Oct. 6, 2021

Bio-integrated Materials Science (Online Lectures)

Atomic Structure & Interatomic Bonding
Lecture 1-2

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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 – [ ] kg
  protons, neutrons } [ ] kg

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

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

  A (atomic weight) = ***Z*** (atomic number) +
  N *(number of neutrons)*

C	12.011
H	1.008 etc.

Schematic representation of the Bohr atom

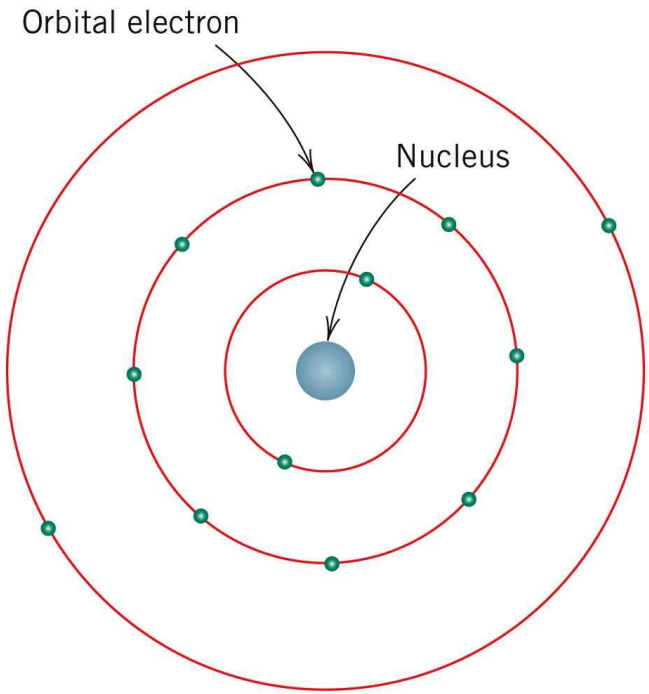


Figure 2.1

The first three electron energy states of Bohr atom

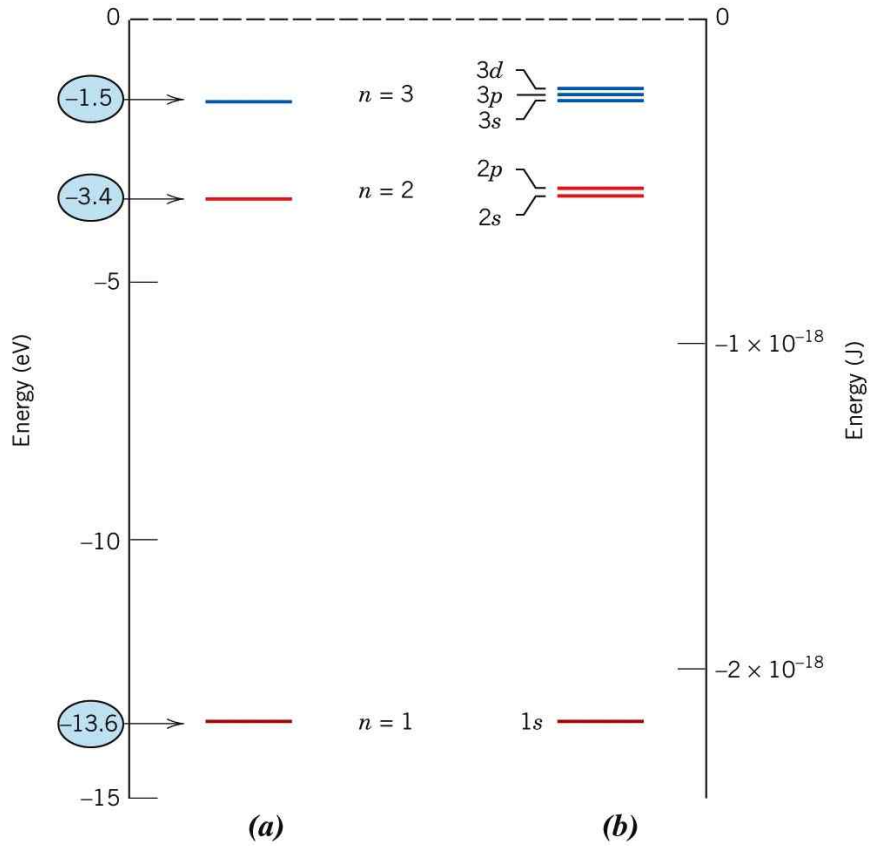


Figure 2.2

Electron Energy States

Electrons...

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

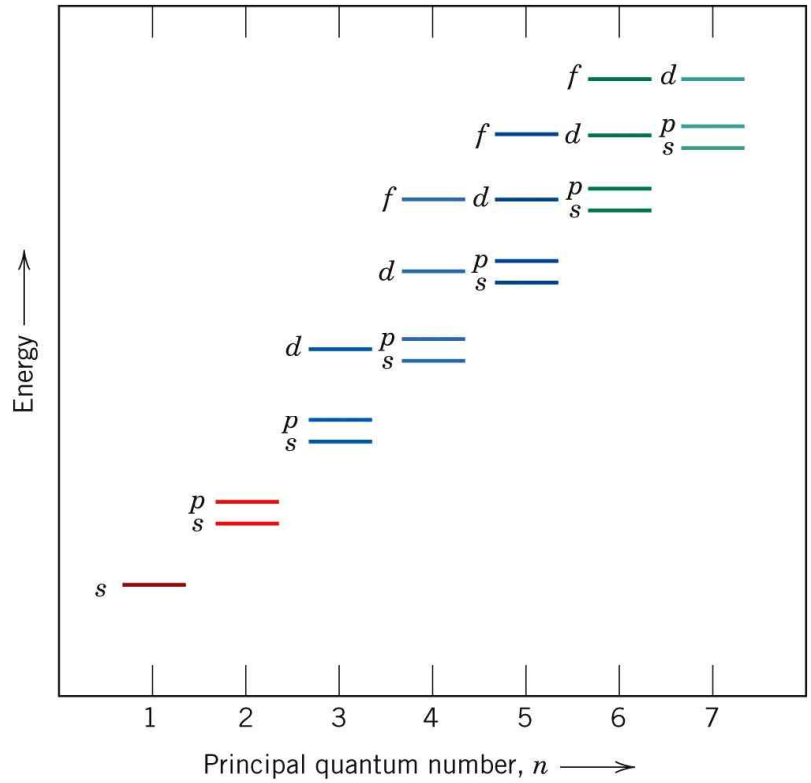


Figure 2.4

Electron configuration of a Na atom

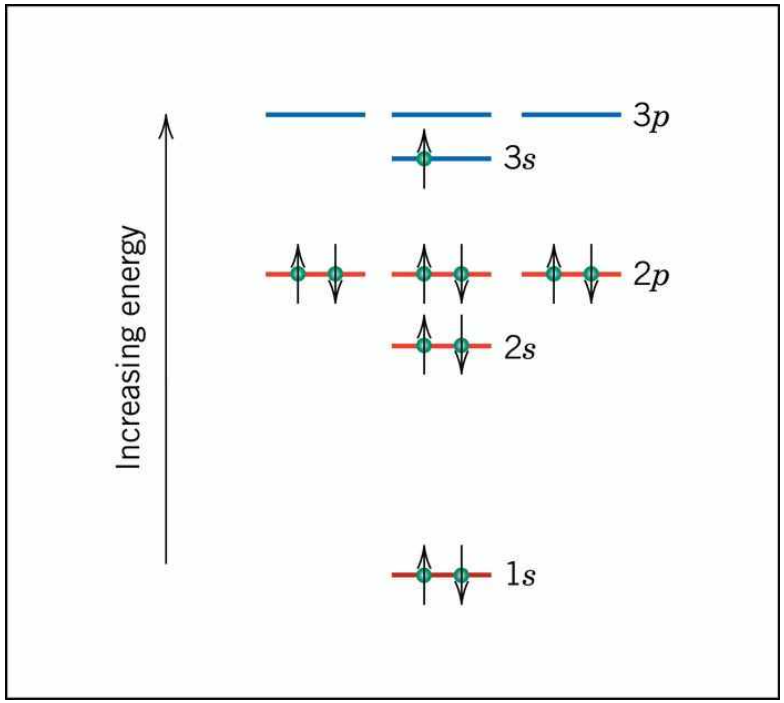


Table 2.2
Expected Electron Configurations for Some Common Elements[a]

Element	*Symbol*	*Atomic Number*	*Electron Configuration*
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
Gallium	Ga	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Arsenic	As	33	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
Selenium	Se	34	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Krypton	Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

[a]When some elements covalently bond, they form *sp* hybrid bonds. This is especially true for C, Si, and Ge.

