# 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 – $9.11 \times 10^{-31}$ kg
  protons } $1.67 \times 10^{-27}$ kg
  neutrons
- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species
- atomic mass unit = amu = 1/12 mass of $^{12}C$

  Atomic wt = wt of $6.022 \times 10^{23}$ molecules or atoms

  1 amu/atom = 1g/mol

  ex) Fe: 55.85 amu/atom = 55.85 g/mol

  C 12.011
  H 1.008 etc. (1 proton, 0 neutron)

## Quiz

- *Chromium has four naturally-occurring isotopes: 4.34% of $^{50}Cr$, with an atomic weight of 49.9460 amu, 83.79% of $^{52}Cr$, with an atomic weight of 51.9405 amu, 9.50% of $^{53}Cr$, with an atomic weight of 52.9407 amu, and 2.37% of $^{54}Cr$, with an atomic weight of 53.9389 amu. On the basis of these data, confirm that the average atomic weight of Cr is amu.*



## 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.

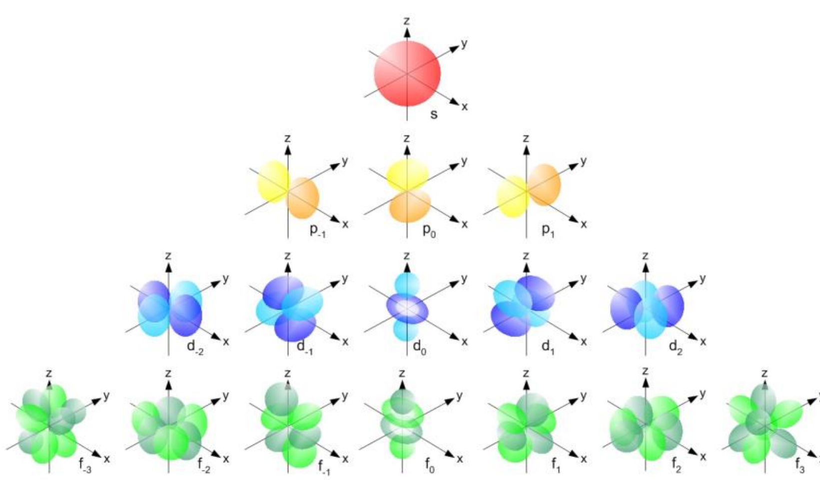
    **double slit experiment :** https://youtu.be/Iuv6hY6zsd0 http://youtu.be/_oWRI-LwyC4

| – Quantum # | Designation |
|---|---|
| $n$ = principal (energy level-shell) | $K$, $L$, $M$, $N$, $O$ (1, 2, 3, etc.) |
| $\ell$ = 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 |

- Particle like characteristics: photoelectric effect
  - a phenomenon where irradiating a blue light on metal emits electrons from it.
  - But not with red light



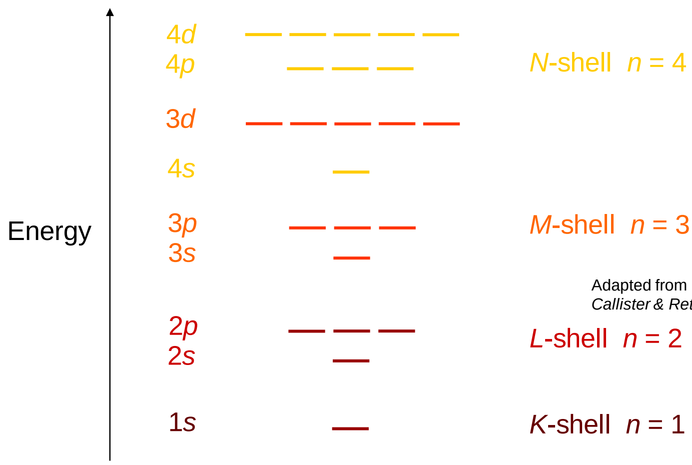
# Orbitals



# Electron Energy States

Electrons...

