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 } 1.67×10^{-27} kg
  neutrons }

- atomic number = # of protons in nucleus of atom
  = # of electrons in 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 = 1 g/mol

C 12.011
H 1.008 etc.

Atomic Structure

- Some of the following properties
    1) Chemical
    2) Electrical
    3) Thermal
    4) Optical

  are determined by electronic structure

Electronic Structure

- Electrons have wavelike and particulate properties.
- Two of the wavelike characteristics are
  - 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 ($-\ell$ to $+\ell$)
m_s = spin	½, -½

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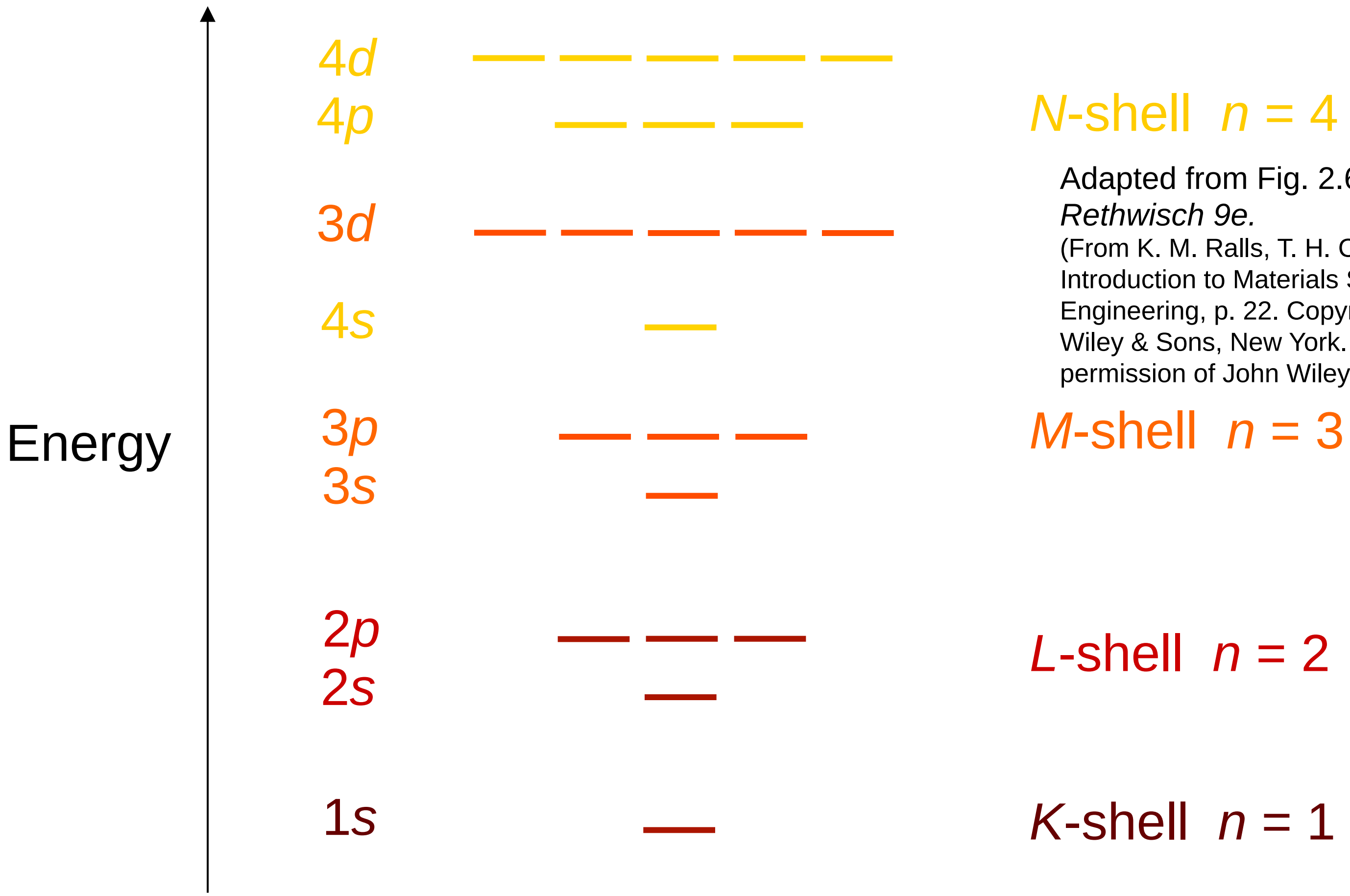
Electron Energy States

Electrons...

