Chapter 2: Atomic Structure & Interatomic Bonding

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Atomic Structure (Freshman Chem.)

- atom – electrons – 9.11×10^{-31} kg
  protons
  neutrons } 1.67×10^{-27} kg

- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species

- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

Atomic wt = wt of 6.022×10^{23} molecules or atoms

1 amu/atom = 1g/mol

C 12.011
H 1.008 etc.

Atomic Structure

- Valence electrons determine all of the following properties
  1) Chemical
  2) Electrical
  3) Thermal
  4) Optical

Electronic Structure

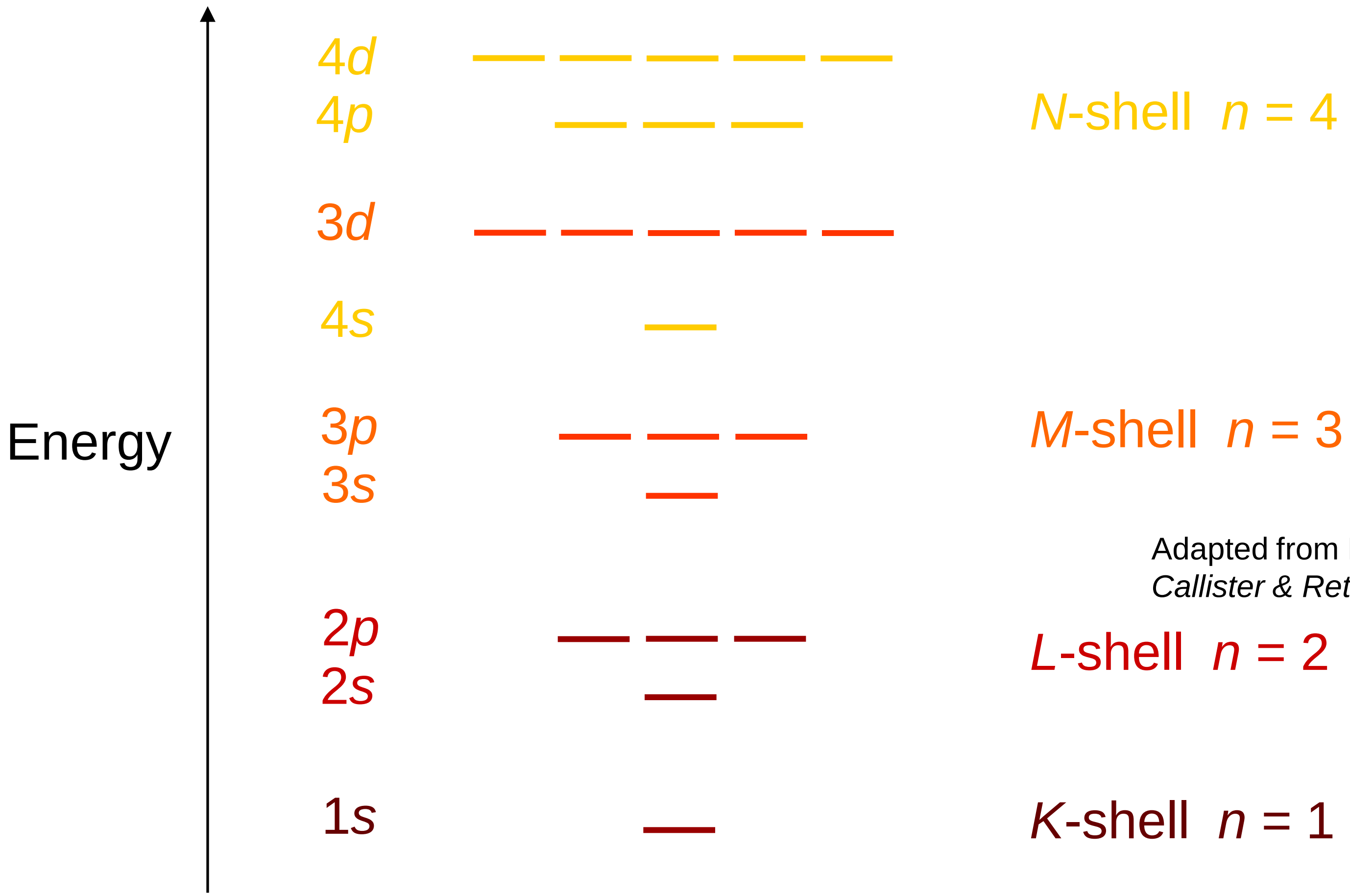
- Electrons have wavelike and particulate properties.
  - This means that electrons are in orbitals defined by a probability.
  - Each orbital at discrete energy level is determined by quantum numbers.

