Chapter #3:
Crystal Binding

Lecture 3: Types of Crystals based on Atomic Bonds

3.3 Types of Crystals (Atomic Bonds)

1. Ionic Bond
2. Covalent Bond
3. Molecular Bond (Van der Waals Bond)
4. Metallic Bond
5. Hydrogen Bon

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3. Metallic Bond

A **metallic bond** arises from the interaction between a lattice of positive ions and a "sea" of delocalized electrons.

In metals:

- Valence electrons are **not bound to individual atoms**
- They are **free to move throughout the crystal**

✓ Metals are characterized by high electrical conductivity due to free electrons.

◇ Origin of Metallic Bonding

Metallic bonding arises due to:

- Attraction between **positive ions** and **delocalized electrons**
- Lowering of total energy when electrons spread over the lattice
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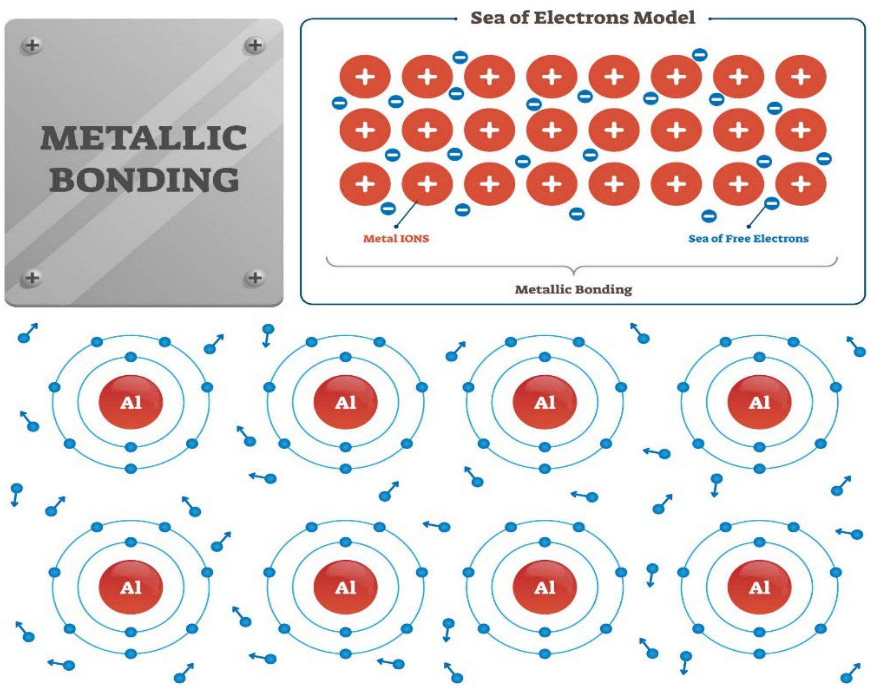
== > Electrons are shared by **all atoms**, not just pairs (unlike covalent bonding).

Example-1:

Discuss the metallic bond in Aluminum.



◇ 1. Aluminum Atoms and Valence Electrons

- Each **Al atom has 3 valence electrons ($3s^2$ $3p^1$)**.
- In the solid metal, these electrons are **not bound to individual atoms**.
- Instead, they become **delocalized** (free to move).

◇ 2. Formation of Positive Ion Cores

- Aluminum atoms effectively lose their 3 valence electrons.
- They become **positively charged ion cores (Al^{3+})** arranged in a **regular lattice**.
- In your diagram, these are the **circles labeled "13+"** (nuclear charge representation).

◇ 3. The "Electron Sea" Model

- The small dots around the lattice represent **delocalized electrons**.
- These electrons:
  - Move freely throughout the structure
  - Are shared by all atoms (not localized between specific atoms)

➡️ This is called the **"electron sea"**.

◇ 4. Nature of the Metallic Bond

The metallic bond in Al is:

The electrostatic attraction between the positively charged Al ion cores and the surrounding sea of delocalized electrons.

◇ 5. The diagram shows physically

- Regular repeating pattern → **crystal lattice**
- Circles (Al cores) → **fixed positive centers**
- Dots (electrons) → **mobile electron cloud**
- Overlap between regions → **electrons are shared globally**

◇ 6. Resulting Properties (Very Important)

Because of this bonding:

☑ Electrical Conductivity

- Free electrons → carry charge easily

☑ Thermal Conductivity

- Electrons transfer energy quickly

☑ Malleability & Ductility

- Layers can slide while the electron sea holds the structure together

☑ Metallic Luster

- Free electrons reflect light

Feature	Metallic	Covalent	Ionic
Electrons	Delocalized	Shared	Transferred
Direction	Non-directional	Directional	Non-directional
Conductivity	High	Low	Low
Mechanical behavior	Ductile	Brittle	Brittle

4. Molecular Bond (Van der Waals Bond)

Van der Waals bonding is a weak interaction between neutral atoms or molecules arising from **fluctuating or induced electric dipoles**.

