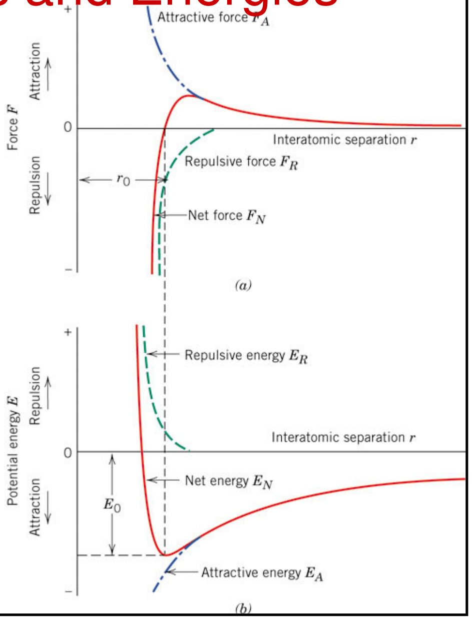
Chapter 2. Atomic Structure and Interatomic Bonding

Interatomic Bonding

–Bonding forces and energies
–Primary interatomic bonds
–Secondary bonding
–Molecules

Bonding Forces and Energies

- Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.
- At larger distances, the interactions are negligible.
- As the atoms approach, each exerts forces on the other.
  - Attractive
  - Repulsive
- Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force comes into play.



Bonding Models

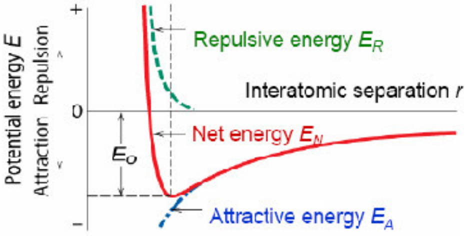
- Bonding holds atoms together to form solids materials
- In solids, atoms are held at preferred distances from each other (equilibrium distances)
- Distances larger or smaller than equilibrium distances are not preferred. Equilibrium spacing r_0 is approximately 0.3nm
- Consequently, as atomic bonds are stretched, atoms tend to attract each other, and as the bonds are compressed, atoms repel each other.
- Simple bonding models assume that the total bonding results from the sum of two forces: an attractive force (F_A) and a repulsive (F_R).

the net force $F_N = F_A + F_R$

- The repulsive force dominates at small distances, and the attractive force dominates at larger distances. At equilibrium they are just equal.

Bonding Forces and Energies

- It is convenient to work with energy than forces.
- Bonding energy (also called interaction energy or potential energy) between two isolated atoms at separation *r* is related to the force by



$$E(r) = \int_{\infty}^{r} F(r')dr'$$
$$= \int_{\infty}^{r} (F_A(r') + F_R(r'))dr'$$
$$= E_A(r) + E_R(r)$$

- The total energy has a minimum at the point of equilibrium separation. Bonding energy E_0 corresponds to the energy at r_o– the energy that would be required to separate these two atoms to an infinite separation.
- Interpretation: holding one atom at the origin, a second atom would repel that atom at separation $r < r_o$ and attract it when $r_o < r$.

Bonding energy between two atoms

- The interaction energy at equilibrium is called the bonding energy between the two atoms.
- To break the bond, this energy must be supplied from outside.
- Breaking the bond means that the two atoms become infinitely separated.
- In real materials, containing many atoms, bonding is studied by expressing the bonding energy of the entire materials in terms of the separation distances between all atoms, see later discussion.