Quantum #	Designation
n = principal (energy level-shell)	K, L, M, N, O (1, 2, 3, etc.)
l = subsidiary (orbitals)	s, p, d, f (0, 1, 2, 3,…, n-1)
m_l = magnetic	1, 3, 5, 7 ($-l$ to $+l$)
m_s = spin	½, -½

Electron Energy States

Electrons...

- have discrete energy states
- tend to occupy lowest available energy state.



Adapted from Fig. 2.4, *Callister & Rethwisch 8e.*

SURVEY OF ELEMENTS

- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Adapted from Table 2.2, *Callister & Rethwisch 8e.*

- Why? Valence (outer) shell usually not filled completely.

Electron Configurations

- Valence electrons – those in unfilled shells
- Filled shells more stable
- Valence electrons are most available for bonding and tend to control the chemical properties

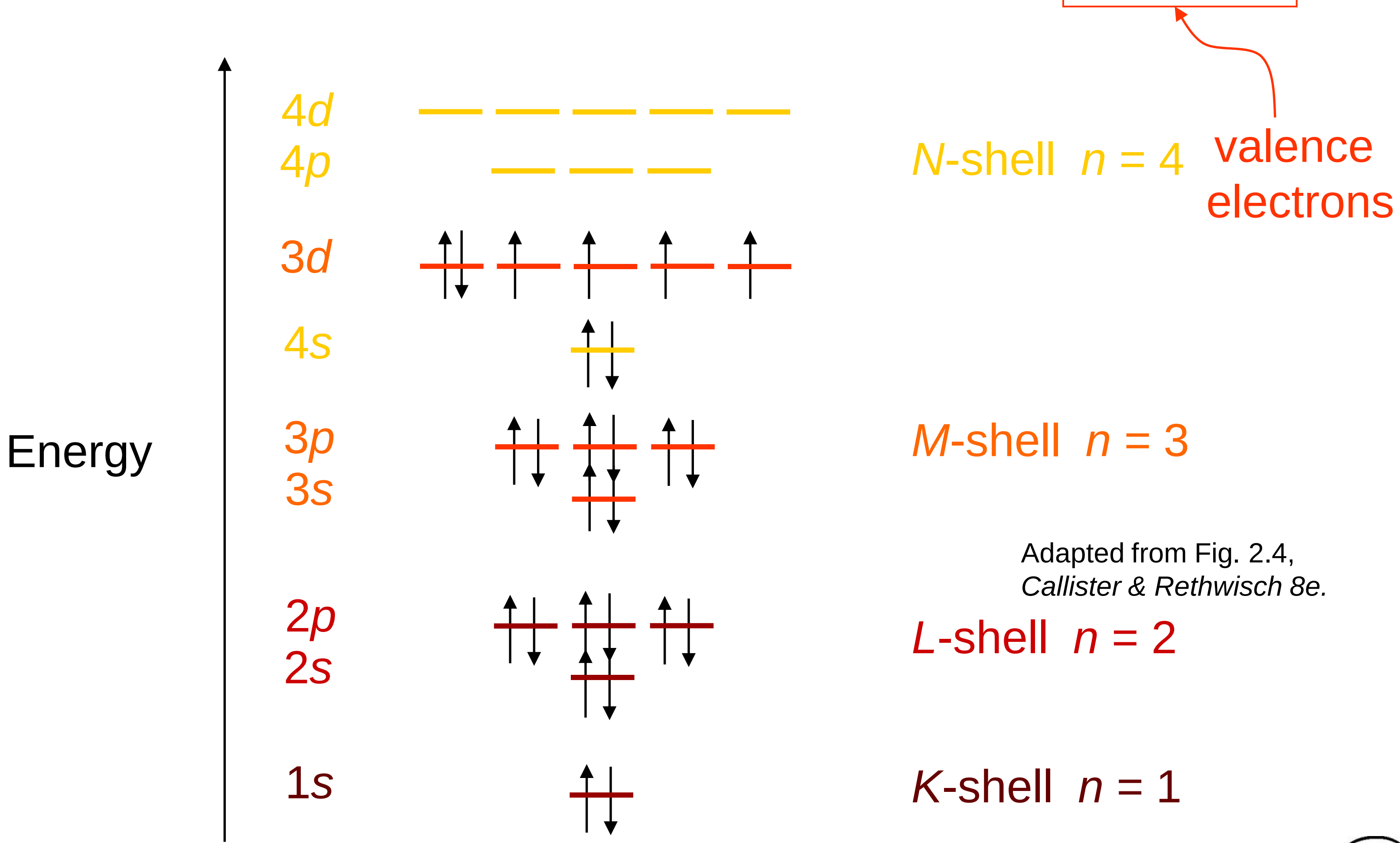
  – example: C (atomic number = 6)

