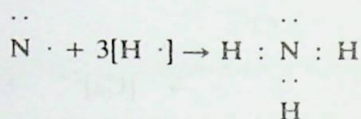


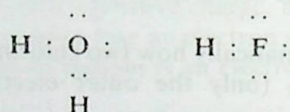
that although it is possible to build up molecules in this way in order to understand their electronic structures, it does not follow that the atoms will react together directly. In this case, carbon and chlorine do not react directly, and tetrachloromethane is made by indirect reactions.

A molecule of ammonia NH_3 is made up of one nitrogen and three hydrogen atoms:



The nitrogen atom is three electrons short of a noble gas structure, and the hydrogen atoms are one electron short of a noble gas structure. Nitrogen forms three bonds, and the hydrogen atoms one bond each, so all four atoms attain a stable configuration. One pair of electrons on the N atom is not involved in bond formation, and this is called a *lone pair* of electrons.

Other examples of covalent bonds include water (with two covalent bonds and two lone pairs of electrons), and hydrogen fluoride (one covalent bond and three lone pairs):



Oxidation numbers

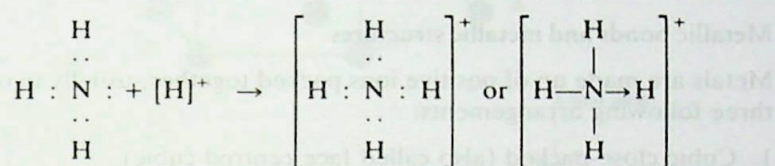
The oxidation number of an element in a covalent compound is calculated by assigning shared electrons to the more electronegative element, and then counting the theoretical charge left on each atom. (Electronegativity is described in Chapter 6.) An alternative approach is to break up (theoretically) the molecule by removing all the atoms as ions, and counting the charge left on the central atom. It must be emphasized that molecules are not really broken, nor electrons really moved. For example, in H_2O , removal of two H^+ leaves a charge of -2 on the oxygen atom, so the oxidation state of O in H_2O is $(-II)$. Similarly in H_2S the oxidation state of S is $(-II)$; in F_2O the oxidation state of O is $(+II)$; in SF_4 the oxidation state of S is $(+IV)$; whilst in SF_6 the oxidation state of S is $(+VI)$. The concept of oxidation numbers works equally well with ionic compounds, and in CrCl_3 the Cr atom has an oxidation state of $(+III)$ and it forms Cr^{3+} ions. Similarly in CrCl_2 , Cr has the oxidation state $(+II)$, and exists as Cr^{2+} ions.

Coordinate bonds

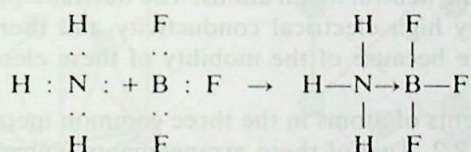
A covalent bond results from the sharing of a pair of electrons between two atoms, where each atom contributes one electron to the bond. It is also

possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called coordinate bonds or dative bonds. Since, in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

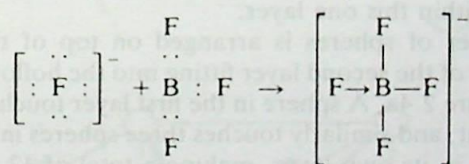
Even though the ammonia molecule has a stable electron configuration, it can react with a hydrogen ion H^+ by donating a share in the lone pair of electrons, forming the ammonium ion NH_4^+ :



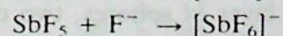
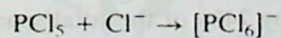
Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bonds as arrows indicating which atom is donating the electrons. Similarly ammonia may donate its lone pair to boron trifluoride, and by this means the boron atom attains a share in eight electrons:



In a similar way, a molecule of BF_3 can form a coordinate bond by accepting a share in a lone pair from a F^- ion.

