INTERATOMIC BONDS

Prof. H. K. Khaira
HoD, MSME Deptt.
MANIT, Bhopal
Atomic Structure and Interatomic Bonding

Goals

– Define basic concepts (*refortify* your chemistry):
  • Types of Bonding between Atoms
  • Bond Energy Curves
– Describe how types of bonding affect Bond-Energy Curves.
– Describe how the Bond-Energy Curve describes macroscale properties.

Learning Objective

– Use the Bond-Energy Curve to describe qualitatively the different types of materials and their macroscale properties.
– Know the origins of stress and strain, melting temperature, and thermal expansion.
How are Macroscopic Properties related to Bonding?

• **Structure of atoms**
  A. Protons, neutrons, and electrons
  B. Electron configurations: shells and subshells
  C. Valence states
  D. Atoms and the periodic table

• **Types of bonding between atoms**
  A. Ionic bonding
  B. Covalent bonding
  C. Metallic bonding
  D. Secondary bonds
    1. Permanent dipoles and the hydrogen bond
    2. Temporary dipoles and the van der Waals bond

• **Influence of Bond Type on Engineering Properties**
  A. Brittle versus ductile behavior
  B. Electrical conductivity
  C. Melting temperature of polymers
Valence Electrons are...?

The Valence electrons are responsible for the chemical properties of atoms, and are those in the outer energy level.

Valence electrons - The s and p electrons in the outer energy level (the highest occupied energy level)

Core electrons – are those in the energy levels below.
The Octet Rule

The noble gases are unreactive in chemical reactions.

In 1916, Gilbert Lewis used this fact to explain why atoms form certain kinds of ions and molecules.

The Octet Rule: in forming compounds, atoms tend to achieve a noble gas configuration; 8 in the outer level is stable.

Each noble gas (except He, which has 2) has 8 electrons in the outer level.
Formation of Cations

Metals *lose* electrons to attain a noble gas configuration. They make positive ions *(cations)*.

If we look at the electron configuration, it makes sense to lose electrons:

\[
\text{Na} \quad 1s^22s^22p^63s^1 \quad \text{1 valence electron}
\]

\[
\text{Na}^{1+} \quad 1s^22s^22p^6 \quad \text{This is a noble gas configuration with 8 electrons in the outer level.}
\]
Formation of Cations

Metals will have few valence electrons (usually 3 or less); calcium has only 2 valence electrons

\( \text{Ca} \)
Formation of Cations

Metals will have few valence electrons
Metals will *lose the valence electrons*

Ca
Formation of Cations

Metals will have few valence electrons
Metals will *lose the valence electrons*
Forming positive ions

\[ \text{Ca}^{2+} \]

This is named the “calcium ion”.
Formation of Anions

Nonmetals gain electrons to attain noble gas configuration.
They make negative ions (anions)

$S = 1s^22s^22p^63s^23p^4 = 6$ valence electrons

$S^{2-} = 1s^22s^22p^63s^23p^6 = $ noble gas configuration.

*Halide ions* are ions from chlorine or other halogens that gain electrons
Formation of Anions

Nonmetals will have many valence electrons (usually 5 or more)

They will gain electrons to fill outer shell.

\[
\begin{array}{c}
\text{P} \\
3^-
\end{array}
\]

(This is called the “phosphide ion”, and should show dots)
Stable Electron Configurations

All atoms react to try and achieve a noble gas configuration.
Noble gases have 2 s and 6 p electrons.
8 valence electrons = already stable!
This is the *octet rule* (8 in the outer level is particularly stable).

\[ \text{Ar} \]
Interatomic Bonds
Interatomic Bonds

Primary Bond
- Ionic Bond
- Covalent Bond
- Metallic Bond

Secondary Bond
- Van der Waals Bond
Primary Bond
Primary Bond

1. Ionic Bond
2. Covalent Bond
3. Metallic Bond
Ionic Bonds
Ionic Bond
Anions and cations are held together by opposite charges (+ and -)

Ionic compounds are called **salts**.

Simplest ratio of elements in an ionic compound is called the **formula unit**.

The bond is formed through the transfer of electrons (lose and gain)

Electrons are transferred **to achieve noble gas configuration**.
Ionic Bond

The metal (sodium) tends to lose its one electron from the outer level. 