$1s^2$ $2s^2\ 2p^2$

valence electrons

Electronic Configurations

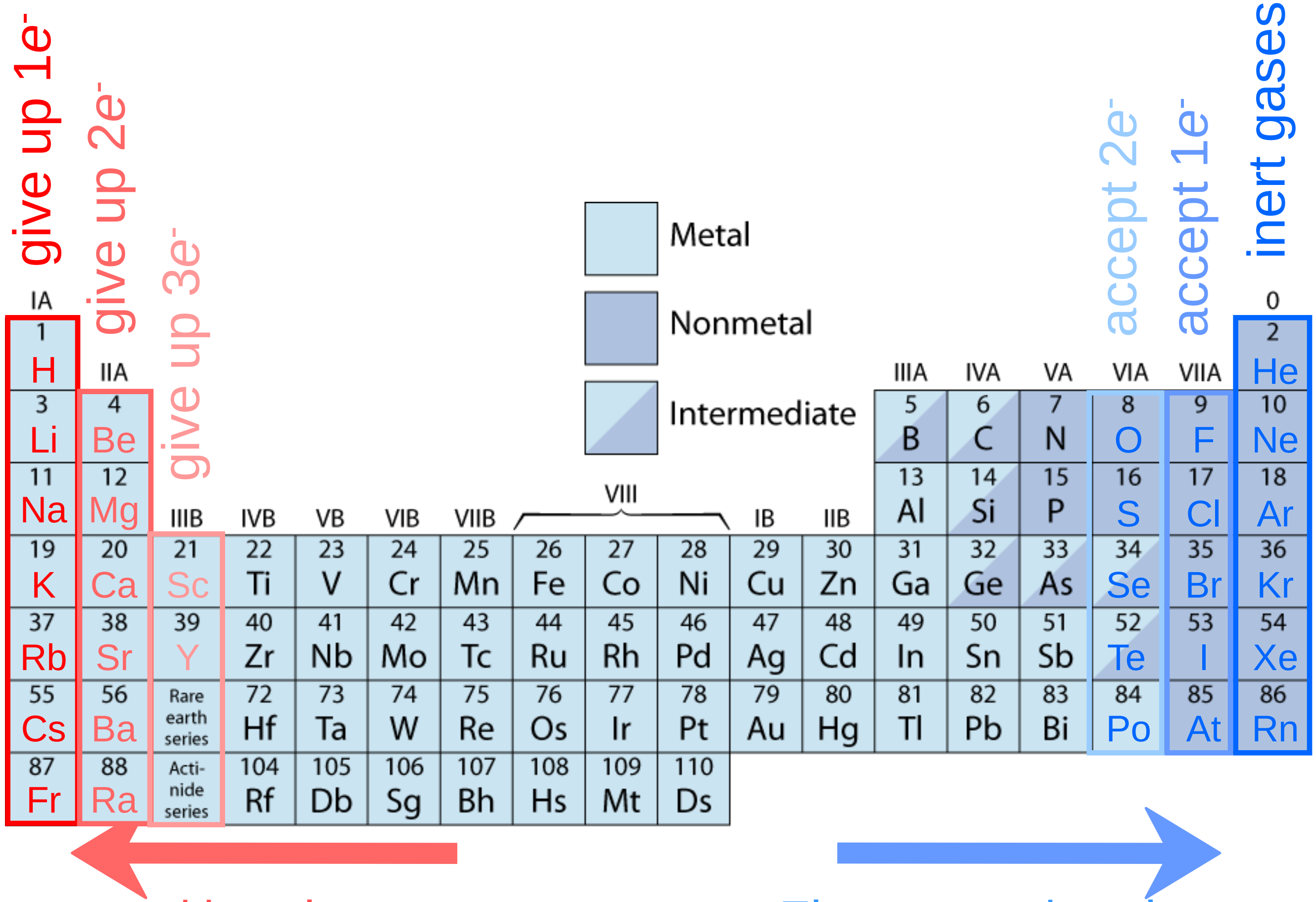
ex: Fe - atomic # = 26 $1s^2$ $2s^2\,2p^6$ $3s^2\,3p^6$ $3d^6$ $4s^2$



Adapted from Fig. 2.4, *Callister & Rethwisch 8e.*

The Periodic Table

- Columns: Similar Valence Structure



Adapted from Fig. 2.6, *Callister & Rethwisch 8e.*

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

Electronegativity

- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Smaller electronegativity

Larger electronegativity

Adapted from Fig. 2.7, *Callister & Rethwisch 8e.* (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.

PRIMARY ATOMIC BONDING

Ionic bond – metal + nonmetal

metal: donates electrons

nonmetal: accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

[Ne] $3s^2$

O $1s^2\ 2s^2\ 2p^4$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$

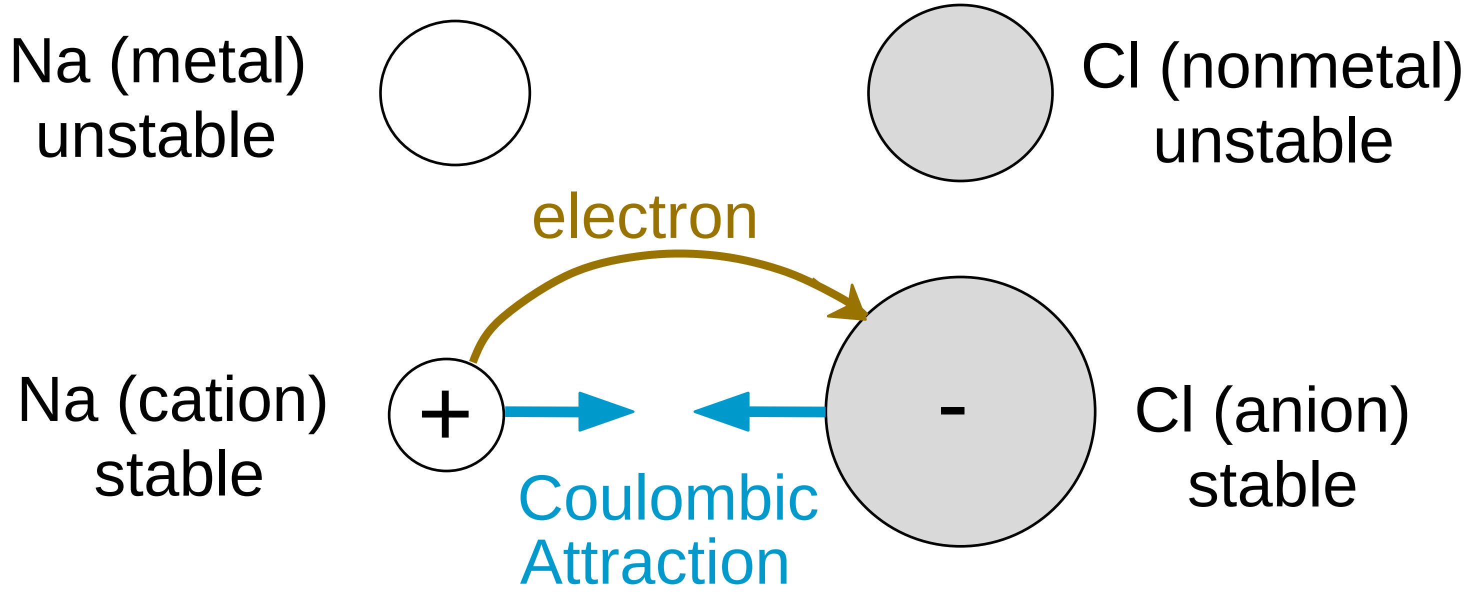
[Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$

[Ne]

Ionic Bonding

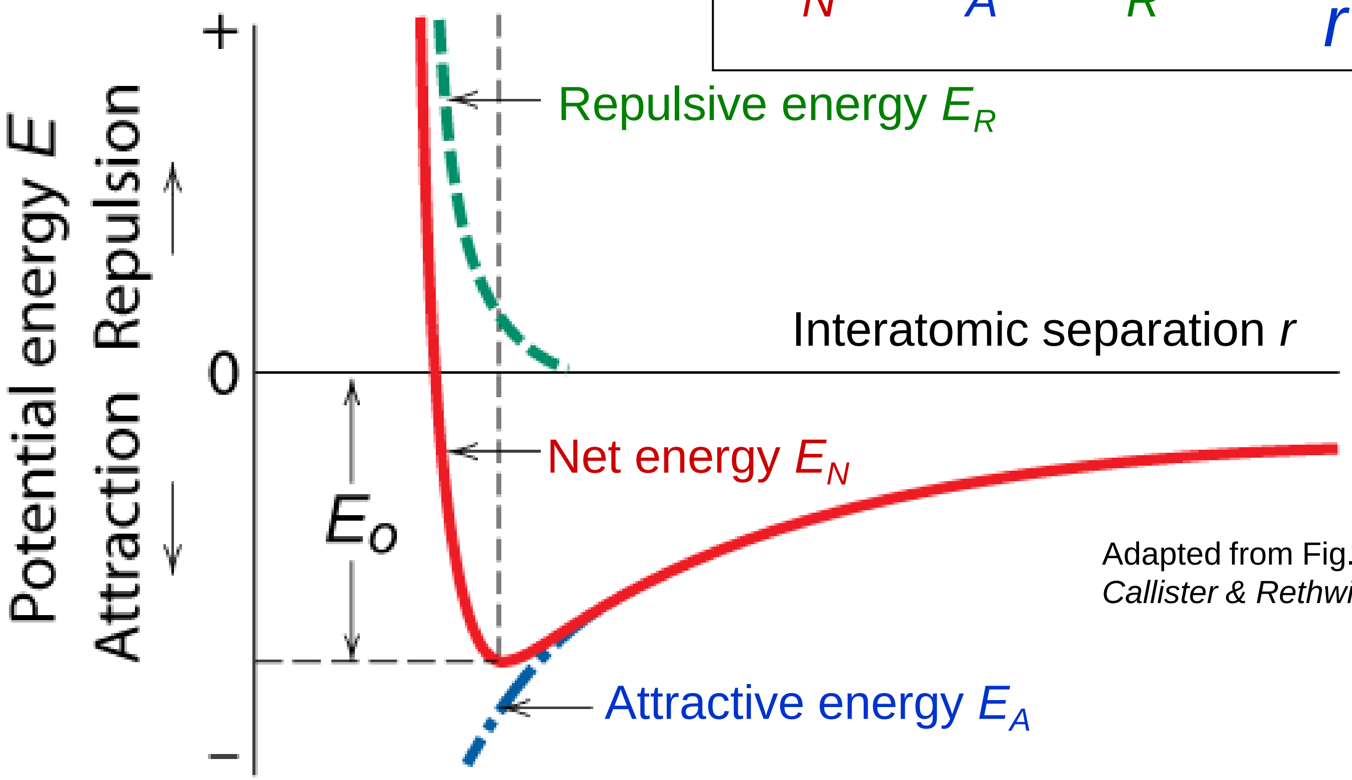
- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



Ionic Bonding

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

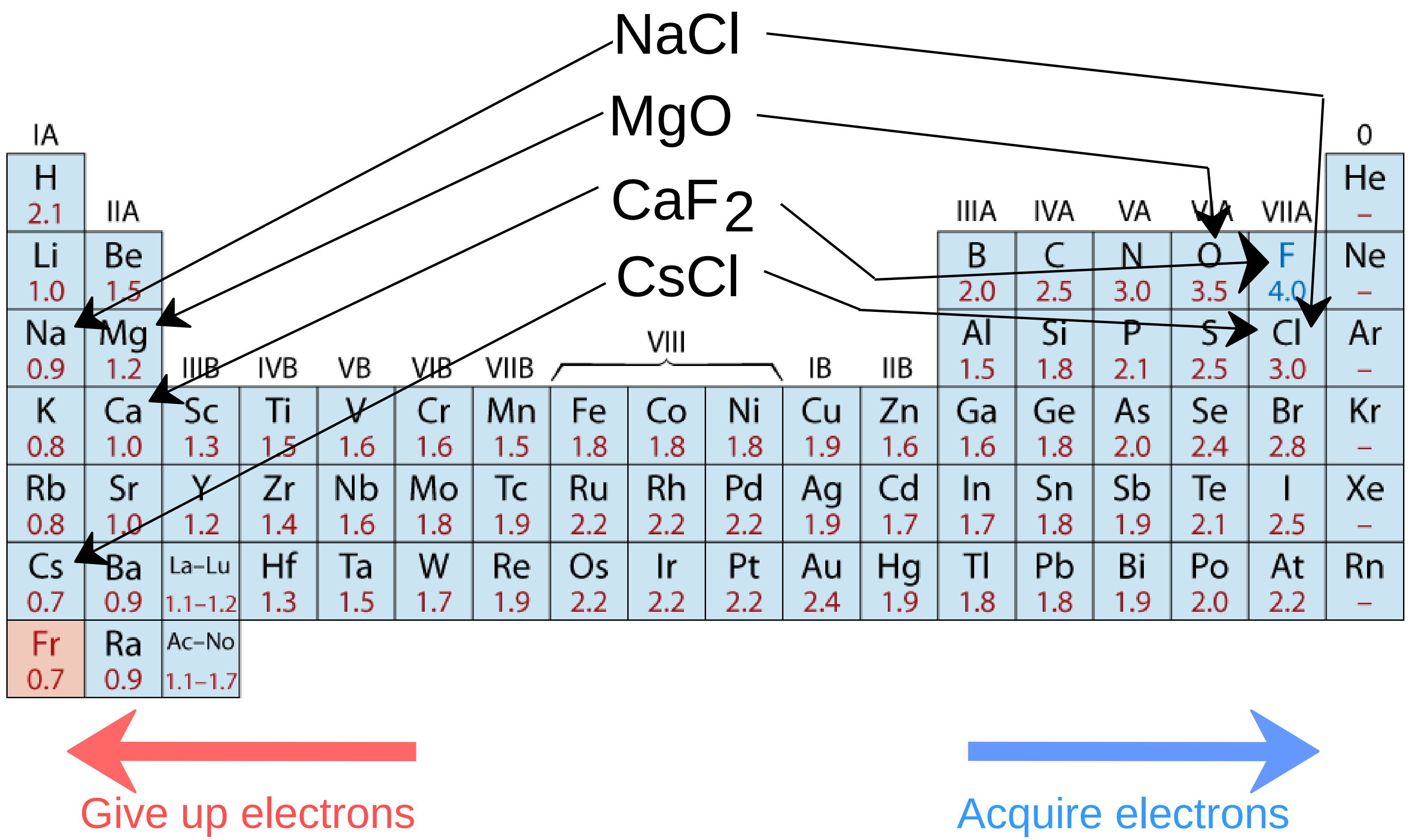
$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$



Adapted from Fig. 2.8(b), *Callister & Rethwisch 8e.*

Examples: Ionic Bonding

- Predominant bonding in Ceramics



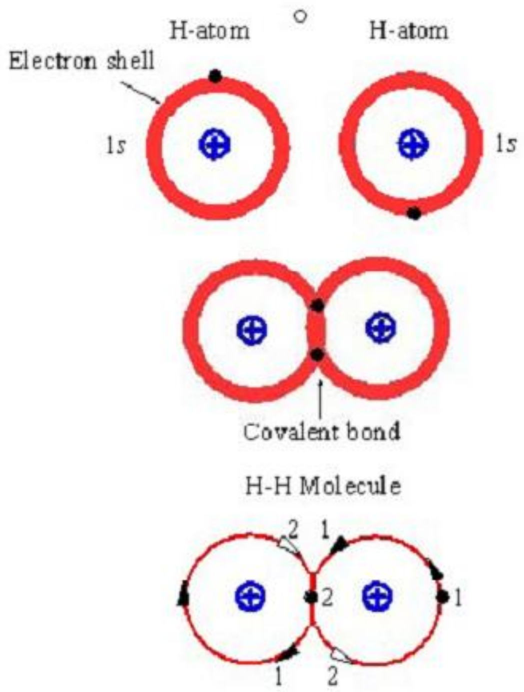
Adapted from Fig. 2.7, *Callister & Rethwisch 8e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Covalent Bonding

Covalent Bonding (Diamond, Silicon,Gemanium, etc.

Covalent bonds – the key to life

• covalent bond: the sharing of valence electrons to complete the subshells of each atom and thereby reducing the overall potential E of the combination.



i.e.) formation of a covalent bond between two H atoms, leading to the H_2 molecule

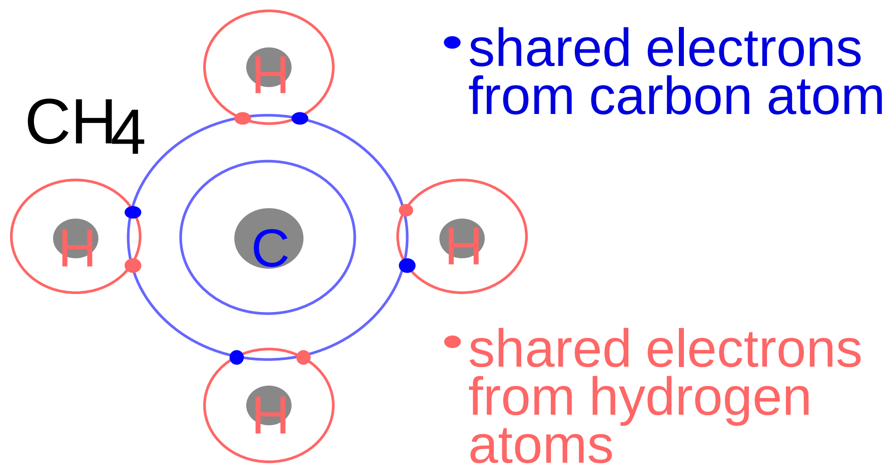
Electron spend a majority of their time between the two nuclei, which results in a net attraction between the electrons and the two nuclei, which is the origin of the covalent bond

Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH_4

  C: has 4 valence e^-,
  needs 4 more

  H: has 1 valence e^-,
  needs 1 more



- Properties :

  - due to strong Coulombic attraction between the shared 'e' and the positive nuclei, the covalent bond E is the highest for all bond type.

  → lead to very high melting temperatures, very hard solids ex) diamond

  - insoluble in nearly all solvents

  - directional nature and strength makes it nonductile (or nonmalleable)

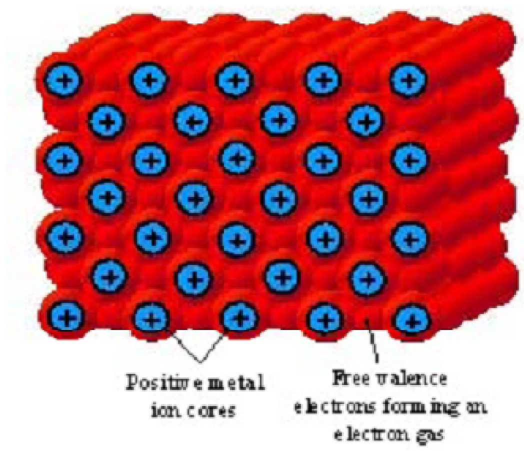
  - poor electrical conductivity because 'e' is not free in a crystal.

METALLIC BONDING

Metallic Bonding (Copper,gold, silver, bronze,brass, etc.)

• Metal atoms have only a few valence electrons; easily lost from individual atoms and become collectively shared by all the ions when many metal atoms are brought together to form a solid (delocalized and form an electron gas or cloud).
• ions are packed as closely as possible by the gluing effect of the electrons between the ions, forming a crystal called the face-centered cubic (FCC)

• the nondirectional nature of the bond (collective sharing of electrons) → ductile
• free valence electrons → the high electrical conductivity
good thermal conductivity



In metallic bonding, the valence electrons from the metal atoms form a "cloud of electrons" which fills the metal ions and "glues" the ions together through Coulmbic attraction between the electron gas and the positive metal ions.

Primary Bonding

- Metallic Bond -- delocalized as electron cloud

- Ionic-Covalent Mixed Bonding

$$\%\text{ ionic character} = \left(1 - e^{-\frac{(X_A - X_B)^2}{4}}\right) \times (100\%)$$

where X_A & X_B are Pauling electronegativities

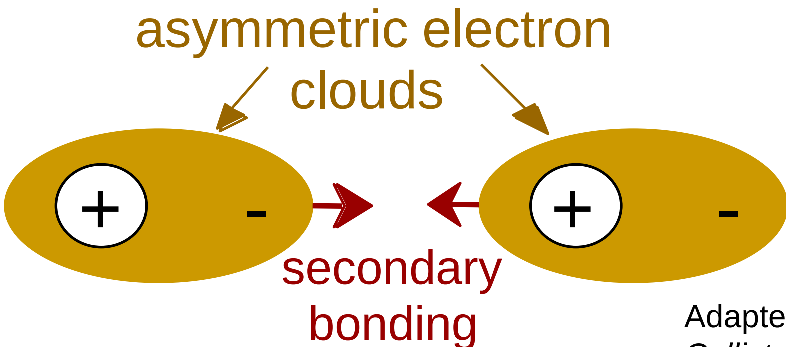
Ex: MgO $\quad X_{Mg} = 1.2$
$\quad X_O = 3.5$

$$\%\text{ ionic character} = \left(1 - e^{-\frac{(3.5-1.2)^2}{4}}\right) \times (100\%) = 73.4\%\text{ ionic}$$

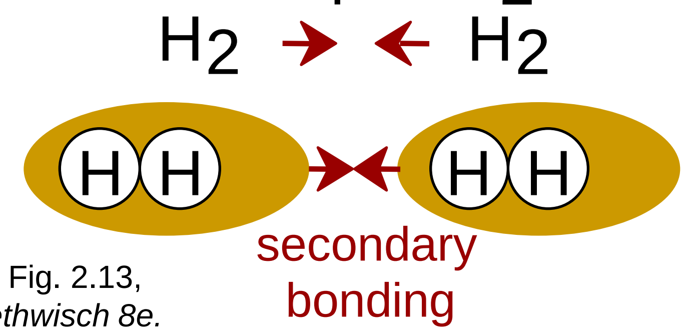
SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles



ex: liquid H_2



Adapted from Fig. 2.13, *Callister & Rethwisch 8e.*

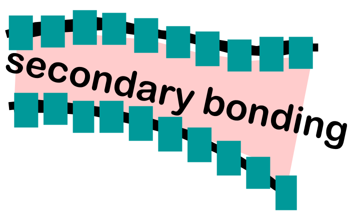
- Permanent dipoles-molecule induced

-general case:

-ex: liquid HCl

Adapted from Fig. 2.15, *Callister & Rethwisch 8e.*

-ex: polymer



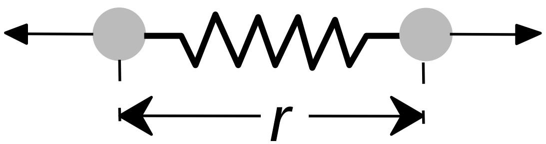
secondary bonding

Summary: Bonding

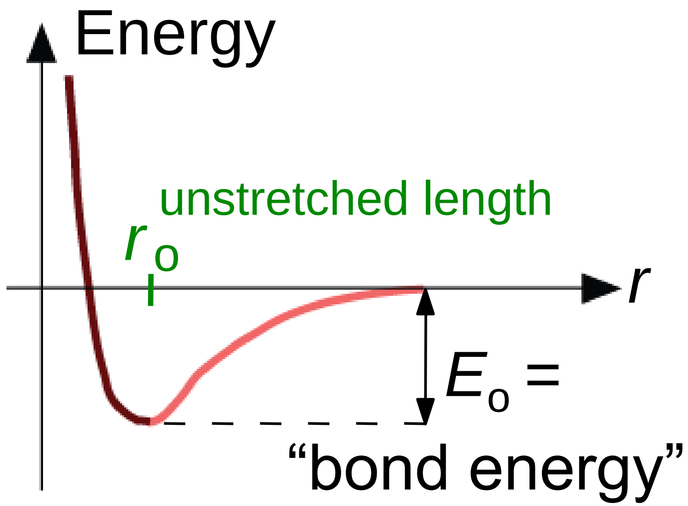
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

