

THE STRUCTURE OF SOLIDS

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Solids, as is well known, are characterised by *incompressibility, rigidity and mechanical strength*. This indicates that the molecules, atoms or ions that make up a solid are *closely packed, i.e.*, they are held together by strong forces and cannot move at random. Thus, *in solids there is well-ordered arrangement of molecules, atoms or ions*. The properties of solids not only depend upon the number and kind of constituents but also on their arrangements.

Solids can be classified into the following two categories.

1. Crystalline Solids. *A substance whose constituents are arranged in an orderly manner in a definite geometric form is called a crystalline solid.* X-ray diffraction studies of these solids reveal that the regular arrangement of the constituents (molecules, atoms or ions) *extends over large distances* in three-dimensional network of crystals. In other words, the crystalline solids are said to exhibit *long range order*. Some common examples of crystalline solids are sodium chloride, sulphur, diamond, sugar, etc.

2. Amorphous Solids. *A substance whose constituents are not arranged in an orderly manner is called an amorphous solid.* These substances do possess properties such as incompressibility and rigidity to a certain extent but they do not have definite geometric forms. Some amorphous solids may have some orderly arrangement but *it does not extend to more than a few Angstrom units*. Thus, amorphous solids have only *short range order*. Some common examples of amorphous solids are glass, rubber, plastics, etc.

Difference between Crystalline and Amorphous Solids. Crystalline and amorphous solids differ from one another in the following respects.

1. Characteristic Geometry. A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in three-dimensional space. An amorphous solid, on the other hand, does not have any pattern or arrangement of its constituents and, therefore, does not have any definite geometric shape.

2. Melting Points. A crystalline substance has a *sharp melting point, i.e.*, it changes abruptly into liquid state at a fixed temperature. An amorphous substance, on the contrary, does not have a sharp melting point. For example, if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change into liquid state. Strictly speaking, *solid state refers only to crystalline state, i.e., only a crystalline material can be considered to be a true solid.*

3. Isotropy and Anisotropy. Amorphous solids differ from crystalline solids in another important respect. *The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index of an amorphous solid are the same in all directions.* Amorphous substances are, therefore, said to be **isotropic**. Liquids and gases are also isotropic.

Crystalline solids, on the other hand, are **anisotropic, i.e.**, *their physical properties are different in different directions.* For example, the velocity of light passing through a crystal varies with the direction

in which it is measured. Thus, a ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction**. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangement in such materials. This can be shown on reference to Fig. 1 in which a simple two-dimensional arrangement of only two different kinds of atoms is depicted. If the properties are measured along the direction indicated by the slanting line CD , they will be different from those measured in the direction indicated by the vertical line AB . The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case, each row is made up of one type of atoms only. In amorphous solids, atoms or molecules are arranged at random and in a disorderly manner and, therefore, all directions are identical and all properties are alike in all directions.

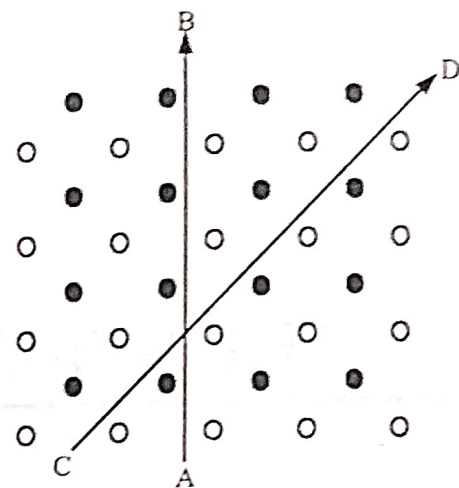


Fig. 1. Anisotropic behaviour of a crystal.

Size and Shape of Crystals. Several naturally occurring solids have definite crystalline shapes which can be recognised easily. There are many other solid materials which occur as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape. *Such solids in which the crystals are so small that they can be recognised only under a powerful microscope, are said to be microcrystalline.* The size of a crystal depends on the rate at which it is formed; the slower the rate, the bigger the crystal. This is because time is needed by the ions or atoms or molecules to get into their proper positions in the crystal structure. Thus, large transparent crystals of sodium chloride, silver chloride, lithium chloride, etc., can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the minerals formed by geological processes are often very large.

Interfacial Angles. Crystals are bound by plane faces. *The angle between any two faces is called an interfacial angle.* It is measured by an instrument called *goniometer*. It may be noted that the size of the faces or even shapes of the crystals of *one and the same substance* may vary widely with conditions of their formation. Although a crystal may have different shapes yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is also known as law of constancy of interfacial angles or law of crystallography. This is illustrated in Fig. 2. Although the external shapes are different yet the interfacial angle is the same.

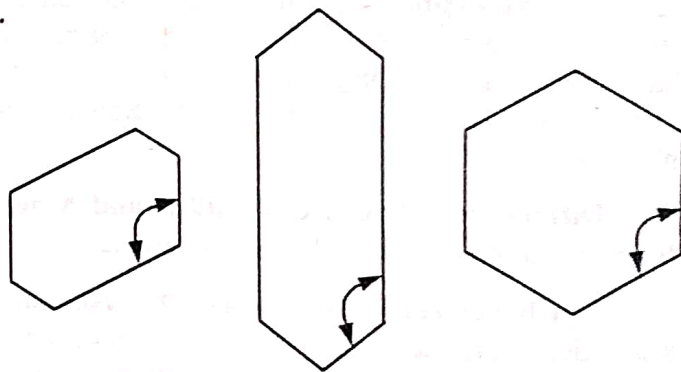


Fig. 2. Interfacial angles in a crystal.

SYMMETRY IN CRYSTALS

Besides the interfacial angles, another characteristic property of crystals is their symmetry. The symmetry of a crystal may be understood in terms of symmetry operation and symmetry elements.

The **symmetry operation** is an operation performed around a line, plane or point on a body so that it yields the same or similar appearance of the body after the operation. To illustrate this, let us consider a symmetry operation such as rotation around an axis. Suppose we are looking at a cube. If we rotate the cube through 90° about an imaginary axis passing through the centres of the top and bottom faces (Fig. 3), the appearance after rotation is exactly similar to the appearance before rotation. The cube on further rotation presents similar appearance three times more in one complete rotation. Thus, a cube gives similar

The important characteristics of molecular crystals are given below.

1. Molecular crystals are generally soft.
2. They have low melting and boiling points.
3. They are bad conductors of electricity because they consist of neutral molecules in solid as well as in dissolved state.
4. They are volatile and have low heats of vaporisation.

Close Packing of Identical Solid Spheres

In order to understand the packing of atoms, molecules or ions in crystals, let us consider the packing of hard spheres of equal size in two dimensions, i.e., in a layer and extend the arrangement to three dimensions by putting such layers above one another. There can be a number of possible arrangements but the one in which maximum available space is occupied will be economical. Such an arrangement is called *close packing*. Hence, the closer the packing, the greater is the stability of the packed system.

