INTERATOMIC BONDS

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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:

Na **$1s^2 2s^2 2p^6 3s^1$** 1 valence electron

Na^{1+} **$1s^2 2s^2 2p^6$** 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

Formation of Cations

Metals will have few valence electrons

Metals will *<u>lose the valence electrons</u>*

Ca

Formation of Cations

Metals will have few valence electrons

Metals will *lose the valence electrons*

Forming positive ions

$$Ca^{2+}$$

This is named the "calcium ion".

Formation of Anions

Nonmetals **gain** electrons to attain noble gas configuration.

They make negative ions **(anions)**

S = $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^4}$ = 6 valence electrons

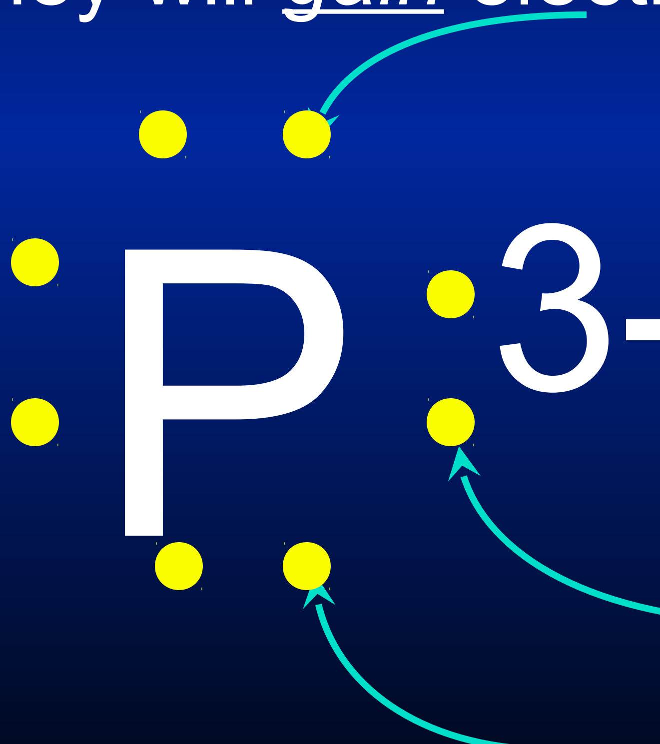
$\mathbf{S^{2-}}$ = $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6}$ = noble gas configuration.

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.



(This is called the “phosphide ion”, and *should show* dots)

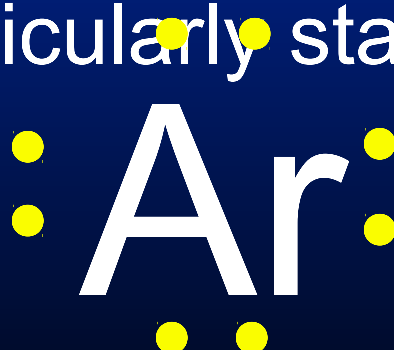
Stable Electron Configurations

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).



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 -)

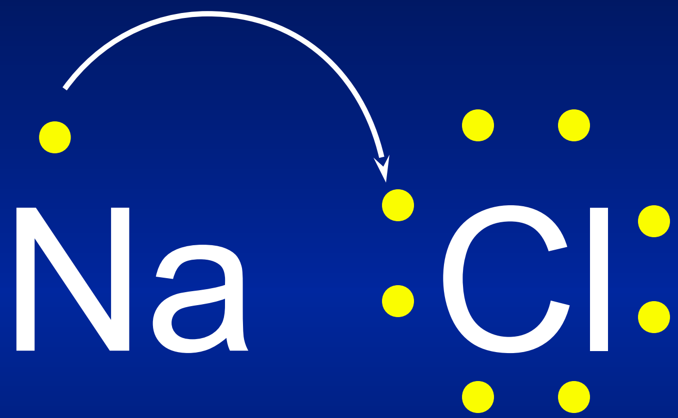
Ionic compounds are called **salts**.

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



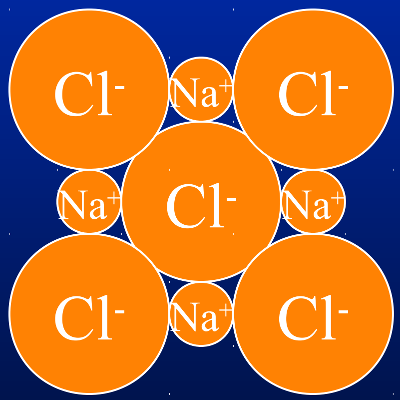
The metal (sodium) tends to lose its one electron from the outer level.

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

$$Na^{+}\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$$

Ionic Bond



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

Ionic Bond

Lets do an example by combining calcium and phosphorus:

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

Ionic Bond

Ionic Bond

Ca^{2+}

Ionic Bond

Ionic Bond

Ca^{2+}

P^{3-}

Ca

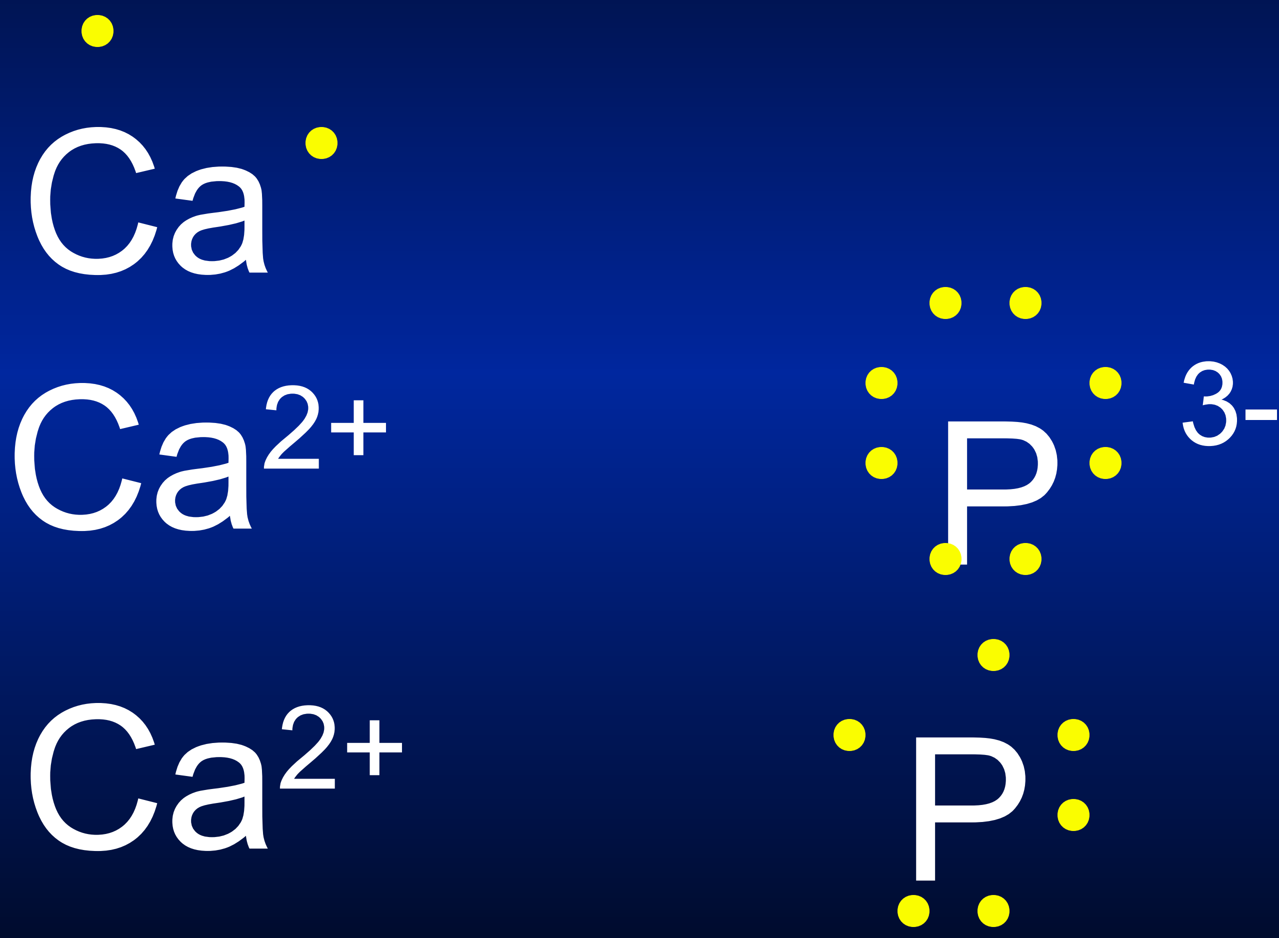
Ionic Bond

Ionic Bond

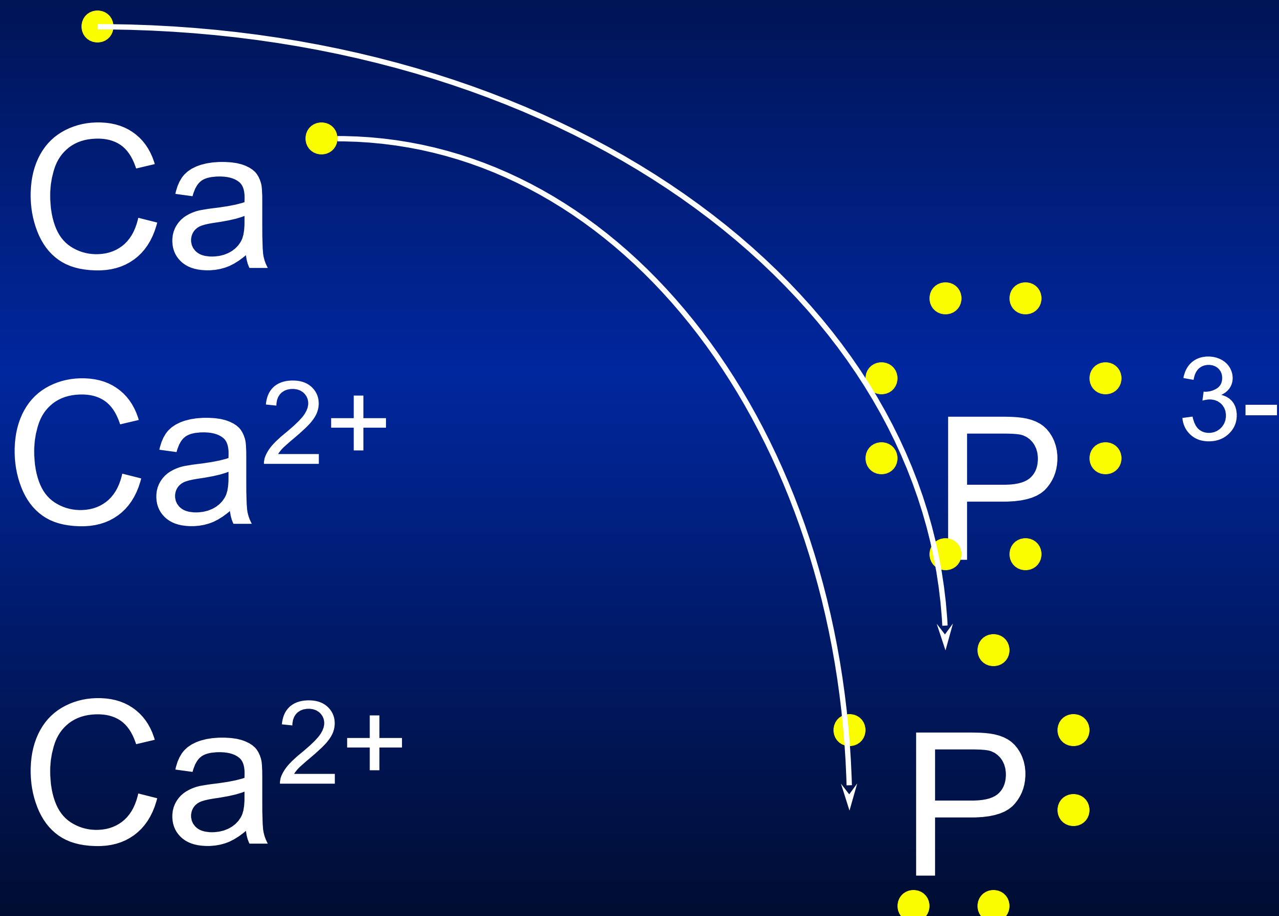
Ca^{2+} P^{3-}

Ca^{2+} P

Ionic Bond



Ionic Bond



Ionic Bond

Ca^{2+}

Ca^{2+} P^{3-}

Ca^{2+} P^{3-}

Ionic Bond

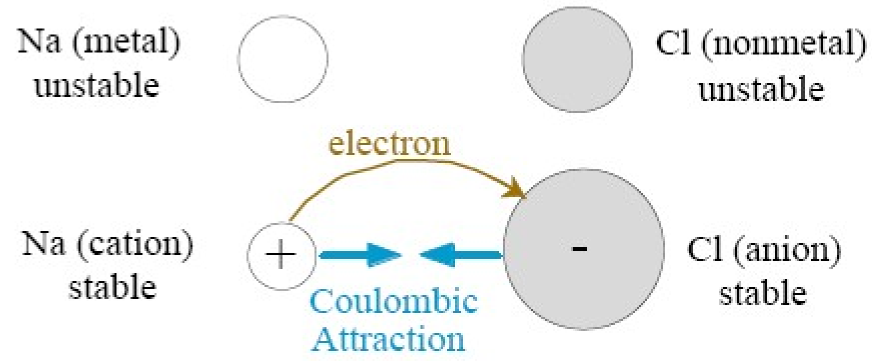
$= Ca_3P_2$ ← Formula Unit

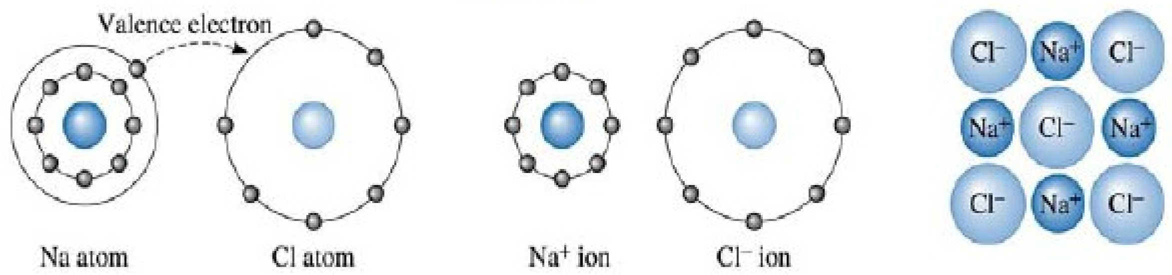
This is a **chemical formula**, which shows the kinds and numbers of atoms in the smallest representative particle of the substance.

For an ionic compound, the smallest representative particle is called a:
Formula Unit

Ionic Bonding

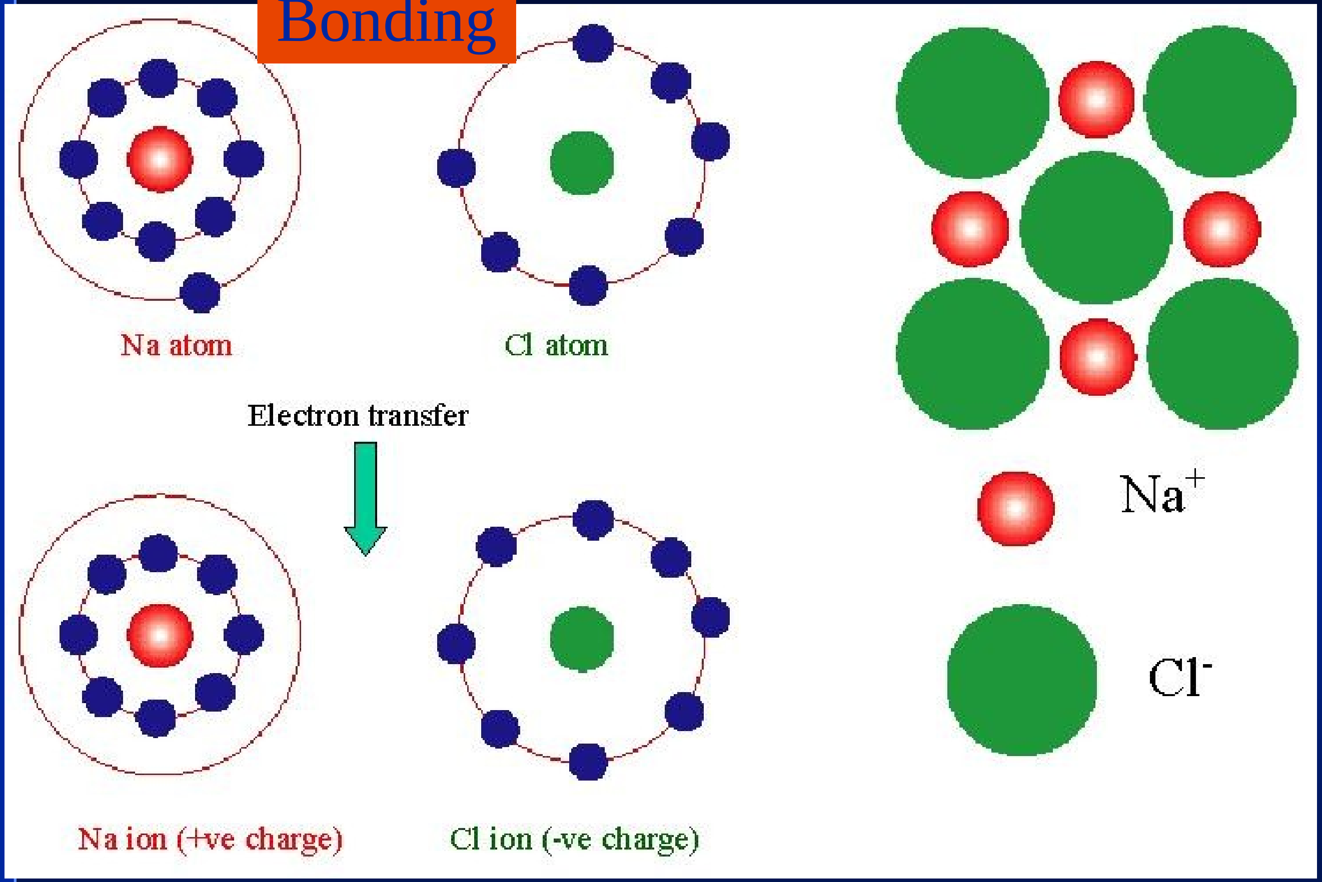
- Occurs between + and - ions
- Requires electron transfer
- Large difference in electronegativity required
- An ionic bond is created between two unlike atoms with different electronegativities
- When sodium donates its valence electron to chlorine, each becomes an ion; attraction occurs, and the ionic bond is formed