Bonding

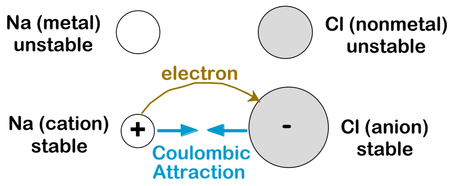
Primary bonding:

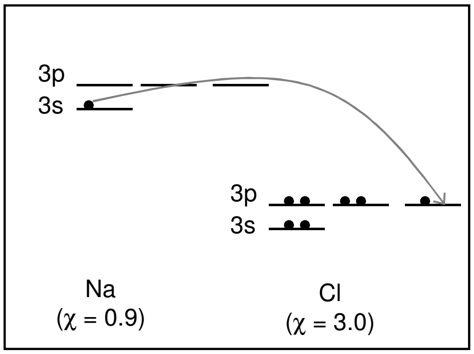
Ionic (transfer of valence electrons)
Covalent (sharing of valence electrons, directional)
Metallic (delocalization of valence electrons)

Secondary or van der Waals Bonding:
(Common, but weaker than primary bonding)
Dipole-dipole
H-bonds
Polar molecule-induced dipole
Fluctuating dipole (weakest)

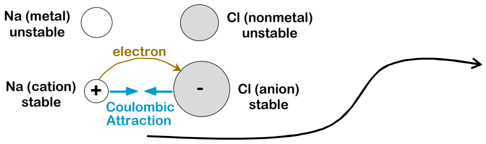
Ionic Bonding

- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl
- Nondirectional





Ionic Bonding



$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_o r}$$

Since z_1 = +1 for Na$^+$ and z_2 = -1 for Cl$^-$

$$E_A = -\frac{e^2}{4\pi\varepsilon_o r} = -\frac{A}{r}$$

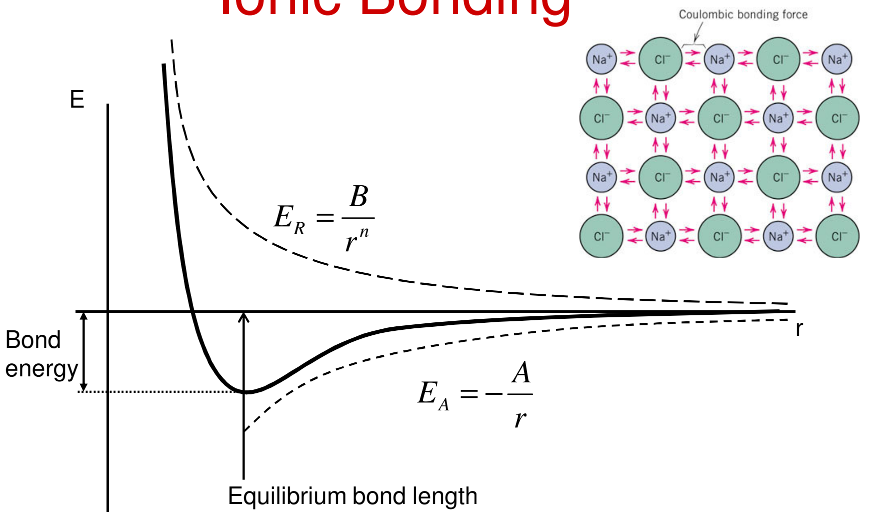
Negative energy means attraction only.
Will the atoms collapse on themselves?

No, there is also repulsive energy (e.g. steric repulsion, e-e repulsion)

$$E_R = \frac{B}{r^n}$$

B and *n* depend on atoms involved.
In many cases *n* ~ *8.*

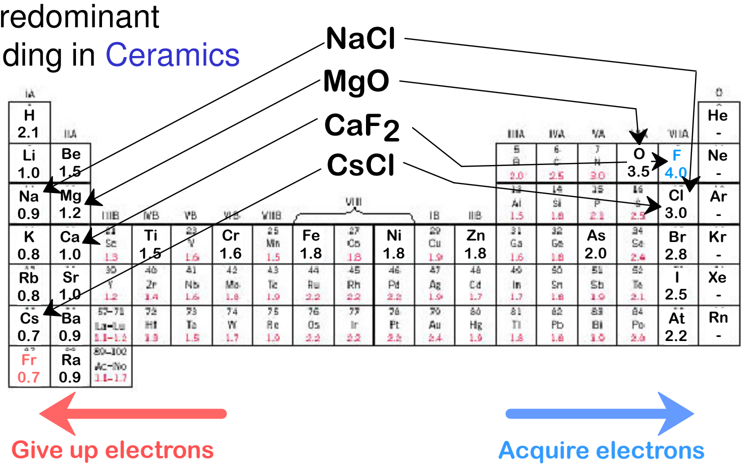
Ionic Bonding



Note: Other types of bonds can also be described in a similar manner

Ionic Bonding: examples

- Predominant bonding in Ceramics



Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

From Callister 6e resource CD.