The nonmetal (chlorine) needs to gain one more to fill its outer level, and will accept the one electron that sodium is going to lose.
Ionic Bond

Na⁺ : Cl⁻
Ionic Bond

- The electron of the Na atom is removed and attached to the Cl atom
- Bonding energy: 1-10 eV (strong)
Ionic Bond

Let's do an example by combining calcium and phosphorus:

Ca  P

All the electrons must be accounted for, and each atom will have a noble gas configuration (which is stable).
Ionic Bond

Ca

P
Ionic Bond

$\text{Ca}^{2+}$ \quad \text{P}
Ionic Bond

$\text{Ca}^{2+}$

$\text{Ca}$

$\text{P}$
Ionic Bond

Ca$^{2+}$

Ca

P$^{3-}$
Ionic Bond

Ca$^{2+}$

Ca

P$^{3-}$

P
Ionic Bond

$\text{Ca}^{2+}$  $\text{P}^{3-}$

$\text{Ca}^{2+}$  $\text{P}$
Ionic Bond

\[
\begin{align*}
\text{Ca}^\cdot & \quad \text{Ca}^{2+} \\
\text{Ca}^{2+} & \quad \text{P}^{3-} \\
\end{align*}
\]
Ionic Bond

Ca
Ca$^{2+}$
Ca$^{2+}$

P$^{3-}$
Ionic Bond

$\text{Ca}^{2+}$
$\text{Ca}^{2+}$
$\text{Ca}^{2+}$
$\text{P}^{3-}$
$\text{P}^{3-}$
Ionic Bond

\[ \text{Ca}_3\text{P}_2 \]

This is a chemical formula, which shows the kinds and numbers of atoms in the smallest representative particle of the substance.

For an ionic compound, the smallest representative particle is called a: **Formula Unit**
Occurs between + and - ions

Requires electron transfer

Large difference in electronegativity required

An ionic bond is created between two unlike atoms with different electronegativities

When sodium donates its valence electron to chlorine, each becomes an ion; attraction occurs, and the ionic bond is formed

Na (metal) unstable
Cl (nonmetal) unstable

Na (cation) stable
Cl (anion) stable

Coulombic Attraction

Valence electron

Na atom Cl atom Na⁺ ion Cl⁻ ion
Primary Bonding Types: IONIC

Bonding

Electron transfer

Na atom

Cl atom

Na ion (+ve charge)

Cl ion (-ve charge)

Structure

Na^+  Cl^-

Na^+  Cl^-
Primary Bonding Types: IONIC

Na ion (+ve charge)  Cl ion (-ve charge)

Structure
Ionic Compounds

1) Also called SALTS

2) Made from: a CATION with an ANION
   (or literally from a metal combining with a nonmetal)
Properties of Ionic Compounds

1. **Crystalline** solids - a regular repeating arrangement of ions in the solid
   - Ions are strongly bonded together.
   - Structure is rigid.

2. **High melting points**
Ionic Crystal

- each positive ion is surrounded by several negative ions and vice versa
When voltage is applied to an ionic material, entire ions must move to cause a current to flow. Ion movement is slow and the electrical conductivity is poor.
Electrical Conductivity

Conducting electricity means allowing charges to move.

In a solid, the ions are locked in place. Ionic solids are insulators.

When **melted**, the ions can move around.

3. Melted ionic compounds conduct.
   - NaCl: must get to about 800 °C.
   - **Dissolved in water**, they also conduct (free to move in aqueous solutions)
The ions are free to move when they are molten (or in aqueous solution), and thus they are able to conduct the electric current.
Ionic solids are brittle
Ionic solids are brittle

**Strong Repulsion** breaks a crystal apart, due to similar ions being next to each other.

*Force*
Covalent Bond
Covalence bond

- Bonding energy: ~1-10 eV (strong)
- Two atoms share a pair of electrons
- Examples: C, Ge, Si, H₂
**Covalent Bonding**

- Requires *shared electrons*
- Example: $\text{CH}_4$
  - C: has 4 valence $e$, needs 4 more
  - H: has 1 valence $e$, needs 1 more
  - Electronegativities are comparable

Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer $sp$ orbital filled. In Si, with a valence of four, four covalent bonds must be formed.
Covalent Bonding