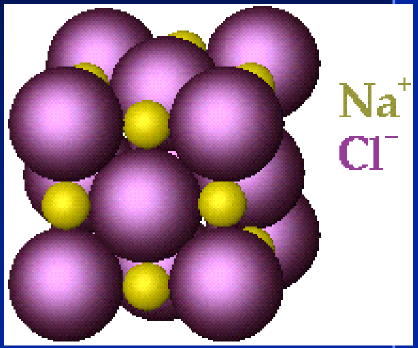


Primary Bonding Types: IONIC

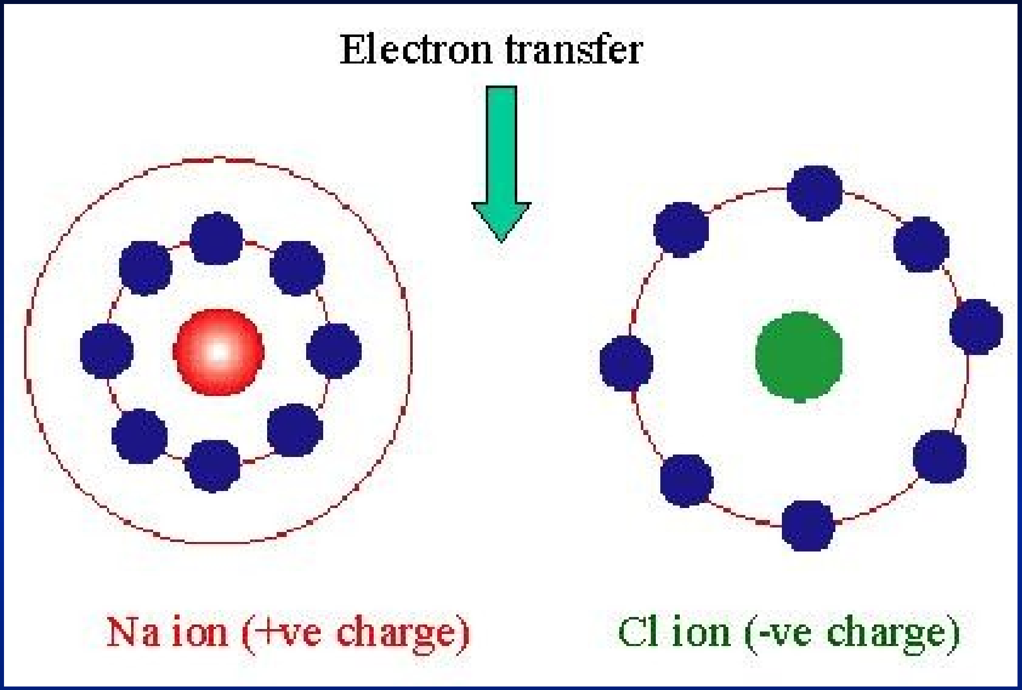
Bonding



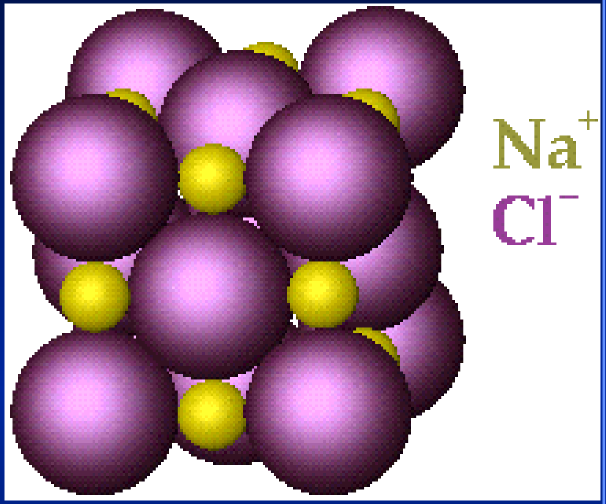
Structure



Primary Bonding Types: IONIC



Structure



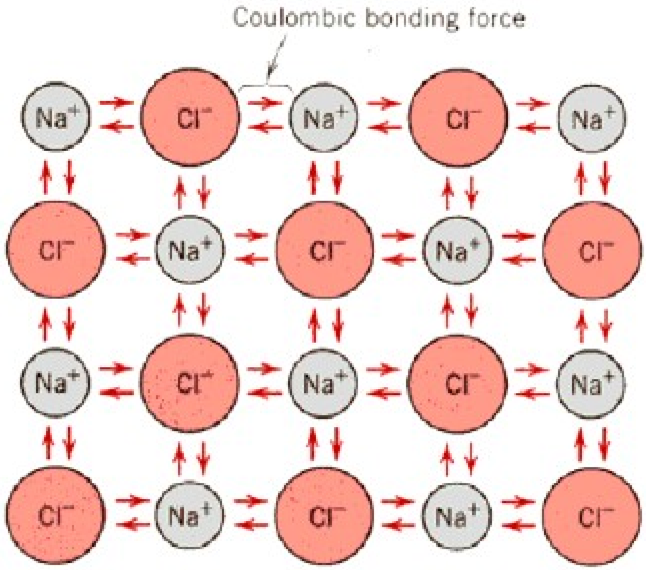
Ionic Compounds

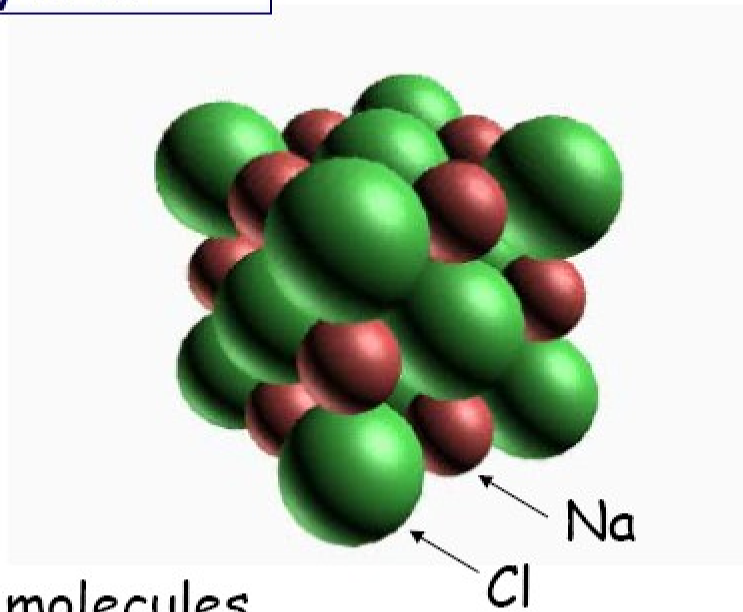
1) Also called SALTS
2) Made from: a CATION with an ANION (or literally from a *metal* combining with a *nonmetal*)

Properties of Ionic Compounds

1. <u>Crystalline</u> solids - a regular repeating arrangement of ions in the solid
   – Ions are <u>strongly</u> bonded together.
   – Structure is rigid.
2. <u>High melting points</u>

Ionic Crystal

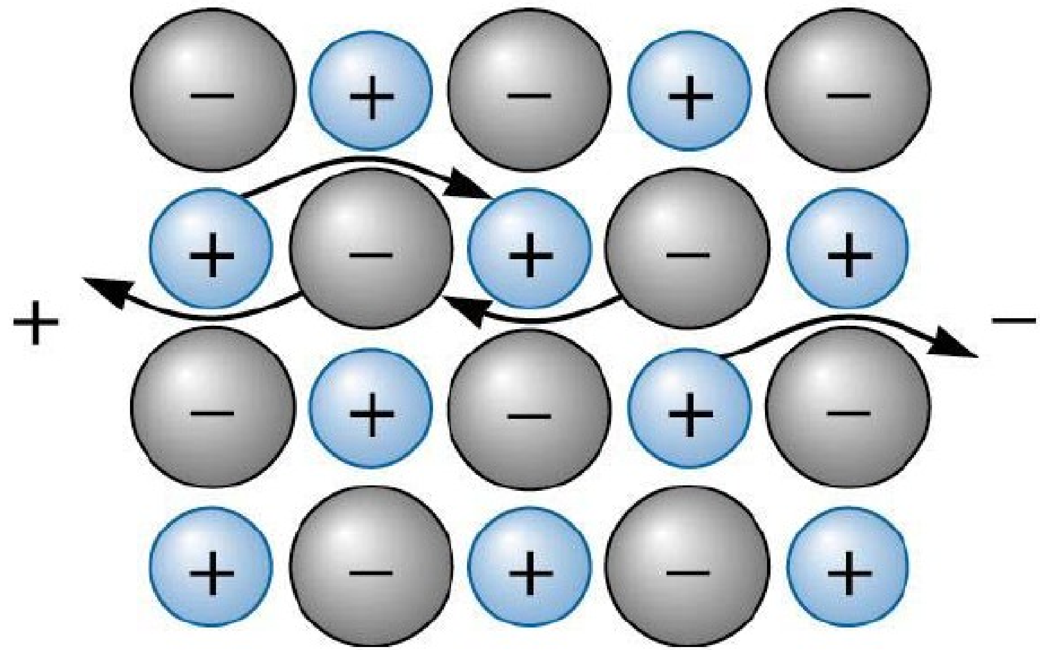




N molecules

- each positive ion is surrounded by several negative ions and vice versa

Electrical Conductivity



- 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.

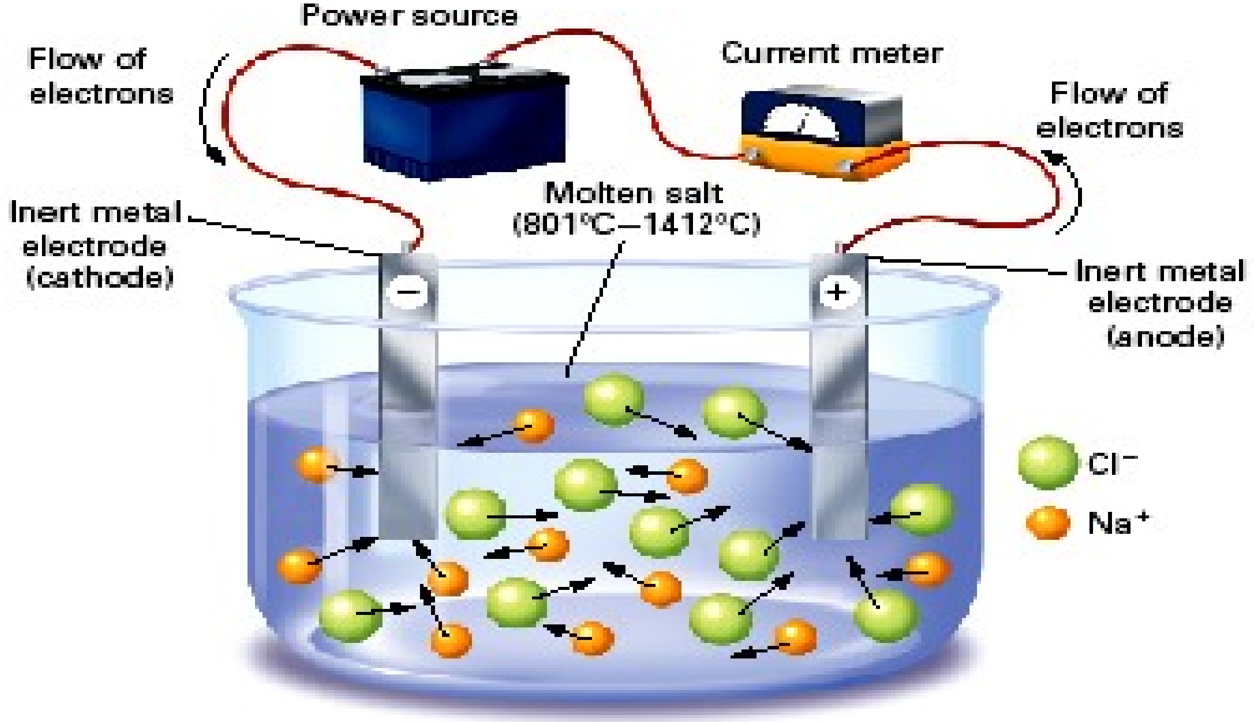
Ionic solids are insulators.

When melted, the ions can move around.

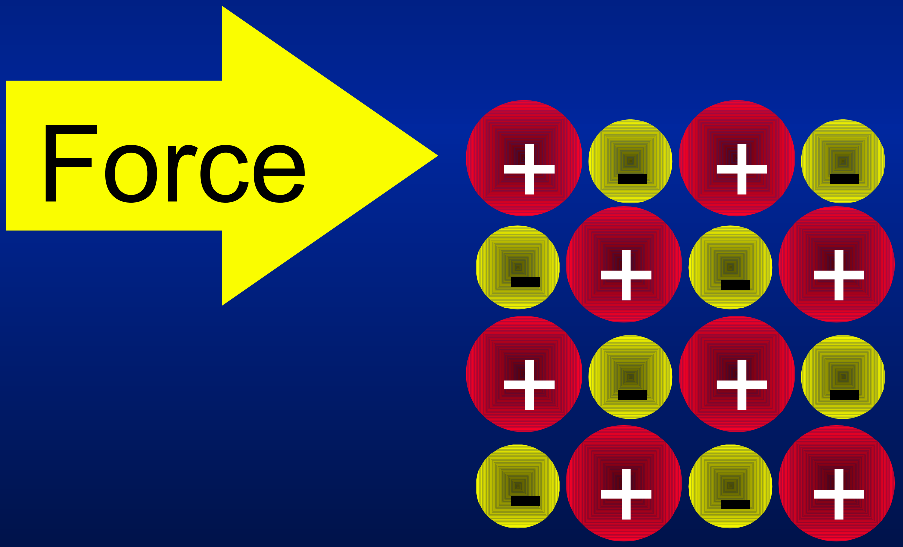
3. Melted ionic compounds conduct.
   - NaCl: must get to about 800 ºC.
   - Dissolved in water, they also conduct (free to move in aqueous solutions)

Figure 7.11 Electrical Conductivity of Molten Sodium Chloride

The ions are free to move when they are **molten** (or in **aqueous solution**), and thus they are able to conduct the electric current.