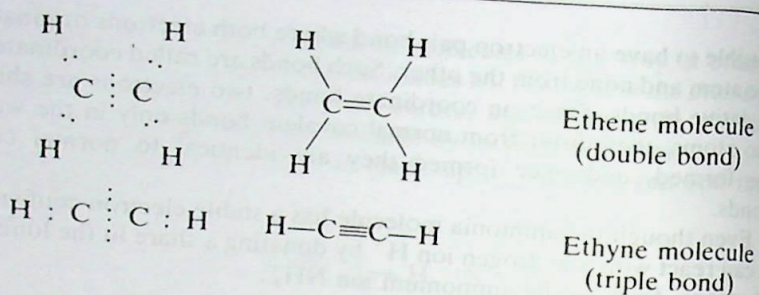


There are many other examples, including:



Double and triple bonds

Sometimes more than two electrons are shared between a pair of atoms. If four electrons are shared, then there are two bonds, and this arrangement is called a double bond. If six electrons are shared then there are three bonds, and this is called a triple bond:



Metallic bonds and metallic structures

Metals are made up of positive ions packed together, usually in one of the three following arrangements:

1. Cubic close-packed (also called face-centred cubic).
2. Hexagonal close-packed.
3. Body-centred cubic.

Negatively charged electrons hold the ions together. The number of positive and negative charges are exactly balanced, as the electrons originated from the neutral metal atoms. The outstanding feature of metals is their extremely high electrical conductivity and thermal conductivity, both of which are because of the mobility of these electrons through the lattice.

The arrangements of atoms in the three common metallic structures are shown in Figure 2.2. Two of these arrangements (cubic close-packed and hexagonal close-packed) are based on the closest packing of spheres. The metal ions are assumed to be spherical, and are packed together to fill the space most effectively, as shown in Figure 2.3a. Each sphere touches six other spheres within this one layer.

A second layer of spheres is arranged on top of the first layer, the protruding parts of the second layer fitting into the hollows in the first layer, as shown in Figure 2.4a. A sphere in the first layer touches three spheres in the layer above it, and similarly touches three spheres in the layer below it, plus six spheres in its own layer, making a total of 12. The coordination number, or number of atoms or ions in contact with a given atom, is therefore 12 for a close-packed arrangement. With a close-packed arrangement, the spheres occupy 74% of the total space.

When adding a third layer of spheres, two different arrangements are possible, each preserving the close-packed arrangement.

If the first sphere of the third layer is placed in the depression X shown in Figure 2.4a, then this sphere is exactly above a sphere in the first layer. It follows that every sphere in the third layer is exactly above a sphere in the first layer as shown in Figure 2.2a. If the first layer is represented by A, and the second layer by B, the repeating pattern of close-packed sheets is ABABAB. . . . This structure has hexagonal symmetry, and it is therefore said to be hexagonal close-packed.

