LECTURE 2: ATOMIC AND MOLECULAR BONDING

Topics

- Ionic, Covalent, Metallic, van der Waal and mixed bonds
- Bond strength, bond strength and melting point
- Effect of bond type on various physical properties of materials

OBJECTIVES

At the end of the lecture you should be able to

(i) Define and state the characteristics of the following atomic bonds, ionic, covalent, metallic, van der Waal, and mixed bonds.

(ii) Explain bond strength and how it influences the various physical properties of different materials.

A number of physical properties, such as melting point and boiling point, and other many mechanical properties depend on the strength and nature of the bonding between atoms. The various types of bonds can be classified into two groups: primary and secondary bonds, the former being considerably stronger. The primary bonds include the: (i) ionic (electrovalent), (ii) covalent, (iii) metallic, and (iv) molecular bonding.

2.1 Ionic (electrovalent) bonding

An ionic bond is formed between two different atoms, one electropositive and the other electronegative. Electropositive elements readily give up electrons and are usually Group I or II elements, e.g. Na, K, and Ba, whereas electronegative elements readily take up electrons and are typically Group VI or VII elements, e.g. Cl, Br, and O.

An example of ionic bonding is in the common salt, NaCl. When Na and Cl atoms are brought together, it is easy for the outer valence electron of sodium atom to be transferred to the chlorine atom making both more stable rare gas electronic configurations and lowering the overall energy. Consequently there is electrostatic attraction between the two ions as shown in Fig. 2.1b.

Other ionic compounds include MgO, CuO, CrO_2 and MoF_2. In MgO the ions are doubly ionized (i.e. two electrons are transferred from each magnesium to an oxygen atom) leading to stronger interatomic bond and hence a higher melting point (2800°C) compared to 800°C for NaCl.

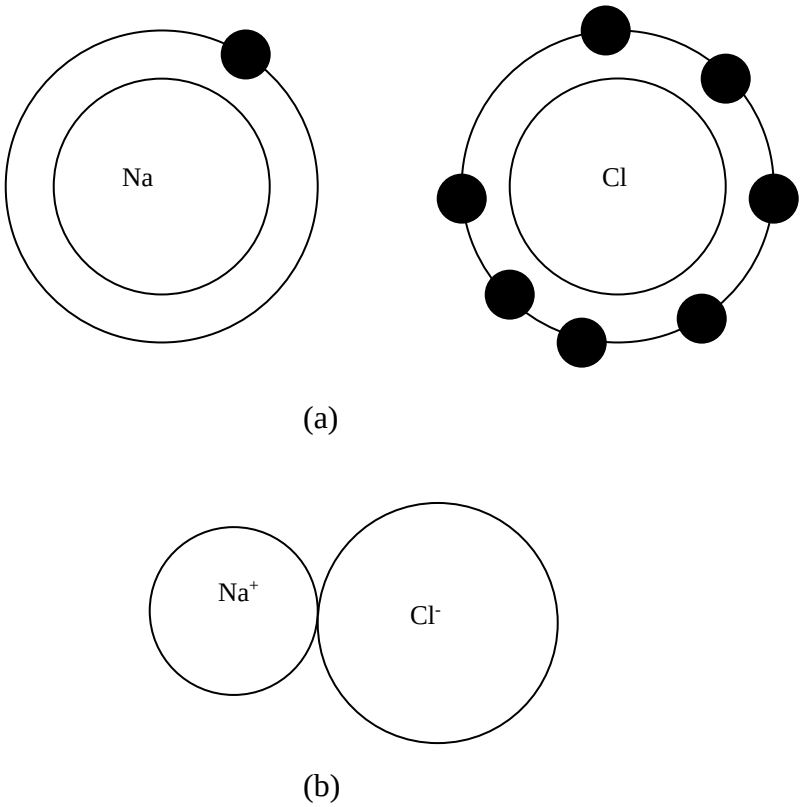

Figure 2.1. (a) Individual atoms (denoting the inner closed shells as a solid sphere) (b) ionic molecule.

2.2 Covalent Bonding

Elements from the central groups of the Periodic Table, chiefly Group IV are not readily reduced to the closed shell configuration because too large an energy would be expended in doing so, thus ionic bond is unlikely. The atoms will complete the outer electron shell by sharing with its neighbours. The sharing gives rise to covalent bonding.

As an example, consider carbon. Its outer shell has four electrons. Four more are required to fill this shell and these may be acquired by sharing an electron with each of four neighbours when carbon is in solid form. Schematically this is shown in Fig. 2.2 below.

