Quadrant II – Transcript and Related Materials (Notes)

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Unit	: 111
Module Name	: Atomic arrangement in crystalline matter, types of Bonds
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Notes:

Atomic Bonding

- The basic unit of all crystal structure is an atom.
- In a crystalline substance the constituent atoms are not only tightly packed on a repetitive pattern but they also bond together by forces of varying strengths, depending on the type of bond that exists between the two atoms.
- The kind of bonds that occur depend upon the electronic configuration which make up the crystalline structure.
- The forces that bind together the atoms of crystalline solids are electrical in nature.
- Their type and intensity are largely responsible for the physical and chemical properties of minerals. Hardness, Cleavage, electrical and thermal conductivity are directly related to binding forces.
- In general the stronger the bond the harder the crystal, the higher its melting point.

• The structural patterns of the mineral Periclase and NaCl Halite are similar, yet Periclase melts at 2800degC and Halite at 801degC. The greater amount of heat energy required to separate the atoms in Periclase indicates it has a stronger electrical bond than Halite

These electrical forces are chemical bonds and can be described as **ionic, covalent, metallic and Van der Waals bonds and Hydrogen Bonds.** The aim of the above bonds is for each atom to end up with a noble gas configuration in the outer shell of electrons.

Ionic Bond:

- Atoms can attain a stable configuration like that of inert gases by losing or gaining electrons. Ionic Bond is the one in which one or more electrons is transferred from a cation to an anion. Here the outermost electrons are removed from one atom, i.e. the donor, and reside in the electronic orbital of another atom, i.e. the electron acceptor.
- The electron donors reside on the left side of the periodic table while the acceptor are on the right. The donors produce Cations, while the acceptors are referred to as Anions.
- Here the ions are held together by electrostatic forces due to equal and opposite charges, hence the compound formed in this way i.e. by transfer of electrons are said to be electrovalent or lonic compounds.
- Minerals with ionic bonds are mechanically strong and hard and hence have a high melting point. They conduct electricity by ion movement. Large number of minerals are ionic compounds.

Covalent Bond:

- Electrons can also be shared between the two combining atoms and thus the shared electron can contribute towards stable atoms.
- **Covalent bond** is one in which electron is shared between adjacent atoms. These bonds are quite stable as the sharing allows the stable electronic configuration for both elements to occur. Covalent bond exists in gases H₂, N₂, O₂ & Cl₂.
- These types of bonds are common in organic compounds and are rare in minerals

- The best example of mineral is **Diamond exhibiting Covalent bond**
- Diamond is made up of carbon atoms. Each carbon atom is covalently bonded to 4 other Carbon Atoms, held together by strong covalent bonds. This network pattern continues in 3D making diamond the hardest mineral.

Metallic Bonds:

- This bonding is typical in metals.
- Occur when valence electrons are released by a metal atom. These electrons move around the array of cations, binding them together in the structure.
- This electron mobility gives good electrical and thermal conductivity in metals, also malleability and ductility.
- These metallic bonded minerals are opaque to incident light
- The metallic bond occur in sulphide minerals that do not have sufficient electrons to fill all 8 orbitals in their outermost shell. These electrons give sulphides their metallic lustre.
- Examples in minerals include: native metals like Cu, Pb, Ag and sometimes few sulphides and arsenides.

Van der Waals Bonds

- Weak, short-range electrostatic attractive forces between uncharged molecules, arising from the interaction of permanent or transient electric dipole-dipole interactions. That is many molecules, although electrically neutral, have time averaged concentrations of electrons on one side of the molecule creating a distortion in the charge distribution. This creates a positive & negative end to the molecules.
- Helps in understanding bonding between the electrically neutral sheets in phyllosilicates.

Crystals with more than one bond

- Usually most minerals occur as a combination of two or more bond types therefore the crystal will share properties of different bonds and will result in anisotropic properties.
- For example in mineral graphite the cohesion of the thin sheets in which the minerals generally occurs is a result of strong covalent bonding in the planes of the

sheets where as the excellent cleavage reflects the weak van der waal bonding joining the sheets together.

Ionic radius:

- Consider ions as hard spheres. Size of the ions is given by their radii measured in Angstrom Unit = 10⁻⁸ cm.
- For some physical reasons there is a limit to which two ions can approach each other. In such a position, half the distance between their centres, is called Ionic radius.
- The size of the atoms in a crystal structure depends on the number of electronic shells surrounding the nucleus. The type of bond and the size and number of atoms surrounding it.
- A large majority of minerals are Ionic compound.
- Diadochy is the ability of an atom of a different element to occupy a similar positions in the crystal structure , thus it is a replacement of one ion by another in a crystal lattice. E.g. Fe⁺² replacing Mg⁺² in the isomorphous series of Olivines

Radius ratio:

- The strongest forces exist between ions that are the nearest neighbours, each ion tends to surround itself with ions of opposite charges. The number of anions that can surround the cations depends on the relative sizes of the coordinated ions i.e. the cations in relation to the anions.
- The relative size of ion is generally expressed as radius ratio, R(cation)/R(Anion). The radii of the ions are measured in Angstrom Units

For Ex.-

The radius of Na^+ is 0.95 Angstrom and that of Cl^- is 187 Angstrom.

Hence, Radius ratio in NaCl = $r_{Na}^+ / r_{Cl}^- = 0.95 / 0.81 = 0.524$.

• When two or more cations are present in a structure coordinated with the same anion separate radius ratios must be computed for each. Thus in spinel (MgAl₂O₄) both magnesium and Aluminium coordinate oxygen anions.