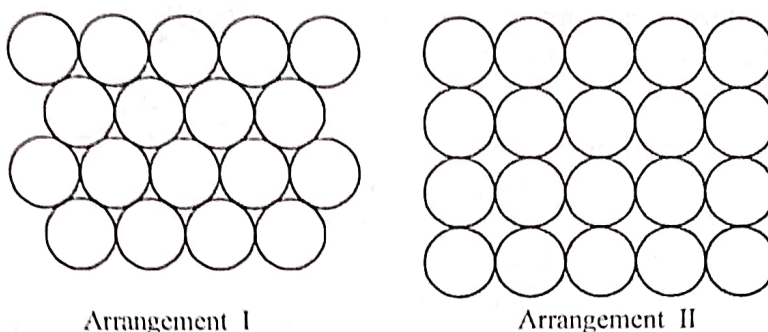


Fig. 17. Two common ways of packing of spheres of equal size. In arrangement I, 60.4% of the volume is occupied and in arrangement II, 52.4% of the volume is occupied.

There are two common ways of packing spheres of equal size in a layer. These are shown in Fig. 17.

A comparison of the two ways of packing of spheres shows that in arrangement I, the spheres are more closely packed than in arrangement II. It has been calculated that in the first arrangement, 60.4% of the available space is occupied by the spheres. The remaining 39.6% of the space is empty and is called **void volume**. In the second arrangement, only 52.4% of the space is filled and 47.6% of the space is empty. Thus, the arrangement I is more economical and it represents a *close packing of spheres*.

It can be seen that in the close packing arrangement, the spheres arrange themselves in such a way that their centres are at the corners of an equilateral triangle. Each sphere is in contact with six other similar spheres shown shaded in Fig. 18. The number of nearest neighbours with which a given sphere is in contact is called the **coordination number**. Thus, the coordination number of each sphere packed in the above manner in a layer is 6.

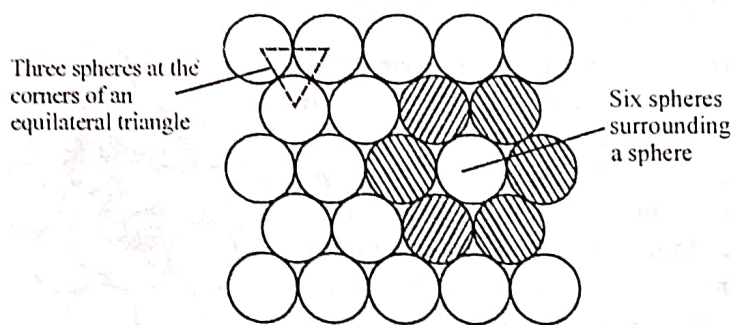
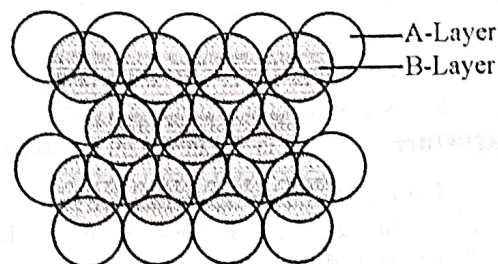
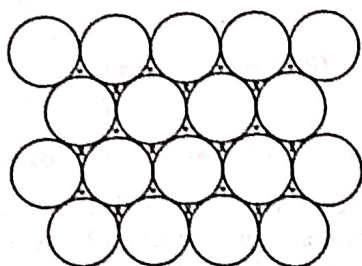


Fig. 18. Close packing of spheres.

The above arrangement can be extended in three dimensions by placing other closest packed layers on the top of hollows (or voids) of the first layer. Let us label the first layer as *A* layer.



There are two types of hollows in the first layer

Fig. 19. Building of second layer (*B*, shown shaded) covering hollows marked by dots (·). The hollows marked by crosses (x) remain unoccupied.

which are marked by dots (\cdot) and crosses (\times). All the hollows are equivalent but the spheres of second layer may be placed either on hollows which are marked by dots or on other set of hollows marked by crosses. It may be noted that it is not possible to place spheres on both types of hollows simultaneously. Let us place spheres on hollows marked by dots to make the second layer which may be labelled as B layer (Fig. 19)

When we come to packing of third layer, there are two alternative ways. One way is to put the spheres of third layer on the hollows of the second layer. In that case it is observed that each sphere of third layer (shown as dark spheres in Fig. 20) lies directly above those in the first layer. In other words, the third layer becomes identical to the first layer. This arrangement if continued indefinitely in the same sequence, is represented as $ABABABA\dots\dots$

This arrangement of layers, viz., $ABABABA\dots$ is shown more clearly in Fig. 20(b). On examination, this arrangement is found to represent **hexagonal close packing symmetry**. This is abbreviated as **hcp**. This means that the structure

has one 6-fold axis of symmetry. This is illustrated in Fig. 20(c). The same or similar appearance is repeated on rotating the crystal through an angle of 60° . It may be noted that the symmetry axis is perpendicular to the layers of close packed spheres.

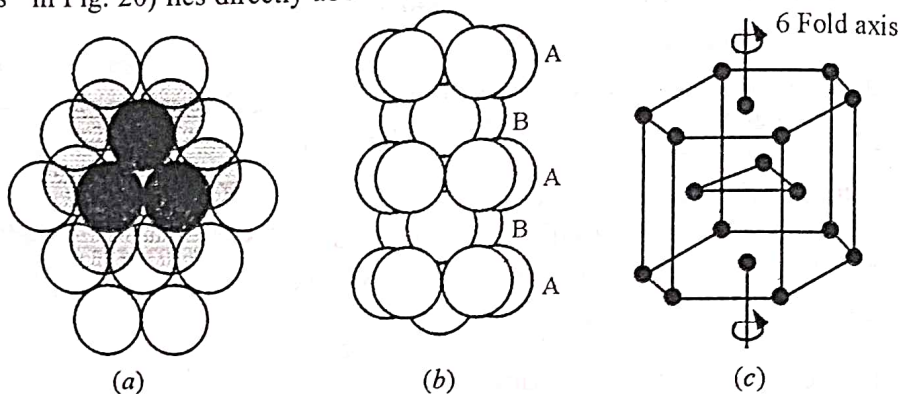


Fig. 20. $ABABABA\dots\dots$ system of close packing or hexagonal close packing (*hcp*) of spheres.

The second way to pack spheres in third layer is to place them over the unoccupied hollows of the first layer marked by crosses. This will give a different type of close-packed arrangement (Fig. 21a). However, it can be shown that now the spheres in the fourth layer will correspond with those in the first layer. This arrangement of stacking, if continued indefinitely, is represented as $ABCABCABC\dots$ (Fig. 21 b). The resulting arrangement has cubic symmetry and, consequently, it is referred to as **cubic close packing of spheres** and is abbreviated as **ccp**.

According to Table 2, this structure has four 3-fold axes of symmetry which pass through the diagonals of the cube. A closer study of $ABCABC\dots$ system of close packing also shows that there is a sphere at the centre of each face of the unit cube and hence this structure is also known as **face centred cubic structure**. The face-centred cubic arrangement has been shown more clearly in Fig. 21(c).