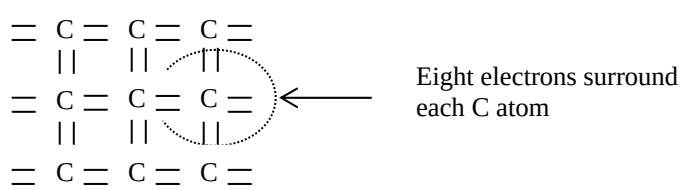

Figure 2.2. Bonding in carbon.

Note that the above arrangement does not occur in practice due to the directional nature of the bonds. This is because the four electrons in the outer shell act so strongly with one another (repulsion) that each electron's cloud concentrates itself away from those of the other three; the four arranging themselves with the largest possible angle, 109.5°, between each pair. Because of the strong repulsion this arrangement is difficult to distort, and the structure so formed is very strong and rigid. Covalent bond is thus very directional. The other Group IV elements, silicon, and germanium are also bond in the same manner.

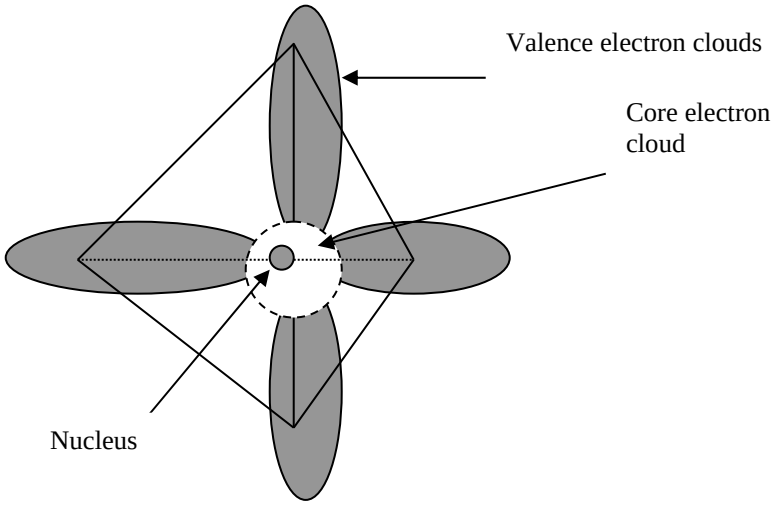

Figure 2.3. The lobe-shaped valence electron cloud in carbon atom.

2.3. Metallic bonding (unsaturated covalent bonding)

This type of bonding is confined to metals and near metals, a number of which are found in Groups I, II and III of the Periodic Table. Consider, as an example, solid copper in which the outer electron is readily released from the parent atom and all the valence electrons can move freely between the copper ions. The positively charged ions are held together by their attraction to the cloud of negative electrons in which they are embedded.

The mobility of the electrons is responsible for the high thermal and electrical conductivities of metals.

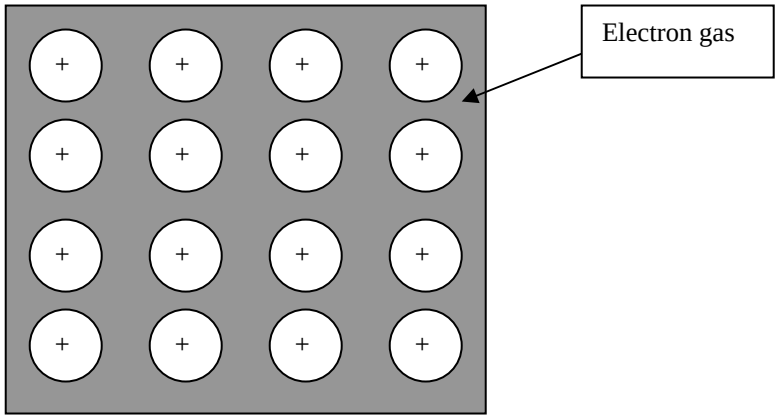

Figure 2.4. A metallic crystal pictured as a lattice of +ve ions embedded in 'sea' of electrons

2.4. Van der Waals bonding

The inert gases condense to form solids of sufficiently low temperatures, yet their closed shell configurations eliminate the formation of any of the three bonds already discussed. Similarly, valency requirements are fulfilled in molecules of the gases (CH_4) methane, CO_2, H_2, etc., and no spare electrons are available forming bonds yet they too can solidify. This points to the presence of another kind of bond called a secondary bond, wherein no major modification of the electronic structure occurs.

An electron with closed electron shells comprise a positive nucleus surrounded by a spherical cloud of negative charge. If the electron clouds of two such atoms were stationary and undeformable, no force would exist between them. In reality the electron cloud results from the motion of various electrons, thus the electrons must be regarded as in motion around the nucleus. While on the average an atom will have no dipole moment, it has a rapidly fluctuating dipole moment. At any instant the centre of the negative charge distribution does not coincide with the nucleus but rapidly fluctuates about it. These rapidly fluctuating dipole moments of atoms affect the motion of electrons in the other atoms and lower energy (i.e. attraction) when they are in sympathy with one another.

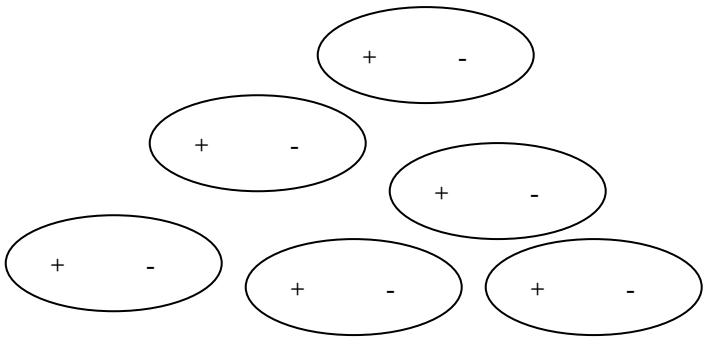

Figure 2.5. Illustrating the origins of Van der Waal force

van der Waal forces, by their nature act over large distances for the electron clouds do not overlap one another. This makes these forces be felt even in the gaseous state, a cause of deviations from the perfect gas laws. The gas equation suggested by van der waal incorporates this effect and the force is known after him.

Examples of substances bonded by van der waal forces include plastics, graphite and the paraffins.

NB: In organic solids the molecules the solids are composed of may have permanent dipoles and the interaction between these dipoles accounts for the cohesive force. One type of permanent dipole interaction is the so-called **hydrogen bond** that occurs only when a hydrogen atom is present in the dipole. The hydrogen bond is important in many biological molecules such as DNA, and in certain ferroelectric crystals.

Reading Exercise: Explain in details the formation of hydrogen bonds.

2.5. Comparison of Bonds-Mixed Bonds

Though the primary bonds seem quite different the bonding in many substances does not fit easily into just one or other of the three categories. That is, quite often we have situations of mixed bonds.

The formation of mixed bonds is related to the electronegativity series, i.e., the degree to which an atom can attract electrons to itself. In general electronegativity increases steadily across the Periodic Table from Group I to Group VIII. It also varies within a group, decreasing with increasing atomic number except in the case of transition elements.

Given the electronegative series, rules about bonding is as follows:

1. Two atoms of similar electronegativity form either metallic bond or covalent bond according to whether they can release or accept electrons.
2. When electronegativities differ the bond is partially ionic, the ionic character increasing with the difference in electronegativity.
3. Since the covalent bond is directional, while the ionic bond is not, the degree of directionality changes with the bond character with, consequently, marked influence on the crystal structure.

2.6. Bond Strength

This is the measure of the energy required to break a bond, that is, the amount of energy required to vapourize the solid and hence separate the constituent atoms. From the measure of heat required to vapourize 1 Kg mole (i.e. energy necessary to break N_o (N_o = Avogadros number)), it is found out that the weakest bonds in decreasing order are van ver Waals, then metallic, followed by ionic and covalent bonds whose strengths are nearly comparable.

2.6.1. Bond Strength and Melting Point.

Melting points are indicative of the bond strengths for the following reason. The atoms in a solid are in constant vibration at normal temperatures. When the temperature is raised the heat is stored in the vibrational energy of the atoms which is proportional to the absolute temperature. Thus melting point occurs when the vibration becomes so great that the bonds are broken and the atoms become mobile. We already know that the bond strength in the ionic bond increases with increase in valency; this is also reflected in the melting point. Further, the melting point decreases with increasing atomic number as shown in Table 2.1 below.

Table 2.1. Melting point and atomic number

Material	Atomic Number	Melting Point (°C)
Carbon (diamond)	6	3,750
Silicon	14	1,421
Germanium	32	937
Tin	50	232

SUMMARY

1. There are two categories of bonds: primary and secondary bonds.
2. Bond strength is the amount of energy expended to break of bond.

EXERCISES

1. Account for the different melting points of the materials given in Table 2.1.
2. Describe the atom structure of helium, aluminum, and bromine, and hence determine what types of chemical bond each can form.
3. Discuss the formation of ionic and covalent bonding between atoms in terms of the electron structure.
4. What is a dipole? Explain the meaning of a dipole moment.

SOME REFERENCES

1. B.H. Flowers and E. Mendoza, Properties of Matter, John Wiley and Sons Ltd, Chichester (2000)
2. K.J. Pascoe, An Introduction to the Properties of Engineering Materials, English Language Book Society and Van Nostrand Reinhold (UK) Co. Ltd. (1982)
3. D. Tabor, Gases, Liquids and Solids and Other States of Matter (3rd edition), Cambridge University Press (1995)