Co-Ordination Principle:

- When oppositely charged ions unite to form a crystal structure in which the binding forces are dominantly electrostatic each ion tends to gather to itself or coordinate with as many ions of opposite sign as the size permits.
- The number of anions surrounding the cation is a coordination number (C.N) of the cation with respect to anion.
- E.g. NaCl, each Na+ has six closest Cl- neighbours and is said to be in 6 coordination with Cl (C.N. 6)
- In fluorite: CaF2, Calcium ion is at the centre of a coordination polyhedron consisting of 8 fluorine ions and hence is in (8 C.N) with respect to Fluorine. This is determined by their relative sizes, so if the radii of anion and cation are known the radius ratio is calculated and this will give us the coordination number.
- Also Anions may also be regarded as occupying the centres of coordination polyhedron formed of cations.
- In NaCl each Chloride ion has 6 Na neighbours and hence is in 6 coordination w.r.t. Na. Because both Sodium and chlorine are in 6 coordination, there must be equal numbers of both in agreement with the formula NaCl.
- On the other hand examination of the fluorite structure reveals that each fluorine ion has four closest calcium neighbours and hence is in 4 coordination with respect to calcium (C.N 4).
- Because each calcium ion has 8 Flourine neighbours whereas each fluorine ion has only 4 calcium neighbours it is appears that there are twice as many Flourine as calcium ions in the structure in accordance with the formula CaF₂
- The total no of ions of all kinds in any stable crystal structure must be as such that the crystal as a whole is electrically neutral. That is the total number of positive charges must be equal the total no of negative charges, hence in Fluorite there can be only half as many divalent positive calcium ions as there are monovalent fluorine ions
- It is found that there is a close relation between the predicted Coordination number and those seen in nature, confirming the assumption that ions behave as spheres of definite radius.

- The greater the distance between the radius of the two types of atoms, the lower is the coordination no.
- Assuming that the ions are rigid spheres the following limiting values of radius ratios for particular co-ordinations have been calculated.

Radius Ratio		Co-ordination No	Arrangement of Anions around Cation
0.00 0.15	to	2	Linear
0.16 0.22	to	3	Corners of Equilateral Triangle
0.23 0.41	to	4	Corners of Tetrahedron
0.42 0.73	to	6	Corners of Octahedron
0.74 0.99	to	8	Corners of Cube
1		12	Closes Packing/Dodecahedral (HCP & CCP)

For Ex.-

1) The radius of Na+ is 0.95 Angstrom and that of Cl– is 187 Angstrom.

Hence, Radius ratio in NaCl = rNa + / r Cl = 0.95 / 0.81 = 0.524

Limiting radius ratio is 0.524, therefore coordination number is six and shape is octahedral. It is proved by X-ray study of NaCl crystal that each Na+ is surrounded by six Cl– which are arranged octahedrally. Each Cl– is surrounded by six Na+.

2. Consider 4 fold coordination of O2- around Si 4+ , Radius for Si =0.34Ao & O=1.30Ao, the radius ratio of Si 4+ /O2-=0.262, consistent to tetrahedral close packing.

Mineral Stability

• Mineral form to lower the internal energy of the mass of the system. This is accomplished by building 3D repeating arrangement of atoms using chemical bonds of the shorted possible length.

- **Valency:** Valency refers to the ability of an atom or a group of chemically bonded atoms to form chemical bonds with other atoms or groups of atoms. The valency of an element is determined by the number of outer shell (valence) electrons.
- **Electronegativity(EN)**, is the ability of an atom to attract to itself an electron pair shared with another atom in a chemical bond. It is calculated from Bond energies It is proportional to the sum of Ionization Potential(IP) and electron Affinity(EA).
- **Ionisation potential (IP)** is the measure of the energy needed to form a positively charged ion that is a cation by removing electrons from an atom.
- **Electron affinity(EA)** is the amount of energy released if we succeed in adding a valence electron to a neutral atom thus to create a negatively charged anion.
- Elements differing greatly in electronegativity tend to form ionic compounds Those differing moderately in electronegativity form polar covalent compounds.
- While those elements with approximately equal electronegativities form nonpolar covalent compounds, which show little charge separation.

Closest packing structure in 3D: Atomic Arrangement in crystalline matter

- In ionic solids: Anions are often larger than cations and therefore "touch". Small cations then fit in the "holes" between anions.
- Think of co-packing softballs and golf balls in the most efficient way.

This reveals that spherical units may be arranged in 3D either in two ways called as Hexagonal closed packing (HCP) or Cubic closed packing (CCP)

- For practical purposes atoms or ions may be considered as hard spheres
- Within a crystal, these spheres are arranged in such a way that they fit together as closely as possible
- The manner in which different atoms fit together depends largely on their relative sizes
- Simplest case would be to consider the filling of space with atoms of the **same type and size**, that is, all of the same size, radius ratio
- (R _{cation}/R_{anion})=1
- Let us take marbles of uniform sizes, one marble can be surrounded by a minimum of 6 others so that a flat hexagonal pattern is obtained this pattern is called *hexagonal closest packed layer*. This is in 2D.

- **A second layer** of Marbles is now placed in the indentations left by the first layer. There is a space trapped between the layers that is not filled by the solid marbles:
- We see two different type of holes(called intestinal Sites)
- Octahedral(O) holes with six nearest spheres/marbles neighbours around.
- Tetrahedral (T) holes with 4 nearest spheres
- There are two sets of positions in which the **third layer** of spheres could be fitted
- a) Marbles in the 3rd layer are placed on the voids overlying the marbles of the bottom layer **Hexagonal Close Packing,** seen in metals of platinum group.
- b) Positions of the marbles in the 3rd layer are different from the first two Cubic Closest Packing, seen in Native minerals like Cu, Ag & Au
- Hence, we conclude that in a closest packing of similar spheres each must be surrounded by exactly 12 others of the same size