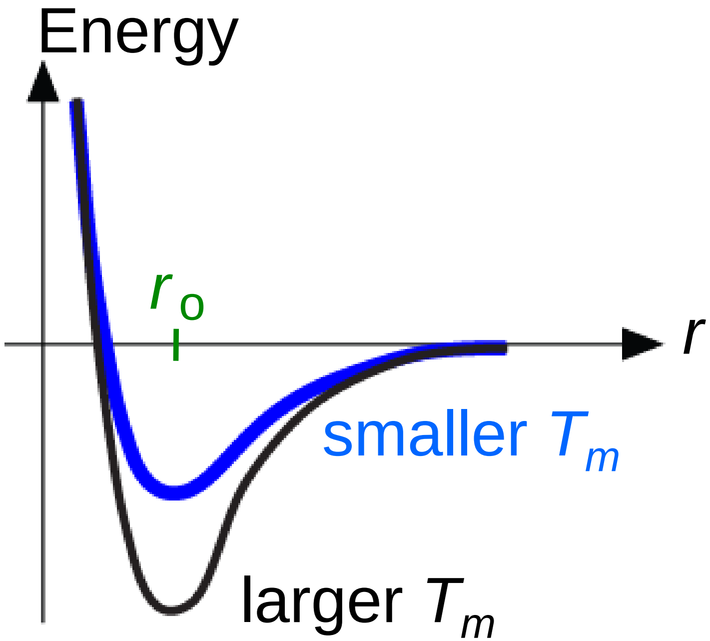
- Bond length, r



- Bond energy, E_o



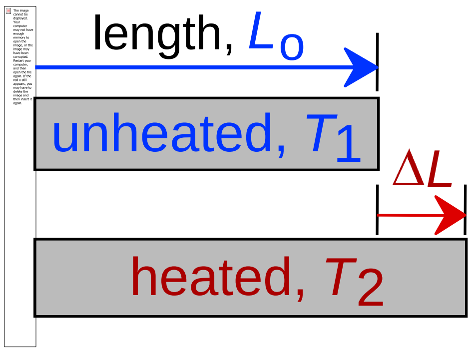
- Melting Temperature, T_m



T_m is larger if E_o is larger.

Properties From Bonding : α

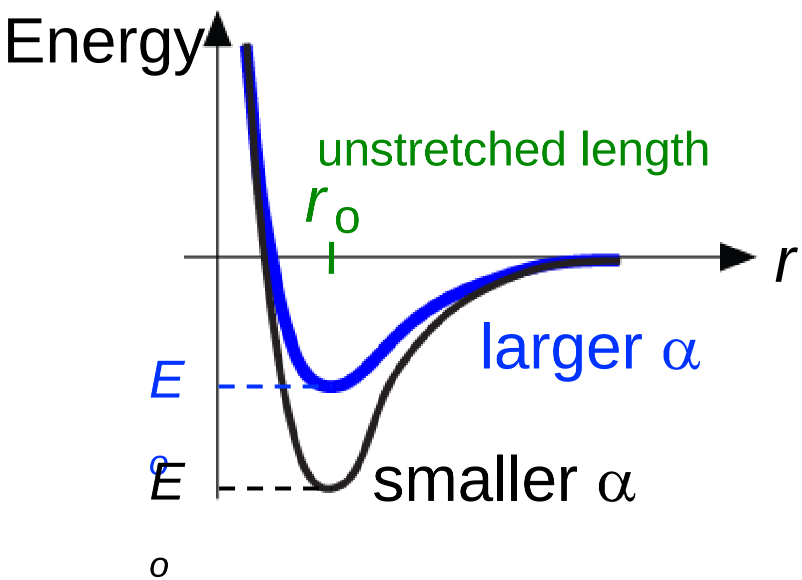
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetric at r_o



α is larger if E_o is smaller.

Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m

large E

small α

Metals

(Metallic bonding):

Variable bond energy

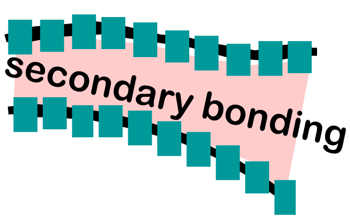
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m

small E

large α