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



Adapted from Fig. 2.6, *Callister & Rethwisch 9e.*
(From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

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 9e.*

- 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)

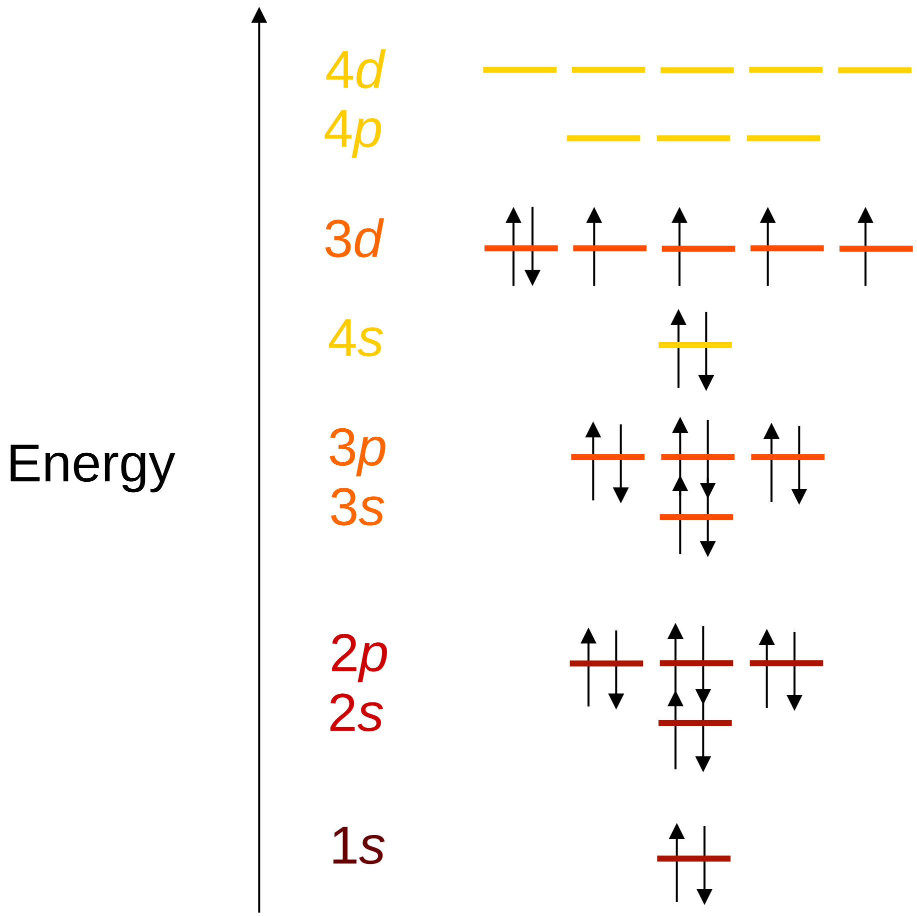
$1s^2$ $2s^2$ $2p^2$

valence electrons

Electronic Configurations

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

valence electrons



N-shell *n* = 4

Adapted from Fig. 2.6, *Callister & Rethwisch 9e.*
(From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

