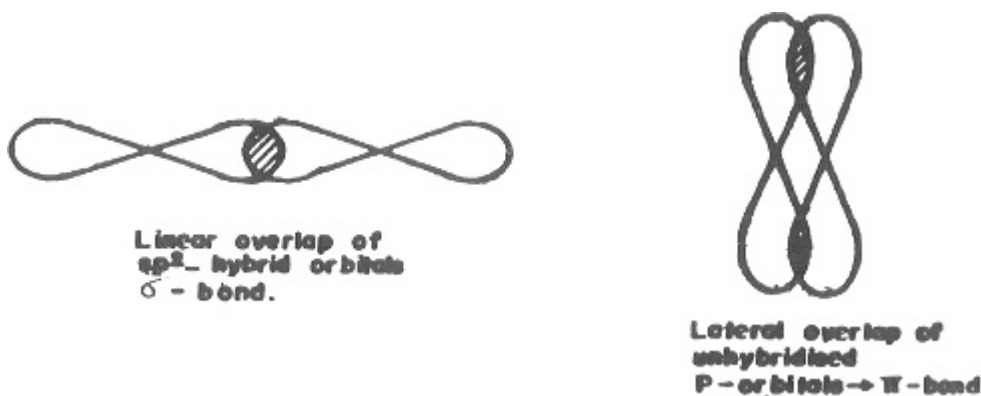Lateral overlap of
unhybridised
P - orbitals → π - bond

Figure 2.6: Formation of a double bond between two carbon atoms

The overlap of the other two hybrid orbitals of each carbon atom with a hydrogen $1s^1$ orbital results in the formation of two Ïf, bonds (i.*e.* between each carbon atom and two hydrogen atoms). The final product is a molecule of ethene.
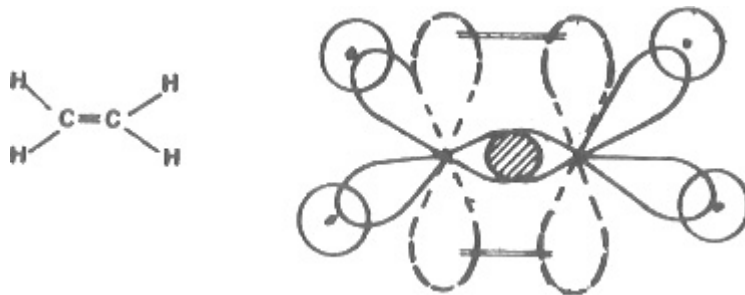

Figure 2.7: Molecular orbitals of Ethene

Since the hybrid orbitals are planar, all the atoms overlapping with them, (ie, the two carbon atoms and the four hydrogen atoms) all lie on the same plane. The ethene molecule is therefore plannar.

A triple bond is formed when only one unpaired pâ€"orbital and the $2s^1$ orbital of an excited carbon atom hybridize. This hybridization is termed sp-hybridization. The two hybrid orbitals spread out fully, so that one is 180Â° away from the other.
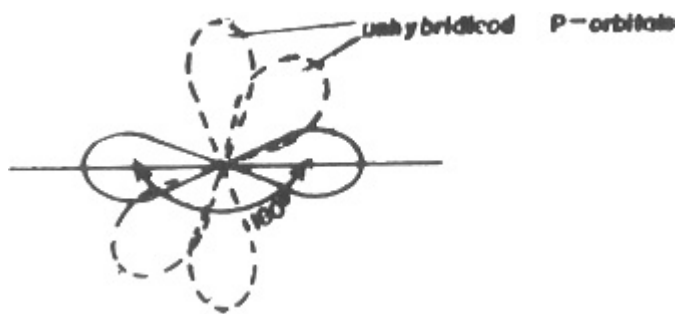