- The tetrahedral structure of silica (SiO$_2$), which contains covalent bonds between Si and oxygen atoms.
Covalent Bonding

- Electron sharing
- Directional

Covalent bond

$Cl_2$

$CH_4$

Shared electron from hydrogen

Shared electron from carbon
Covalent Bonding

- bond energy curve

- high hardness
- high melting point
- strong directional nature of bonding
- low electrical conductivities at low temp when specimens are pure
Metallic Bonds
**Metallic Bonding**

- **delocalized electron**

  Isolated Mg

  - 2 valence electrons

  Can be viewed as

  +2 ion core

  Many Mg atoms combine to form a solid metal

- **Delocalized cloud of valence electrons**

- **Free electrons act as a "glue" to hold the ion core**
Metallic Bonding

- Arises from a sea of donated valence electrons (1, 2, or 3 from each atom)

- Primary bond for metals and their alloys
Metallic Bond

Positive ions in a sea of electrons

- Bonding energy: 
  \(~1\text{-}10 \text{ eV (strong)}\)
Metabolic Bonding

- The metallic bond forms when atoms give up their valence electrons, which then form an electron sea.
- The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.
Primary Bonding Types: METALLIC

Metals share so-called electrons, or a “sea of electron” (electron-glue).

Electrons move (or “hop”) from atom to atom.

*Metallic bonds may be weak or strong*

Bonding energies ($E_0$): range from

- 68 kJ/mol (0.7 eV/atom) for Hg
- to 850 kJ/mol (8.8 eV/atom) for W.

Melting temperatures ($T_{melt} \sim E_0$):
- -39 C for Hg and 3410 C for W.

Stronger bonds lead to higher melting temperature: atomic scale property $\Rightarrow$ macroscale property.
Sea of Electrons

Electrons are free to move through the solid.

Metals conduct electricity.
When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.
Metallic Bonding

- mechanical property

Ionic bonding
brittle

Metallic bonding
ductile
Plastic Deformation

Force
Plastic Deformation

Mobile electrons allow atoms to slide by, sort of like ball bearings in oil.
Metallic Bonds

How metal atoms are held together in the solid?
Metals hold on to their valence electrons very weakly.
Think of them as positive ions (cations) floating in a sea of electrons.
Secondary Bond

van der Waals bond
Secondary Bonding

Arises from interaction between
- Induced dipoles
- Induced dipoles and polar molecules
- Polar molecules

- **Fluctuating dipoles**
  
  ![Fluctuating dipoles diagram](image)

- **Permanent dipoles**

  - general case: ![General case diagram](image)
  - ex: liquid HCl ![Liquid HCl diagram](image)
Secondary Bond (van der Waals)

Two types of Secondary: **induced dipolar** and **permanent dipole**.

- Induced dipolar interactions are weak and depend on molecular environment.
- They are typically caused by vibrational effects within the particular molecule and lead to interactions **between** molecules.
- Hence, they are **weak** secondary bonds to the **stronger** molecular bonds.

**Example of Induced Dipole: Argon Gas**

The positive nuclei repel one another and the electron cloud deforms in the neighboring atoms such that the two dipoles align and their is a weak attraction via dipolar forces, $1/r^4$. 

![Diagram of induced dipolar interaction between Argon atoms](image.png)
van der Waals bond

- Bonding energy: ~0.01 eV (weak)
- Compared to thermal vibration energy $k_B T \sim 0.026$ eV at $T = 300$ K
- Examples: inert gases