M-shell *n* = 3

L-shell *n* = 2

K-shell *n* = 1

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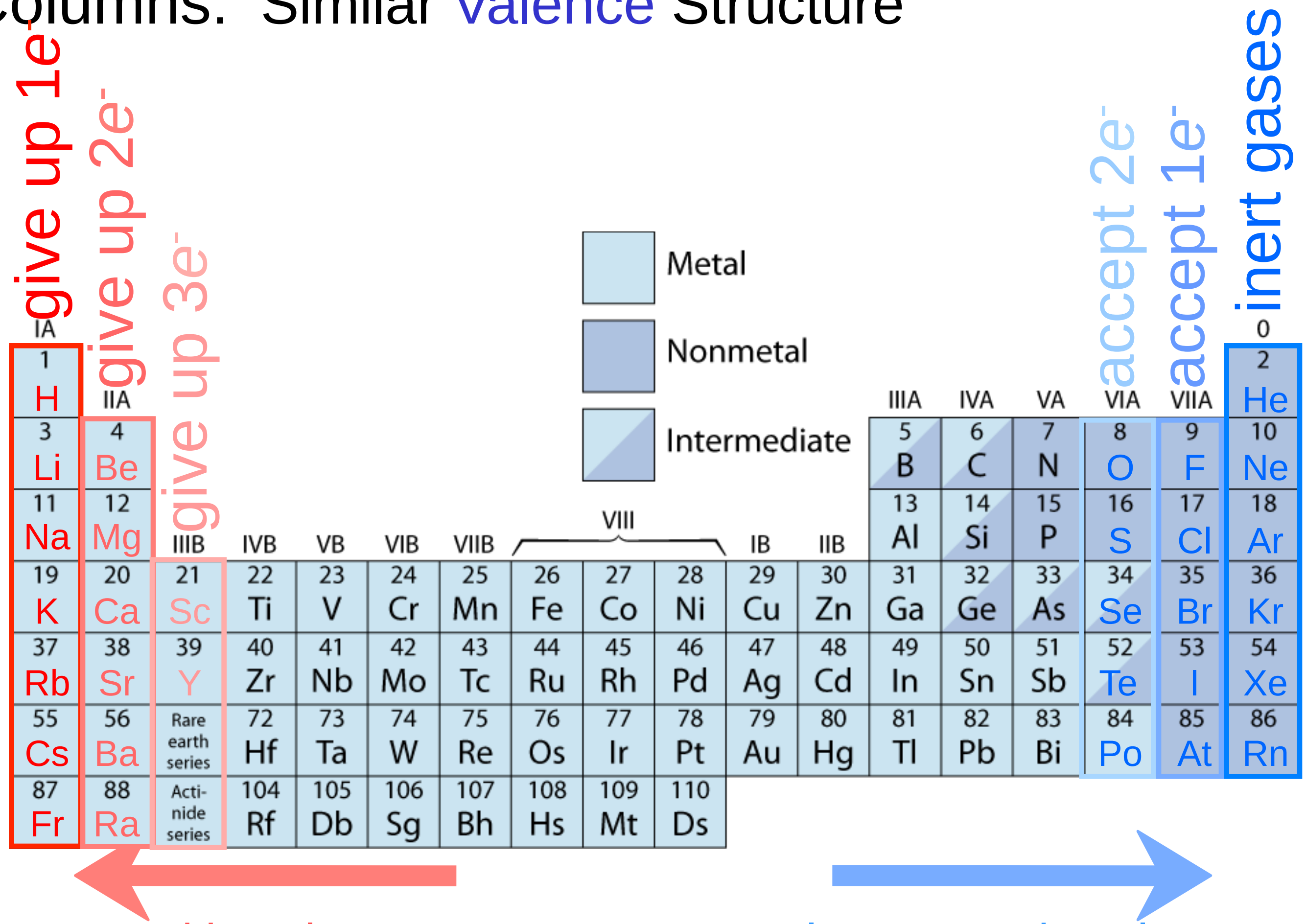
The Periodic Table

- Columns: Similar Valence Structure



Adapted from Fig. 2.8, *Callister & Rethwisch 9e.*

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

Electronegative elements: Readily acquire electrons to become - ions.

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Electronegativity

- Ranges from 0.9 to 4.1,
- 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 3.1	O 3.5	F 4.1	Ne –
Na 1.0	Mg 1.3											Al 1.5	Si 1.8	P 2.1	S 2.4	Cl 2.9	Ar –
K 0.9	Ca 1.1	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.8	Kr –
Rb 0.9	Sr 1.0	Y 1.1	Zr 1.2	Nb 1.3	Mo 1.3	Tc 1.4	Ru 1.4	Rh 1.5	Pd 1.4	Ag 1.4	Cd 1.5	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2	Xe –
Cs 0.9	Ba 0.9	La 1.1	Hf 1.2	Ta 1.4	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.5	Au 1.4	Hg 1.5	Tl 1.5	Pb 1.6	Bi 1.7	Po 1.8	At 2.0	Rn –
Fr 0.9	Ra 0.9	Ac 1.0															

Lanthanides: 1.0-1.2

Actinides: 1.0-1.2

Smaller electronegativity

Larger electronegativity

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

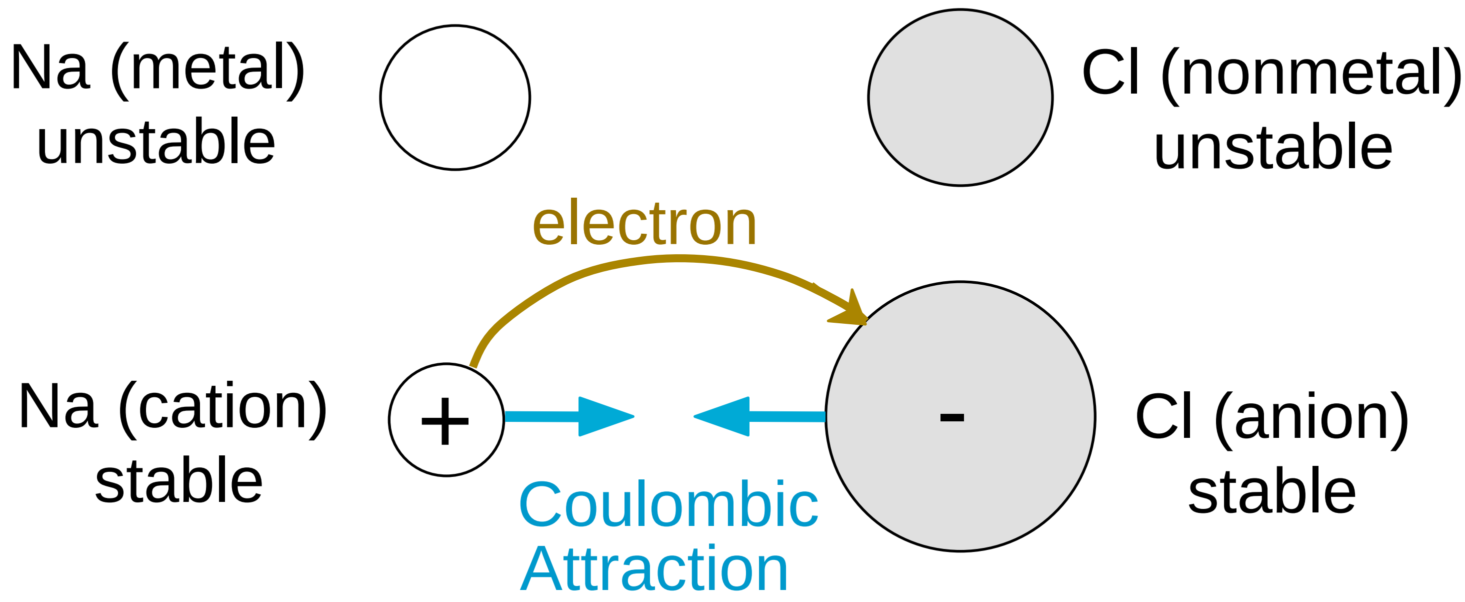
[Ne]