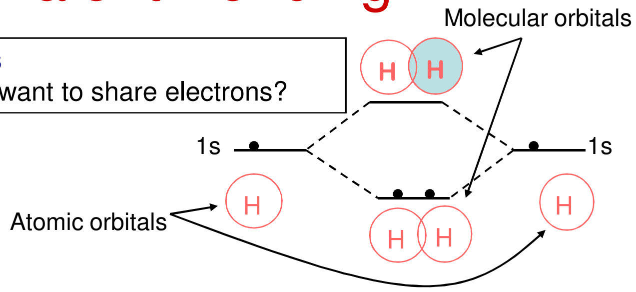
Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	*Substance*	*Bonding Energy* *kJ/mol*	*Bonding Energy* *eV/Atom, Ion, Molecule*	*Melting Temperature (°C)*
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	>3550
Metallic	Hg	68	0.7	−39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	−189
	Cl_2	31	0.32	−101
Hydrogen	NH_3	35	0.36	−78
	H_2O	51	0.52	0

Covalent Bonding

- "Sharing" of electrons
- Why do some atoms want to share electrons?

- Example1: H_2

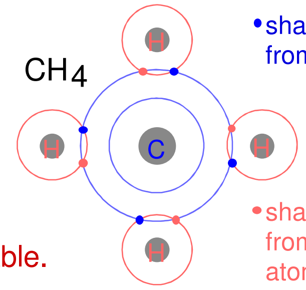


- Example2: CH_4

C: has 4 valence e,
needs 4 more

H: has 1 valence e,
needs 1 more

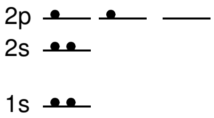
Electronegativities
are same or comparable.



- shared electrons from carbon atom
- shared electrons from hydrogen atoms

Adapted from Fig. 2.10, *Callister 6e.*

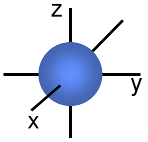
atomic orbitals for carbon:



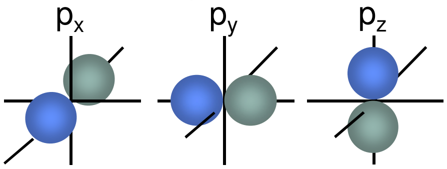
4 valence electrons but two different types orbitals.
H's on CH_4 should be equivalent.