Unlike:

- Ionic → charge transfer
- Covalent → electron sharing
- Metallic → delocalized electrons

Van der Waals bonding occurs **without a permanent charge or strong bonding**.

◇ Where Does It Occur?

✔ Noble gas solids (Ne, Ar, Kr, Xe)
✔ Molecular crystals (e.g., CO_2, CH_4)
✔ Between layers in graphite

The Lennard-Jones equation:

Atoms attract each other when they are far apart, but strongly repel when pushed too close — the Lennard-Jones equation captures this behavior in one formula.

◇ Distance Dependence

Attraction varies as:

$$\sim 1 / R^6$$

Repulsion varies as:

$$\sim 1 / R^{12}$$

The Lennard-Jones potential:

$$U(R) = 4\varepsilon \left[(\sigma/R)^{12} - (\sigma/R)^6 \right]$$

Total energy for N atoms:

$$U_{total} = (1/2) \Sigma_{ij} 4\varepsilon \left[(\sigma/R_{ij})^{12} - (\sigma/R_{ij})^6 \right]$$

Where:

- ϵ = depth of potential well (bond strength)
- σ = characteristic distance

◇ Key Properties of Van der Waals Solids

✔ Very weak bonding
✔ Low melting and boiling points
✔ Soft materials
✔ Poor electrical conductivity

◇ Why Is This Bond Weak?

Because:

- No charge transfer
- No electron sharing
- Only induced dipoles

=➔ The energy scale is much smaller than that of other bonds.

Feature	Electrostatic Energy	Lennard–Jones
Based on	Real charges	Neutral atoms
Formula origin	Fundamental (Coulomb law)	Empirical/model
Attraction	(1/r)	($1/r^6$)
Repulsion	From same charges	Artificial ($1/r^{12}$) term
Used for	Ionic solids, electrons	Noble gases, molecules

Example-2
If the total energy of a noble gas crystal is given by the Lennard-Jones potential:

$$E = \frac{1}{2}(4\varepsilon)\sum_{ij}\left[\left(\frac{\sigma}{R_{ij}}\right)^{12} - \left(\frac{\sigma}{R_{ij}}\right)^{6}\right]$$

$$\sum_{ij} R_{ij}^{-12} = 12.13188 R_0^{-12} \quad , \quad \sum_{ij} R_{ij}^{-6} = 14.45392 R_0^{-6}$$

ε and σ are constants, and R0 is the nearest-neighbor distance.

Given:
σ = 3.98 Å
ε = 0.02 eV

Find:
1) The equilibrium nearest-neighbor distance R_0 for Xenon crystal.
2) The total energy at equilibrium.

Solution:

$$E = \frac{1}{2}(4\varepsilon)\left[14.45392\left(\frac{\sigma}{R_0}\right)^6 - 12.13188\left(\frac{\sigma}{R_0}\right)^{12}\right]$$

$$\frac{\partial \mathrm{E}}{\partial \mathrm{R}_0} = 0 = 14.45392\left(-6\frac{\sigma^6}{\mathrm{R}_0{}^7}\right) - 12.13188\left(-12\frac{\sigma^{12}}{\mathrm{R}_0{}^{13}}\right)$$

$$-12.13188\left(-12\frac{\sigma^{12}}{\mathrm{R}_0{}^{13}}\right) = 14.45392\left(-6\frac{\sigma^6}{\mathrm{R}_0{}^7}\right)$$

$$12.13188\left(2\frac{\sigma^6}{\mathrm{R}_0{}^6}\right) = 14.45392$$

$$\left(\frac{\mathrm{R}_0}{\sigma}\right)^6 = \frac{12.13188 * 2}{14.45392} = 1.67$$

$$\mathrm{R}_0 = 1.09\sigma = 4.338\dot{A}$$

2- The total energy at equilibrium

$$E = 2\varepsilon\left[12.13188\left(\frac{1}{1.09}\right)^{12} - 14.45392\left(\frac{1}{1.09}\right)^6\right] = -0.17eV$$