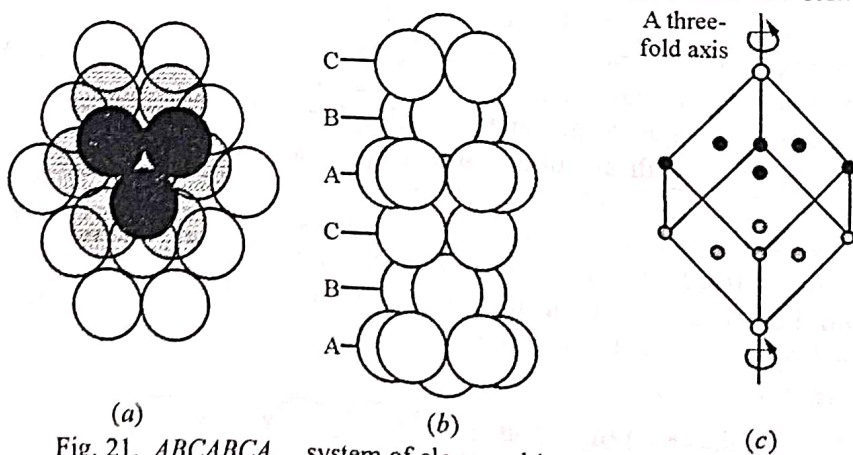


Fig. 21. $ABCABC\dots\dots$ system of close packing or cubic close packing (*ccp*) of spheres.

It may be noted that in both the types of structures discussed above, each sphere is surrounded by twelve other spheres. For example, a sphere marked x is in contact with six nearest spheres (marked 1, 2, 3, 4, 5 and 6) in the same layer, as shown in Fig. 22. In addition to this, the sphere marked x is also in contact with three spheres (marked 7, 8, 9) in the layer above and three spheres (marked 10, 11, 12) in the layer

below (shown at some distance for the sake of clarity). Thus, the coordination number in the *hcp* as well as in the *ccp* structure is 12.

In addition to the above two close packed arrangements, another arrangement of packing of spheres is the **body centred cubic arrangement**. In this arrangement, the spheres in the first layer of close packing are slightly opened up. As a result, the spheres are not in contact with each other. This is shown in Fig. 23. To build the second layer (shown by dotted spheres in Fig. 23a), the spheres are placed at the top of hollows in the first layer. Each sphere in the second layer is in contact with four spheres of the first layer. In the third layer, spheres are placed exactly above the first layer. Thus, each sphere in this system of close packing is in contact with eight spheres, four in the layer below it and four in the layer above it. In other words, coordination number of each sphere is 8. In this arrangement, as can be easily visualised, there are eight spheres at the corners of a cube and one sphere is in the centre (or body) of the cube. Therefore, the structure is known as **body centred cubic** and is abbreviated as *bcc*.

It can be shown by simple geometry that while the volume occupied in *ccp* arrangement is 74%, that in *bcc* arrangement is 68% of the total volume (see below).

Volume occupied in *ccp* arrangement. Consider the cubic close packed arrangement, as shown in Fig. 24*. Let the length of each side be *a* so that the volume of the cube is *a*³. Let us now calculate the volume occupied by spheres.

As shown in the figure, there are eight spheres at the corners and six spheres at the faces. But, each sphere at the corner is shared by eight unit cells and its contribution per unit cell is 1/8. Similarly, each sphere in the face is shared by two unit cells and its contribution per unit cell is 1/2. Thus, the number of spheres per unit cell = 8×(1/8) + 6×(1/2) = 4.

Consider Δ ABC. Since it is a right angled triangle, hence

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

$$\therefore \text{Face diagonal, } AC = \sqrt{2}a$$

But, as is evident from the figure, AC = 4 *r* where *r* is the radius of the sphere.

$$\therefore 4r = \sqrt{2}a \text{ or } r = \frac{\sqrt{2}a}{4}$$

Since, as mentioned above, there are 4 spheres per unit cell, hence the volume occupied by 4 spheres

$$= 4 \times \frac{4}{3} \pi r^3 = 4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3$$

$$\text{Ratio of the volume occupied to total volume} = \frac{\text{Volume occupied by spheres}}{\text{Volume of the cube}}$$

$$= \frac{4 \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{\sqrt{2}a}{4}\right)^3}{a^3} = 0.7406$$

Thus, the volume occupied in *ccp* arrangement = 74.06%

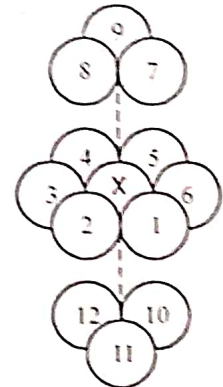


Fig. 22. Coordination number in *hcp* and *ccp* structures.

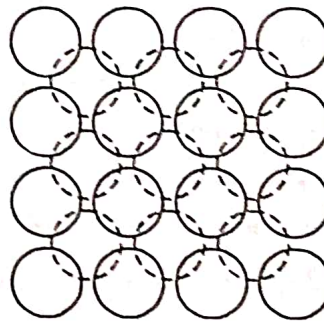


Fig. 23. Body centred cubic packing of spheres.

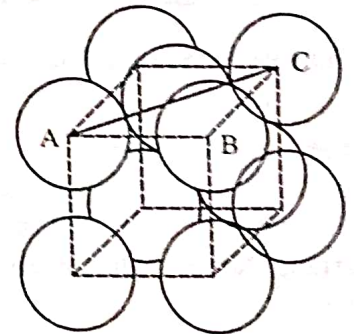


Fig. 24. Volume occupied in *ccp* arrangement. Only one face centred sphere is shown here.

Volume occupied in *bcc* arrangement. Consider the body-centred cubic arrangement, as shown in Fig. 25**. As before, let the length of each side be a so that the volume of the cube is a^3 .

It is clear from the figure that there are eight spheres at the corners and one in the body of the unit cell. But, each sphere at the corner is shared by eight unit cells and its contribution per unit cell is $1/8$. However, the sphere at the body centre of the cube contributes fully to the cube. Thus,

$$\text{The number of spheres per unit cell} = 8 \times (1/8) + 1 = 2 \quad \dots(i)$$

$$\begin{aligned} \text{In right angled triangle ABC, } AC^2 &= AB^2 + BC^2 = a^2 + a^2 \\ \text{or } AC^2 &= 2a^2 \text{ or } AC = \sqrt{2}a \quad \dots(ii) \end{aligned}$$

$$\text{Similarly, in right angled triangle ACD, } AD^2 = AC^2 + CD^2 = (\sqrt{2}a)^2 + a^2 = 3a^2$$

$$\text{or } AD = \sqrt{3}a \quad \dots(iii)$$

But, as is evident from the figure,

$$\text{the body diagonal } AD = 4r$$

where r is the radius of the sphere.

$$\text{From Eqs. (iii) and (iv), } 4r = \sqrt{3}a \text{ or } r = \sqrt{3}a/4$$

Since there are 2 spheres per unit cell (Eq. (i)), hence,

$$\text{Volume occupied by 2 spheres} = 2 \times 4/3 \pi r^3 = 2 \times 4/3 \times 22/7 \times (\sqrt{3}a/4)^3$$

$$\text{Ratio of volume occupied to total volum} = 2 \times 4/3 \times 22/7 \times (\sqrt{3}a/4)^3 / a^3 = 0.6805$$

Thus, the volume occupied in *bcc* arrangement = 68.05%

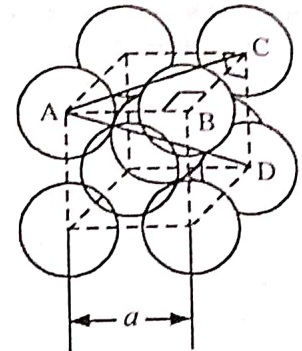


Fig. 25. Volume occupied in *bcc* arrangement.