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

[Ne]

Ionic Bonding

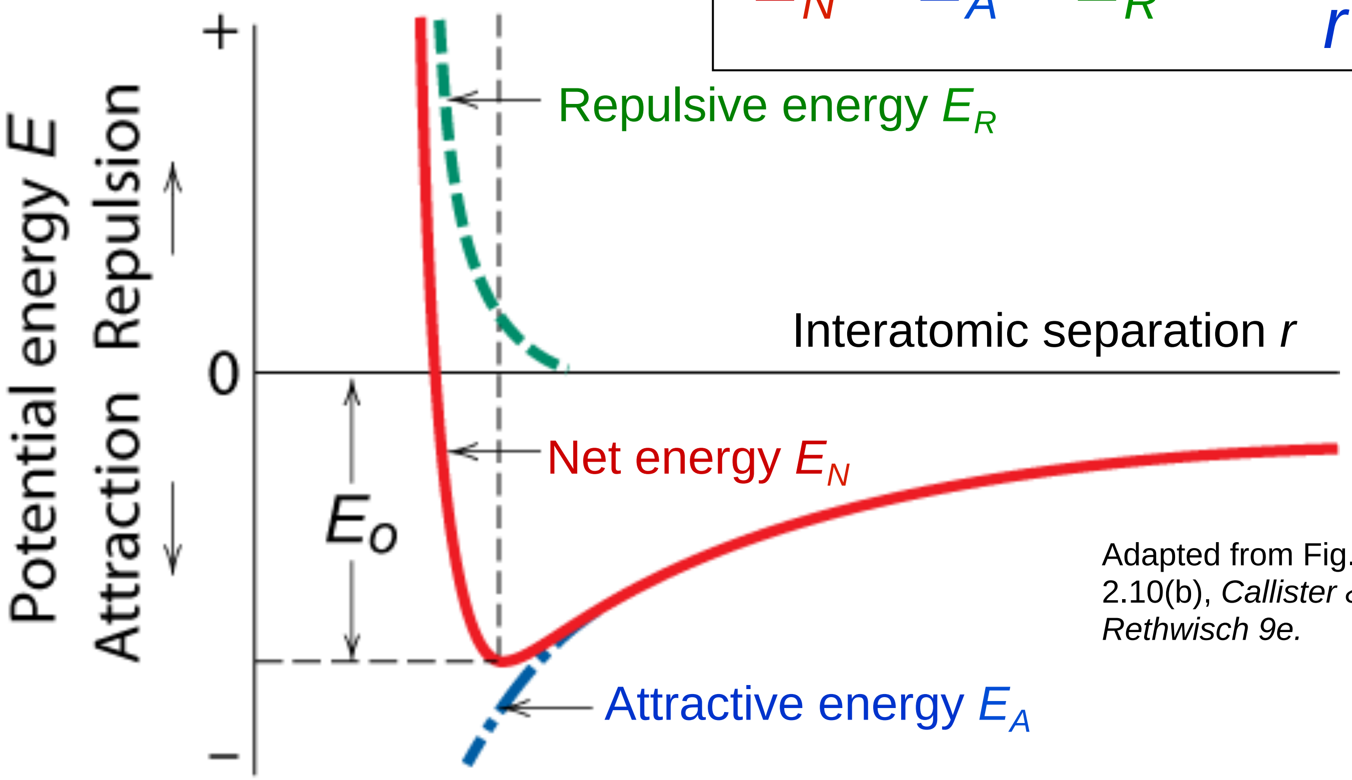
- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