Table 2.2

Survey of elements

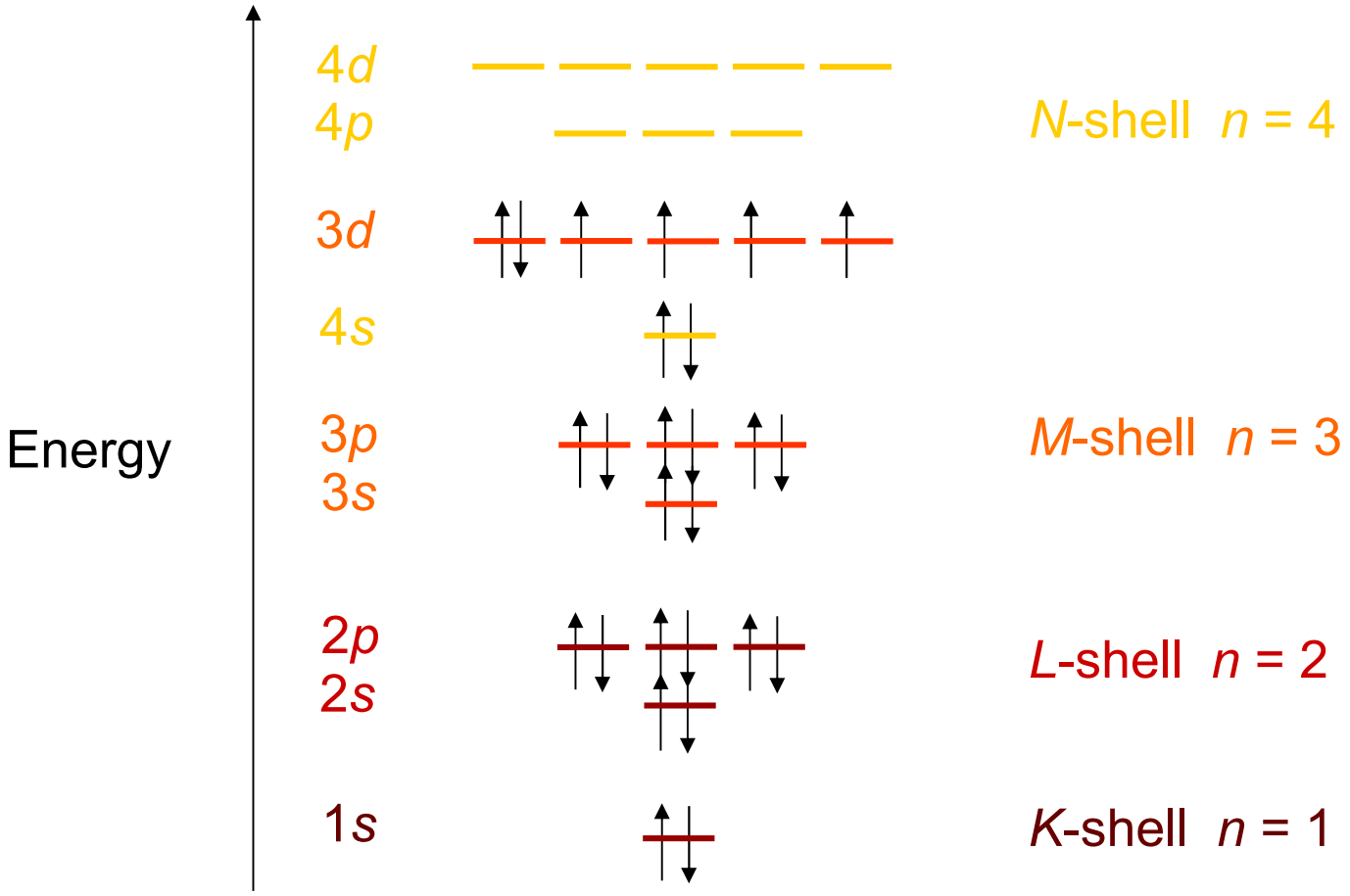
- Most elements: Electron configuration not stable.

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)