Interstitial Sites in Close Packing of Spheres

We have seen before that even in the closest packing of spheres, there is some empty space left in between the spheres. This is known as an interstitial site. For example, when the spheres are closely packed in a single plane, the centres of three adjacent spheres lie at the vertices of an equilateral triangle. In between these three spheres, there is some empty space. This empty space (hole or void) is called **triangular** or **trigonal site**. In addition to this, we come across two more common interstitial sites, *viz.*, *tetrahedral* and *octahedral sites*, in closely packed lattices. These are discussed below.

Tetrahedral Sites. If one sphere is placed upon three other spheres which are touching one another, *tetrahedral structure* results. This is shown in Fig. 26. Since the four spheres touch one another at one point only, they leave a small space in between which is called a **tetrahedral site**. The size of the site is much smaller than that of the spheres. However, the bigger the spheres, the larger is the size of the tetrahedral site formed by them. We have seen already that in *hexagonal close packing (hcp)* as well as in *cubic close packing (ccp)* arrangement, each sphere is in contact with *three spheres* in the layer above and *three spheres* in the layer below. Thus, there would be *two tetrahedral sites associated with each sphere*. One of these sites will be immediately above and the other immediately below the sphere. It may be noted that tetrahedral site does not mean that the shape of

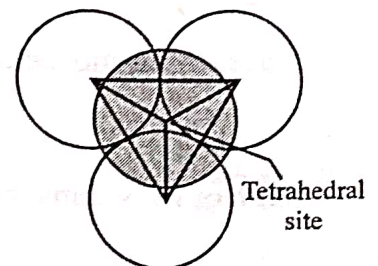


Fig. 26. A tetrahedral site.

Hence, for maximum stability, the oppositely charged ions should be as close to one another and similarly charged ions as far away from one another as possible.

The structure of an ionic crystal depends, to a large extent, on relative sizes of the cations and anions concerned. If, for example, anions are larger, they form a close-packed arrangement and the cations just fit into (or occupy) the resulting interstitial sites of tetrahedral or octahedral type, as the case may be.

In the case of a substance of general formula AX, like sodium chloride (NaCl) or zinc sulphide (ZnS), in which the number of each kind of ions is the same, the coordination number of the positive ion is the same as that of the negative ion. But in the case of a substance of general formula AX₂ or A₂X (e.g., CaCl₂ or Na₂S) in which the number of each kind is not the same, the coordination number of positive ion is different from that of negative ion. In calcium chloride, for example, chloride ions are twice as many as calcium ions. The coordination number of calcium ion, therefore, is *twice* the coordination number of chloride ion.

Let us discuss the structures of a few common crystals of the formula AX and AX₂. The structures can be described in terms of close-packed arrangements of large anions with small cations occupying the interstitial sites such as tetrahedral or octahedral.

CRYSTALS OF THE TYPE AX

Structure of Sodium Chloride (NaCl). The unit cell of sodium chloride crystal is shown in Fig. 34. In this structure, the sodium ions are represented by hollow circles and chloride ions by solid circles.

The salient features of this structure are as follows :

1. The chloride ions are arranged in *cubic close packing (ccp)* arrangement. In this arrangement, there are Cl⁻ ions at the corners of the cube as well as at the centre of each face (*face centred cubic arrangement*).

2. The sodium ions occupy all the *octahedral sites*.

3. There is only one octahedral site per atom in a close packed lattice. Therefore, there will be one Na⁺ ion for every Cl⁻ ion. This corresponds to 1 : 1 stoichiometry of sodium chloride crystal. This stoichiometry can also be understood by counting the number of Na⁺ and Cl⁻ ions which contribute to the unit cell, as discussed below.

It is clear from Fig. 34 that there are eight Cl⁻ ions at the corners and six at the faces of the unit cell. We can easily understand from the figure that each ion at the corner is shared between eight unit cells and its contribution per unit cell is 1/8. Similarly, each ion on a face is shared by two unit cells so that its contribution per unit cell is 1/2. Therefore, the number of Cl⁻ ions for the unit cell is equal to $8 \times (1/8) + 6 \times (1/2) = 4$. The number of sodium ions can also be calculated in a similar way. There are twelve Na⁺ ions on the edges and one inside the cell. It can be easily seen that each ion on the edge is shared by four unit cells and its contribution per unit cell is 1/4, while the ion at

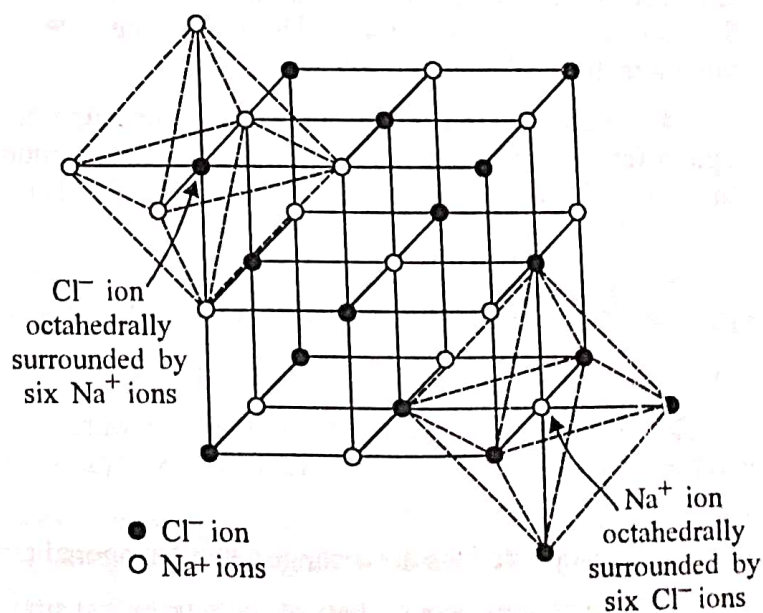


Fig. 34. Unit cell representation of NaCl structure, Hollow circles represent Na⁺ ions and solid circles represent Cl⁻ ions.

the body centre contributes only to one unit cell. Therefore, the number of Na^+ ions for the unit cell is equal to $12 \times (1/4) + 1 = 4$. Thus, the stoichiometry is 1 : 1.

4. In this structure, each Na^+ ion is surrounded by six Cl^- ions which are disposed towards the corners of a regular octahedron. This has also been shown in the figure. Similarly, each Cl^- ion is surrounded by six Na^+ ions. Thus, the coordination number of Na^+ ion as well as that of Cl^- ion is 6.