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




Adapted from Fig. 2.4, *Callister & Rethwisch 4e.*



# 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 4e.*

- 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)

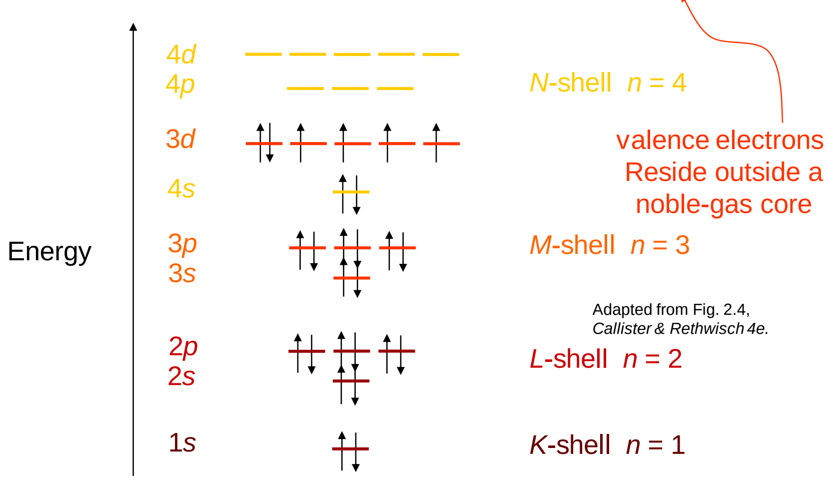
$1s^2$ $\boxed{2s^2\ 2p^2}$

valence electrons



# Electronic Configurations

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




Adapted from Fig. 2.4, *Callister & Rethwisch 4e.*

# quiz

- *Give the electron configurations for the following ions: $Fe^{3+}$, $Ga^{3+}$, $Cr^{+}$, $Ca^{2+}$, $Na^{-}$, and $S^{2-}$.*



$Fe^{3+}$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

$Ga^{3+}$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

$Cr^{+}$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

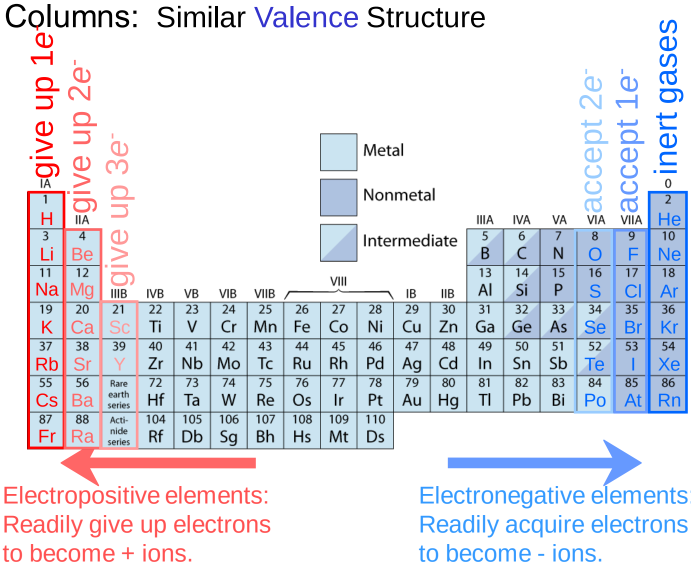
$Ca^{2+}$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6$

$Na^{-}$ ion is $1s^2 2s^2 2p^6 3s^2$

$S^{2-}$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6$

# The Periodic Table

- Columns: Similar Valence Structure




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



# 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 | | | | | | | | | | | | | | | |

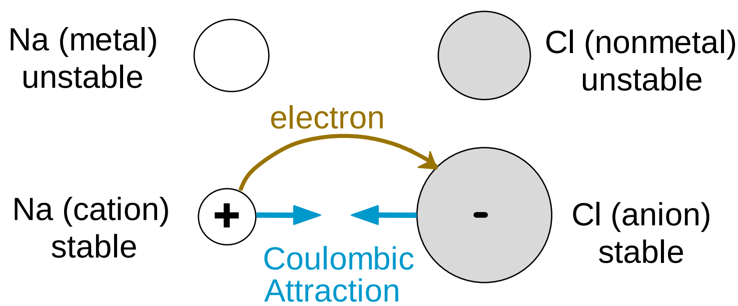
Smaller electronegativity

Larger electronegativity

Adapted from Fig. 2.7, *Callister & Rethwisch 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 Bonding