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

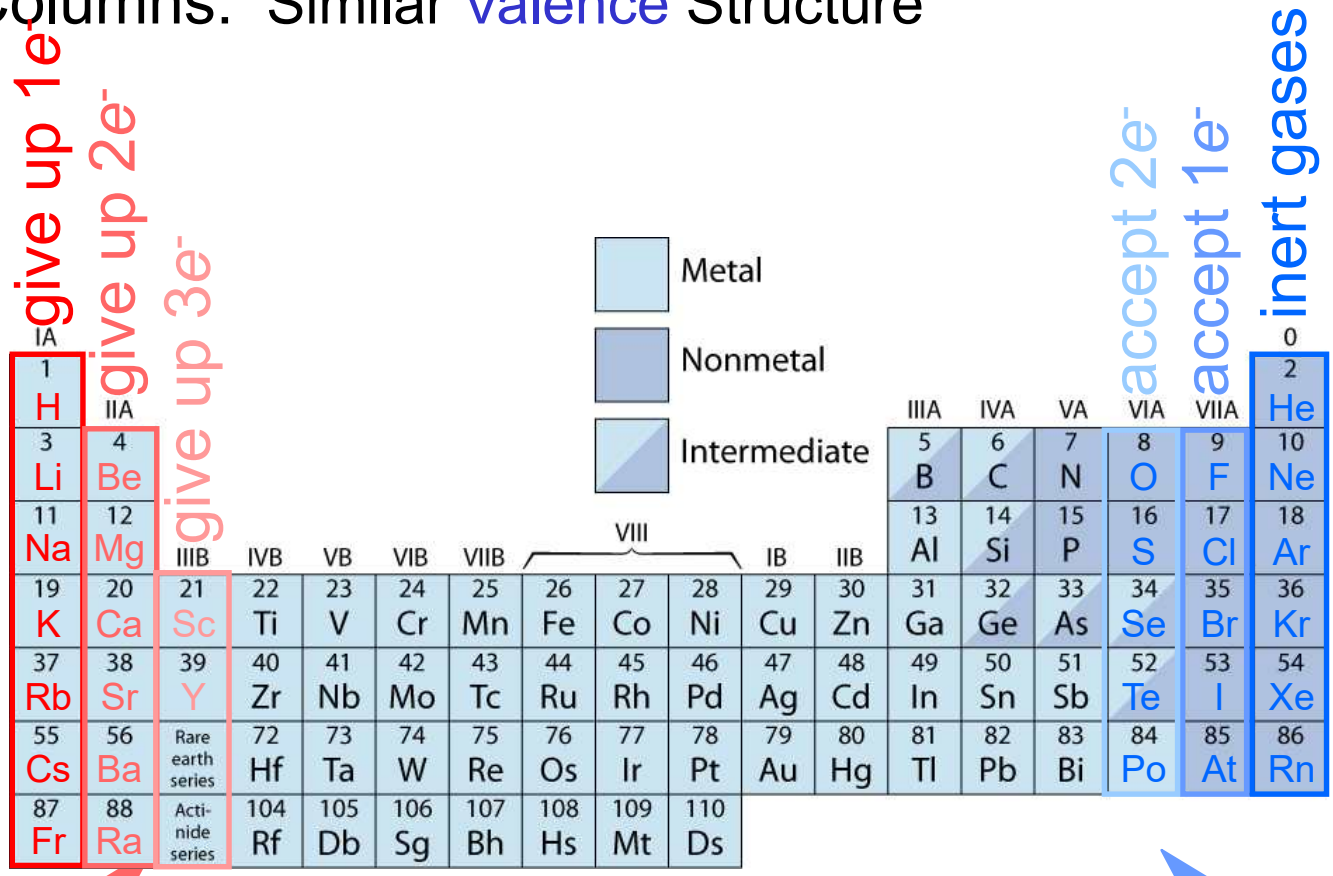
Electronic Configurations

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



The Periodic Table

- Columns: Similar Valence Structure



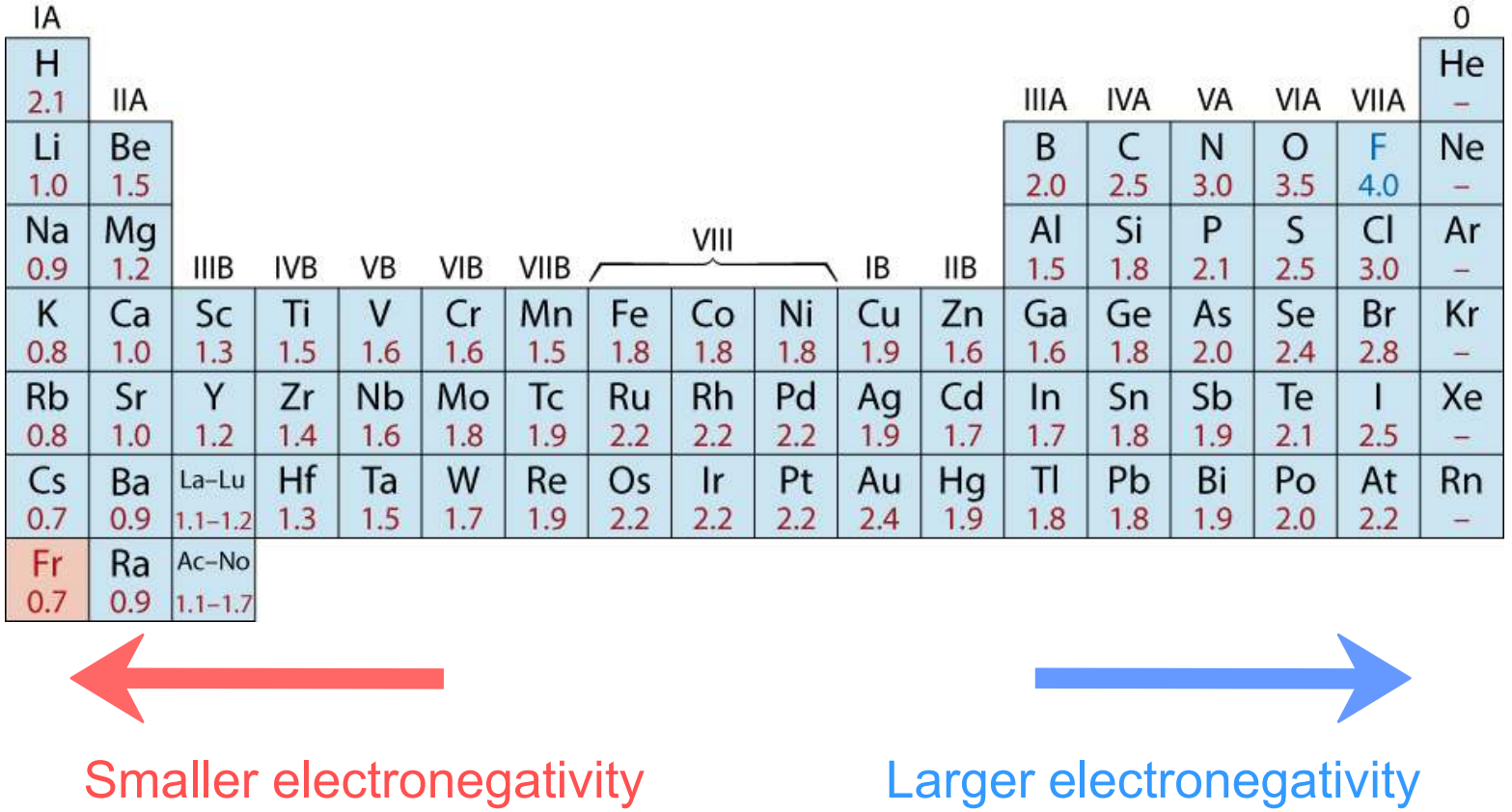
Adapted from Fig. 2.6, *Callister & Rethwisch 4e.*

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

Electronegative elements:
Readily acquire electrons
to become - ions.

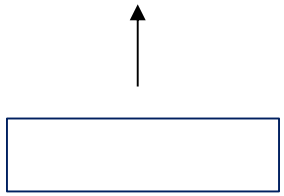
Electronegativity

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



Adapted from Fig. 2.7, *Callister & Rethwisch 4e.* (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.

Ionic bond – metal + nonmetal



electrons

accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

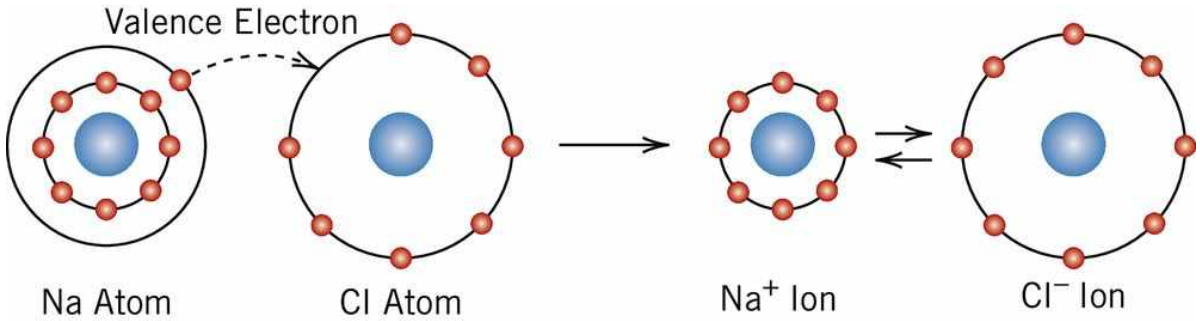
O $1s^2\ 2s^2\ 2p^4$

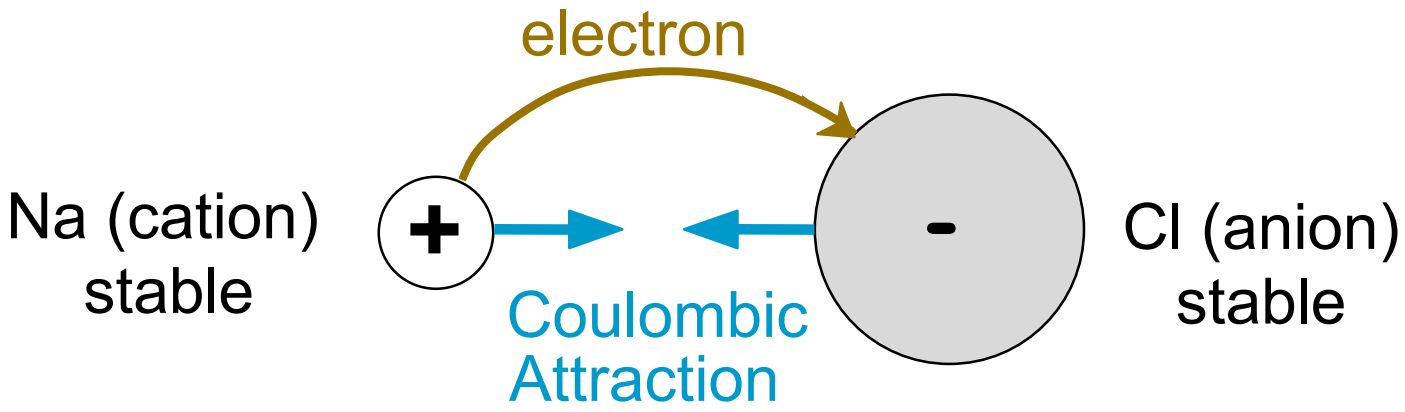
Mg^{2+} $1s^2\ 2s^2\ 2p^6$ or [Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$ or [Ne]

Ionic Bonding

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





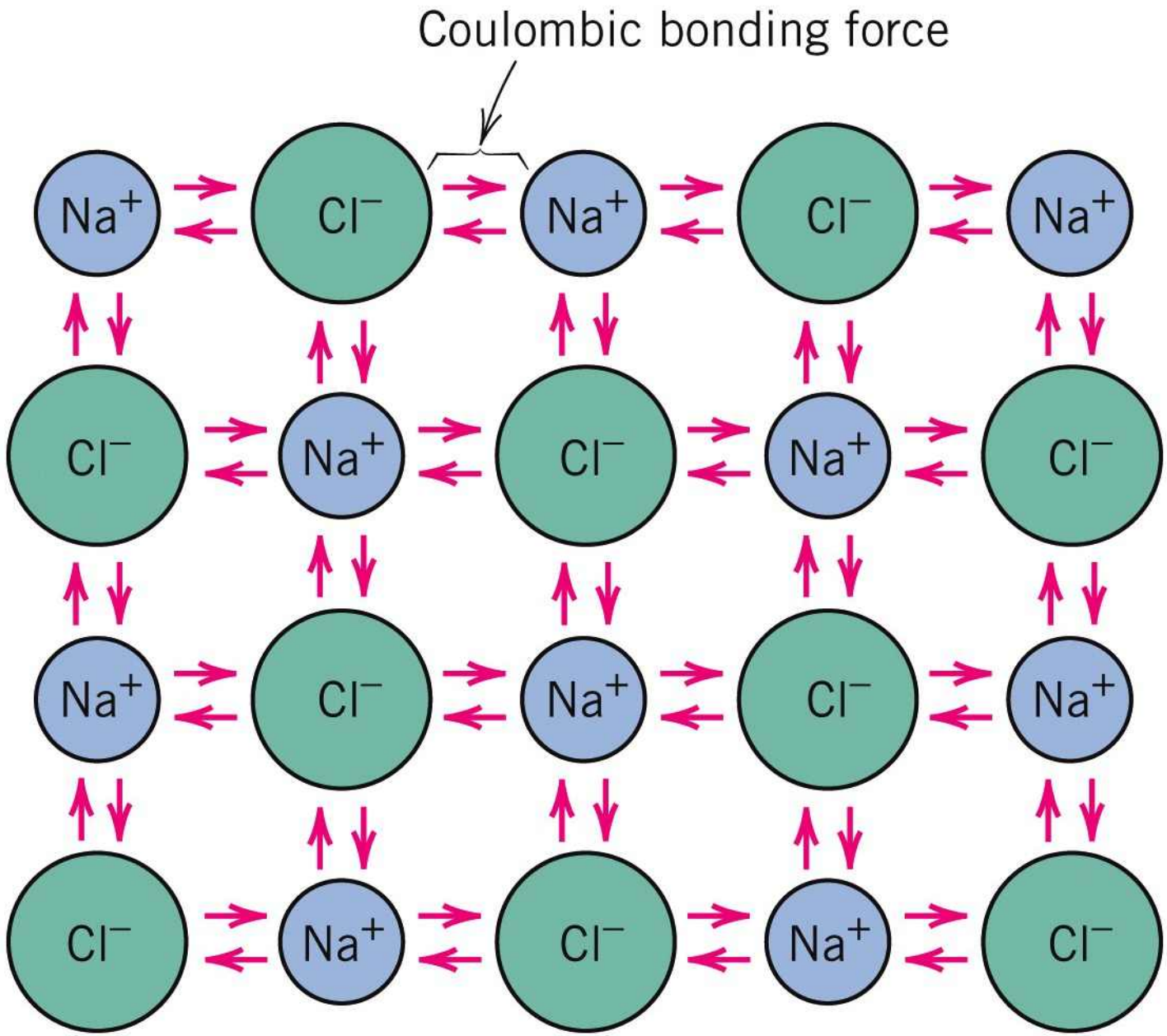


Figure 2.9

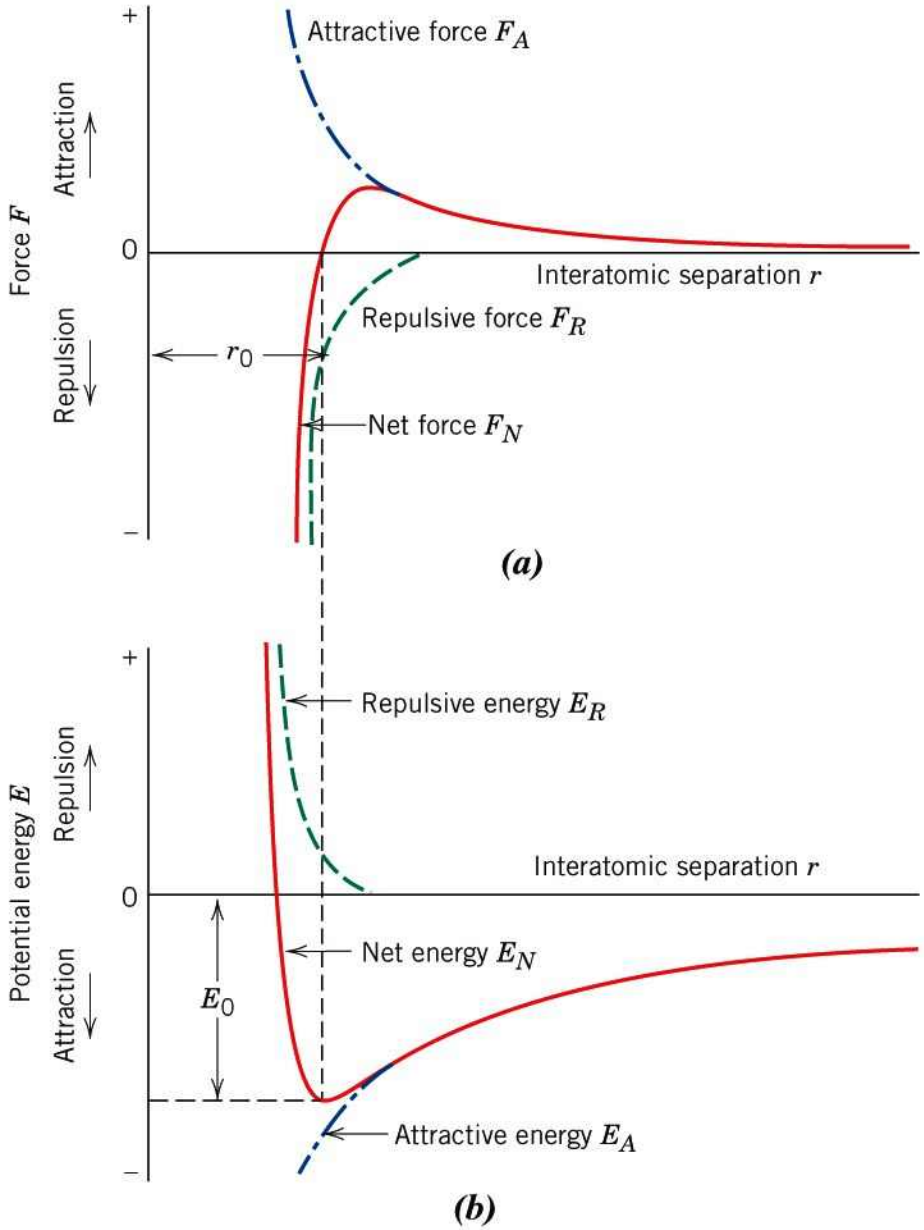
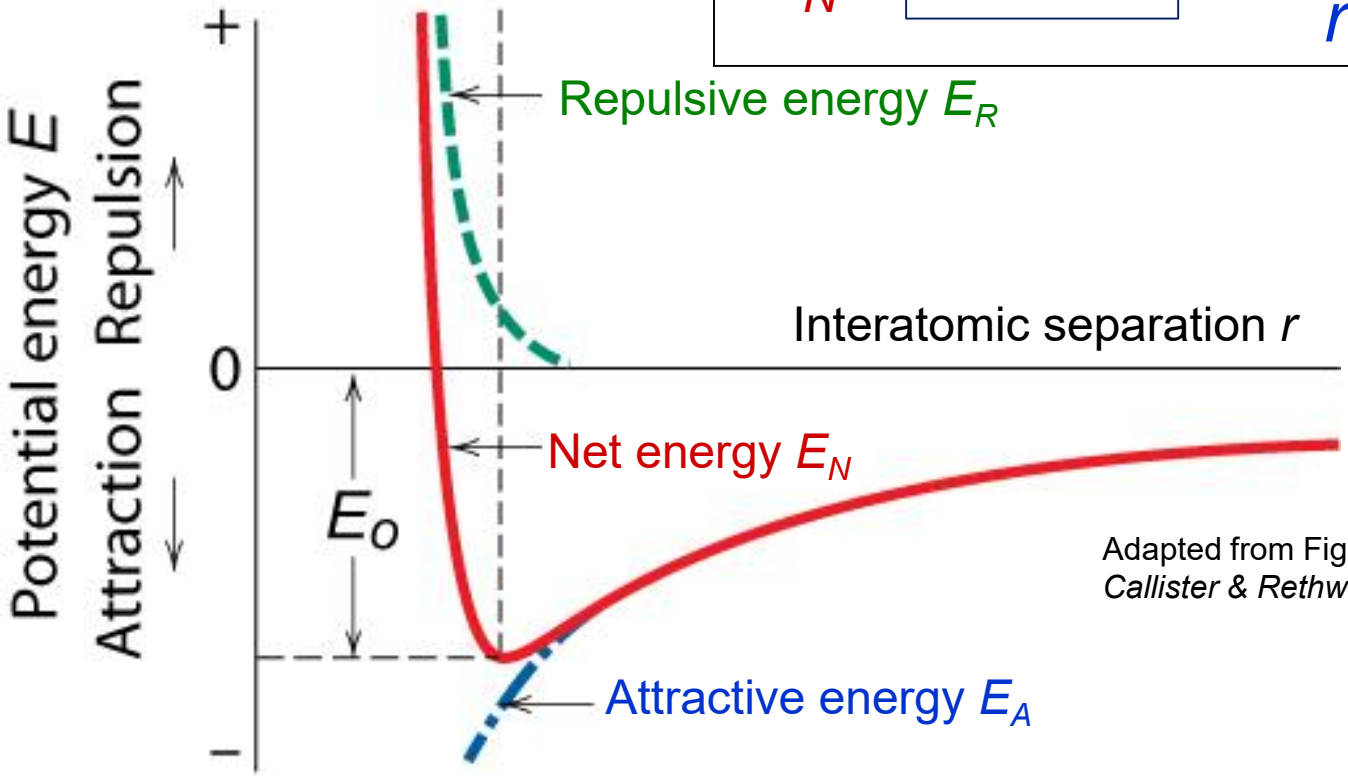


Figure 2.8

Ionic Bonding

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

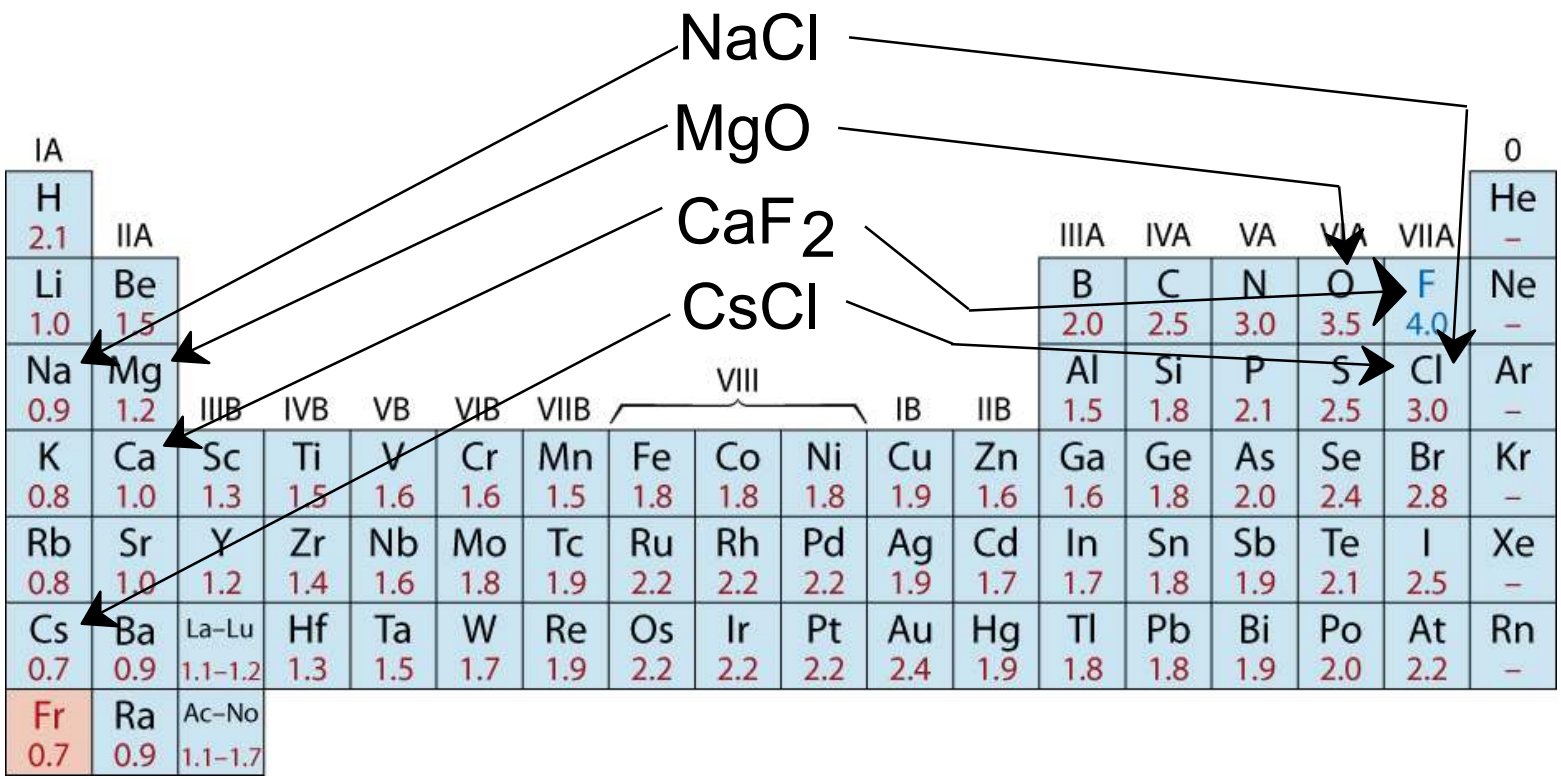
$$E_N = \boxed{} = -\frac{A}{r} + \frac{B}{r^n}$$



Adapted from Fig. 2.8(b), *Callister & Rethwisch 4e.*

Examples: Ionic Bonding

- Predominant bonding in

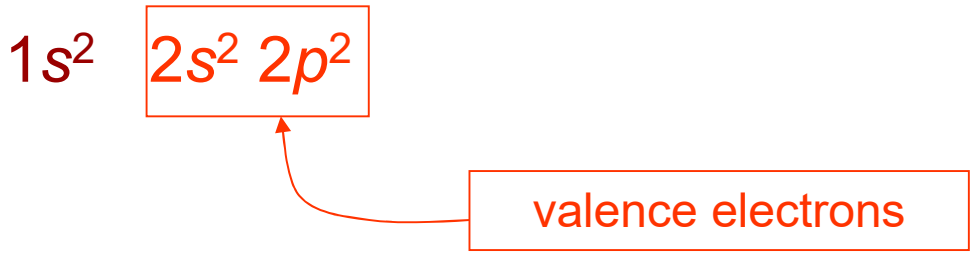


Adapted from Fig. 2.7, *Callister & Rethwisch 4e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Electron Configurations

- [ ] 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)



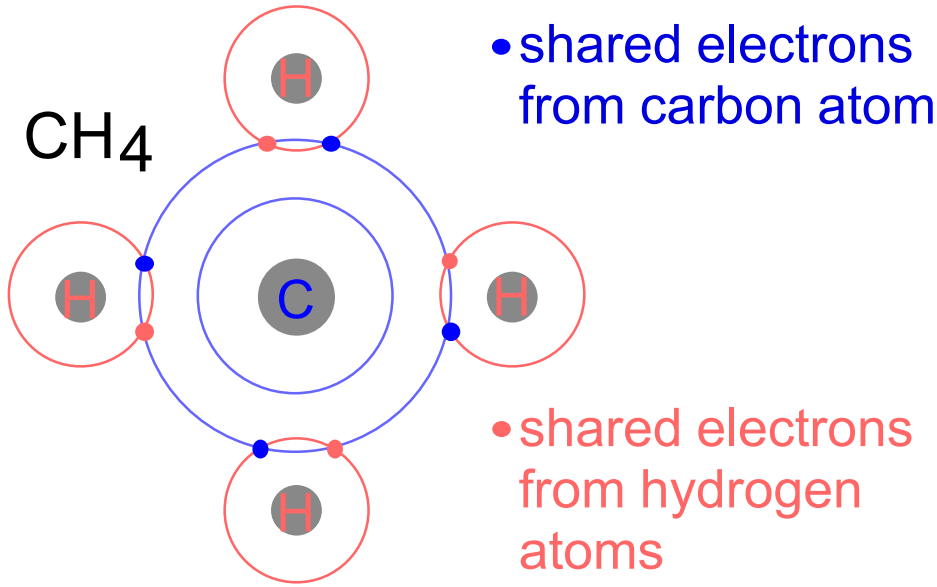
Covalent Bonding

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

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

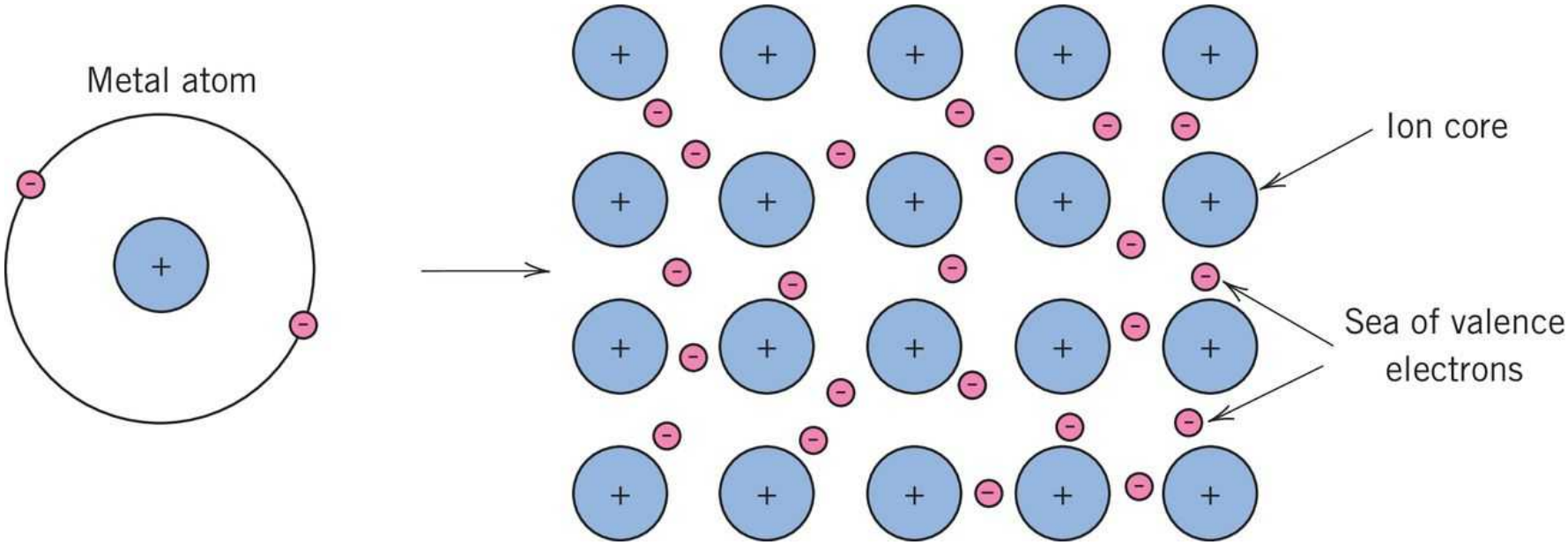
H: has 1 valence e^-, needs 1 more

Electronegativities are comparable.



Adapted from Fig. 2.10, *Callister & Rethwisch 4e.*

Metallic Bonding



Metallic Bonding

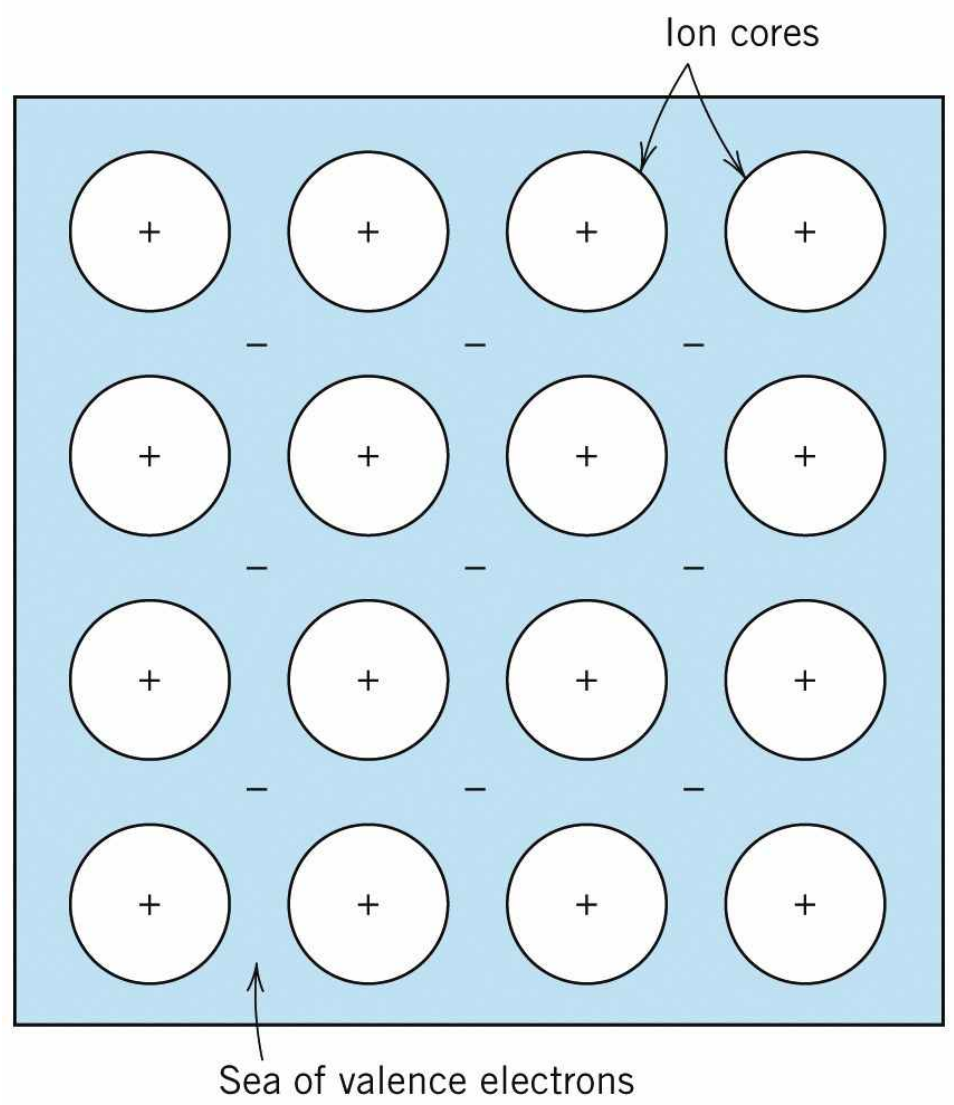


Figure 2.11

Primary Bonding

- Metallic Bond -- delocalized as electron cloud

- Ionic-Covalent Mixed Bonding

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

where X_A & X_B are Pauling electronegativities

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

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

Fluctuating induced dipoles

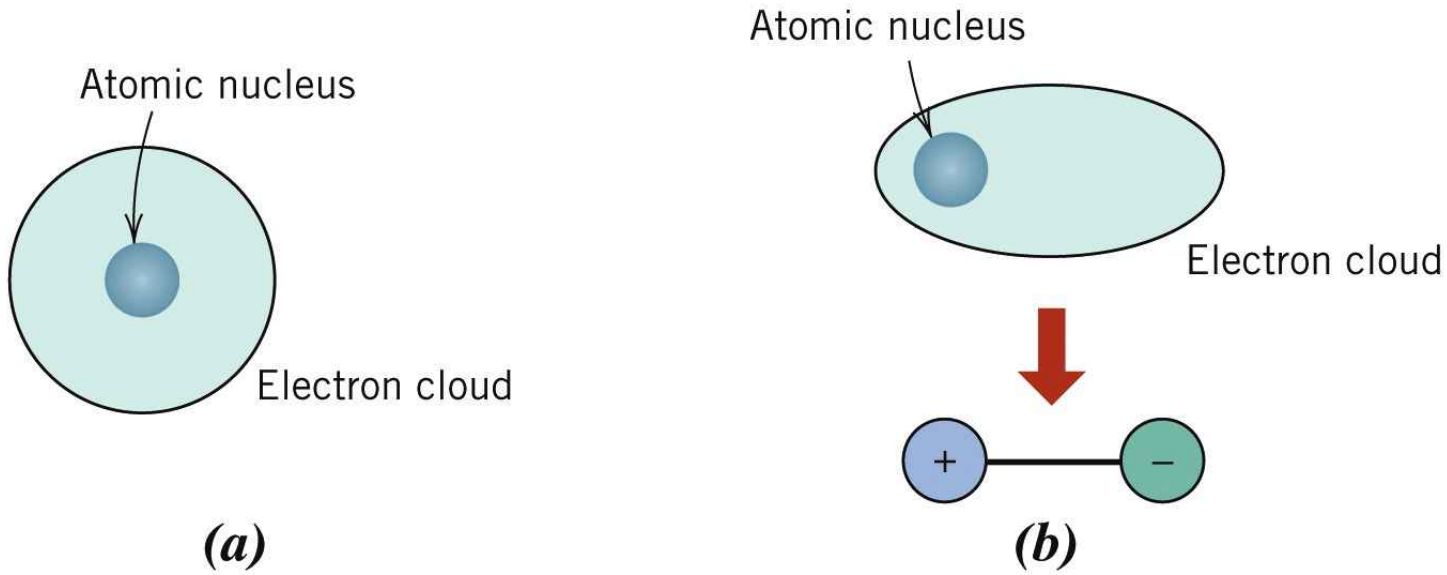


Figure 2.13

Permanent dipoles

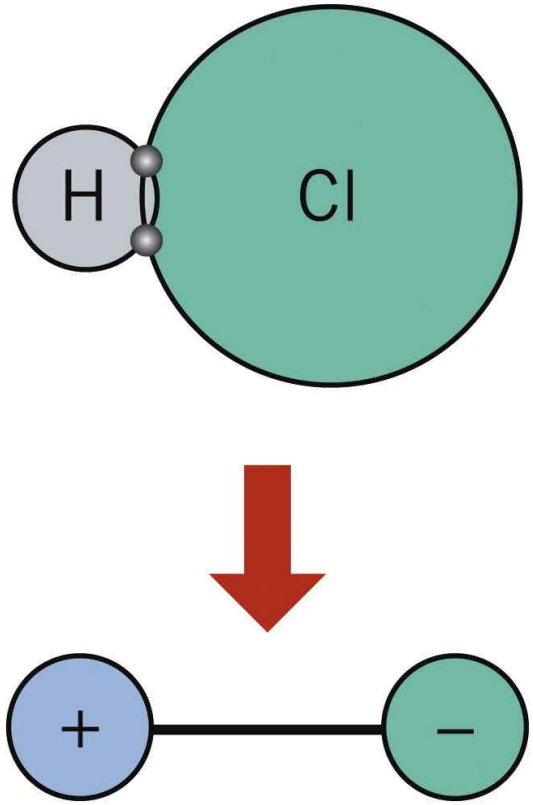
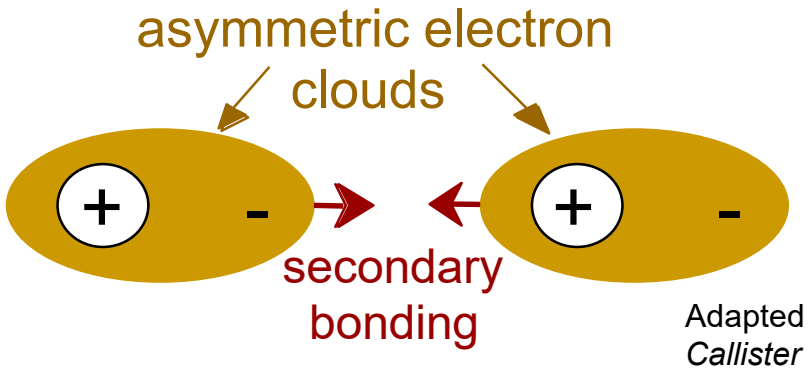


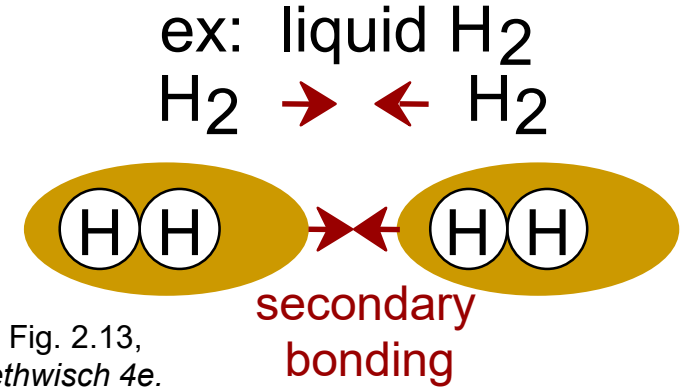
Figure 2.14

SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles





Adapted from Fig. 2.13, *Callister & Rethwisch 4e.*

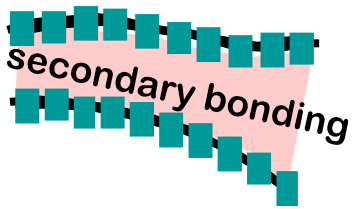
- Permanent dipoles-molecule induced

-general case:

Adapted from Fig. 2.14, *Callister & Rethwisch 4e.*

-ex: liquid HCl

-ex: polymer



secondary bonding

Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	Ionic	
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF_2	1548	1418
	Covalent	
Cl_2	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
	Metallic	
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
	van der Waals[a]	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101
	Hydrogen[a]	
HF	29	−83
NH_3	35	−78
H_2O	51	0

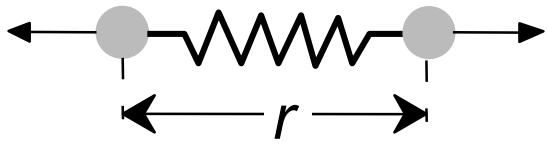
[a]Values for van der Waals and hydrogen bonds are energies *between* molecules or atoms (*inter*molecular), not between atoms within a molecule (*intra*molecular).

Summary: Bonding

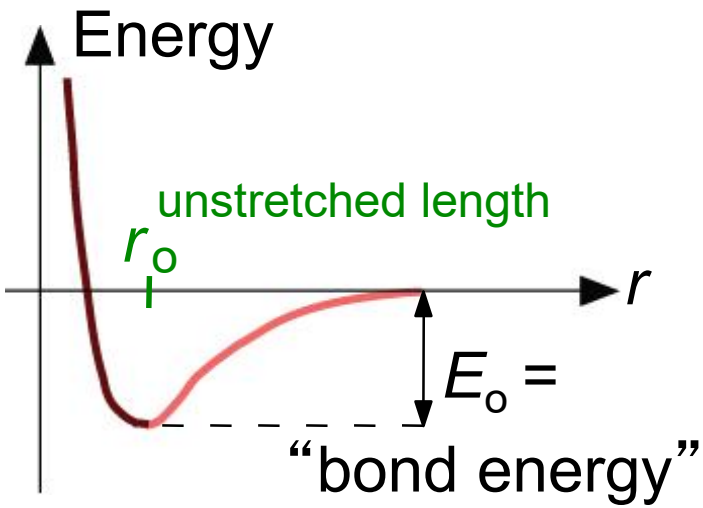
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

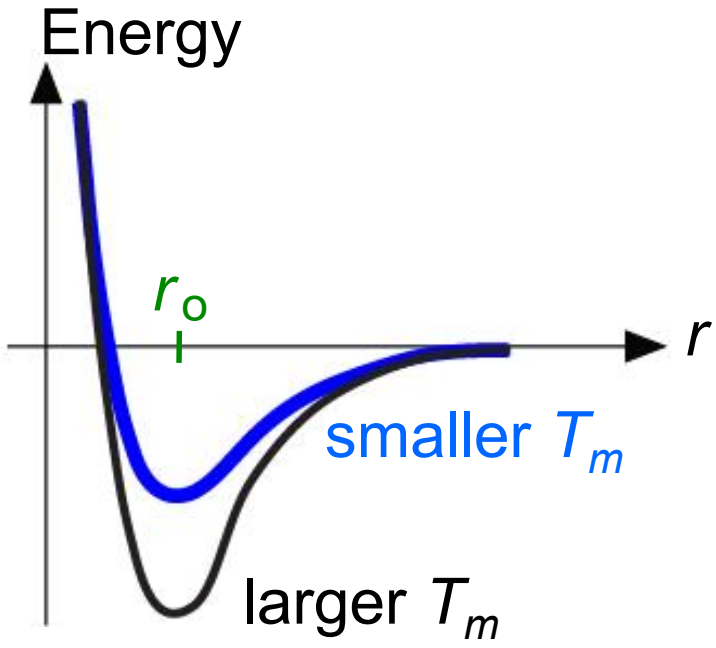
- Bond length, r



- Bond energy, E_o



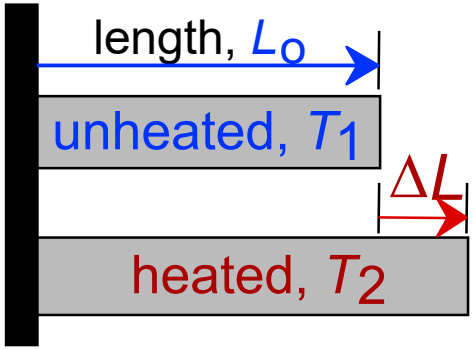
- Melting Temperature, T_m



T_m is [ ] if E_o is larger.

Properties From Bonding : α

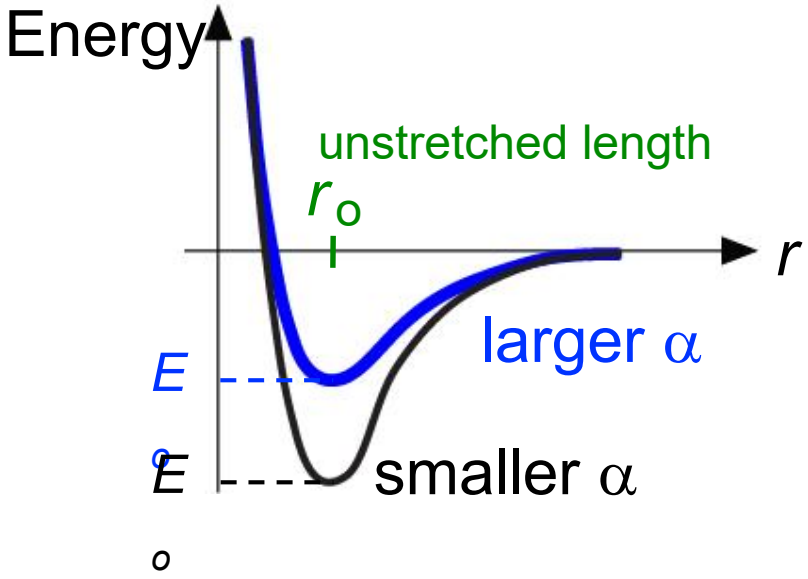
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \boxed{}$$

- α ~ symmetric at r_o



α is [ ] 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

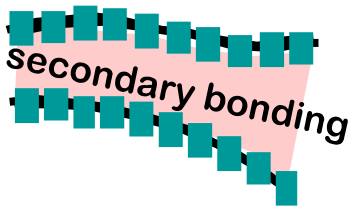
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m

small E

large α