5. We have seen that for cations to fit into octahedral sites, the radius ratio r_+/r_- should be equal to 0.414 (Table 4). The radius of Na^+ ion is 0.95 Å and that of Cl^- ion is 1.81 Å so that $r_{\text{Na}^+}/r_{\text{Cl}^-}$ is 0.524. Therefore, to accommodate somewhat larger sized Na^+ ions, Cl^- ions move apart slightly. In other words, the *ccp* arrangement of Cl^- ions is slightly opened up. This type of structure is adopted by most of the alkali metal halides, the alkaline earth metal oxides and AgF , AgCl , AgBr , NH_4Cl and NH_4Br , etc.

Structure of Zinc Sulphide (ZnS). It has two types of structures known as

1. Zinc blende Structure

1. Zinc Blende Structure. The unit cell of zinc blende structure is shown in Fig. 35. In this structure, the zinc ions are represented by hollow circles and the sulphide ions are represented by solid circles. The salient features of this structure are as follows :

1. The sulphide ions are arranged in *ccp* arrangement, *i.e.*, at the corners of the cube and at the centre of each face.

2. The zinc ions occupy half of the tetrahedral sites.

3. Since there are two tetrahedral sites per atom in a close packed lattice, this means that there are two tetrahedral sites per S^{2-} ion. In this arrangement, only half of the tetrahedral sites are occupied by Zn^{2+} ions so that each S^{2-} ion has one Zn^{2+} ion. Therefore, the stoichiometry of the compound is 1 : 1.

4. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions. The arrangement around one Zn^{2+} ion and one S^{2-} ion is also shown in Fig. 35. Thus, the coordination numbers of Zn^{2+} and S^{2-} ions in zinc blende are described as 4 : 4.

5. In zinc sulphide, the radius ratio r_+/r_- is 0.40. This suggests that the coordination number is 4 (Table 4). This supports the structure presented in Fig. 35.

Zinc blende structure is also adopted by some other compounds such as ZnO , CuCl , CuBr , CuI , etc.

2. Wurtzite Structure. The unit cell for wurtzite structure is shown in Fig. 36 in which each Zn^{2+} ion is represented by a hollow circle and each S^{2-} ion is represented by a solid circle. The wurtzite structure may be described as follows :

1. The sulphide ions are arranged in a hexagonal close packed (*hcp*) arrangement.

2. The zinc ions occupy half of the tetrahedral sites.

3. There are two tetrahedral sites for each S^{2-} ion in the lattice. Since only half of them are occupied by Zn^{2+} ions, the stoichiometry of the compound is 1 : 1.

2. Wurtzite Structure

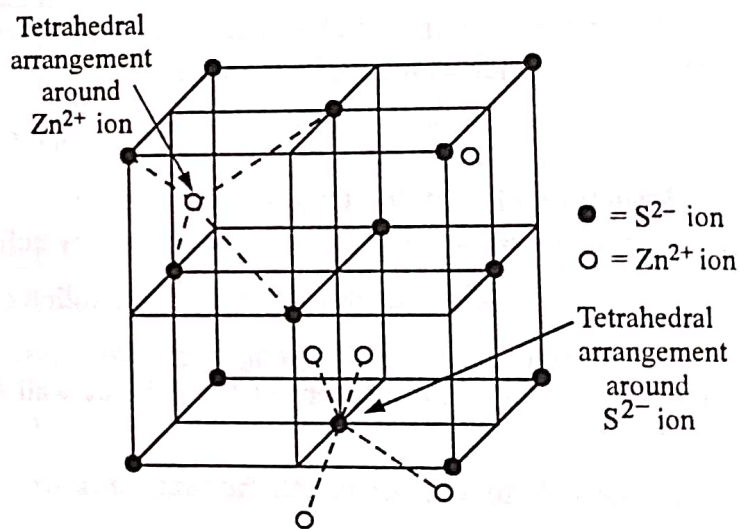


Fig. 35. Unit cell representation of zinc blende structure. Hollow circles represent Zn^{2+} ions and solid circles represent S^{2-} ions.

4. Each S^{2-} ion is surrounded by four Zn^{2+} ions which are disposed towards the corners of a regular tetrahedron. Similarly, each Zn^{2+} ion is surrounded by four S^{2-} ions. The arrangement around one Zn^{2+} ion and one S^{2-} ion is shown in Fig. 36. Therefore, the coordination numbers of Zn^{2+} and S^{2-} ions in wurtzite structure are 4 : 4.

5. The radius ratio r_+/r_- in this structure is 0.40 which also suggests that the coordination number is 4 (Table 4) and that the crystal has a tetrahedral structure. Thus, the radius ratio rule supports the above structure. The compounds such as AgI, ZnO, NH_4F and AlN have wurtzite structure.

It will be noted that the basic difference between *zinc blende* and *wurtzite* structure is that whereas in the former case the sulphide ions are arranged in *ccp* type of packing, in the latter case they are arranged in *hcp* type of packing.

Structure of Cesium Chloride (CsCl). The unit cell of CsCl is shown in Fig. 37. In this structure, cesium ions are represented by hollow circles whereas chloride ions are represented by solid circles. The structure of CsCl may be described as follows :

1. The Cl^- ions form the simple cubic arrangement and the Cs^+ ions occupy the cubic interstitial sites. In other words, the Cl^- ions may be regarded as lying at the corners of a cube and cesium ions are present at the body centre of each cube.

2. Each Cs^+ ion is surrounded by eight Cl^- ions which are disposed towards the corners of a cube. This is clear from Fig. 37(a). When the unit cell is extended as shown in Fig. 37(b), it becomes clear that each Cl^- ion is also surrounded by eight Cs^+ ions. Thus, both types of ions are in equivalent positions. Therefore, the coordination numbers of Cs^+ and Cl^- ions are 8 : 8.

The above structure may be described as body centred cubic. But, this would be a misnomer because the body centred cubic structure is one which has the same atoms at the body centre as well as the corners. But in CsCl, the atoms at the corners are different from the atoms at the centre. This type of structure is adopted by CsBr, CsI, TlCl, TlBr, etc.

Since coordination numbers of ions in CsCl (8 : 8) are higher than those in NaCl (6 : 6), we might expect that cesium chloride lattice would be more stable since each ion would have more ions of opposite charge as its neighbours. This is actually the case. The cesium chloride lattice is 1 per cent more stable than the sodium chloride lattice.

Here question arises that if CsCl lattice is more stable then why do the halides of Li, Na, K and Rb not have this lattice ? The answer lies in the radius ratio effect. The radius ratio in the halides of Li, Na,

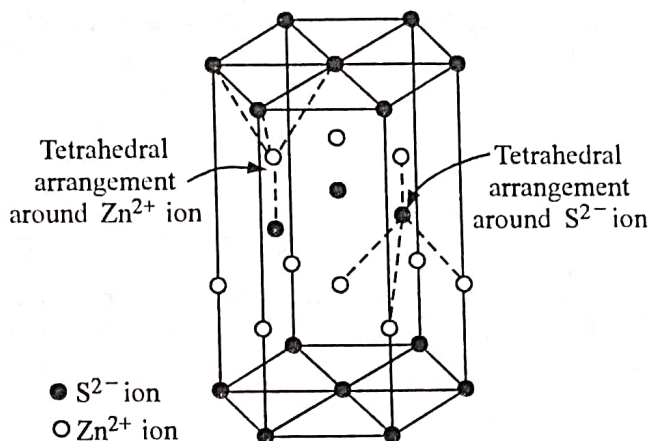


Fig. 36. Unit cell representation of wurtzite structure. S^{2-} ions (solid circles) adopt *hcp* arrangement and Zn^{2+} ions (hollow circles) occupy half of the tetrahedral sites.