Atomic Orbitals

an s-orbital

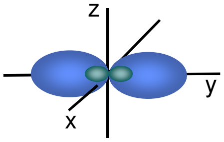


the three p orbitals

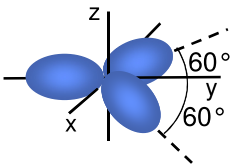


Hybridization

1s + 1p = sp-orbitals

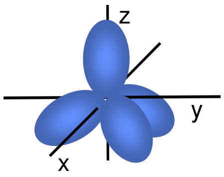


1s + 2p = sp^2-orbitals

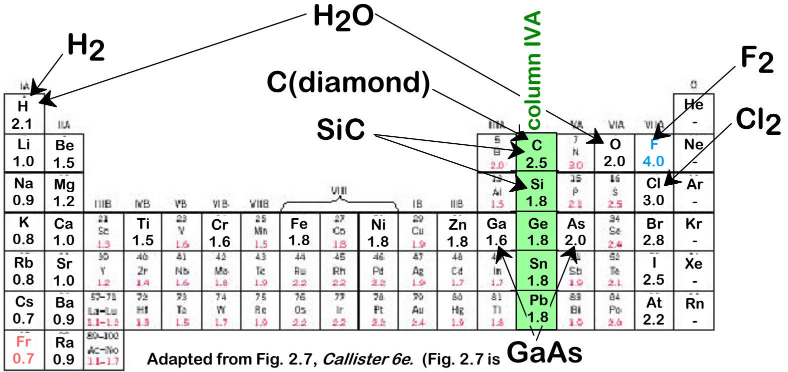


sp3 hybridization for C in CH_4

1s + 3p = sp^3-orbitals



Examples: Covalent Bonding



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From Callister 6e resource CD.

- Molecules with nonmetals
- Molecules with metals and nonmetals
- Elemental solids (RHS of Periodic Table)
- Compound solids (about column IVA)

% ionic character

- The covalent bond is directional.

- The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons.

- Most bonds between two different types of atoms are somewhere in between ionic and covalent. Very few compounds exhibit pure ionic or covalent bonding.

- % ionic character = $\{1-\exp[-0.25(\chi_A-\chi_B)^2]\}\times 100$

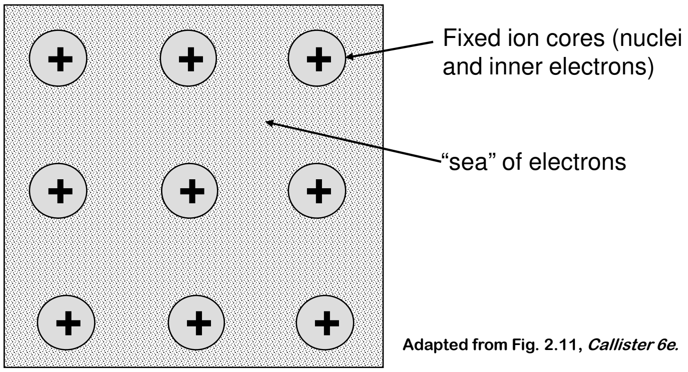
χ_j = electronegativity of atom j

Example problem

- Order the following semiconductors from most covalent to most ionic.
  1) ZnS, GaP, CuCl
  2) ZnS, ZnSe, ZnO

Metallic Bonding

- Arises from a sea of donated valence electrons



Adapted from Fig. 2.11, *Callister 6e.*

- Primary bond for metals and their alloys.
- Large atomic radius and small IP will more likely lead to metallic bonding.

Metallic Bonding

- Valence electrons are completely delocalized to form an electron cloud, in which positive ionic cores are embedded.
- The remaining nonvalence electrons and atomic nuclei form "ion cores", which posses a net positive charge equal in magnitude to the total valence electron charge per atom.
- The metallic bond is nondirectional.
- Metallic bonding is found in the periodic table for Group IA and IIA elements.
- Electron delocalization is the origin of good electrical and thermal conductivities in metals. (Ionically and covalently bonded materials are typically electrical and thermal insulators, due to the absence of large numbers of free electrons) .

Secondary Bonds: Intermolecular Forces

- **Secondary, Van der Waals, or physical bonds** are weak in comparison to the primary bonds.

- Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present.

- Secondary bonding forces arise from atomic or molecular dipoles. An electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.

- Dipole interactions occur between induced dipoles, between induced dipoles and polar molecules (which have permanent dipoles), and between polar molecules.

- Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents.

Secondary Bonds: Intermolecular Forces

- **Dipole-dipole interaction**: secondary bond between molecules with permanent dipole moments

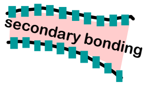
-general case:

Adapted from Fig. 2.14, *Callister 6e.*

-ex: liquid HCl

Adapted from Fig. 2.14, *Callister 6e.*

-ex: polymer



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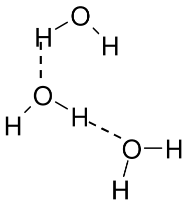
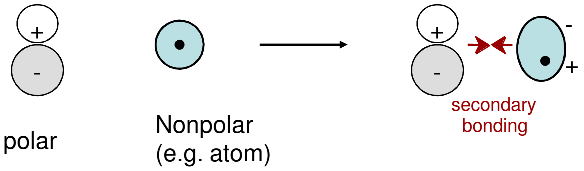
- **Hydrogen bonding**