unhybridicod P-orbitals

Figure 2.8: sp hypridization in carbon

The two unhybridized pâ€"orbitals remain at right angles with the

hybrid ones. When two carbon atoms involved in sp hybridization come close to one another, their hybrid orbitals overlap effectively to form σ- bond. At the same time, their two unhybridized p–orbitals also overlap. Thus, there are three bonds between the two carbon atoms. One is a σ–bond resulting the effective overlap of hybrid orbitals. The other two are π–bonds, resulting from a less effective overlap of unhybridized orbitals at right angles with the hybrid orbitals (Figure 2.9).
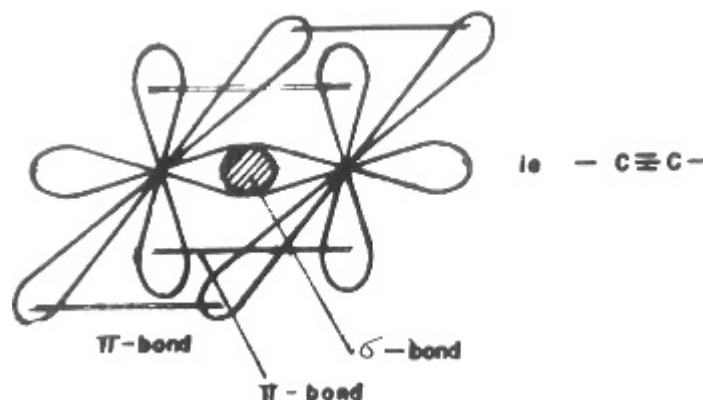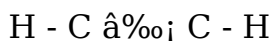

Figure 2.9: Formation of a triple bond between two carbon atoms

The overlap of the second hybrid orbital of each carbon atom with a $1s^1$ orbital to form a σ–bond, results in a molecule of ethyne. This molecule must be linear since the hybrid orbitals are linear.

$$H - C ≡ C - H$$

Properties of Covalent Compounds

(a) Covalent compounds exist as discrete molecules. They are therefore gaseous or volatile liquids. If solid, their melting and boilding points are usually low.

(b) Since ions are not present, they do not conduct electricity in the molten state or in solution.

(c) They are usually insoluble in water but dissolve in non-polar solvents such as ethers, acetone, ethanol.

(d) Covalency is common with elements with high ionization energies and between elements with similar electronegativities.

2.3 Polar Bonds

A bond between two atoms of the same non-metallic element is purely covalent. This is so because the electronegativities of the two atoms are equal. A bond between an atom at the bottom of group I of the periodic table and one on top of group 7 should be purely ionic. This is expected to be so because the two elements have widely different

electronegativities. Between these extreme cases of pure covalent and ionic bonds, covalent bonds have some ionic character, and ionic bonds some covalent character.

The hydrogen chloride bond is covalent, with some ionic character. The chlorine atom is more electronegative than the hydrogen atom. So, the pair of electrons which both elements share are closer to the chlorine atom, which therefore acquires a partial negative charge, designated (Î´-). The hydrogen atom acquires a partial positive charge (Î´+). The bond is said to be polar and is designated as:

$$\text{Î´+} \qquad \text{Î´-}$$
$$\text{H} \qquad \text{-Cl.}$$
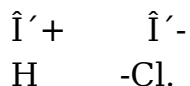
The greater the difference in electronegativities between atoms forming a covalent bond, the more polar the covalent bond formed between them.

2.4   Intramolecular Forces

Although covalent compounds are said to exist as discrete molecules, some intramolecular forces exist between them, tending to bring the discrete molecules together. This is why covalent compounds are not always gaseous. However, the intramolecular forces are usually very weak forces. Even when they bring molecules close together to form a solid, the melting points of such solids like candle wax and ice are low. If they form liquids, the boiling points of most of such liquids like methanol, ethanol, liquid ammonia, are low.

Two such intramolecular forces are well known. They are hydrogen bonding and van der Waalsâ€™ forces.
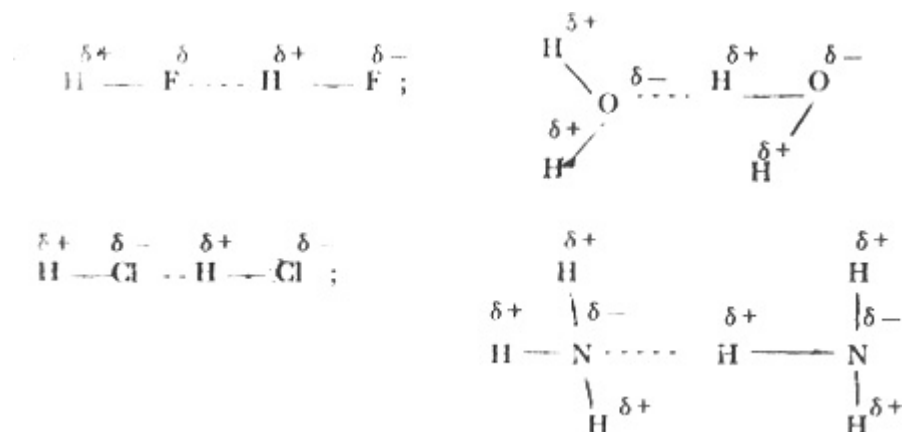
Hydrogen Bonding