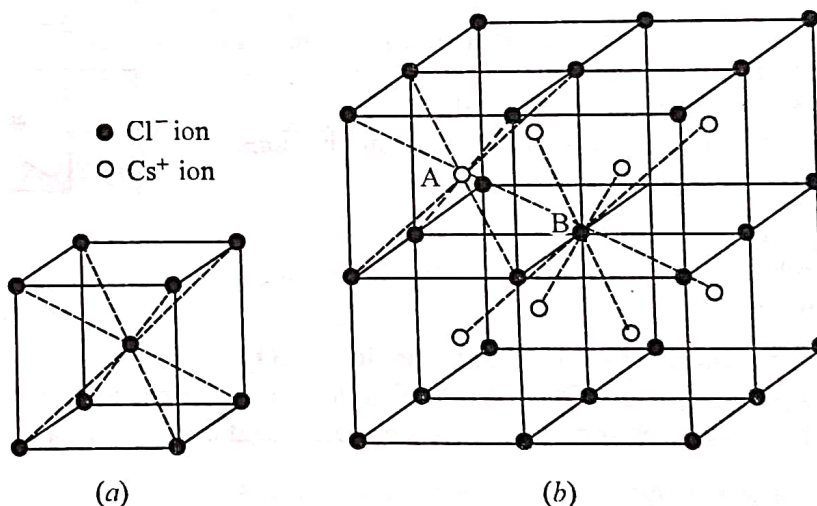


Fig. 37. (a) Unit cell representation of CsCl. The Cl^- ions adopt simple cubic arrangement and Cs^+ ions occupy cubic sites. (b) The extended unit cell.

K and Rb lies between 0.73 and 0.41 and, therefore, the coordination number has to be 6 (Table 4). If an attempt is made to pack 8 halide ions around a *smaller* positive ion, say, Na^+ ion, then some of the negative ions will touch each other sooner than they can approach a positive ion, as shown in Fig. 38. The lattice would thus be unstable. This difficulty can be overcome by packing 6 negative ions around the central positive ion. Hence, the coordination number of 6 is preferred.

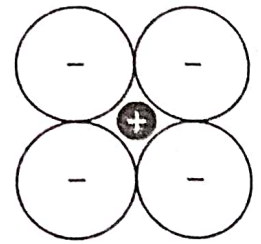


Fig. 38. Cross-section of unstable structure with 8 halide ions around an alkali metal ion other than Cs^+ .

CRYSTALS OF THE TYPE AX_2

Structure of Calcium Fluoride (CaF_2). The unit cell of CaF_2 is shown in Fig. 39. The calcium ions are represented by hollow circles and fluoride ions are represented by solid circles. The CaF_2 structure may be described as follows :

1. The Ca^{2+} ions are arranged in *ccp* arrangement so that there are Ca^{2+} ions at all the corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites.

2. Since there are two tetrahedral sites for each Ca^{2+} ion and F^- ions occupy all the tetrahedral sites, there will be two F^- ions for each Ca^{2+} ion. Thus, the stoichiometry of the compound is 1 : 2.

3. In this arrangement, each F^- ion is surrounded by four Ca^{2+} ions whereas each Ca^{2+} ion is surrounded by eight F^- ions. Thus, the coordination numbers of Ca^{2+} and F^- ions are 8 : 4.

This structure is adopted by a large number of fluorides such as BaF_2 , SrF_2 , PbF_2 , HgF_2 , CuF_2 , etc.

Structure of Titanium Dioxide, TiO_2 (Rutile Structure). The unit cell of rutile structure is shown in Fig. 40 in which titanium ions are represented by hollow circles and oxide ions are represented by solid circles.

The structure may be described as follows :

1. The titanium ions are arranged in a *distorted body centred cubic arrangement* in which these ions are present at all the corners and at the centre of the distorted cube. This structure cannot be described as cubic because one of the axes is shorter than the other by 30 per cent. The structure is, therefore, described as **distorted cubic**.

2. As shown in Fig. 40, each titanium ion is surrounded octahedrally by six oxide ions, as, for example, the titanium ion marked A in the figure. On the other hand, each oxide ion is surrounded by three titanium ions disposed towards the corners of an equilateral triangle. Thus, the coordination numbers of Ti^{4+} and O^{2-} ions are 6 : 3.

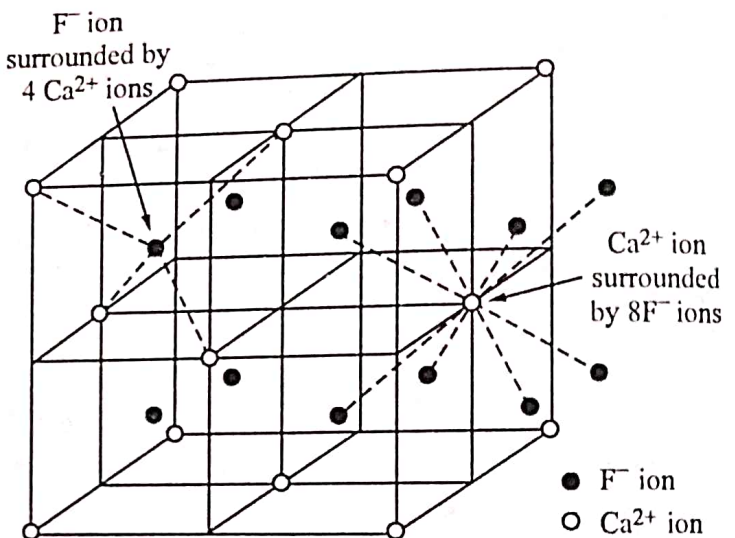


Fig. 39. Unit cell representation of CaF_2 . The Ca^{2+} ions adopt *ccp* arrangement and F^- ions occupy all the tetrahedral sites.

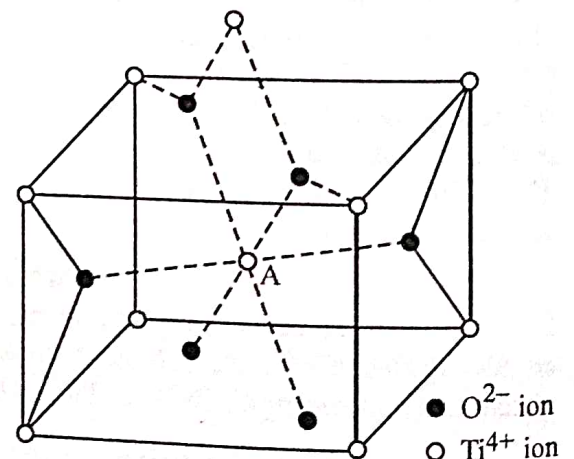


Fig. 40. Structure of titanium dioxide.