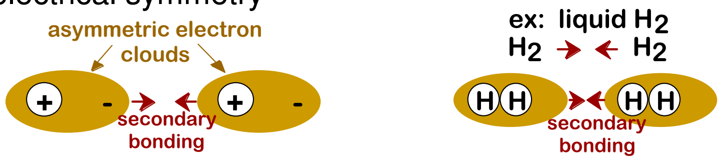
- **Polar molecule-induced dipole interaction**:

  Polar molecules (with asymmetric arrangement of positively and negatively charged regions) can induce dipoles in adjacent nonpolar molecules



- **Fluctuating dipoles**

  Constant vibrational motion can cause distortions of electrical symmetry



Adapted from Fig. 2.13, *Callister 6e.*

SUMMARY: BONDING

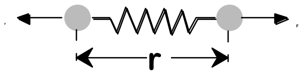
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Bonding and materials properties

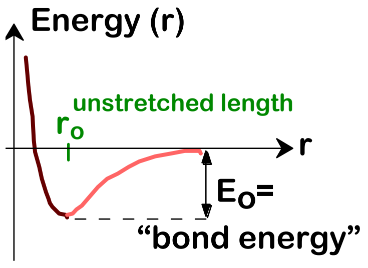
- Materials with large bonding energies usually have high melting temperatures.
- There is a correlation between the magnitude of the bonding energy and the state of materials
  - Solids have large bonding energies
  - Liquids tend to have relatively lower energies
- The expansion/contraction during heating/cooling of materials is related to the shape of its *E*(r) curve.
- A deep and narrow ‘trough,’ which typically occurs for materials having large bonding energies, usually imply a low coefficient of thermal expansion.

PROPERTIES FROM BONDING: T_M

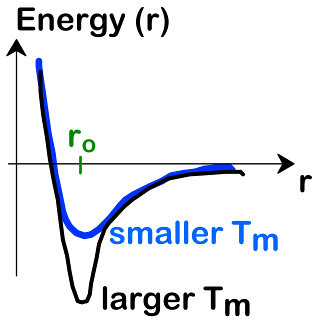
- **Bond length**, **r**



- **Bond energy**, **E_o**



- **Melting Temperature**, **T_m**



T_m is larger if E_o is larger.

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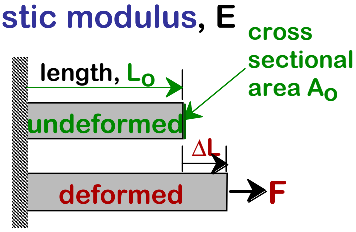
PROPERTIES FROM BONDING: E

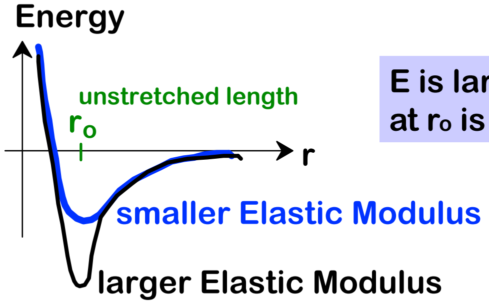
- **Elastic modulus, E**



Elastic modulus

$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$

- E ~ curvature at r_o



E is larger if curvature at r_o is larger.

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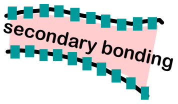
SUMMARY: BONDING and Materials' properties

Ceramics (Ionic & covalent bonding):	**Large bond energy** large T_m large E small α
Metals (Metallic bonding):	**Variable bond energy** moderate T_m moderate E moderate α
Polymers (Covalent & Secondary):	**Directional Properties** Secondary bonding dominates small T small E large α



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