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






## Ionic bond – metal + nonmetal

donates electrons (metal) — accepts electrons (nonmetal)

Dissimilar electronegativities

ex: MgO — Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ — O $1s^2\ 2s^2\ 2p^4$

[Ne] $3s^2$

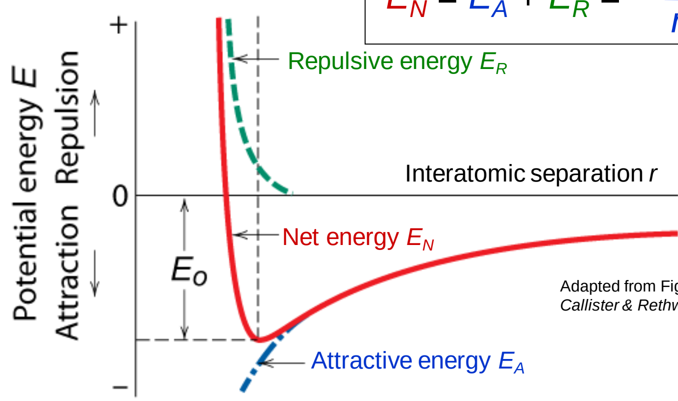
$Mg^{2+}$ $1s^2\ 2s^2\ 2p^6$ — $O^{2-}$ $1s^2\ 2s^2\ 2p^6$

[Ne] — [Ne]

# Ionic Bonding

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

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

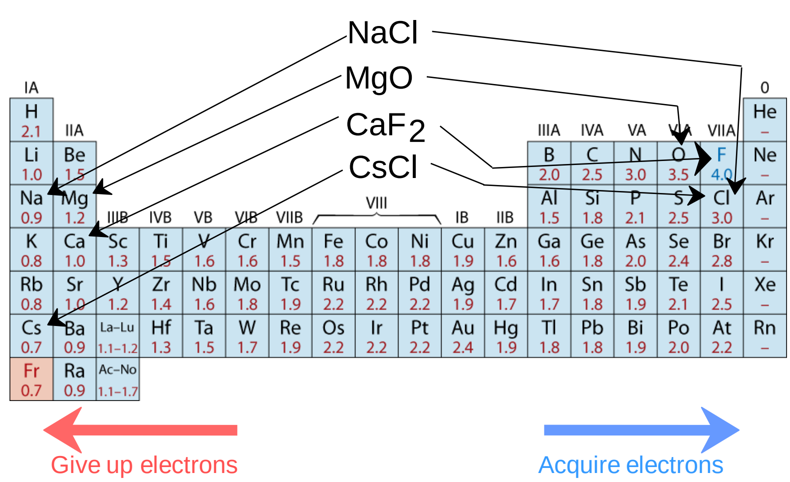



Adapted from Fig. 2.8(b), *Callister & Rethwisch 4e.*



# Examples: Ionic Bonding

- Predominant bonding in Ceramics




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.

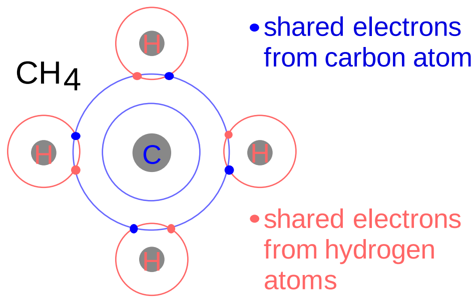
# Covalent Bonding

- similar electronegativity $\therefore$ 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.*



# Primary Bonding

- Ionic-Covalent Mixed Bonding

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

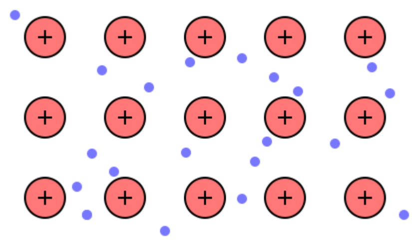
where $X_A$ & $X_B$ are Pauling electron negativities

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

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

# Metallic Bonding

- Metallic Bond -- delocalized as electron cloud
- Found in metals and their alloys
- described as the sharing of free electrons among a lattice of positively charged ions (cations)





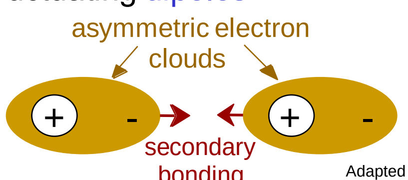
# SECONDARY BONDING

Arises from interaction between dipoles (−259.14 C (14.01 K)

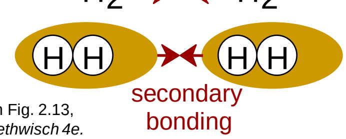
- Fluctuating dipoles

ex: liquid $H_2$

$H_2$ → ← $H_2$



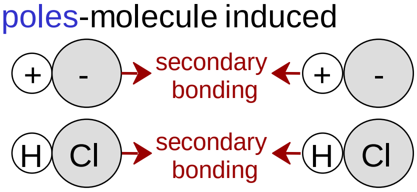

Adapted from Fig. 2.13, *Callister & Rethwisch 4e.*




- Permanent dipoles-molecule induced

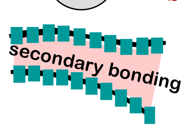
-general case:

-ex: liquid HCl




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

-ex: polymer




secondary bonding

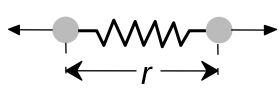
# Summary: Bonding

| Type | Bond Energy | Comments |
|---|---|---|
| Ionic | Large! | Nondirectional (ceramics)<br>(same attraction from all directions)<br>- No sharing e or no overlaping orbitals<br># of nearest atoms decided by charges and sizes. |
| Covalent | Variable<br>large-Diamond<br>small-Bismuth | Directional<br>(semiconductors, ceramics<br>polymer chains) |
| Metallic | Variable<br>large-Tungsten<br>small-Mercury | Nondirectional (metals) |
| Secondary | smallest | Directional<br>inter-chain (polymer)<br>inter-molecular |

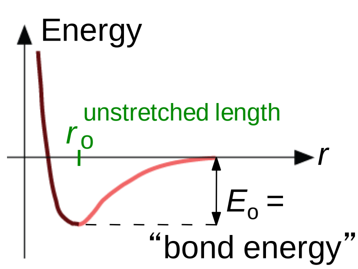


# Properties From Bonding: $T_m$

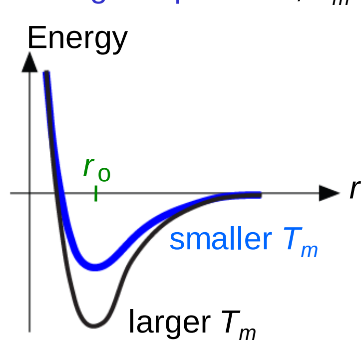
- Bond length, $r$




- Bond energy, $E_o$



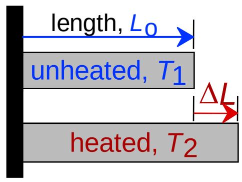

- Melting Temperature, $T_m$




$T_m$ is larger if $E_o$ is larger.

# Properties From Bonding : $\alpha$

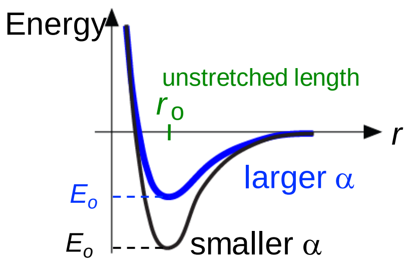
- Coefficient of thermal expansion, $\alpha$




coeff. thermal expansion

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

- $\alpha$ ~ symmetric at $r_o$




$\alpha$ Depends on curvature



# Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large $T_m$
large $E$
small $\alpha$

Metals

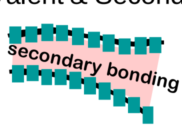
(Metallic bonding):

Variable bond energy

moderate $T_m$
moderate $E$
moderate $\alpha$

Polymers

(Covalent & Secondary):




Directional Properties

Secondary bonding dominates

small $T_m$
small $E$
large $\alpha$

*The net potential energy between two adjacent ions, $E_N$, may be represented by*

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

*Calculate the bonding energy $E_0$ in terms of the parameters A, B, and n*

Chapter 2 - 29