Structure of Calcium Carbide (CaC_2). The unit cell of calcium carbide is shown in Fig. 41. The structure of calcium carbide is similar to that of sodium chloride (Fig. 34). Here sodium ions are replaced by

calcium ions and chloride ions by C_2 groups. The carbon atoms are associated in pairs, as shown in Fig. 41, forming the C_2 groups. The C_2 groups are aligned in parallels as shown. The cubic symmetry observed in sodium chloride is, however, distorted considerably in the case of calcium carbide for obvious reasons.

The structure of FeS_2 is similar to that of CaC_2 . However, the S_2 units are not aligned in parallels as are the C_2 units in the case of CaC_2 .

✓ **Structure of Cadmium Iodide (CdI_2)** The unit cell of cadmium iodide is shown in Fig. 42 in which Cd^{2+} ions are represented by hollow circles and iodide ions are represented by solid circles.

The salient features of this structure are described below :

1. The iodide ions are arranged in a *hexagonal close packed (hcp)* arrangement while cadmium ions lie in *octahedral sites between every two layers of iodide ions*.

2. Each Cd^{2+} ion is surrounded octahedrally by six I^- ions, as shown in Fig. 42. On the other hand, each I^- ion has three Cd^{2+} ions as nearest neighbours. The three Cd^{2+} ions surround the I^- ion in an arrangement in which Cd^{2+} ions form the base of a trigonal pyramid whose apex is the I^- ion.

3. The arrangement of the three layers corresponds to the composition CdI_2 .

This arrangement is continued as shown and the structure is referred to as a layer lattice. The forces operating in between the $I - Cd - I$ layers to hold them together are weak. As a result, this compound is flaky and can be easily cleaved.

.....I.....

.....Cd.....

.....I.....

.....I.....

.....Cd.....

.....I.....

● Cd^{2+} ion
○ I^- ion

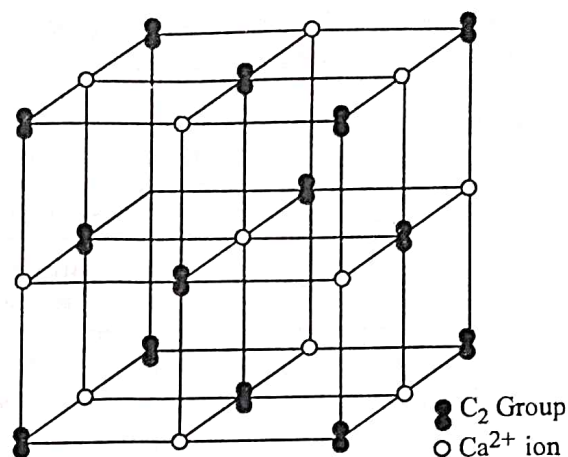


Fig. 41. Structure of calcium carbide.

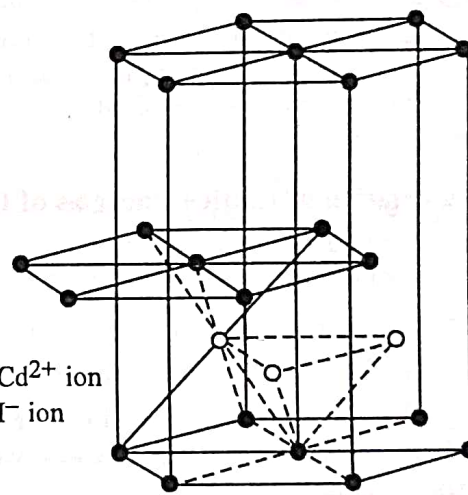
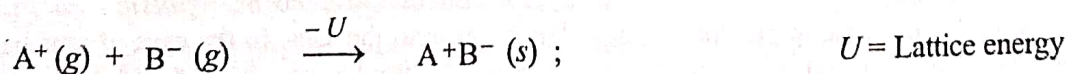


Fig. 42. Structure of cadmium iodide.

Lattice Energy of an Ionic Crystal

The **lattice energy U of an ionic crystal** is defined as the amount of energy released when cations and anions in their gaseous states are brought from infinity to their respective lattice sites in a crystal to form one mole of the ionic crystal.

The formation of a mole of an ionic crystal from the constituent gaseous ions may be represented as follows :



With the coming together of positive and negative ions, there is a considerable *decrease in potential energy* of the system. Hence, in the formation of an ionic crystal from the constituent gaseous ions, as in the above example, there is considerable *release of energy in the form of heat*. Hence, U is negative.

It is obvious that the greater the magnitude of the lattice energy of an ionic crystal, the greater would be its stability. Lattice energies of a few ionic crystals are given in Table 7.

TABLE 7
Lattice Energies of Some Common Ionic crystals

Uni-Univalent Crystals		Bi-Bivalent Crystals	
Ionic Crystal	Lattice Energy (kJ mol ⁻¹)	Ionic Crystal	Lattice Energy (kJ mol ⁻¹)
LiF	- 1033	CaF ₂	- 2581
CsF	- 748	MgF ₂	- 2882
NaCl	- 778	MgO	- 3932
LiI	- 140	BcO	- 3125
CsI	- 601	MgS	- 3254
AgCl	- 895	ZnO	- 4032

As can be seen, lattice energies of ionic crystals are quite high. This is on account of strong electrostatic attraction between oppositely charged ions present in the crystals. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the valency (charge) of the ions, the greater would be the lattice energy of the ionic crystals. Thus, lattice energy increases as we move from uni-univalent ionic crystals to uni-bivalent ionic crystals and then to bi-bivalent ionic crystals.

Calculation of Lattice Energies of Ionic Crystals

The lattice energy of ionic crystals can be calculated theoretically on the basis of coulombic interactions between the ions present in the crystals. There are two types of interactions :

1. *Attractive interactions between oppositely charged ions.*
2. *Repulsive interactions because of interpenetration of electron charge clouds.*

1. Attractive Interactions between Oppositely Charged Ions. The potential energy (*P.E.*) of a pair of ions of opposite charges varies inversely as the distance *r* between the ions. This may be expressed as

$$P.E. (\text{attraction}) = z_1 z_2 \frac{(+e)(-e)}{r} = - \frac{z_1 z_2 e^2}{r} \quad \dots(2)$$

where *e* is the electronic charge and *z*₁ and *z*₂ are the charges on the oppositely charged ions (being, for example, 1 and 1 in the case of NaCl and 2 and 1 in the case of CaCl₂).

2. Repulsive Interactions due to Interpenetration of Electron Charge Clouds. As a cation and an anion come very close to each other, there is repulsion between them because of interpenetration of similarly charged electron charge clouds. The potential energy due to this repulsion has been shown to be inversely proportional to the *n*th power of the distance between the ions, i.e.,

$$P.E. (\text{repulsion}) = b e^2 / r^n \quad \dots(3)$$

when *n* is called *Born exponent* while *b* is a constant termed as *repulsion coefficient*. The value of *n* increases with increase in electron charge density around the ions. In the case of ions having Ne configuration (e.g., Na⁺ and F⁻ ions), *n* = 7 while in the case of ions having Ar, Kr and Xe configurations, *n* = 9, 10 and 12, respectively.