Ionic Bonding

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

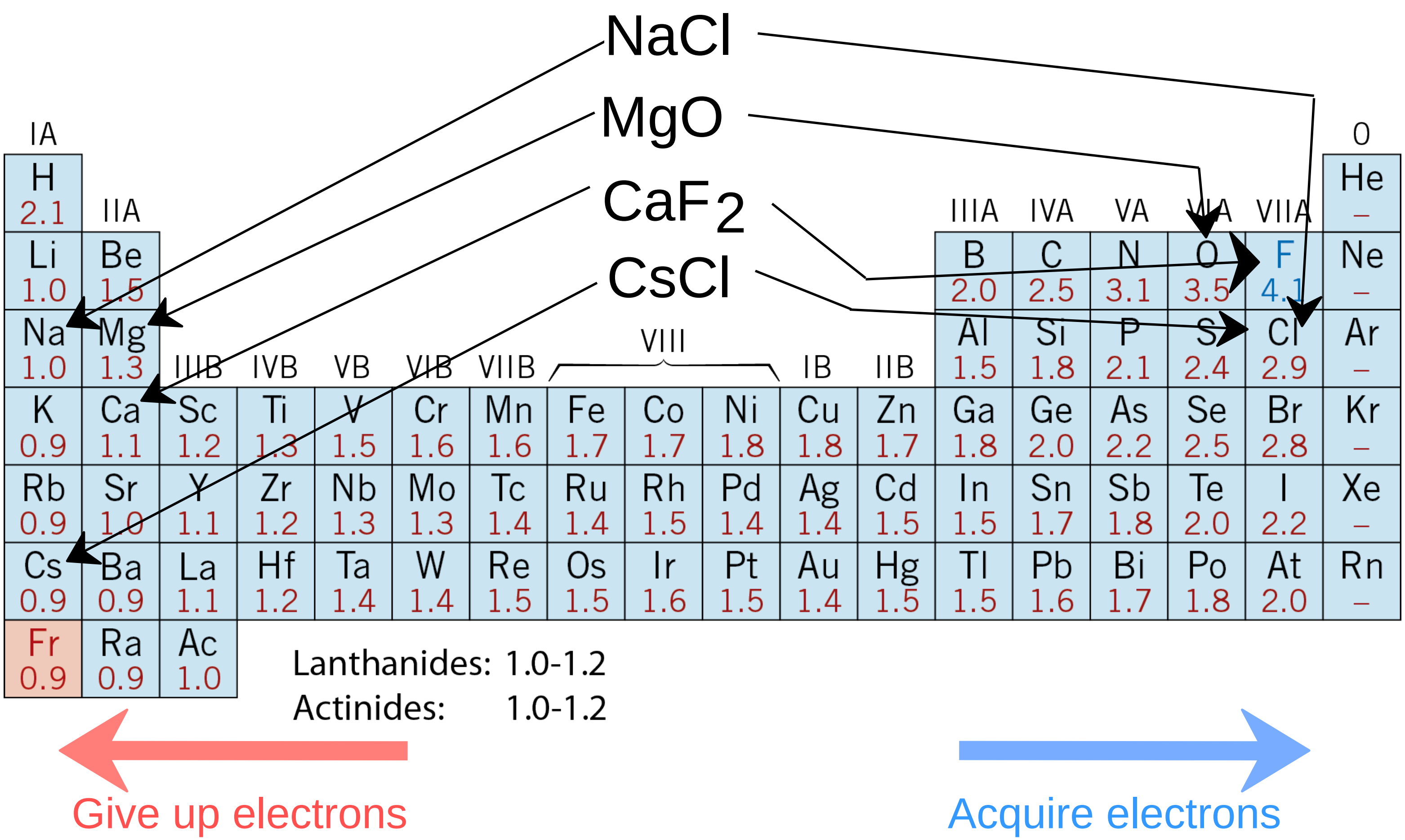
$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$



Adapted from Fig. 2.10(b), *Callister & Rethwisch 9e.*

Examples: Ionic Bonding

- Predominant bonding in Ceramics



Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: H_2

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

Electronegativities
are the same.