Hydrogen forms highly polar bonds with the elements at the top right hand corner of the periodic table. These elements:â€“ fluorine,chlorine, oxygen and nitrogen have high electronegativities. These highly electronegative elements strongly attract the bonding pair of electrons to themselves and become partially nega-tively charged, leaving the hydrogen atom partially positively charged.
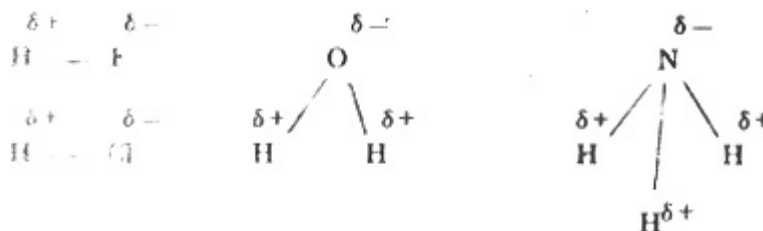

Since hydrogen has no shielding electrons, its proton becomes almost exposed, it therefore approaches the electronegative atom of another molecule of the polar compound so closely that electrostatic

force of attraction exists between them. This force, between molecules, is called hydrogen bonding. The usual notation for a hydrogen bond is the dotted lines between partially positively charged hydrog a *atom* in one molecule and partially negatively charged electronegative atom in another molecule, thus:

In the liquid state of these compounds, many molecules are held together by hydrogen bonding as shown below:
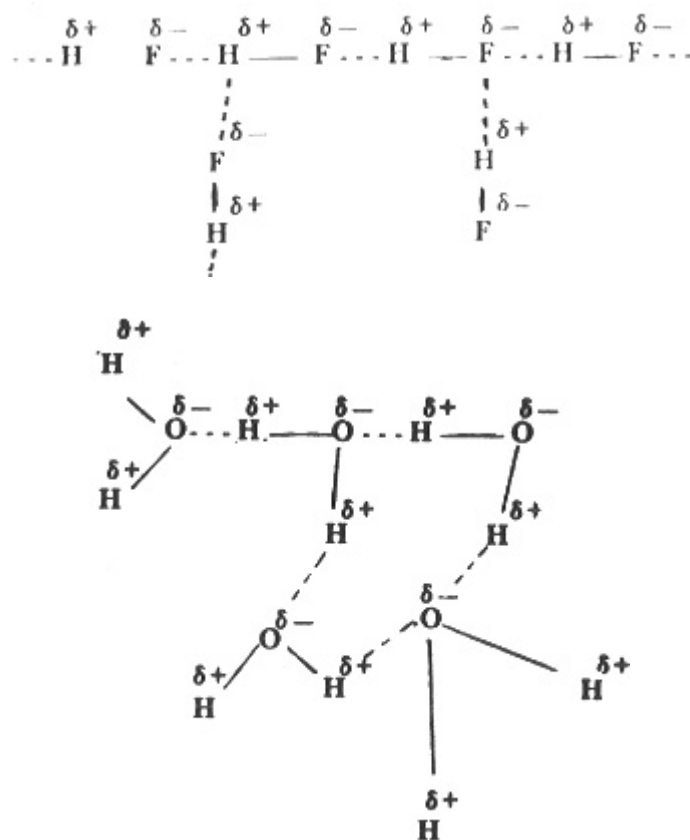
In the gaseous state, hydrogen bonding exists only in hydrogen fluoride. The molecules exist only as Hâ€"F----H â€" F. The other extensions are broken. Hydrogen fluoride exists as a dimer, $H_2 F_2$, in the gaseous state.

Hydrogen bonding accounts for many observations in chemistry.

Examples are:

(a) The boiling point of water is unusually high compared to that of hydrogen sulphide even though the molar mass of hydrogen sulphide is higher. This is due to the stronger hydrogen bonding between hydrogen and oxygen in water, than between sulphur and hydrogen in hydrogen sulphide. The electronegativity of sulphur is less than that of oxygen, hence there is a stronger and more extensive bonding in water than in hydrogen sulphide.

(b) Ammonia is easily liquefied. This is because compression brings the molecules together and establishes hydrogen bonding between them, since nitrogen is highly electronegative.

(c)   The molar mass determination of ethanoic acid gives a figure which is double the actual figure because the molecule dimerises i.e. two molecules join to become one, due to hydrogen bonding.

Van der Waals' forces

The two atoms in the iodine molecule behave like noble gas atoms towards each other because each iodine atom has attained a stable electronic configuration in the molecule. But iodine is a solid at room temperature. There must be a force binding the molecules together in the crystalline solid. This force is called van der Waals' force.

Van der Waals' forces are the result of the attraction between the temporary positive and negative charges which exist for very short periods between neighbouring atoms in molecules. The electrons of atom A in one molecule repel those of atom B in another molecule, but attract the nucleus of atom B and vice versa. The nuclear charges of atoms A and B also repel each other when the molecules approach one another. The repulsive and attractive forces are in a balance at an internuclear distance of about 0.4 nm. A little before this internuclear distance is approached, the attractive forces dominate. They are strong enough to bind iodine molecules into solid crystals and also make bromine molecules exist as liquid. But they are not strong enough to unite chlorine or fluorine molecules. This is because van der Waals' forces increase with increasing atomic number. Van der Waals' forces account for the liquefaction of gases such as carbon(IV) oxide, under pressure.

2.5   Structures of Simple Solids

We have noted that the properties of ionic compounds are very different from those of covalent compounds. But why do solids, both ionic and covalent, have regular crystalline shapes? An explanation could be that the particle of which these solids are composed are arranged in patterns. Let us look at the arrangement of the particles of ionic and covalent compounds to see how these affect the

crystalline shapes of the solids.

Ionic Lattices

In a solid substance composed of ions, each ion is surrounded by neighbouring ions of opposite charge (Figure 2.10)
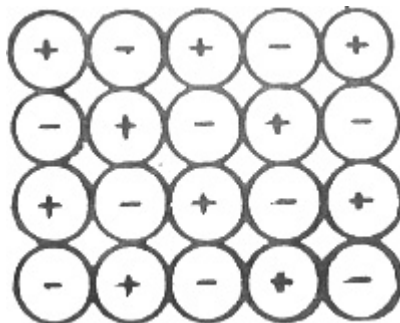


Figure 2.10: Arrangement of ions in the solid state

Because of the closeness of ions with opposite charges, the particles are held by strong electrostatic forces. Their melting points are therefore high.

In sodium chloride, for example, sodium and chloride ions are arranged in the pattern of cubes (Figure 2.11).
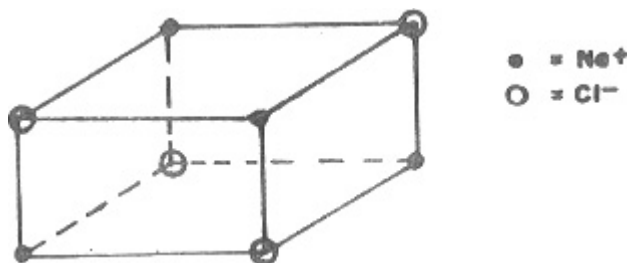
*Figure 2.11: Arrangement of sodium chloride ions in a cubic pattern*

The extension of this pattern many million times will result in the sodium chloride crystal lattice which is also a cube (Figure 2.12). The arrangement of ions of other compounds form other lattice structures.
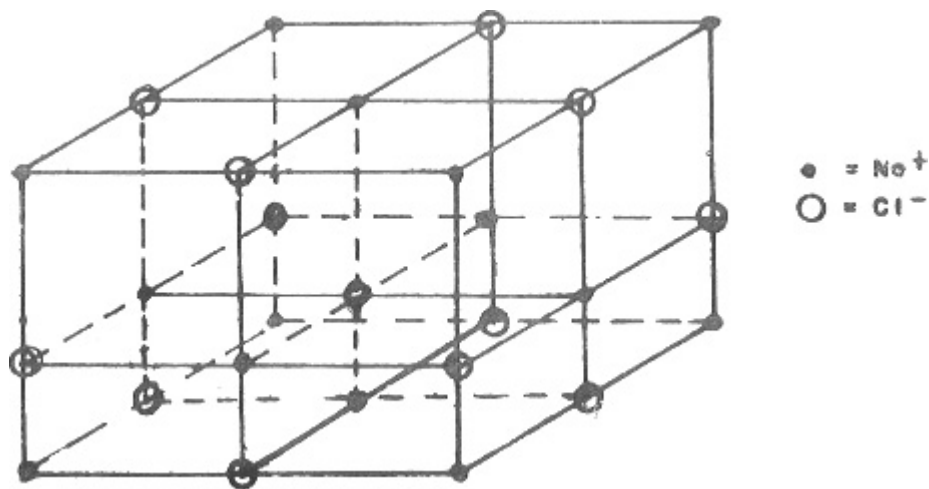
Figure 2.12: Sodium chloride lattice structure

Molecular Lattices

Substances which form crystalline solids with low melting and boiling points, and low heats of vapourization (sublimation), have lattices in which the component particles are molecules. Only weak forces, usually van der Waals' forces, hold the molecules together in the crystalline lattice. They are usually soft, nonconductors of heat and electricity even in the molten state, and have low densities. Iodine is an example.
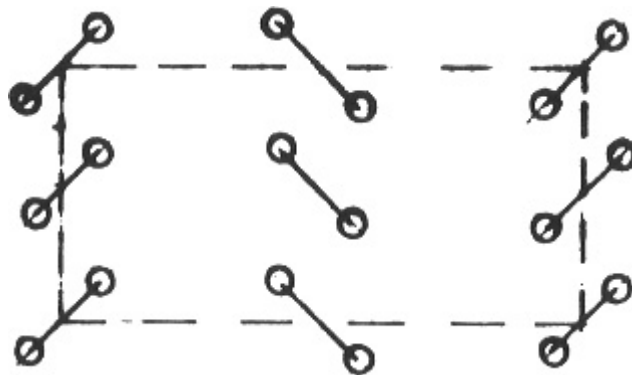
Figure 2.13: Lattice structure of iodine showing iodine molecules

Solid carbon(IV) oxide, known as dry ice, is another example. The basic pattern is a molecule at each corner of a cube, and a molecule at the centre of the face of each cube (Figure 2.14).

$O \bullet O$ = a molecule of CO_2
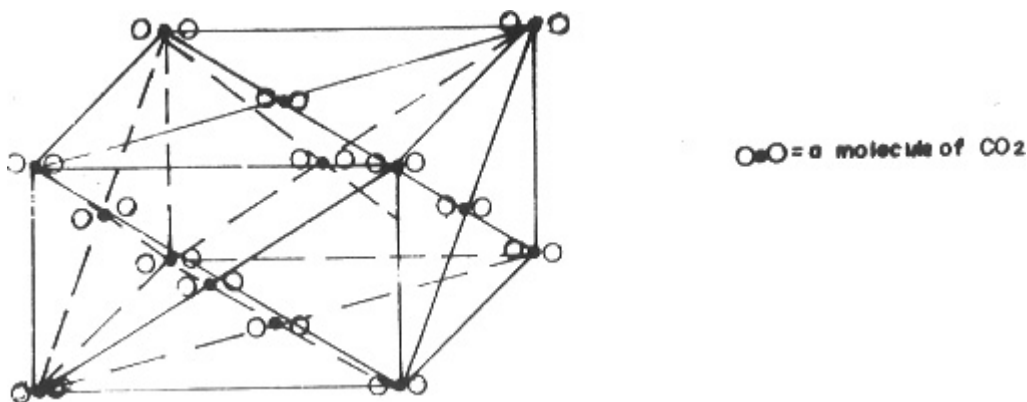
Figure 2.14: Crystal lattice structure of solid carbon (IV) oxide.

Net-work Covalent Lattices

The structures of diamond and graphite have already been described in Book 1. They are examples of net-work covalent lattices.

In diamond, each carbon atom is covalently bonded to four other carbon atoms arranged tetrahedrally. The carbon atoms at. the corners of each tetrahedron form centres of other tetrahedral arrangements. This gives the giant net-work structure of diamond.
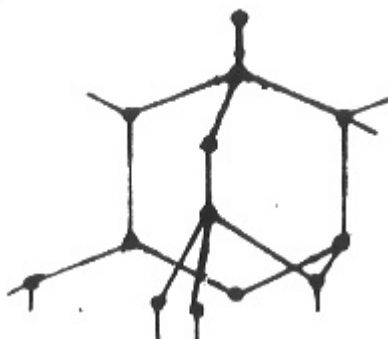
Figure 2.15: Structure of diamond.

This arrangement of the carbon atoms in diamond confers on the substance some characteristic properties such as hardness, bright lustre, non-conductivity, etc.

Graphite also has a giant net-work structure. A crystal of graphite consists of layers of carbon atoms. Each atom is joined to three others in the same plane. The layers are therefore made up of hexagonally arranged carbon atoms Only weak van der Waals forces hold the layers together.
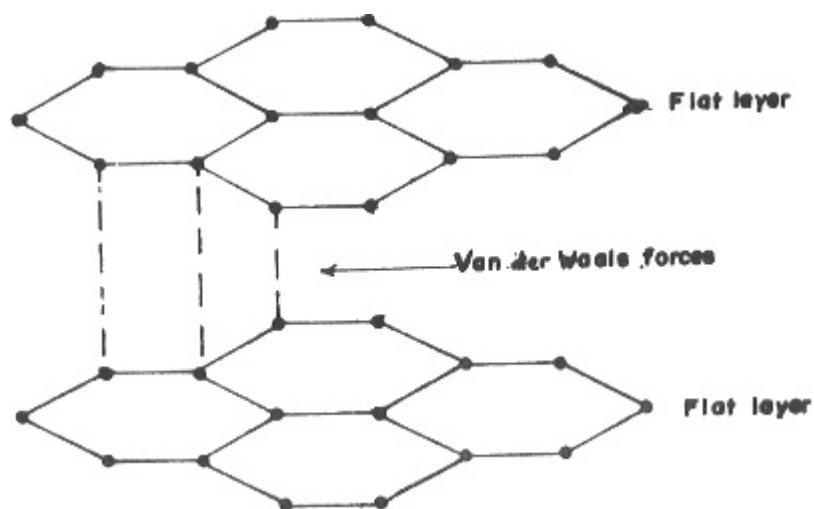
Figure 2.16: Structure of graphite

The weak van der Waals forces are easily overcome. Graphite is therefore soft and greasy. The fourth valence electron of each carbon atom in graphite is delocalised. Graphite therefore conducts electricity since electric current (electrons in motion) merely join the free electrons in graphite to move from one end of a graphite rod to the other.

EXERCISE 2.2.

Phosphorus forms tetrahedrally arranged P_4 molecules in which each phosphorus atom is linked covalently to three others. Would you expect solid phosphorus to be:

(a) high or low melting?

(b) hard or soft?

(c) a conductor or a non-conductor of electricity?
Explain your answers.

2.6   Shapes of some Simple Molecules

We noted earlier that the four hybrid orbitals of sp^3 hybridization point to the corners of a regular tetrahedron. Their overlap with the 1s orbitals of four hydrogen atoms results in a tetrahedral methane molecule. Similarly, their overlap with the unpaired p–orbitals of four chlorine atoms yields a tetrahedral tetrachloromethane. All other compounds with an sp^3 hybridized central atom have a tetrahedral structure. Thus silane, SiH_4 , is tetrahedral in structure.

Ethene and all other compounds involving a central sp^2 hybridized atom are planar in structure, while ethyne and all sp hybridized compounds are linear. Table 2.2 summarises the shapes of molecules arising from different bonding orbitals.

TABLE 2.2: Relationship of bonding orbitals to shapes of molecules

Bonding capacity	Bonding orbital	Molecular Shape	Examples
1	s	linear	H—H
1	p	linear	F_2, Cl_2
2	sp	linear	C_2H_2, BeF_2
2	p^2	bent	H_2O.
3	sp^2	triangular planar	C_2H_4, BF_3
3	p^3	pyramidal	NH_3
4	sp^3	tetrahedral	CH_4, CCl_4
4	dsp^2	square plaınar	$[Cu(NH_3)_4]^{2+}$
6	d^2sp^3	octahedral	$[Cr(NH_3)_6]^{3+}$, SF_6

Structure of Water Molecule

The electronic configuration of oxygen is $1s^2\ 2s^2\ 2p_x^2.\ 2p_y^1\ 2p_z^1$. The $2p^y$ and $2p_z$ orbitals, which are unpaired, are at right angles. Their overlap with the $1s^1$ orbitals of two hydrogon atoms should result in a water molecule, H - O - H, with a bond angle of 90° as shown in Figure 2.17.
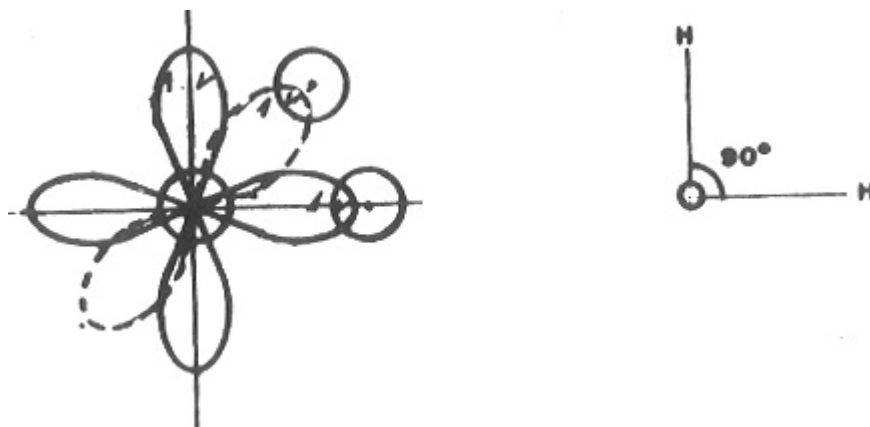
Figure 2.17: Molecular Orbital of H^2O if oxygen is unhybridised

But the actual H - O - H angle in water is 104.5°. This is closer to the tetrahedral angle of sp^3 hybridization. So, sp^3 hybridization is proposed. The tetrahedral angle which should have resulted is reduced by the repulsion between the paired non–bonding electrons, Figure 2.18.
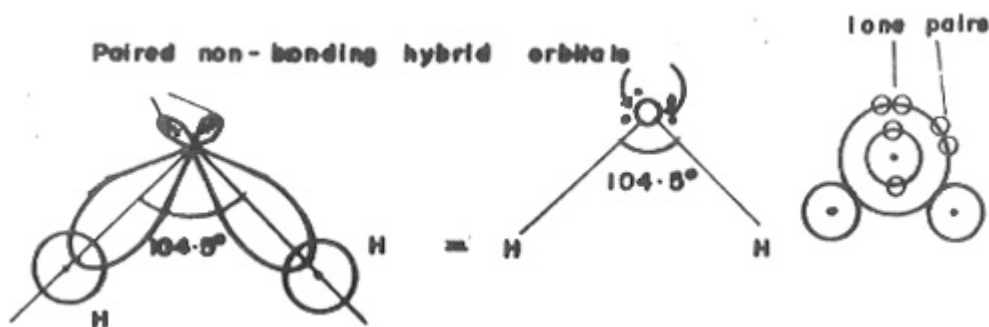
Figure 2.18: Bent structure of water.

Structure of Ammonia Molecule

The electronic configuration of nitrogen is $1s^2\ 2s^2\ 2P_x^1\ 2P_y^1\ 2P_z^1$. The overlap of the three unpaired p–orbitals with 1s–orbitals of three hydrogen atoms will form an ammonia molecule in which each H - N - H angle is 90°. Hybridization between the 2s– and 3 p–orbitals, followed by repulsion of the unpaired hybrid orbitals by the paired one, is responsible for the H - N - H angle of 107° in ammoiua.
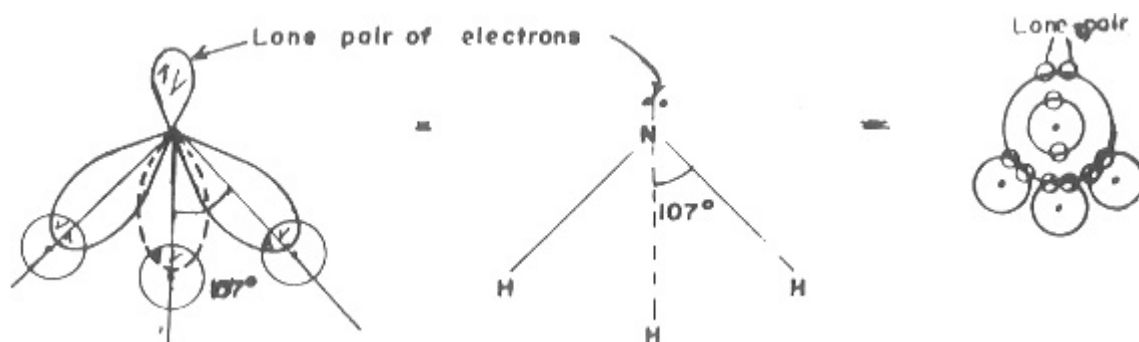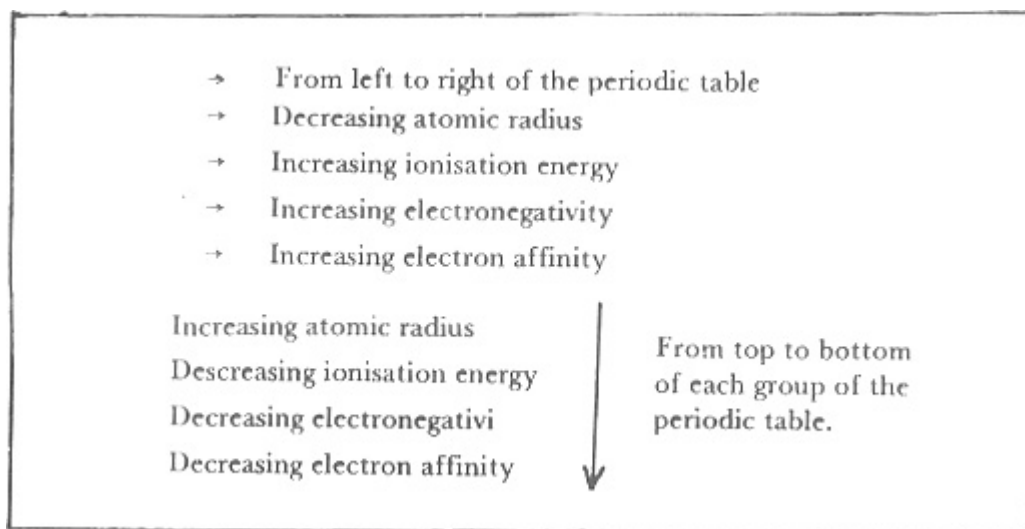

Figure 2.19: Structure of ammonia

CHAPTER SUMMARY

Bonding and the Periodic Table

• The variations in the fundamental properties of atoms on which bonding depends are summarised below. Taking the box below as the periodic table, we *have:*

```
→   From left to right of the periodic table
→   Decreasing atomic radius
→   Increasing ionisation energy
→   Increasing electronegativity
→   Increasing electron affinity

Increasing atomic radius
Descreasing ionisation energy          From top to bottom
Decreasing electronegativi             of each group of the
Decreasing electron affinity           periodic table.
                                    ↓
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• Elements with low ionisation energies form ionic compounds with elements with high electron affinities.

• Elements with widely different electronegativities form ionic compounds.

• Elements with high ionization energies form covalent compounds with elements with low electron affinities.

• Elements with nearly equal electronegativities form covalent compounds.

• Hydrogen bonding is a weak bond existing between molecules which have highly electronegative atoms such as fluorine, oxygen and nitrogen attached to a hydrogen atom. The positive end of one molecule attracts the negative end (the electronegative atom) of another molecule to give rise to the weak hydrogen bond indicated by dotted lines:

$$H\_\_\_\_\_F........F\_\_\_\_\_F........H\_\_\_\_\_F$$

• van der Waals' forces are weak inter-molecular forces which arise as a result of attraction between molecules resulting from the movement of electrons. The forces are used to explain a number of phenomena including the solid State of iodine and the liquefaction of gases.

Structure of ions and molecules

• Since bonds are directional, the geometry of simple molecules formed by covalency are definite.

• In ionic compounds, each ion is surrounded by a definite number of oppositely charged ions, thus giving rise to a lattice of characteristic shape.

• Net-work structures such as diamond extend in all directions but it is always possible to identify their repeating units.

ASSESSMENT

1. (a) Name three examples each of compounds containing these types of bonding:
   (i) ionic bonding,
   (ii) covalent bonding,
   (iii) hydrogen bonding.

   (b) State with reasons, if they:
   (i) have high or low melting points.
   (ii) conduct electricity when dissolved in water.
   (iii) are brittle or hard.

2. (a) An element, X, is represented as $^{40}_{20}X$
   (i) How many electrons and neutrons are present in the atom of X?
   (ii) Write the electronic configuration of the atom.

   (b) Chlorine, whose atomic number is 17, reacts with the element $^{40}_{20}X$ to form a compound.
   (i) What type of bond is formed between X and chlorine?
   (ii) Explain how the bond between X and chlorine is formed.
   (iii) Write the formula of the compound formed and state three properties of the compound.

   (WAEC).

3. Two elements, Y and Z, have the electronic structures 2,8,7 and 2,4 respectively. If Y is diatomic,
   (i) write a balanced equation for the reaction between Y and Z.
   (ii) what type of bond will be present in the compound formed?
   (iii) what would you expect the physical state of the compound formed in the reaction to be, at room temperature? Explain.
   (iv) Are Y and Z metals or non-metals? Explain.

4. (a) Define the terms
   (i) ionization energy
   (ii) atomic radius
   (iii) electron affinity
   (iv) electronegativity

   (b) How does each of these vary from
   (i) left to right across the periods
   (ii) top to bottom along the groups of the periodic table.

5. State and explain the shapes of:
   (i) methane molecule
   (ii) ethane molecule

(iii) ethyne molecule
(iv) ammonia molecule
(v) water molecule