Dipole-dipole interaction
## Bonding

<table>
<thead>
<tr>
<th>Type of Bond</th>
<th>Substance</th>
<th>Bond Energy* kcal/mole</th>
<th>Melting Temperature (°C)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>CaCl</td>
<td>155</td>
<td>646</td>
<td>Low electrical conductivity; transparent; brittle; high melting temperature</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>183</td>
<td>801</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiF</td>
<td>240</td>
<td>870</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuF₂</td>
<td>617</td>
<td>1360</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>3618</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>Covalent</td>
<td>Ge</td>
<td>≈ 75</td>
<td>958</td>
<td>Low electrical conductivity; very hard; very high melting temperature</td>
</tr>
<tr>
<td></td>
<td>GaAs</td>
<td>≈ 75</td>
<td>1238</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>84</td>
<td>1420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>283</td>
<td>2600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diamond</td>
<td>170</td>
<td>3550</td>
<td></td>
</tr>
<tr>
<td>Metallic</td>
<td>Na</td>
<td>26</td>
<td>97.5</td>
<td>High electrical and thermal conductivity; easily deformable; opaque</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>74</td>
<td>660</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>81</td>
<td>1083</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>97</td>
<td>1535</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>201</td>
<td>3370</td>
<td></td>
</tr>
<tr>
<td>Van der Waals</td>
<td>Ne</td>
<td>0.59</td>
<td>-248.7</td>
<td>Weak binding; low melting and boiling points; very compressible</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>1.8</td>
<td>-189.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>2.4</td>
<td>-184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kr</td>
<td>2.8</td>
<td>-157</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl₂</td>
<td>7.4</td>
<td>-103</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>HF</td>
<td>7</td>
<td>-92</td>
<td>Higher melting points than Van der Waals bonding; tendency to form groups of many molecules</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>12</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Important Properties

1. Melting temperature
2. Elastic modulus
3. Thermal expansion coefficient
Interatomic Forces

Here we will discuss the forces between atoms.

The forces may be both attractive and repulsive.

The net force is important to decide the bonding strength between atoms.
Origin of Bonding Curve

arises from **attractive** plus **repulsive** interactions between atoms(ions)

\[
\text{Energy} : E_{\text{total}} = E_A + E_R
\]

\[F = 0 \text{ at equilibrium } r_0; \text{ can find } r_0.\]
How are Macroscopic Properties related to Bonding?

The Bond-Energy Curve
A. Dependence of potential energy on atomic spacing
   1. Long-range attraction versus short-range repulsion
   2. Superposition of attractive and repulsive potentials

B. The bond-energy curve and engineering properties
   1. Melting temperature
   2. Elastic modulus
   3. Thermal expansion coefficient

• How are macroscopic properties (mechanical, structural, thermal, electrical, optical, ...) most simply related to bonding?
Melting Temperature

- Bond Length, \( r_0 \)
- Binding Energy, \( U_0 \)
- Melting Temperature, \( T_m \) (really \( T_{\text{sublimation}} \))

\[
\text{equil. bond } r_0 : F = \frac{dU}{dr} \bigg|_{r_0} = 0
\]

\[
\text{min. energy } E_0 : U(r_0)
\]

Stored energy goes ↑ as \( U_0 \) goes ↓

\[ T_m \text{ goes } \uparrow \text{ as } U_0 \text{ goes } \downarrow \]

Larger \( T_m \)

Smaller \( T_m \)
### Table 2.3  Bonding Energies and Melting Temperatures for Various Substances

<table>
<thead>
<tr>
<th>Bonding Type</th>
<th>Substance</th>
<th>Bonding Energy (kJ/mol kcal/mol)</th>
<th>Bonding Energy (eV/Atom, Ion, Molecule)</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>NaCl</td>
<td>640 (153)</td>
<td>3.3</td>
<td>801</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>1000 (239)</td>
<td>5.2</td>
<td>2800</td>
</tr>
<tr>
<td>Covalent</td>
<td>Si</td>
<td>450 (108)</td>
<td>4.7</td>
<td>1410</td>
</tr>
<tr>
<td></td>
<td>C (diamond)</td>
<td>713 (170)</td>
<td>7.4</td>
<td>&gt;3550</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>68 (16)</td>
<td>0.7</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>324 (77)</td>
<td>3.4</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>406 (97)</td>
<td>4.2</td>
<td>1538</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>849 (203)</td>
<td>8.8</td>
<td>3410</td>
</tr>
<tr>
<td>Metallic</td>
<td>Ar</td>
<td>7.7 (1.8)</td>
<td>0.08</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Cl₂</td>
<td>31 (7.4)</td>
<td>0.32</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td>NH₃ 51 (12.2)</td>
<td>0.52</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O 51 (12.2)</td>
<td>0.52</td>
<td>—</td>
</tr>
</tbody>
</table>

What is the relationship between Bonding Energy and $T_{\text{melt}}$?
\[ E = \frac{d^2 U}{dr^2}(r_0) \]

which is the curvature at \( r_0 \)

like “spring constant”
\[ F = k(r-r_0) \]
and linear near equilibrium.