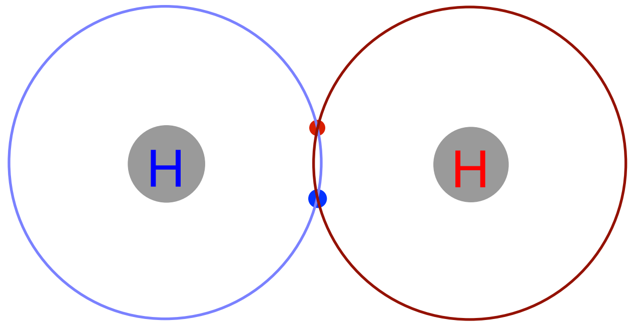


Fig. 2.12, *Callister & Rethwisch 9e.*

Bond Hybridization

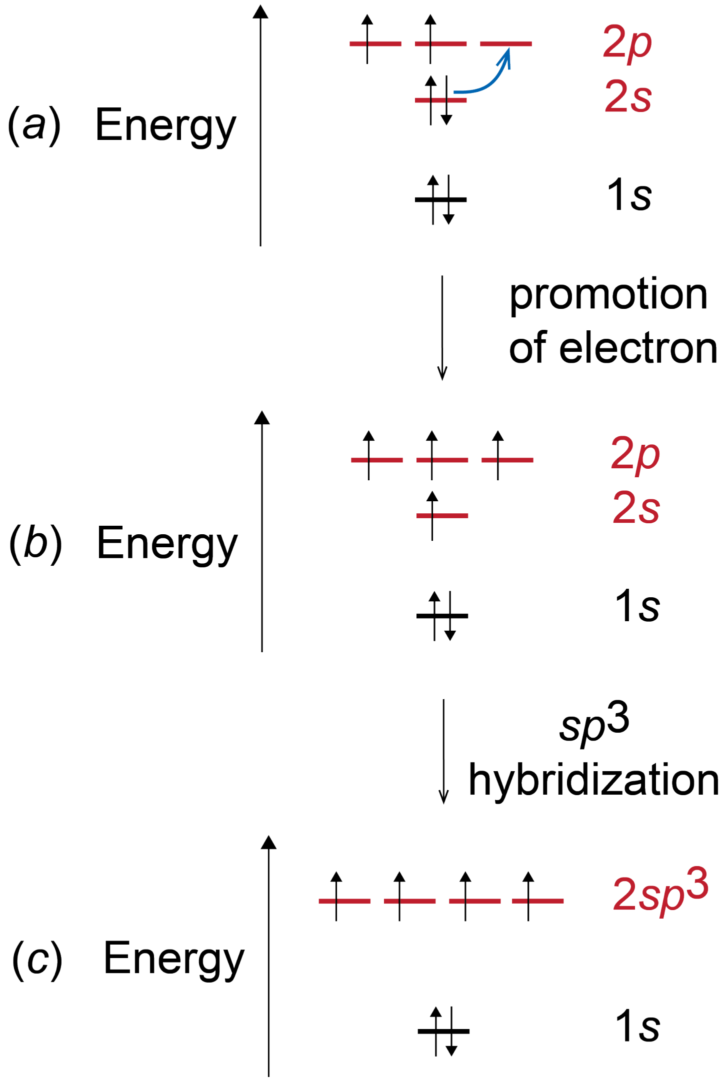


Fig. 2.13, *Callister & Rethwisch 9e.*

- Carbon can form *sp*^{3} hybrid orbitals

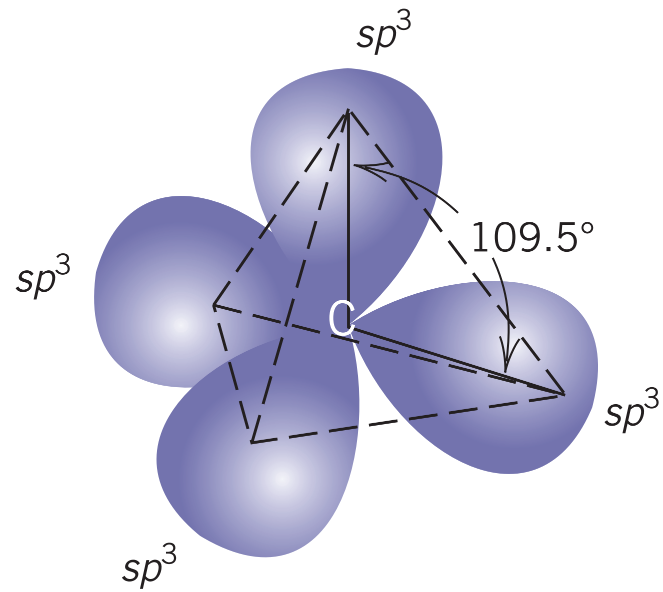


Fig. 2.14, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Covalent Bonding: Carbon *sp*^{3}

- Example: CH_4

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

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

Electronegativities of C and H are comparable so electrons are shared in covalent bonds.