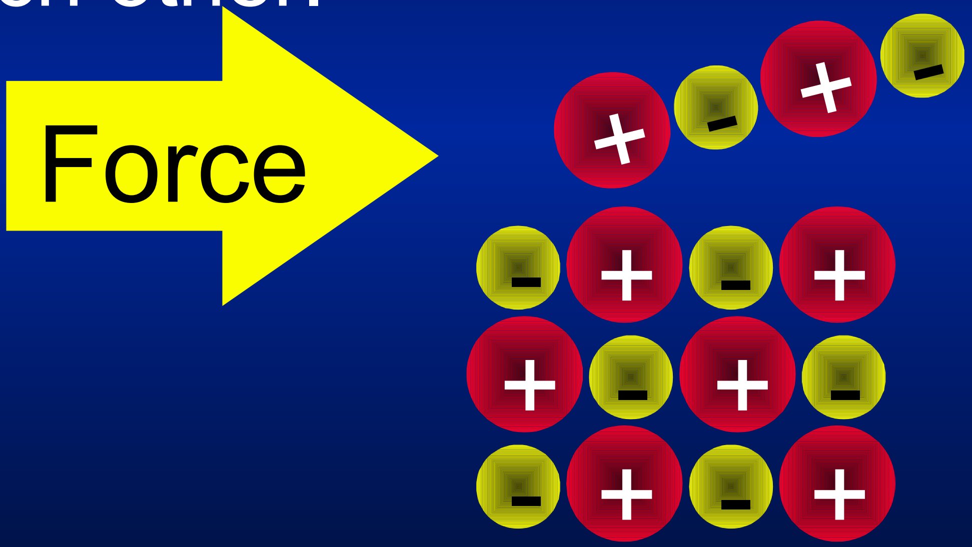


Ionic solids are brittle



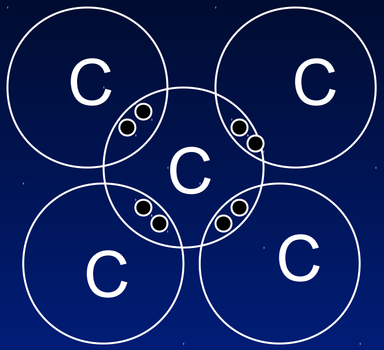
Ionic solids are brittle

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



Covalent Bond

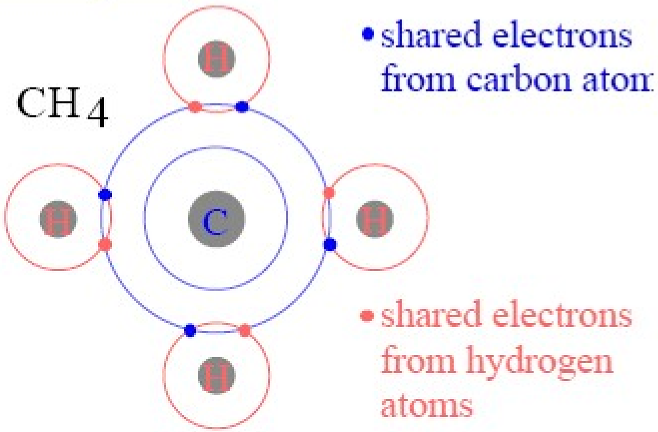
Covalence bond

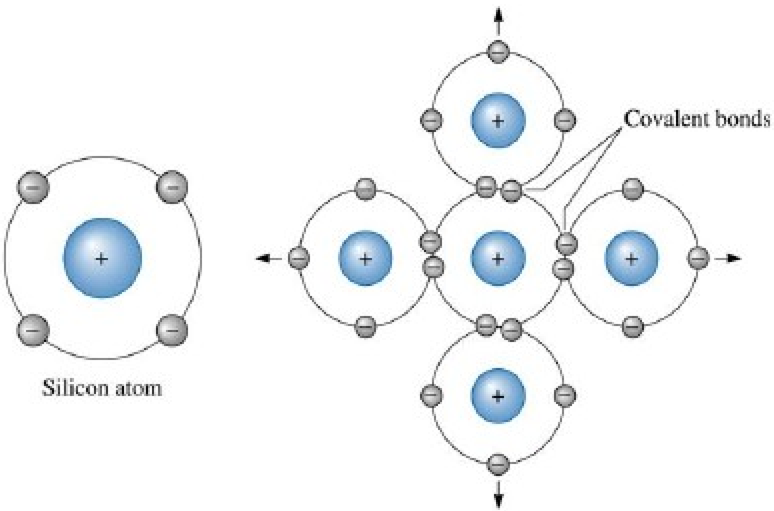


- Bonding energy: ~1-10 eV (strong)
- Two atoms share a pair of electrons
- Examples: C, Ge, Si, H_2

Covalent Bonding

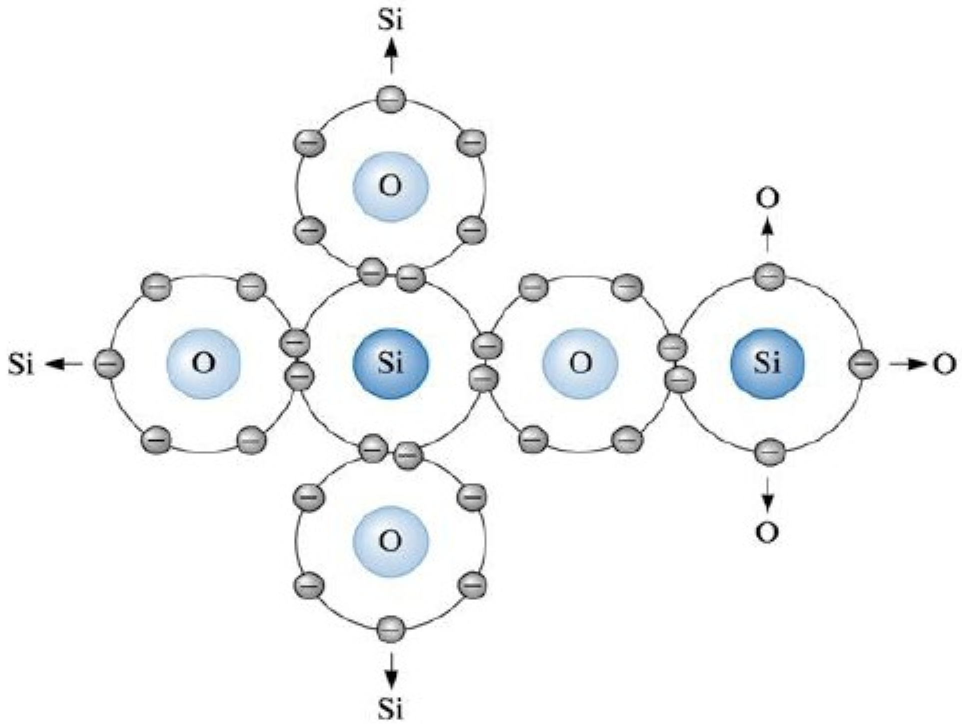
- Requires shared electrons
- Example: CH_4
  - ✓ C: has 4 valence e, needs 4 more
  - ✓ H: has 1 valence e, needs 1 more
  - ✓ Electronegativities are comparable

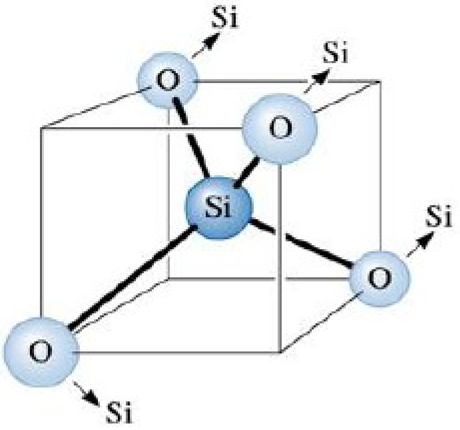




Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled. In Si, with a valence of four, four covalent bonds must be formed.

Covalent Bonding





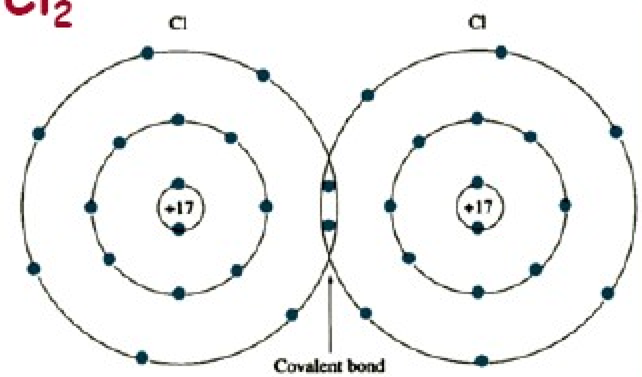
- The tetrahedral structure of silica (SiO_2), which contains covalent bonds between Si and oxygen atoms

Covalent Bond

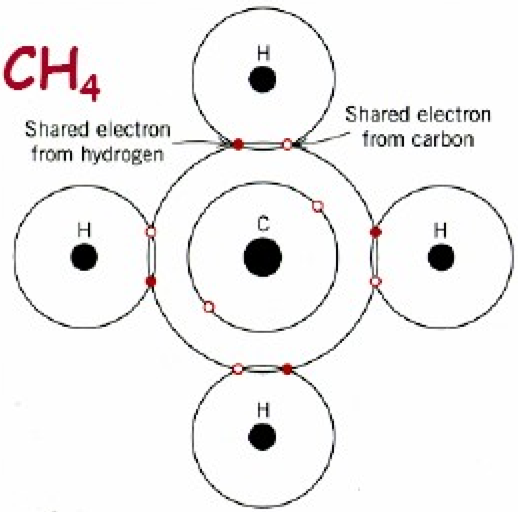
Covalent Bonding

- Electron sharing
- Directional

Cl_2

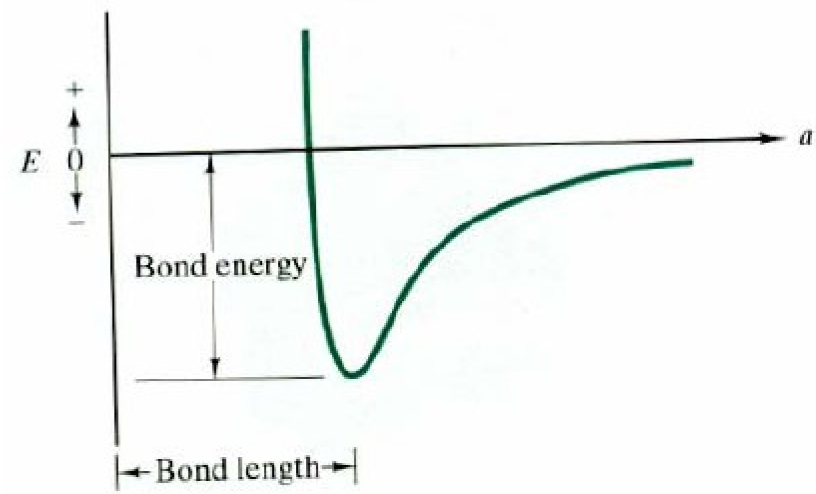


CH_4



Covalent Bonding

- bond energy curve

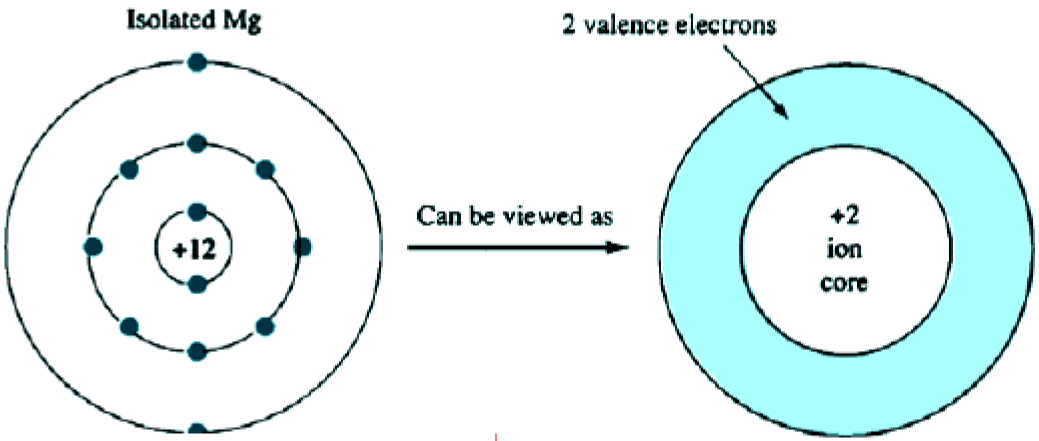


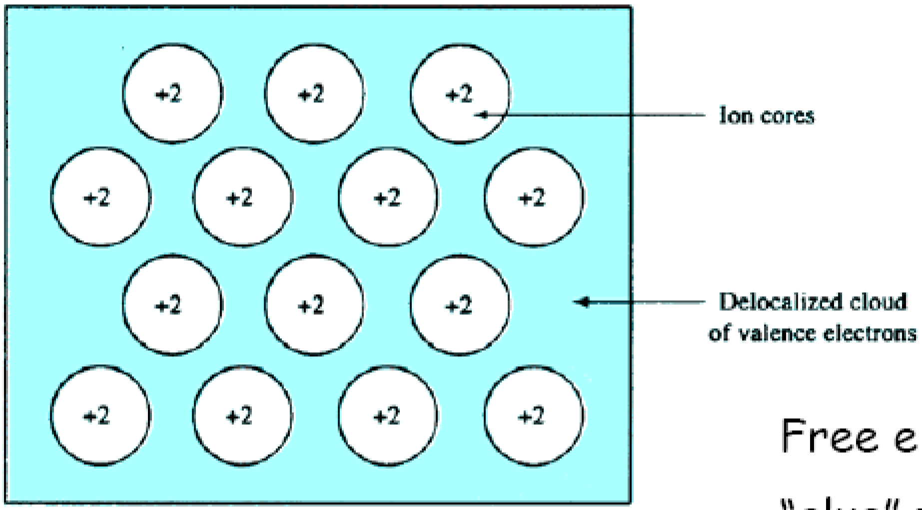
- high hardness
- high melting point
- <u>strong directional nature of bonding</u>
- low electrical conductivities at low temp when specimens are pure

Metallic Bonds

Metallic Bonding

- delocalized electron



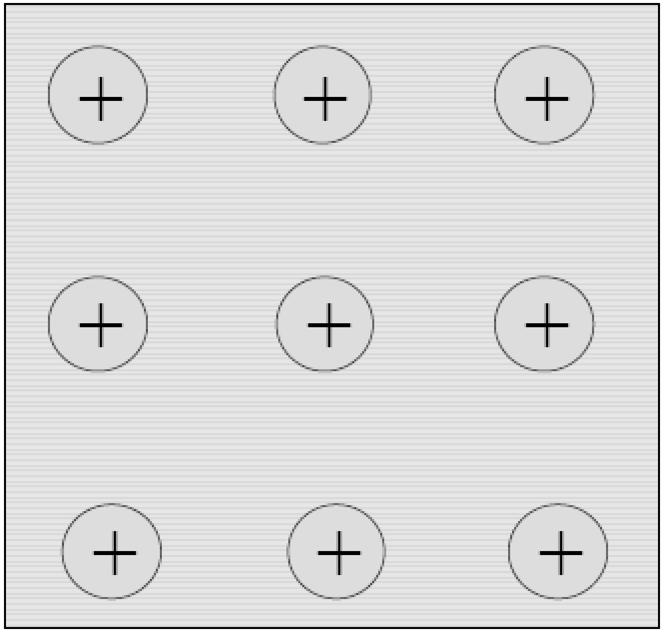


Many Mg atoms combine
to form a solid metal

Free electrons act as a "glue" to hold the ion core

Metallic Bonding

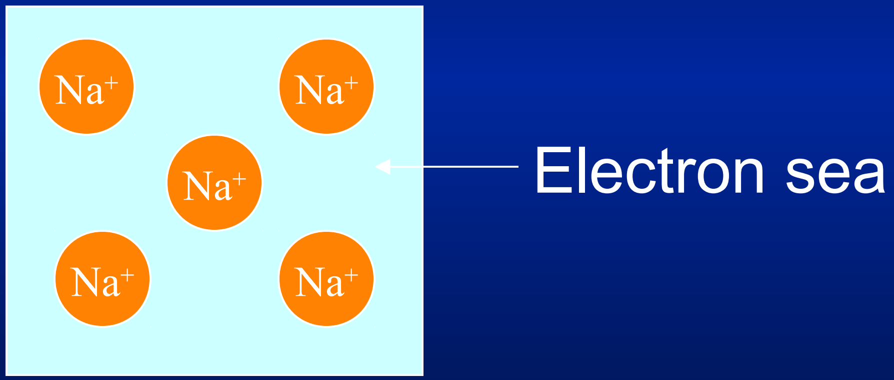
- Arises from a sea of donated valence electrons (1, 2, or 3 from each atom)



- Primary bond for metals and their alloys

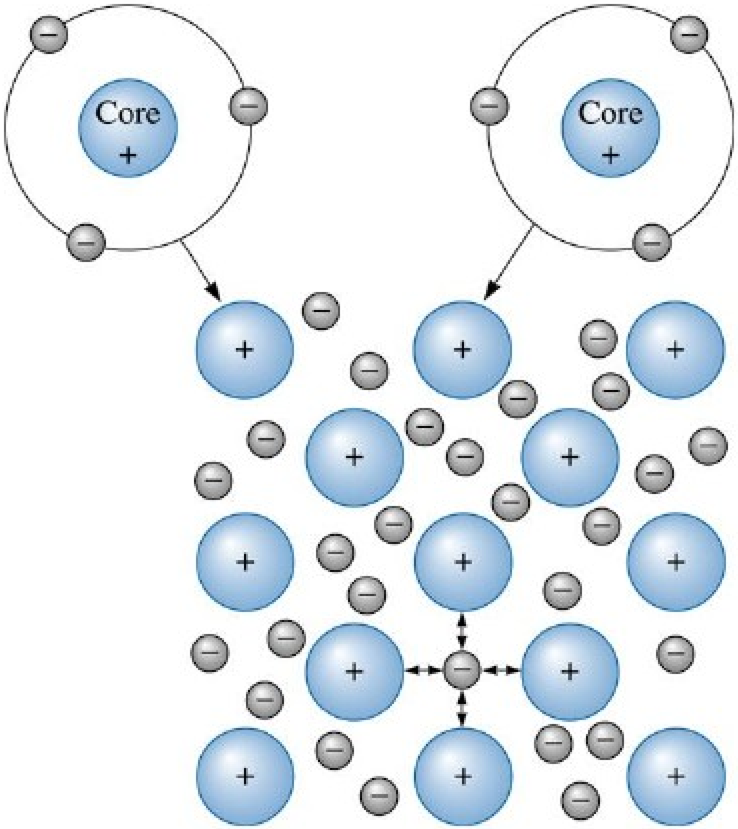
Metallic Bond

Positive ions in a sea of electrons



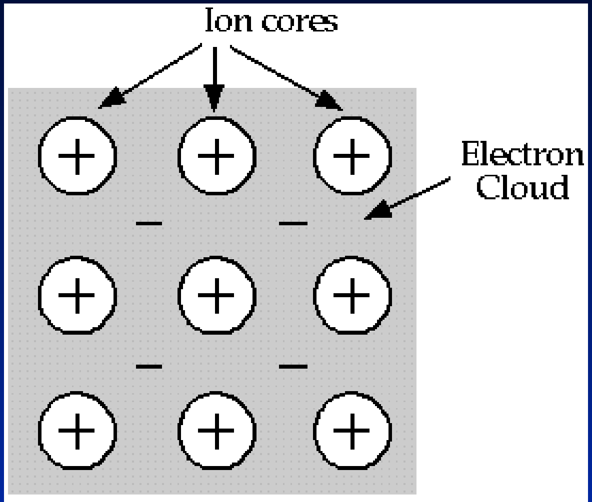
- Bonding energy:
  ~1-10 eV (strong)

Metallic 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

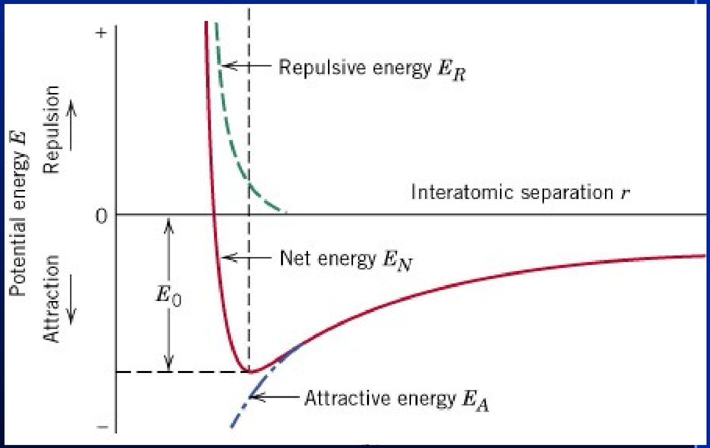
68 kJ/mol (0.7 eV/atom) for Hg

to 850 kJ/mol (8.8 eV/atom) for W.

Melting temperatures (T_{melt}~E_0):

-39 C for Hg and 3410 C for W.

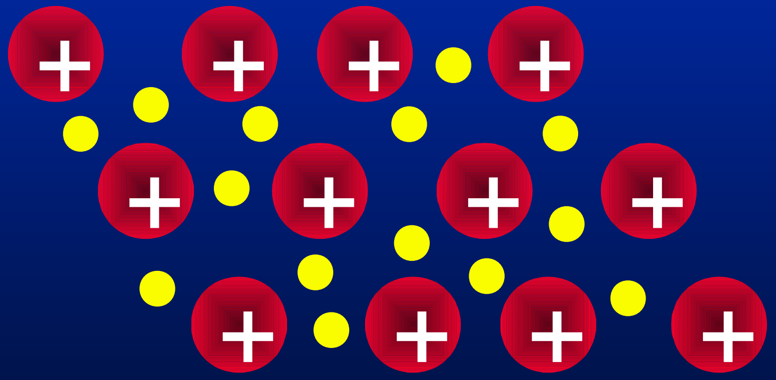
Stronger bonds lead to higher melting temperature:
atomic scale property ➔ macroscale property.



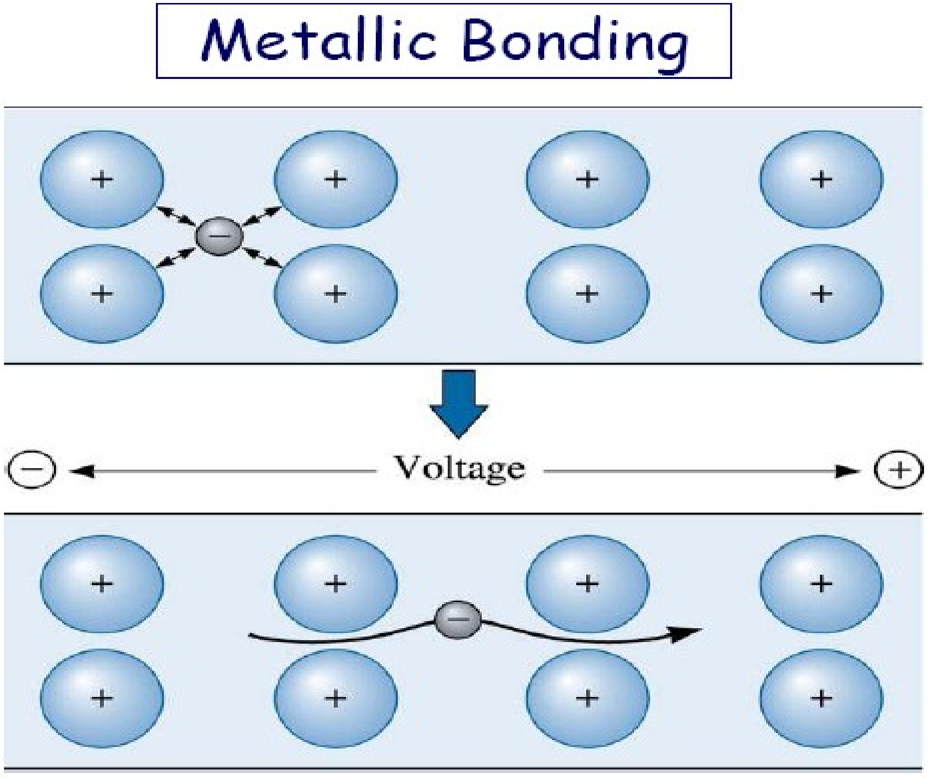
Sea of Electrons

Electrons are free to move through the solid.

Metals conduct electricity.



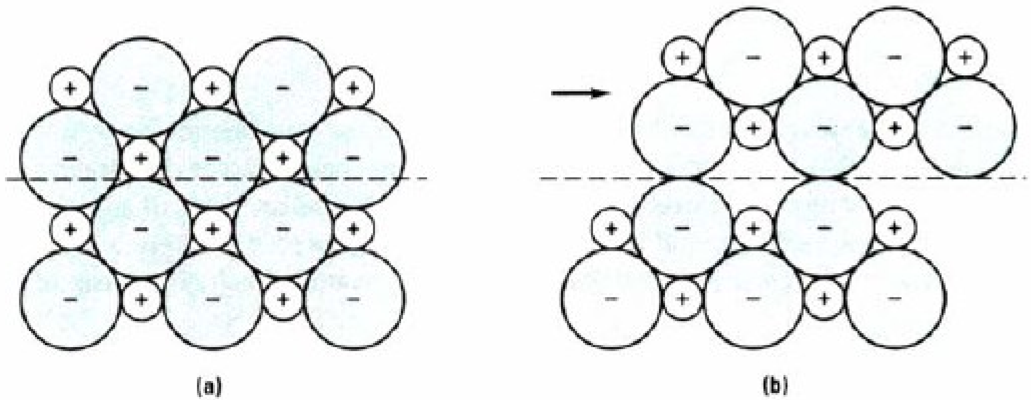
Electrical Conductivity



➢ When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.

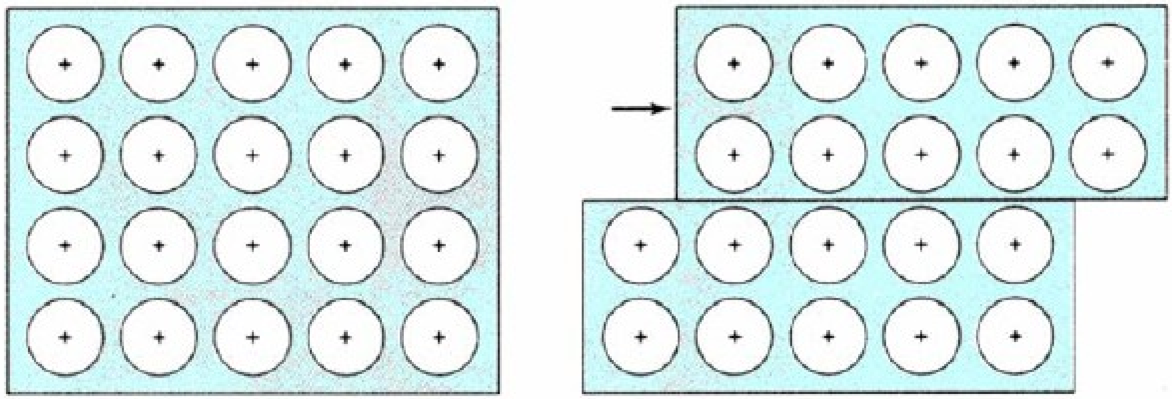
Metallic Bonding

- mechanical property



Ionic bonding

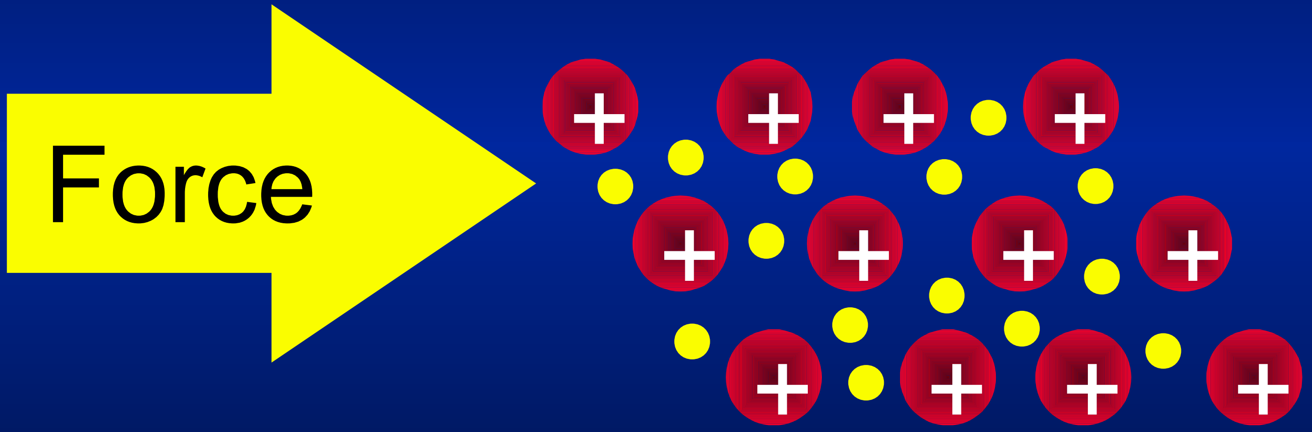
brittle



Metallic bonding

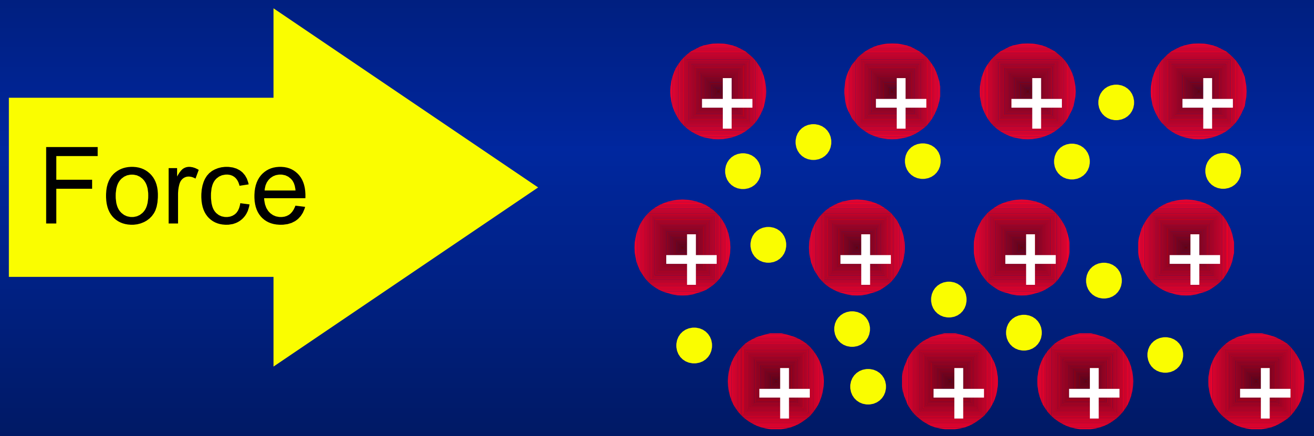
ductile

Plastic Deformation



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

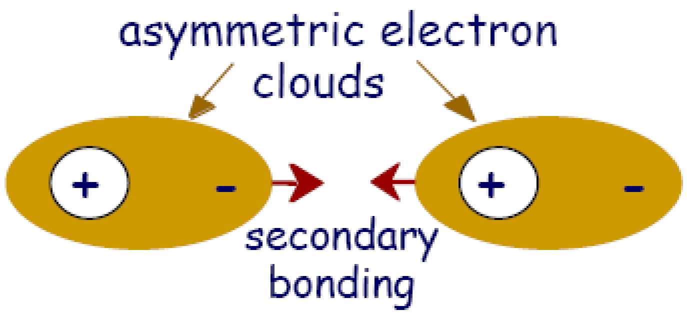
van der Waals bond

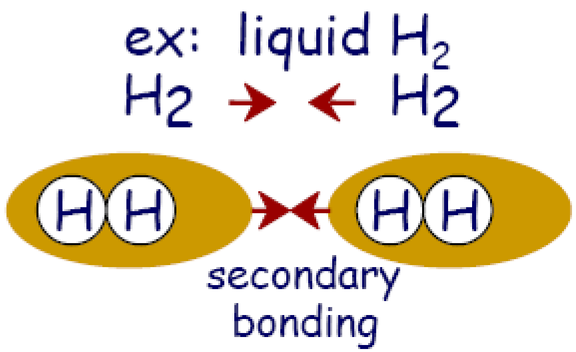
Secondary Bonding

Arises from interaction between

- Induced dipoles
- Induced dipoles and polar molecules
- Polar molecules

- Fluctuating dipoles

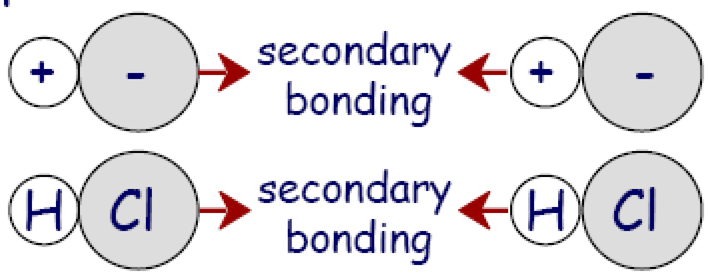




- Permanent dipoles

-general case:

-ex: liquid HCl



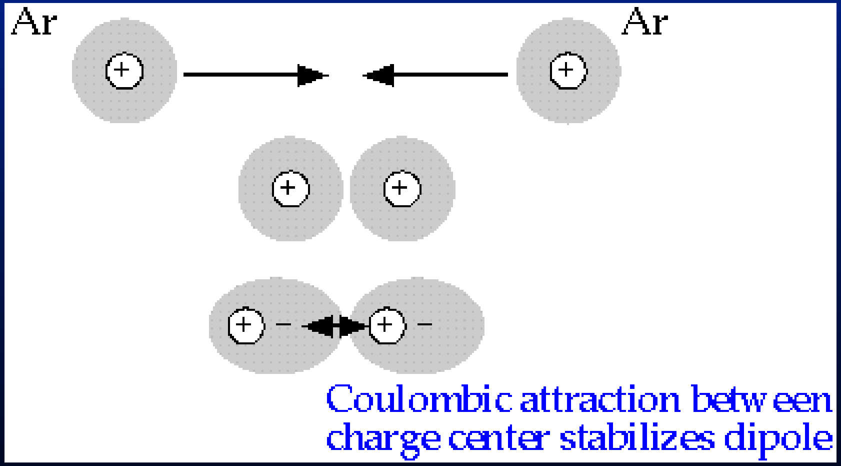
Secondary Bond (van der Waals)

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

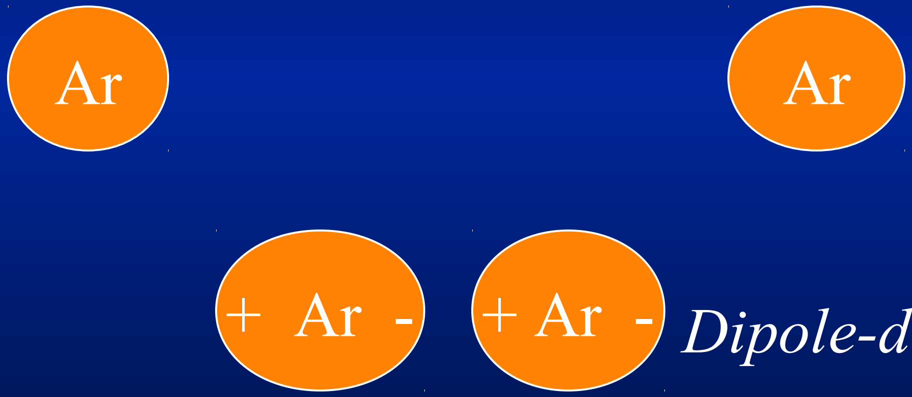
- Induced dipolar interactions are weak and depend on molecular environment.
- They are typically caused by vibrational effects within the particular molecule and lead to interactions **between** molecules.
- Hence, they are **weak** secondary bonds to the stronger molecular bonds.

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, $1/r^4$.



van der Waals bond



Dipole-dipole interaction

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

Bonding

Type of Bond	Substance	Bond Energy* kcal/mole	Melting Temperature (°C)	Characteristics
Ionic	CaCl	155	646	Low electrical conductivity; transparent; brittle; high melting temperature
	NaCl	183	801	
	LiF	240	870	
	CuF_2	617	1360	
	Al_2O_3	3618	3500	
Covalent	Ge	75	958	Low electrical conductivity; very hard; very high melting temperature
	GaAs	≈75	1238	
	Si	84	1420	
	SiC	283	2600	
	Diamond	170	3550	
Metallic	Na	26	97.5	High electrical and thermal conductivity; easily deformable; opaque
	Al	74	660	
	Cu	81	1083	
	Fe	97	1535	
	W	201	3370	
Van der Waals	Ne	0.59	−248.7	Weak binding; low melting and boiling points; very compressible
	Ar	1.8	−189.4	
	CH_4	2.4	−184	
	Kr	2.8	−157	
	Cl_2	7.4	−103	
Hydrogen	HF	7	−92	Higher melting points than Van der Waals bonding; tendency to form groups of manv molecules
	H_2O	12	0	

Important Properties

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

Interatomic Forces

Here we will discuss the forces between atoms

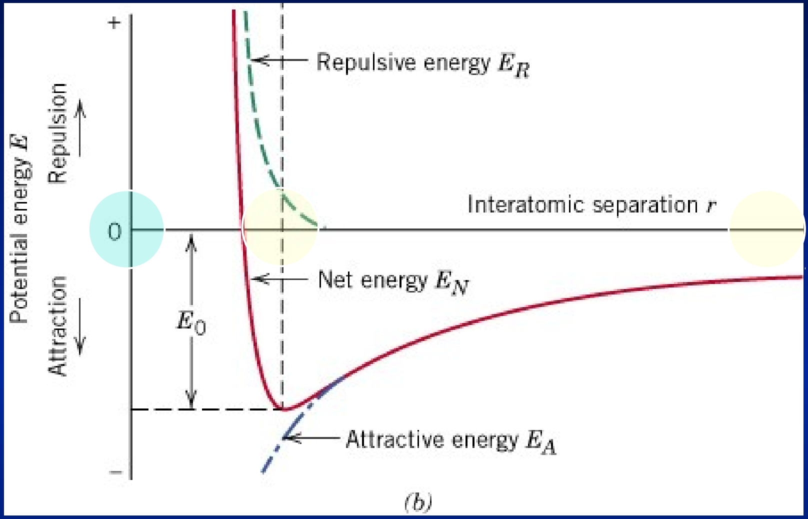
The forces may be both attractive and repulsive

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)

$$Energy : E_{total} = E_A + E_R$$



F = 0 at equilibrium r_0: can find r_0.

How are Macroscopic Properties related to Bonding?

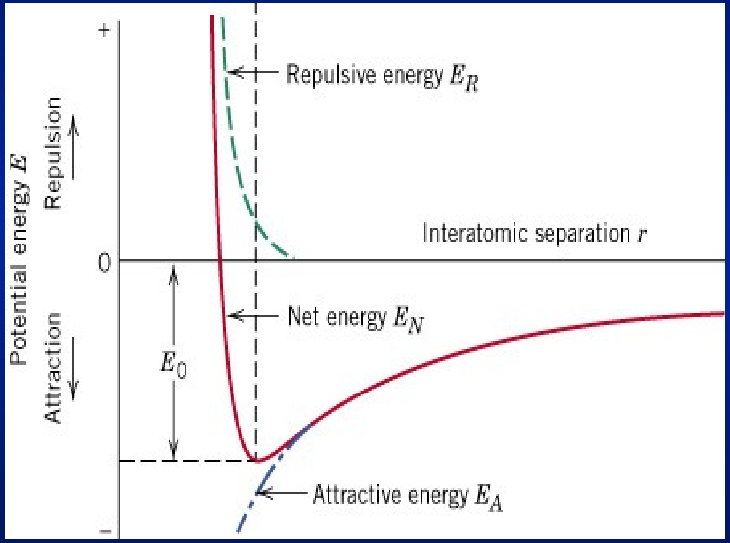
The Bond-Energy Curve

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

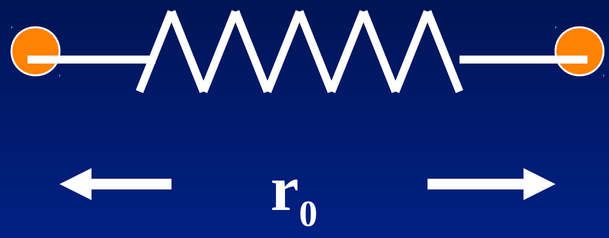
1. Melting temperature
2. Elastic modulus
3. Thermal expansion coefficient



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

Melting Temperature

- Bond Length, r_0



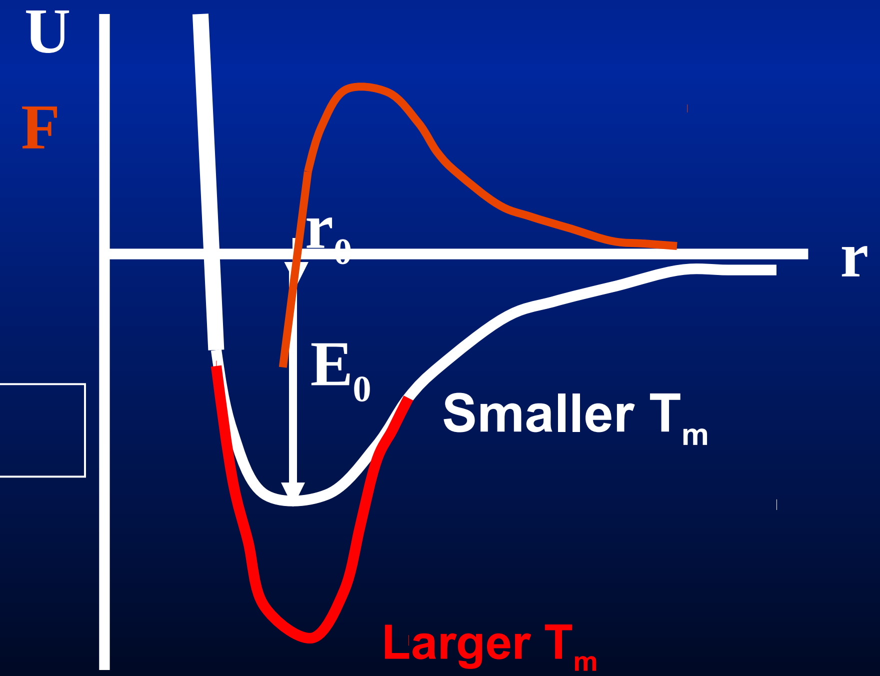
- Binding Energy, U_0
- Melting Temperature, T_m (really $T_{sublimation}$)

T_m goes ↑ as U_0 goes ↓

$$\text{equil. bond } r_0 : F = -\left.\frac{dU}{dr}\right|_{r_0} = 0$$

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

Stored energy goes ↑ as U_0 goes ↓



Bond Energy and Melting Temperature

Callister

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	*Substance*	*Bonding Energy* kJ/mol (kcal/mol)	*Bonding Energy* eV/Atom, Ion, Molecule	*Melting Temperature* (°C)
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

What is relationship between Bonding Energy and T_{melt}?

Elastic Moduli, *E* (Young's Modulus)

$E = d^2U/dr^2(r_0)$

which is the curvature at r_0

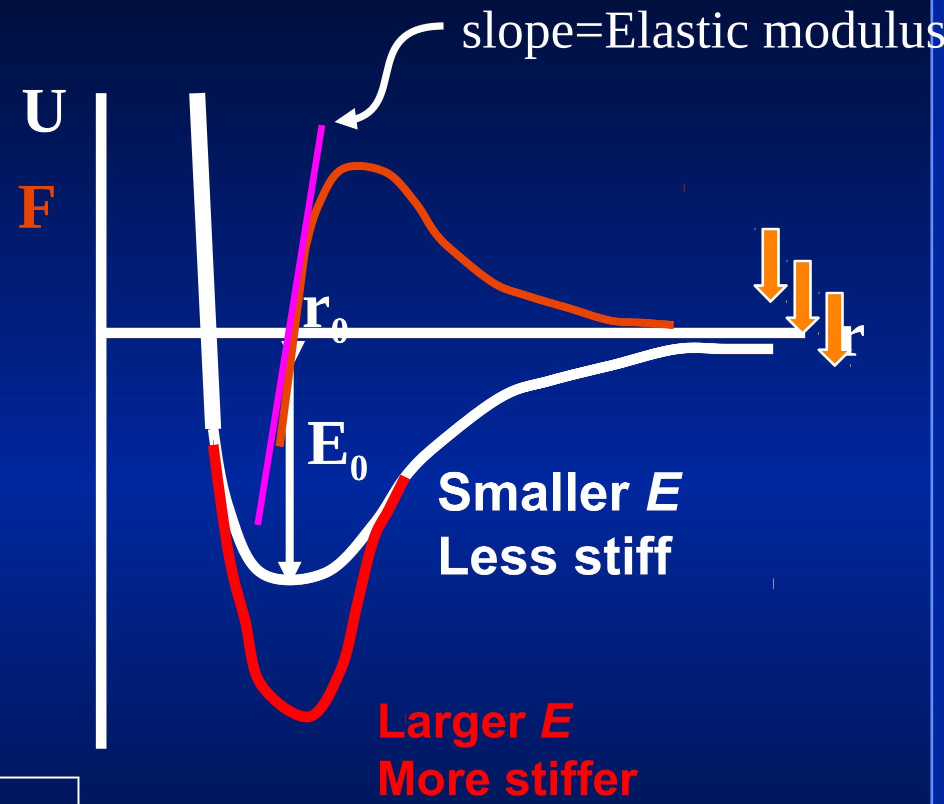
like "spring constant"

$F = k(r - r_0)$

and linear near equilibrium.

Negative F - compression

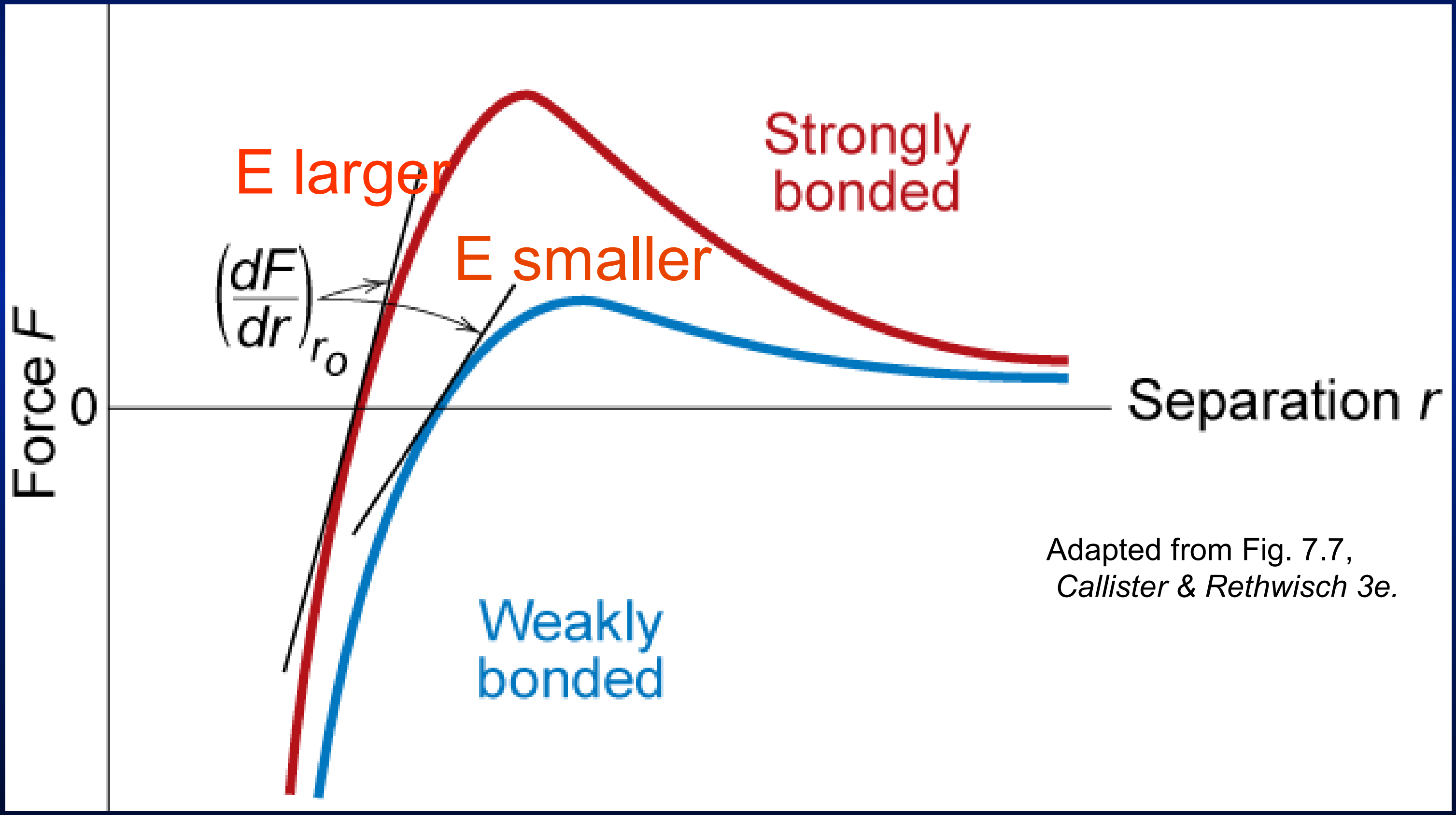
Positive F - tension



E modulus ↑ as E_0 ↓ (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.*

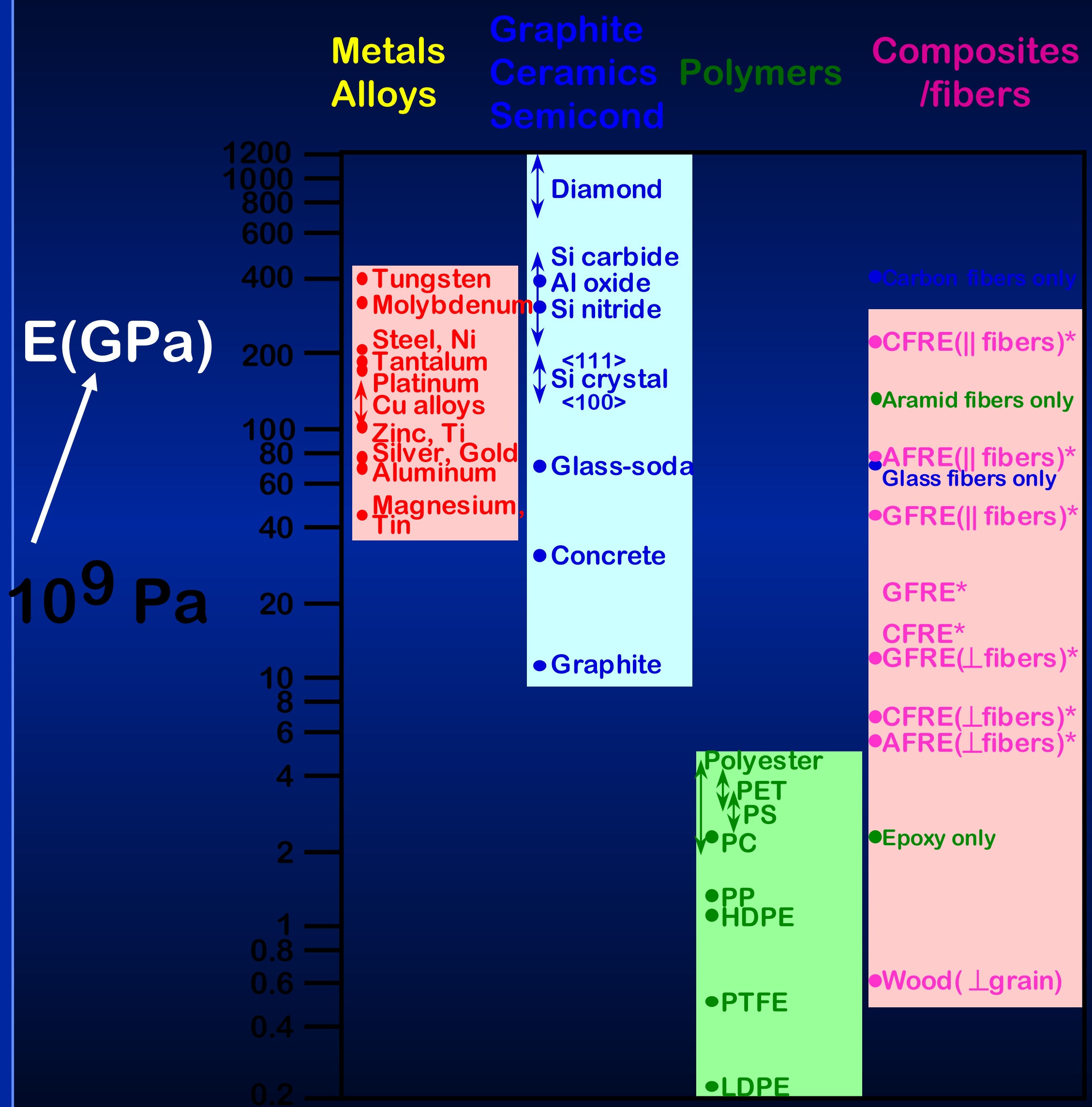
Comparison of Elastic Moduli

Table 7.1 Room-Temperature Elastic and Shear Moduli, and Poisson's Ratio for Various Materials

Material	*Modulus of Elasticity*		*Shear Modulus*		*Poisson's Ratio*
	GPa	*10^6 psi*	*GPa*	*10^6 psi*	
Metal Alloys					
Tungsten	407	59	160	23.2	0.28
Steel	207	30	83	12.0	0.30
Nickel	207	30	76	11.0	0.31
Titanium	107	15.5	45	6.5	0.34
Copper	110	16	46	6.7	0.34
Brass	97	14	37	5.4	0.34
Aluminum	69	10	25	3.6	0.33
Magnesium	45	6.5	17	2.5	0.35

Silicon (single xtal)	120-190	(depends on crystallographic direction)
Glass (pyrex)	70	
SiC (fused or sintered)	207-483	
Graphite (molded)	~12	
High modulus C-fiber	400	
Carbon Nanotubes	**~1000**	Normalize by density, 20x steel wire. strength normalized by density is 56x wire.

Young's Modulus, E



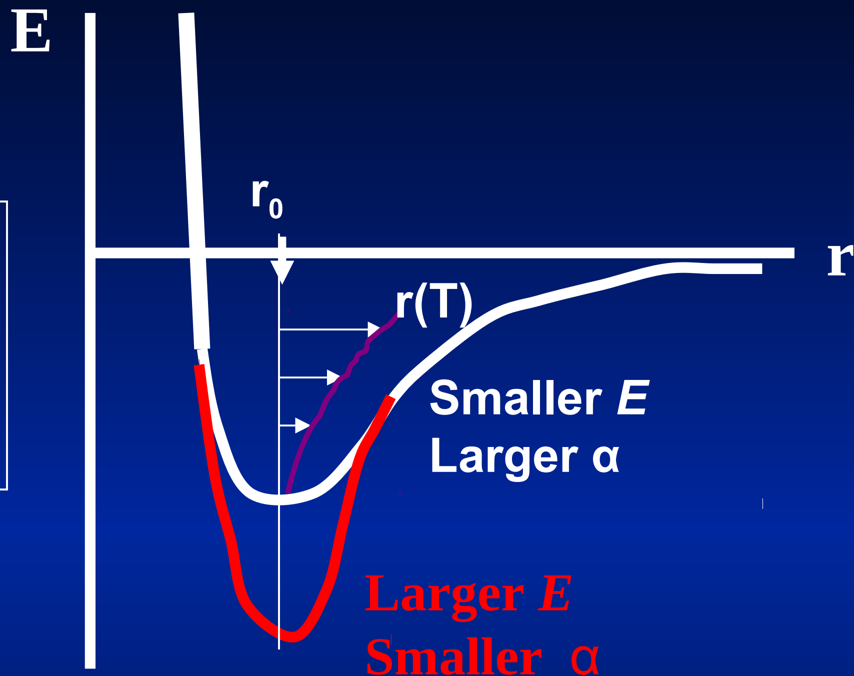
$E_{ceramics} > E_{metals} >> E_{polymers}$

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, α, or dL/dT

Linear Thermal Strain

$$\Delta L(T)/L_0 = \alpha_L\,(T - T_0)$$



α ~ asymmetry at r_0

No asymmetry at r_0

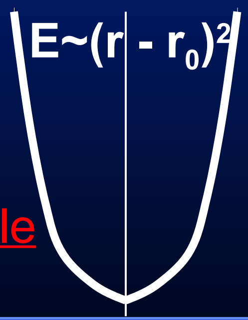
No affect on r(T) or V(T)

α ↑ as E_0 ↑ (less negative)

Volume Thermal Strain

$$\Delta V/V_0 = \alpha_V\,(T - T_0)$$

Parabolic E vs. r shape



Symmetric well $r(T)=r_0$: No expansion possible

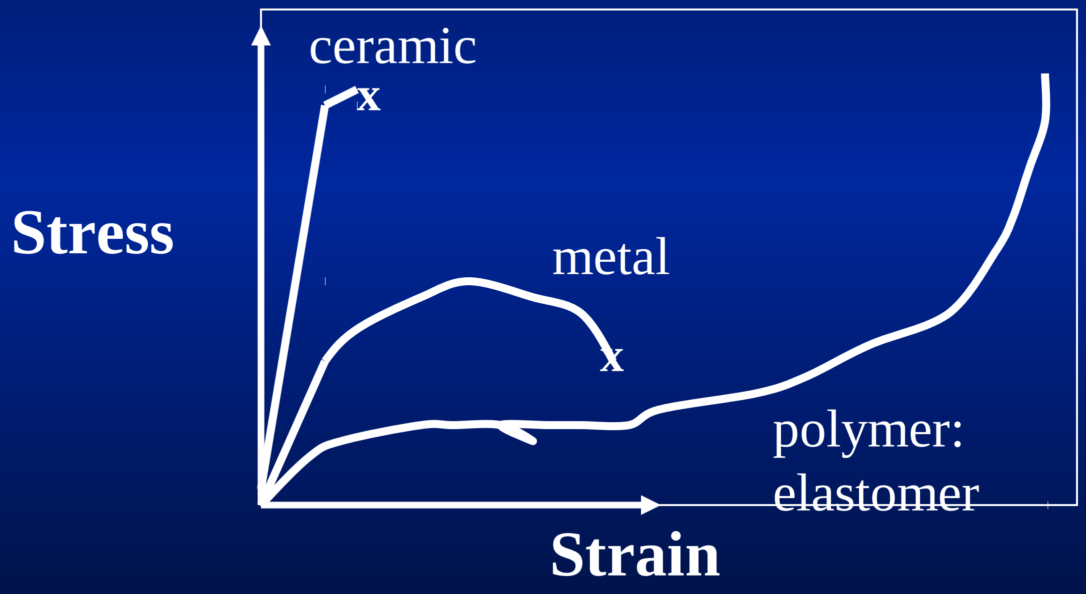
Atoms just vibrate back and forth!

What can you now say about ...

What is T_{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?

Summary: Bonding, Structure, Properties

Ceramics	Large bond energies
Ionic and Covalent bonds	large T_m, E Small α
Metals	Varying bond energy
Metallic bonding	intermediate T_m, E, α
Polymers	directional properties
Covalent and Secondary	secondary dominates outcome
	small T_m, E large α

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).