The net potential energy for a pair of ions of opposite charges is thus given by combining Eqs. 2 and 3, i.e.,

$$P.E. (\text{net}) = -z_1 z_2 e^2 / r + b e^2 / r^n \quad \dots(4)$$

Substituting the value of B in Eq. 6, we have

$$\begin{aligned} (P.E.)_0 &= -\frac{Ae^2z^2}{r_0} + \frac{Az^2e^2}{nr_0^n}r_0^{n-1} = \frac{-Az^2e^2}{r_0} + \frac{Az^2e^2}{nr_0} \\ &= \frac{Az^2e^2}{r_0} \left(\frac{1}{n} - 1 \right) \end{aligned} \quad \dots(9)$$

The lattice energy U_0 is defined as the amount of energy released in the formation of a *mole* of a crystal from the constituent gaseous ions separated at infinite distance from one another. Thus,

$$U_0 = N_A \times (\text{Potential energy}) = \frac{N_A Az^2e^2}{r_0} \left(\frac{1}{n} - 1 \right) \quad \dots(10)$$

Since n is always more than 1, U_0 would be negative, as expected.

In the above equation, all the quantities are known for a given crystal except the value of n which can be calculated from the compressibility of the crystal if the crystal spacing parameters are known.

The values of lattice energies calculated by means of this equation have been found to be in good agreement with those obtained experimentally, as shown for some of the compounds in Table 9.

The Born equation leads to the following conclusions :

1. The higher the charge on cation and anion, the greater would be the magnitude of lattice energy and, therefore, the greater would be the stability of the crystal.

2. Since lattice energy is inversely proportional to the interionic distance which is taken as the sum of the radii of the cation and the anion, hence the smaller the size of the ions, the smaller would be the interionic distance, the higher would be the magnitude of lattice energy and the greater would be the stability of the ionic crystal.

3. The lattice energy and hence stability of an ionic crystal is directly proportional to the Madelung constant which depends upon the coordination number of each ion and the geometric pattern of the ions in the crystal lattice of the crystal.

Experimental Determination of Lattice Energy. The Born-Haber Cycle. Since direct experimental determination of lattice energies is not so easy, these are determined indirectly with the help of a thermo-chemical cyclic process known as **Born-Haber cycle**. We would illustrate this by taking into consideration the determination of the lattice energy of NaCl.

The various steps involved in the formation of NaCl (*s*) in crystalline state are as follows :

1. *Conversion of Metallic Sodium into Gaseous Sodium Atoms.* The energy required for the conversion of one mole of metallic sodium into gaseous sodium atoms is called **sublimation energy**. It is represented by S .



2. *Dissociation of Gaseous Chlorine Molecules into Gaseous Chlorine Atoms.* This step involves the dissociation of gaseous chlorine molecules into gaseous chlorine atoms. The amount of energy required to dissociate one mole of gaseous chlorine molecules into gaseous atoms is called **dissociation energy**. It is represented by D .



TABLE 9

Lattice Energies of Some Common Compounds

Compound	Lattice Energy (kJ mol ⁻¹)	
	Experimental	Theoretical
MgF ₂	-2882	-2920
CaF ₂	-2581	-2585
AgCl	-895	-849
AgBr	-883	-824
AgI	-870	-795

Evidently, the energy required to produce one mole of gaseous chlorine atoms would be $D/2$.

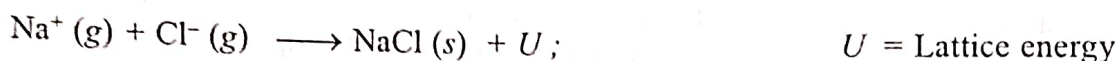
3. *Conversion of Gaseous Sodium Atoms into Sodium Ions.* The amount of energy required to convert one mole of gaseous sodium atoms into sodium ions in the gaseous state is called **ionisation energy**. This may be represented by IE .



4. *Conversion of Gaseous Chlorine Atoms into Chloride Ions.* The amount of energy released when one mole of gaseous chlorine atoms are converted into chloride ions in the gaseous state is called **electron affinity**. It is represented by EA .



5. *Combination of Gaseous Ions to form a Solid Crystal.* This step involves the combination of gaseous Na^+ and Cl^- ions to give one mole of sodium chloride crystal. The amount of energy released when one mole of solid crystalline compound is formed from gaseous ions of opposite charges is called **lattice energy**. It is denoted by U .



The overall change may be represented as



The enthalpy change for this reaction is called **enthalpy of formation** of sodium chloride and may be denoted as ΔH_f .

The various steps may be represented in the form of **Born-Haber cycle**, as shown in Fig. 44.

According to Hess's law, the enthalpy of formation of sodium chloride should be the same irrespective of the fact whether it takes place directly in one step or through a number of steps, as illustrated above. Hence,

$$\Delta H_f = S + (1/2) D + IE + EA + U$$

Using positive sign for energy *absorbed* and negative sign for energy *released*, we have

$$\text{Heat of sublimation of sodium } (S) = 108.5 \text{ kJ mol}^{-1}$$

$$\text{Dissociation energy of } \text{Cl}_2 \quad (D) = 243.0 \text{ kJ mol}^{-1}$$

$$\text{Ionisation energy of sodium } (IE) = 495.2 \text{ kJ mol}^{-1}$$

$$\text{Electron affinity of chlorine } (EA) = -348.3 \text{ kJ mol}^{-1}$$

$$\text{Enthalpy of formation of NaCl } (\Delta H_f) = -381.8 \text{ kJ mol}^{-1}$$

Substituting the various values in the above equation, we get

$$-381.8 \text{ kJ mol}^{-1} = 108.5 \text{ kJ mol}^{-1} + \frac{1}{2} (243.0) \text{ kJ mol}^{-1} + 495.2 \text{ kJ mol}^{-1} - 348.3 \text{ kJ mol}^{-1} + U$$

$$\therefore \text{Lattice energy of sodium chloride, } U = -758.7 \text{ kJ mol}^{-1}$$

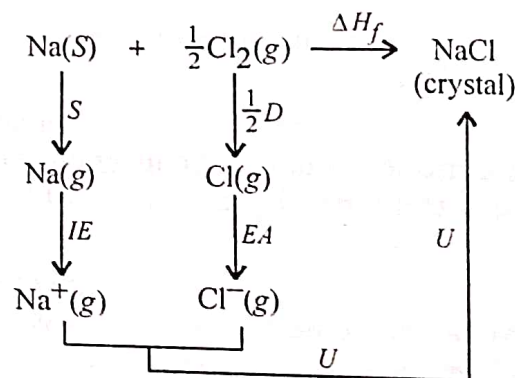


Fig. 44. Born-Haber cycle for the formation of NaCl.

Explanation of Some Properties of Ionic Crystals on the Basis of Lattice Energy

1. **Solubility of Ionic Crystals in Various Solvents.** When an ionic solid goes into solution, its *crystal lattice gets ruptured*. The ions which occupied certain fixed positions in the crystal now move farther apart in the solution. The *question* arises. *How is the energy required to cause the rupture of the lattice obtained?* The answer is not far to seek. There is a *strong interaction between the solvent and the ions* resulting in the *solvation of the ions*. If water is the solvent, the process is called *hydration of the ions*. The ionic solvation or hydration is an exothermic process releasing a considerable amount of