Negative \( F \) - compression
Positive \( F \) - tension

\[ E \text{ modulus } \uparrow \text{ as } E_0 \downarrow \text{ (deeper)} \]
Elastic Moduli, $E$ (Young’s Modulus)

- Recall: Slope of stress strain plot (proportional to the $E$) depends on bond strength of metal

Adapted from Fig. 7.7, *Callister & Rethwisch 3e.*
## Comparison of Elastic Moduli

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Modulus of Elasticity</th>
<th>Shear Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GPa</td>
<td>10^6 psi</td>
</tr>
<tr>
<td><strong>Metal Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tungsten</td>
<td>407</td>
<td>59</td>
</tr>
<tr>
<td>Steel</td>
<td>207</td>
<td>30</td>
</tr>
<tr>
<td>Nickel</td>
<td>207</td>
<td>30</td>
</tr>
<tr>
<td>Titanium</td>
<td>107</td>
<td>15.5</td>
</tr>
<tr>
<td>Copper</td>
<td>110</td>
<td>16</td>
</tr>
<tr>
<td>Brass</td>
<td>97</td>
<td>14</td>
</tr>
<tr>
<td>Aluminum</td>
<td>69</td>
<td>10</td>
</tr>
<tr>
<td>Magnesium</td>
<td>45</td>
<td>6.5</td>
</tr>
</tbody>
</table>

- Silicon (single xtal): 120-190 GPa (depends on crystallographic direction)
- Glass (pyrex): 70 GPa
- SiC (fused or sintered): 207-483 GPa
- Graphite (molded): ~12 GPa
- High modulus C-fiber: 400 GPa
- Carbon Nanotubes: ~1000 GPa

Normalize by density, 20x steel wire. Strength normalized by density is 56x wire.
Based on data in Table B2, *Callister 6e.* Composite data based on reinforced epoxy with 60 vol% of aligned carbon (CFRE), aramid (AFRE), or glass (GFRE) fibers.
Coefficient of Thermal Expansion, $\alpha$, or $dL/dT$

**Linear Thermal Strain**

$$\frac{\Delta L(T)}{L_0} = \alpha_L (T - T_0)$$

- $\alpha \sim$ asymmetry at $r_0$
  - No asymmetry at $r_0$
  - No affect on $r(T)$ or $V(T)$
- $\alpha \uparrow$ as $E_0 \uparrow$ (less negative)

**Volume Thermal Strain**

$$\frac{\Delta V}{V_0} = \alpha_V (T - T_0)$$

- Symmetric well $r(T) = r_0$: **No expansion possible**
- Atoms just vibrate back and forth!

Parabolic $E$ vs. $r$ shape

Larger $E$ Smaller $\alpha$

Smaller $E$ Larger $\alpha$
What is $T_{\text{melt}}$ of ceramic, metal, polymer? Why?

What is $E$ of ceramic, metal, polymer? Why?

What do force-extension or stress-strain curves look like?

What is stress-strain curve of human tissue?
<table>
<thead>
<tr>
<th>Material Type</th>
<th>Bonding Type</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramics</td>
<td>Large bond energies</td>
<td></td>
</tr>
<tr>
<td>Ionic and Covalent bonds</td>
<td>large $T_m$, $E$, Small $\alpha$</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Varying bond energy</td>
<td></td>
</tr>
<tr>
<td>Metallic bonding</td>
<td>intermediate $T_m$, $E$, $\alpha$</td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>directional properties</td>
<td></td>
</tr>
<tr>
<td>Covalent and Secondary</td>
<td>secondary dominates outcome</td>
<td>small $T_m$, $E$, large $\alpha$</td>
</tr>
</tbody>
</table>
Synopsis

• Bonding between atoms dictates macroscale properties in solids, e.g. mechanical and electrical, as well as molecules.
  • Binding energies related to melting temperature.
  • Thermal expansion related to curvature of binding curve.
  • Initial stress-strain behavior (elastic moduli) dictated by binding curve. (NOT TRUE for plasticity, which is controlled by line defects - later!)
• Point defects do not affect mechanical properties to a large extent, but could affect electrical properties (resistivity).