Alternatively, the first sphere of the third layer may be placed in a

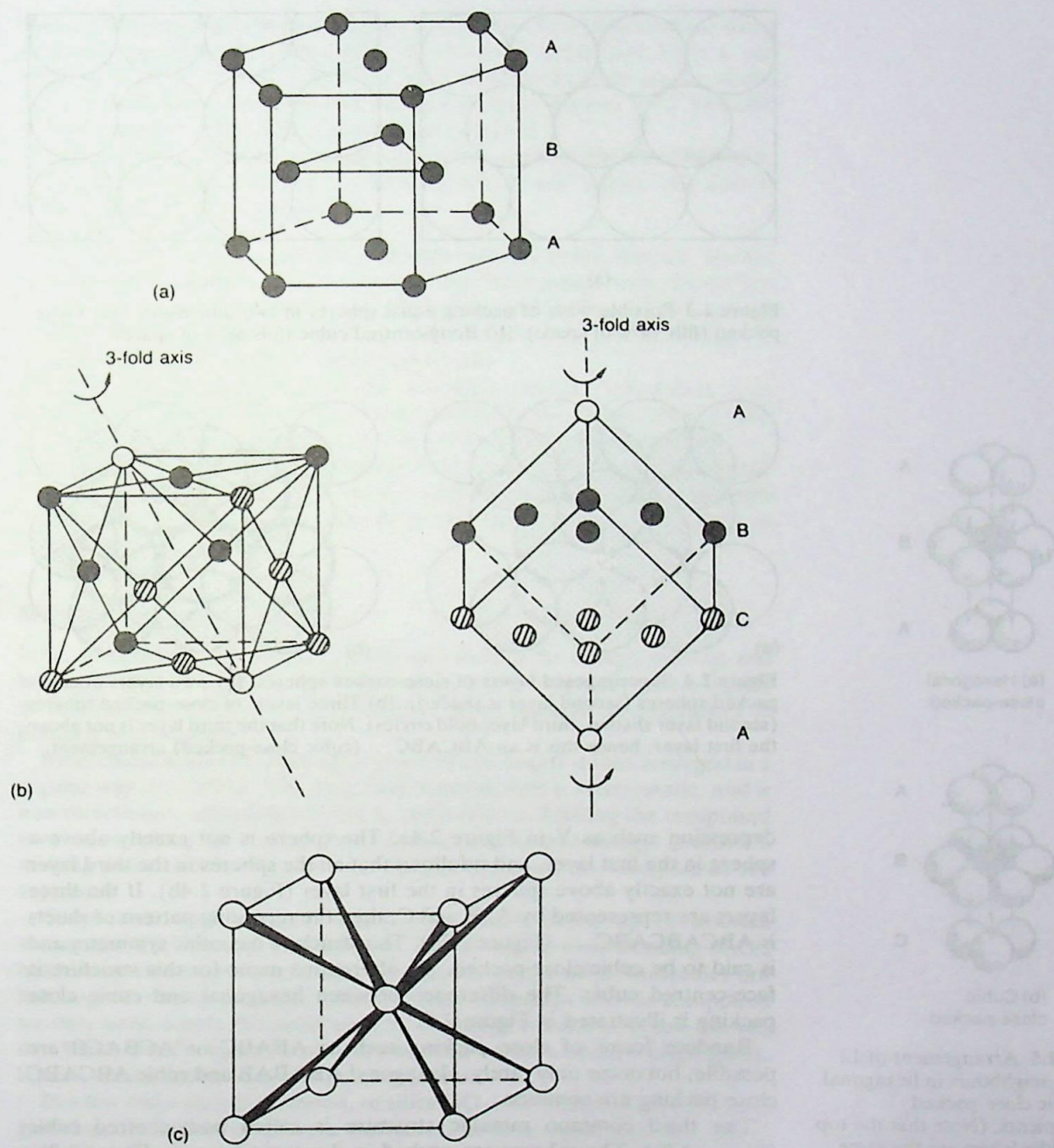


Figure 2.2 The three metallic structures. (a) Hexagonal close-packed structure showing the repeat pattern of layers ABABAB... and the 12 neighbours surrounding each sphere. (b) Cubic close-packed structure (coordination number is also 12) showing repeat pattern of layers ABCABC. (c) Body-centred cubic structure showing the 8 neighbours surrounding each sphere.

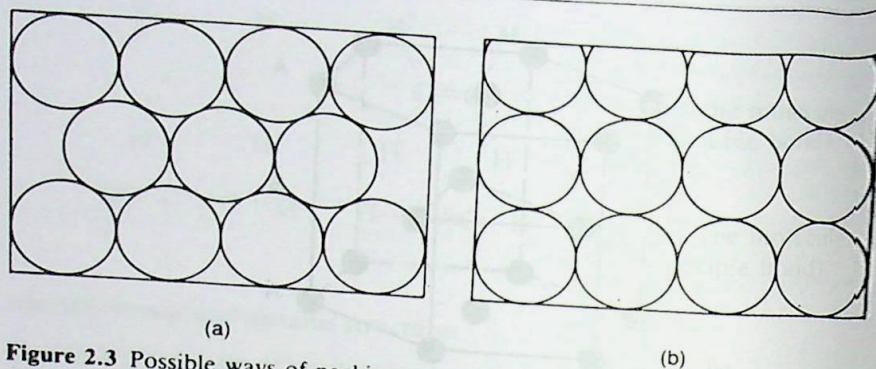


Figure 2.3 Possible ways of packing equal spheres in two dimensions. (a) Close-packed (fills 74% of space). (b) Body-centred cubic (fills 68% of space).

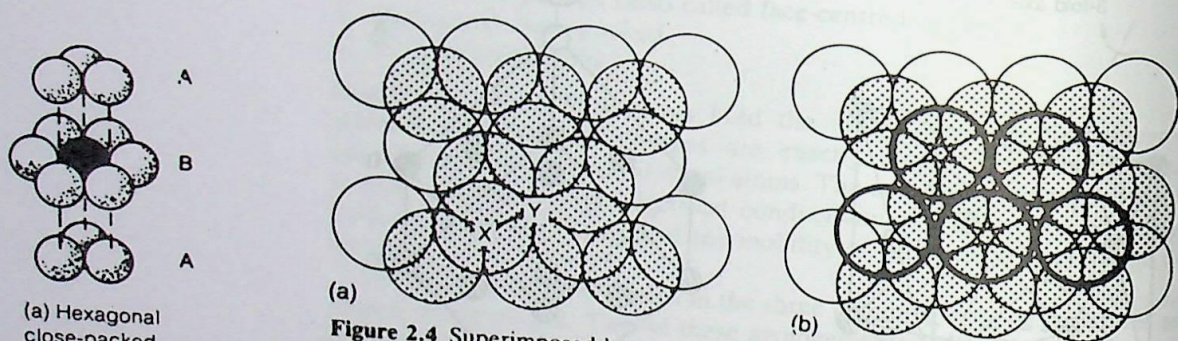
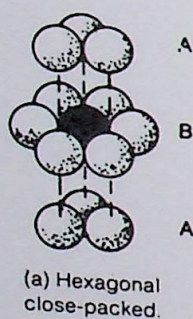
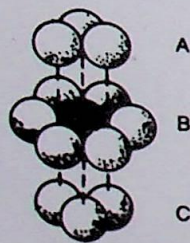


Figure 2.4 Superimposed layers of close-packed spheres. (a) Two layers of close-packed spheres (second layer is shaded). (b) Three layers of close-packed spheres (second layer shaded, third layer bold circles). Note that the third layer is not above the first layer, hence this is an ABCABC... (cubic close-packed) arrangement.



(a) Hexagonal close-packed.



(b) Cubic close-packed.

Figure 2.5 Arrangement of 12 nearest neighbours in hexagonal and cubic close-packed arrangements. (Note that the top and middle layers are the same, but in the cubic close-packed structure the bottom layer is rotated 60° relative to the hexagonal close-packed.

depression such as Y in Figure 2.4a. The sphere is not exactly above a sphere in the first layer, and it follows that all the spheres in the third layer are not exactly above spheres in the first layer (Figure 2.4b). If the three layers are represented by A, B and C, then the repeating pattern of sheets is ABCABCABC... (Figure 2.2b). This structure has cubic symmetry and is said to be cubic close-packed. An alternative name for this structure is face-centred cubic. The difference between hexagonal and cubic close packing is illustrated in Figure 2.5.

Random forms of close packing such as ABABC or 'ACBACB are possible, but occur only rarely. Hexagonal ABABAB and cubic ABCABC close packing are common.

The third common metallic structure is called body-centred cubic (Figure 2.2c). The spheres are packed in sheets as shown in Figure 2.3b. The second layer occupies the hollows in this first sheet. The third layer occupies hollows in the second layer, and the third layer is immediately above the first layer. This form of packing is less efficient at filling the space

than closest packing (compare Figures 2.3a and b). In a body-centred cubic structure the spheres occupy 68% of the total space and have a coordination number of 8, compared with close-packed structures where 74% of the space is occupied and the coordination number is 12. Metallic structures always have high coordination numbers.

The theories of bonding in metals and alloys are described in Chapter 5.

Metallic bonding is found not only in metals and alloys, but also in several other types of compound:

1. Interstitial borides, carbides, nitrides and hydrides formed by the transition elements (and by some of the lanthanides too). Some low oxidation states of transition metal halides also belong to this group, where the compounds show electrical conductivity, and are thought to contain free electrons in conduction bands.
2. Metal cluster compounds of the transition metals, and cluster compounds of boron, where the covalent bonding is delocalized over several atoms, and is equivalent to a restricted form of metallic bonding.
3. A group of compounds including the metal carbonyls which contain a metal-metal bond. The cluster compounds, and the compounds with metal-metal bonds, may help to explain the role of metals as catalysts.

Melting points

Ionic compounds are typically solids and usually have high melting and boiling points. In contrast covalent compounds are typically gases, liquids or low melting solids. These differences occur because of differences in bonding and structure.

Ionic compounds are made up of positive and negative ions arranged in a regular way in a lattice. The attraction between ions is electrostatic, and is non-directional, extending equally in all directions. Melting the compound involves breaking the lattice. This requires considerable energy, and so the melting point and boiling point are usually high, and the compounds are very hard.

Compounds with covalent bonds are usually made up of discrete molecules. The bonds are directional, and strong covalent bonding forces hold the atoms together to make a molecule. In the solid, molecules are held together by weak van der Waals forces. To melt or boil the compound we only need supply the small amount of energy needed to break the van der Waals forces. Hence covalently bonded compounds are often gases, liquids or soft solids with low melting points.

In a few cases such as diamond, or silica SiO_2 , the structures are covalent giant lattices instead of discrete molecules. In these cases there is a three-dimensional lattice, with strong covalent bonds in all directions. It requires a large amount of energy to break this lattice, and so diamond, silica and other materials with giant three-dimensional lattices are very hard and have high melting points.

Conductivity

Ionic compounds conduct electricity *when the compound is melted, in solution*. Conduction is achieved by the ions migrating towards the electrodes under the influence of an electric potential. If an electric current is passed through a solution of sodium chloride, Na^+ ions are attracted to the negatively charged electrode (cathode), where they gain an electron and form sodium atoms. The Cl^- ions are attracted to the positive electrode (anode), where they lose an electron and become chlorine atoms. This process is called electrolysis. The changes amount to the transfer of electrons from cathode to anode, but *conduction occurs by an ionic mechanism involving the migration of both positive and negative ions in opposite directions*.

In the solid state, the ions are trapped in fixed places in the crystal lattice, and as they cannot migrate, they cannot conduct electricity in this way. It is, however, wrong to say that ionic solids do not conduct electricity without qualifying the statement. The crystal may conduct electricity to a *very small extent* by semiconduction if the crystal contains some defects. Suppose that a lattice site is unoccupied, and there is a 'hole' where an ion is missing. An ion may migrate from its lattice site to the vacant site, and in so doing it makes a 'hole' somewhere else. The new 'hole' is filled by another ion, and so on, so eventually the hole migrates across the crystal and a charge is carried in the other direction. Plainly the amount of current carried by this mechanism is extremely small, but semiconductors are of great importance in modern electronic devices.

Metals conduct electricity better than any other material, but the mechanism is by the movement of electrons instead of ions.

Covalent compounds contain neither ions (as in ionic compounds) nor mobile electrons (as in metals), so they are unable to conduct electricity in either the solid, liquid or gaseous state. Covalent compounds are therefore insulators.

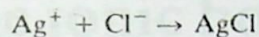
Solubility

If they dissolve at all, ionic compounds are usually soluble in polar solvents. These are solvents of high dielectric constant such as water, or the mineral acids. Covalent compounds are not normally soluble in these solvents but if they dissolve at all they are soluble in non-polar (organic) solvents of low dielectric constant, such as benzene and tetrachloromethane. The general rule is sometimes stated that 'like dissolves like', and so ionic compounds usually dissolve in ionic solvents, and covalent compounds usually dissolve in covalent solvents.

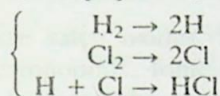
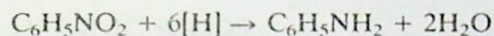
Speed of reactions

Ionic compounds usually react very rapidly, whilst covalent compounds usually react slowly. For ionic reactions to occur, the reacting species are

ions, and as these already exist, they have only to collide with the other type of ion. For example, when testing a solution for chloride ions (by adding silver nitrate solution), precipitation of AgCl is very rapid.

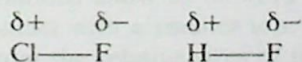


Reactions of covalent compounds usually involve breaking a bond and then substituting or adding another group. Energy is required to break the bond. This is called the activation energy, and it often makes reactions slow. Collisions between the reactant molecules will only cause reaction if they have enough energy. For example, reduction of preparative amounts of nitrobenzene to aniline takes several hours. Similarly the reaction of H_2 and Cl_2 is typically slow except in direct sunlight when the mixture may explode!



It is important to realize that bonds are not necessarily 100% covalent or 100% ionic, and that bonds of intermediate character exist. If a molecule is made up of two identical atoms, both atoms have the same electronegativity, and so have an equal tendency to gain electrons. (See Chapter 6.) In such a molecule the electron pair forming the bond is equally shared by both atoms. This constitutes a 100% covalent bond, and is sometimes called a *non-polar covalent bond*.

More commonly molecules are formed between different types of atoms, and the electronegativity of the two atoms differs. Consider for example the molecules ClF and HF. Fluorine is the most electronegative atom, and it attracts electrons more strongly than any other element when covalently bonded. The bonding electrons spend more time round the F than round the other atom, so the F atom has a very small negative charge δ^- and the atom (Cl or H) has a small positive charge δ^+ .



Though these bonds are largely covalent, they possess a small amount of ionic character, and are sometimes called *polar covalent bonds*. In such molecules, a positive charge, and an equal negative charge, are separated by a distance. This produces a permanent dipole moment in the molecule.

The dipole moment measures the tendency of the molecule to turn and line up its charges when placed in an electric field. Polar molecules have a high dielectric constant, and non-polar molecules have a low dielectric constant. The dielectric constant is the ratio of the capacitance of a condenser with the material between the plates, to the capacitance of the same condenser with a vacuum between them. By measuring the capacitance with the substance between the plates and then with a vacuum, we

can obtain the dielectric constant. Its size indicates whether the material is polar or non-polar.

Ionic, covalent and metallic bonds are considered in more detail in following chapters.