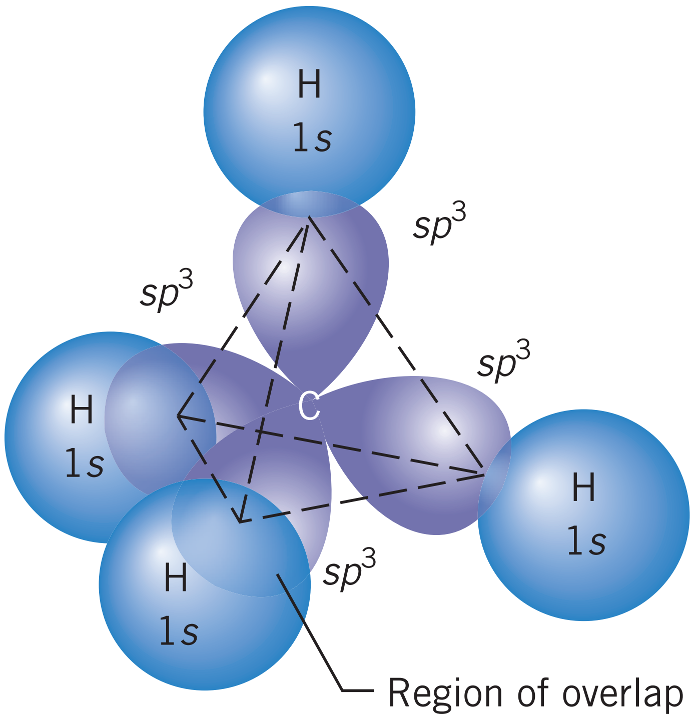


Fig. 2.15, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Primary Bonding

- Metallic Bond -- delocalized as electron cloud

- Ionic-Covalent Mixed Bonding

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

where X_A & X_B are Pauling electronegativities

Ex: MgO $\quad X_{Mg} = 1.3$

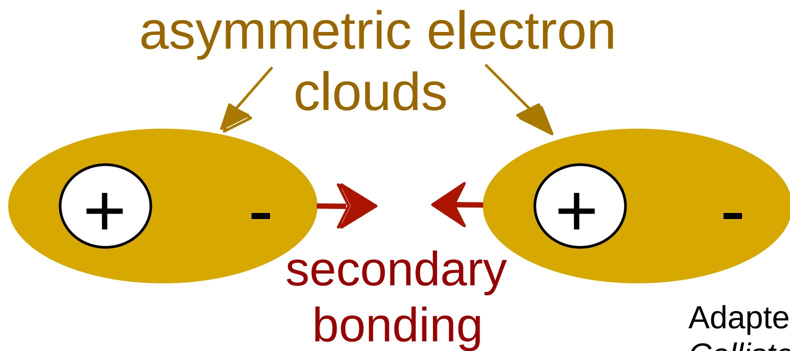
$X_O = 3.5$

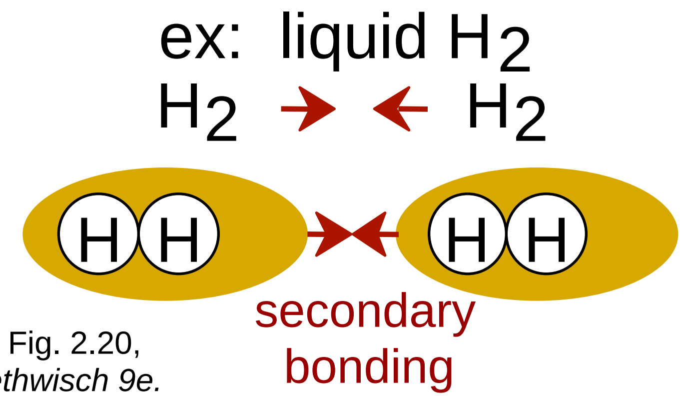
$$\% \text{ ionic character} = \left(1 - e^{-\frac{(3.5-1.3)^2}{4}}\right) \text{x} \, (100\%) = 70.2\% \text{ ionic}$$

Secondary Bonding

Arises from interaction between dipoles

- Fluctuating dipoles





Adapted from Fig. 2.20, *Callister & Rethwisch 9e.*

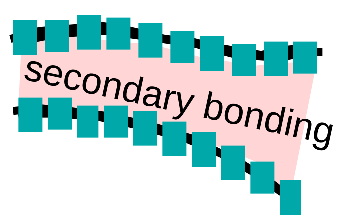
- Permanent dipoles-molecule induced

-general case:

-ex: liquid HCl

Adapted from Fig. 2.22, *Callister & Rethwisch 9e.*

-ex: polymer



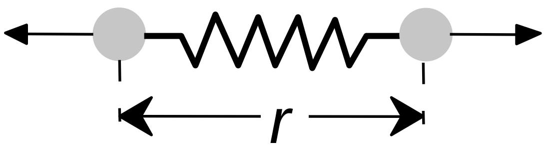
secondary bonding

Summary: Bonding

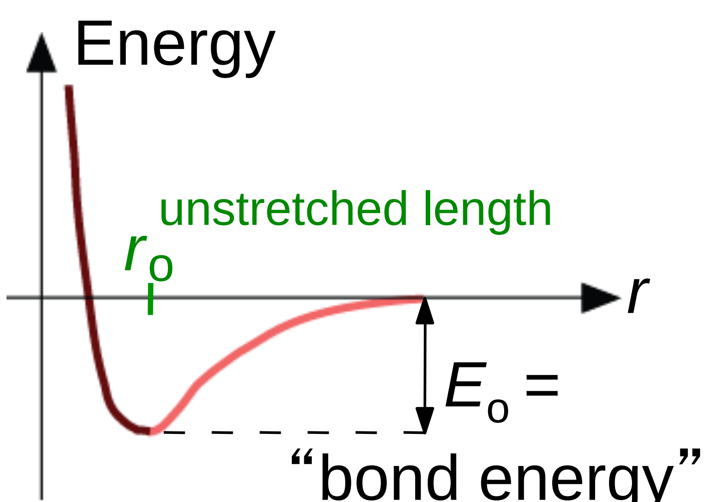
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

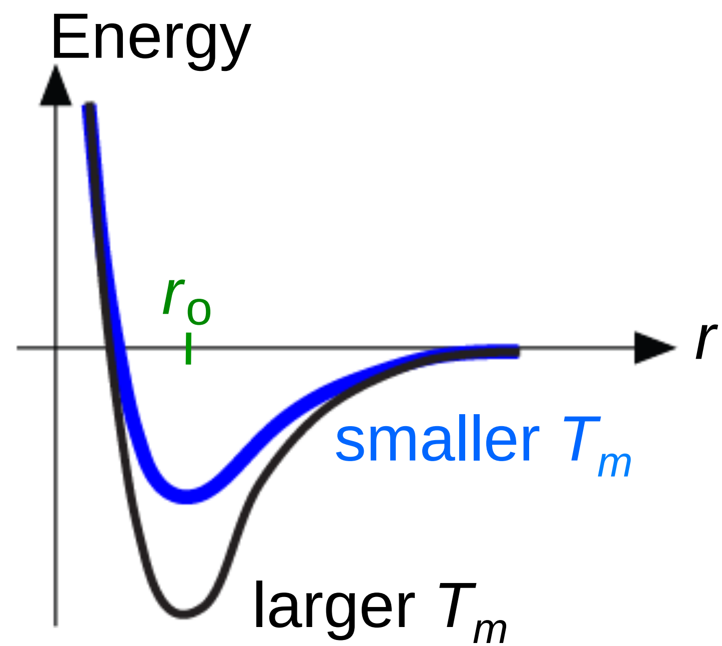
- Bond length, r



- Bond energy, E_o



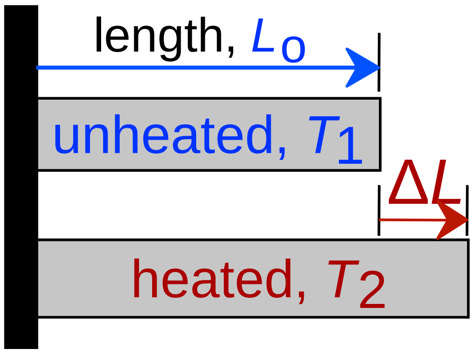
- Melting Temperature, T_m



T_m is larger if E_o is larger.

Properties From Bonding: α

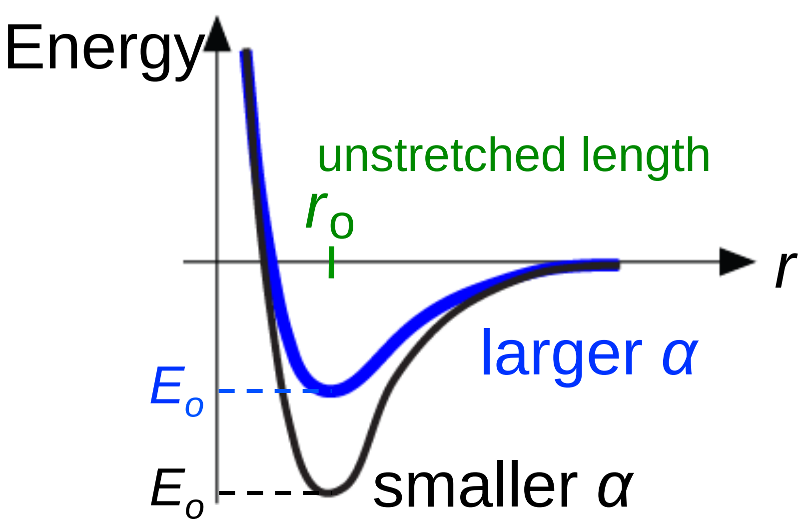
- Coefficient of thermal expansion, α



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

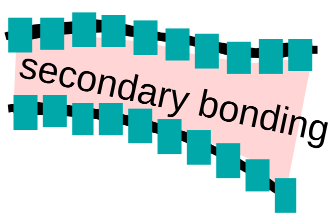
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m

small E

large α

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: