## C1403 Lecture 13, Wednesday, October 19, 2005

**Chapter 17 Many-Electron Atoms and Chemical Bonding**

17.1 Many-Electron Atoms and the Periodic Table (Done)
17.2 Experimental Measures of Orbital Energies
17.3 Sizes of Atoms and Ions
17.4 Properties of the Chemical Bond
17.5 Ionic and Covalent Bonds
17.6 Oxidation States and Chemical Bonding

# Summary: The Periodic Table built up by electron configurations: the ground state electron configurations of the valence electrons of the elements

| 1A | 2A | 3B | 4B | 5B | 6B | 7B | | 8B | | 1B | 2B | 3A | 4A | 5A | 6A | 7A | 8A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 **H** $1s^1$ | | | | | | | | | | | | | | | | | 2 **He** $1s^2$ |
| 3 **Li** $2s^1$ | 4 **Be** $2s^2$ | | | | | | | | | | | 5 **B** $2s^22p^1$ | 6 **C** $2s^22p^2$ | 7 **N** $2s^22p^3$ | 8 **O** $2s^22p^4$ | 9 **F** $2s^22p^5$ | 10 **Ne** $2s^22p^6$ |
| 11 **Na** $3s^1$ | 12 **Mg** $3s^2$ | | | | | | | | | | | 13 **Al** $3s^23p^1$ | 14 **Si** $3s^23p^2$ | 15 **P** $3s^23p^3$ | 16 **S** $3s^23p^4$ | 17 **Cl** $3s^23p^5$ | 18 **Ar** $3s^23p^6$ |
| 19 **K** $4s^1$ | 20 **Ca** $4s^2$ | 21 **Sc** $3d^14s^2$ | 22 **Ti** $3d^24s^2$ | 23 **V** $3d^34s^2$ | 24 **Cr** $3d^54s^1$ | 25 **Mn** $3d^54s^2$ | 26 **Fe** $3d^64s^2$ | 27 **Co** $3d^74s^2$ | 28 **Ni** $3d^84s^2$ | 29 **Cu** $3d^{10}4s^1$ | 30 **Zn** $3d^{10}4s^2$ | 31 **Ga** $4s^24p^1$ | 32 **Ge** $4s^24p^2$ | 33 **As** $4s^24p^3$ | 34 **Se** $4s^24p^4$ | 35 **Br** $4s^24p^5$ | 36 **Kr** $4s^24p^6$ |
| 37 **Rb** $5s^1$ | 38 **Sr** $5s^2$ | 39 **Y** $4d^15s^2$ | 40 **Zr** $4d^25s^2$ | 41 **Nb** $4d^45s^1$ | 42 **Mo** $4d^55s^1$ | 43 **Tc** $4d^55s^2$ | 44 **Ru** $4d^75s^1$ | 45 **Rh** $4d^85s^1$ | 46 **Pd** $4d^{10}$ | 47 **Ag** $4d^{10}5s^1$ | 48 **Cd** $4d^{10}5s^2$ | 49 **In** $5s^25p^1$ | 50 **Sn** $5s^25p^2$ | 51 **Sb** $5s^25p^3$ | 52 **Te** $5s^25p^4$ | 53 **I** $5s^25p^5$ | 54 **Xe** $5s^25p^6$ |
| 55 **Cs** $6s^1$ | 56 **Ba** $6s^2$ | 57 ***La** $5d^16s^2$ | 72 **Hf** $5d^26s^2$ | 73 **Ta** $5d^36s^2$ | 74 **W** $5d^46s^2$ | 75 **Re** $5d^56s^2$ | 76 **Os** $5d^66s^2$ | 77 **Ir** $5d^76s^2$ | 78 **Pt** $5d^96s^1$ | 79 **Au** $5d^{10}6s^1$ | 80 **Hg** $5d^{10}6s^2$ | 81 **Tl** $6s^26p^1$ | 82 **Pb** $6s^26p^2$ | 83 **Bi** $6s^26p^3$ | 84 **Po** $6s^26p^4$ | 85 **At** $6s^26p^5$ | 86 **Rn** $6s^26p^6$ |
| 87 **Fr** $7s^1$ | 88 **Ra** $7s^2$ | 89 **†Ac** $6d^17s^2$ | 104 **Rf** $6d^27s^2$ | 105 **Db** $6d^37s^2$ | 106 **Sg** $6d^47s^2$ | 107 **Bh** | 108 **Hs** | 109 **Mt** | 110 | 111 | 112 | Unknown | 114 | Unknown | ††116 | Unknown | ††118 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * | 58 **Ce** $4f^26s^2$ | 59 **Pr** $4f^36s^2$ | 60 **Nd** $4f^46s^2$ | 61 **Pm** $4f^56s^2$ | 62 **Sm** $4f^66s^2$ | 63 **Eu** $4f^76s^2$ | 64 **Gd** $4f^75d^16s^2$ | 65 **Tb** $4f^96s^2$ | 66 **Dy** $4f^{10}6s^2$ | 67 **Ho** $4f^{11}6s^2$ | 68 **Er** $4f^{12}6s^2$ | 69 **Tm** $4f^{13}6s^2$ | 70 **Yb** $4f^{14}6s^2$ | 71 **Lu** $4f^{14}5d^16s^2$ |
| † | 90 **Th** $6d^27s^2$ | 91 **Pa** $5f^26d^17s^2$ | 92 **U** $5f^36d^17s^2$ | 93 **Np** $5f^46d^17s^2$ | 94 **Pu** $5f^67s^2$ | 95 **Am** $5f^77s^2$ | 96 **Cm** $5f^76d^17s^2$ | 97 **Bk** $5f^97s^2$ | 98 **Cf** $5f^{10}7s^2$ | 99 **Es** $5f^{11}7s^2$ | 100 **Fm** $5f^{12}7s^2$ | 101 **Md** $5f^{13}7s^2$ | 102 **No** $5f^{14}7s^2$ | 103 **Lr** $5f^{14}6d^17s^2$ |

# 17.2 Experimental Measures of Orbital Energies

Photoelectron spectroscopy. Measuring the energy of electrons in orbitals by kicking them out with photons

Ionization energies. How strongly atoms hold on to electrons

Electron affinities. How strongly atoms add an electron

Effective nuclear charge and screening by inner electrons. How these influence ionization energies and electron affinities

Periodic trends in ionization energies and electron affinities

# The Bohr one electron atom as a starting point for the electron configurations of multielectron atoms.

Replace Z (actual charge) with $Z_{eff}$ (effective charge)

$E_n = -(Z_{eff}^2/n^2)Ry$ = energy of electron in orbital

$r_n = (n^2/Z_{eff})a_0$ = "average" radius of a orbital

## Some important periodic properties of atoms:

Energy required to remove and add an electron ($E_n$)
Size of atoms ($r_n$)

Rules: (1) Larger $Z_{eff}$ more energy required to remove $e^-$
(2) Smaller r more energy require to remove $e^-$

# Effective nuclear charge: $Z_{eff}$

Effective nuclear charge, $Z_{eff}$: the net positive charge attracting an electron in an atom.

An approximation to this net charge is

$$Z_{eff}(\text{effective nuclear charge}) = Z(\text{actual nuclear charge}) - Z_{core}(\text{core electrons})$$

The core electrons are in subshell between the electron in question and the nucleus. The core electrons are said to “shield” the outer electrons from the full force of the nucleus

Rule: In many electron atoms, for a given value of n, the value of $Z_{eff}$ decreases with increasing *l*, because screening decreases with increasing *l*

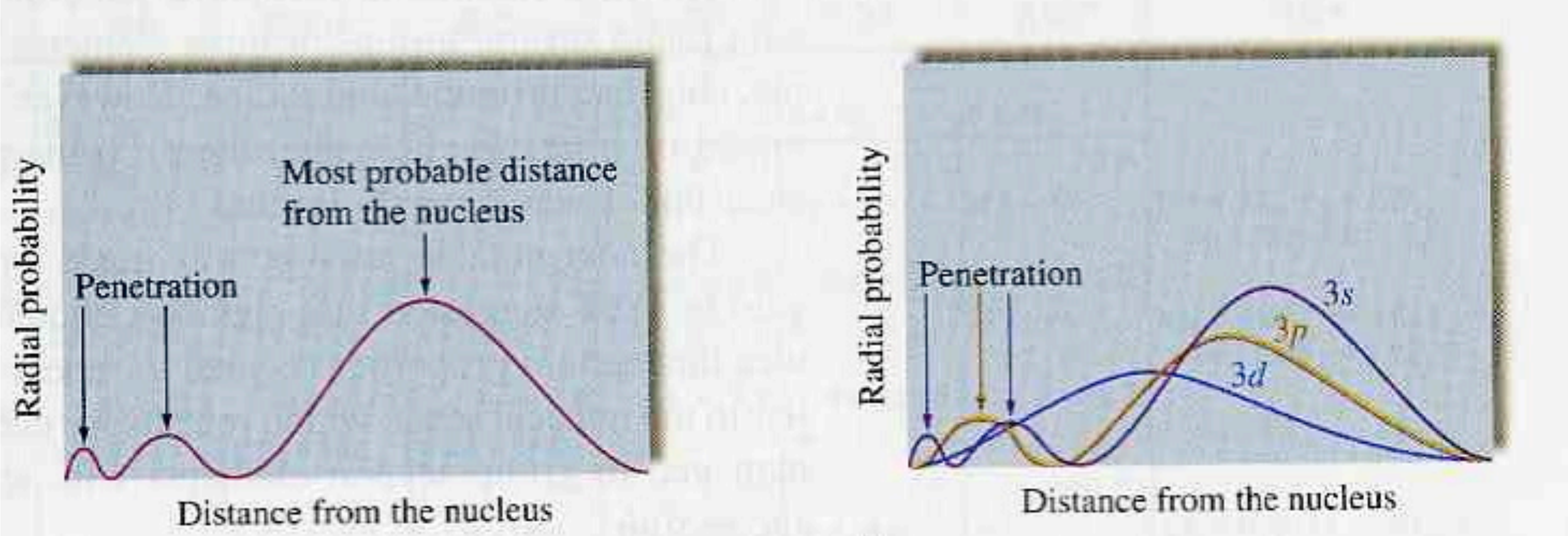
For a given n: $s < p < d < f$

Since the energy of an orbital depends on $Z_{eff}$, in a many electron atom, for a given value of n, the energy of a orbital increases with increasing value of *l*.

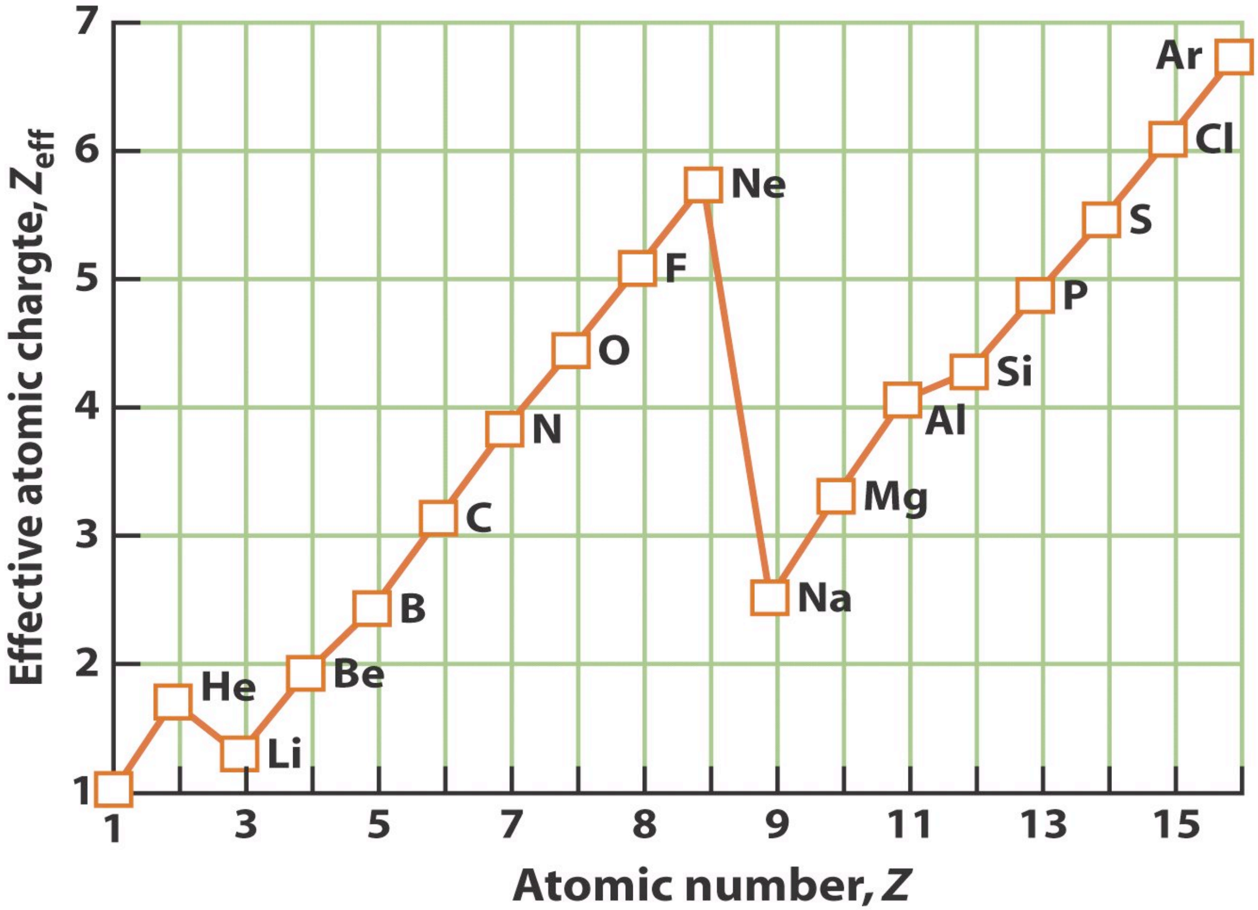
## Electron shielding (screening) of the nuclear charge by other electrons

Why is the energy of a 3s orbital lower than than of a 3p orbital? Why is the energy of a 3p orbital lower than the energy of a 3d orbital?

A qualitative explanation is found in the concept of effective nuclear charge "seen" by an electron



# Effective charge, $Z_{eff}$, seen by valence electrons*:
# Rule: $Z_{eff}$ increases going across a period ot the table




*Note x-axis is incorrect. What should it be?

## Ionization energies (ionization potentials):

The ionization energy (IE) of an atom is the minimum energy required to remove an electron from a gaseous atom.

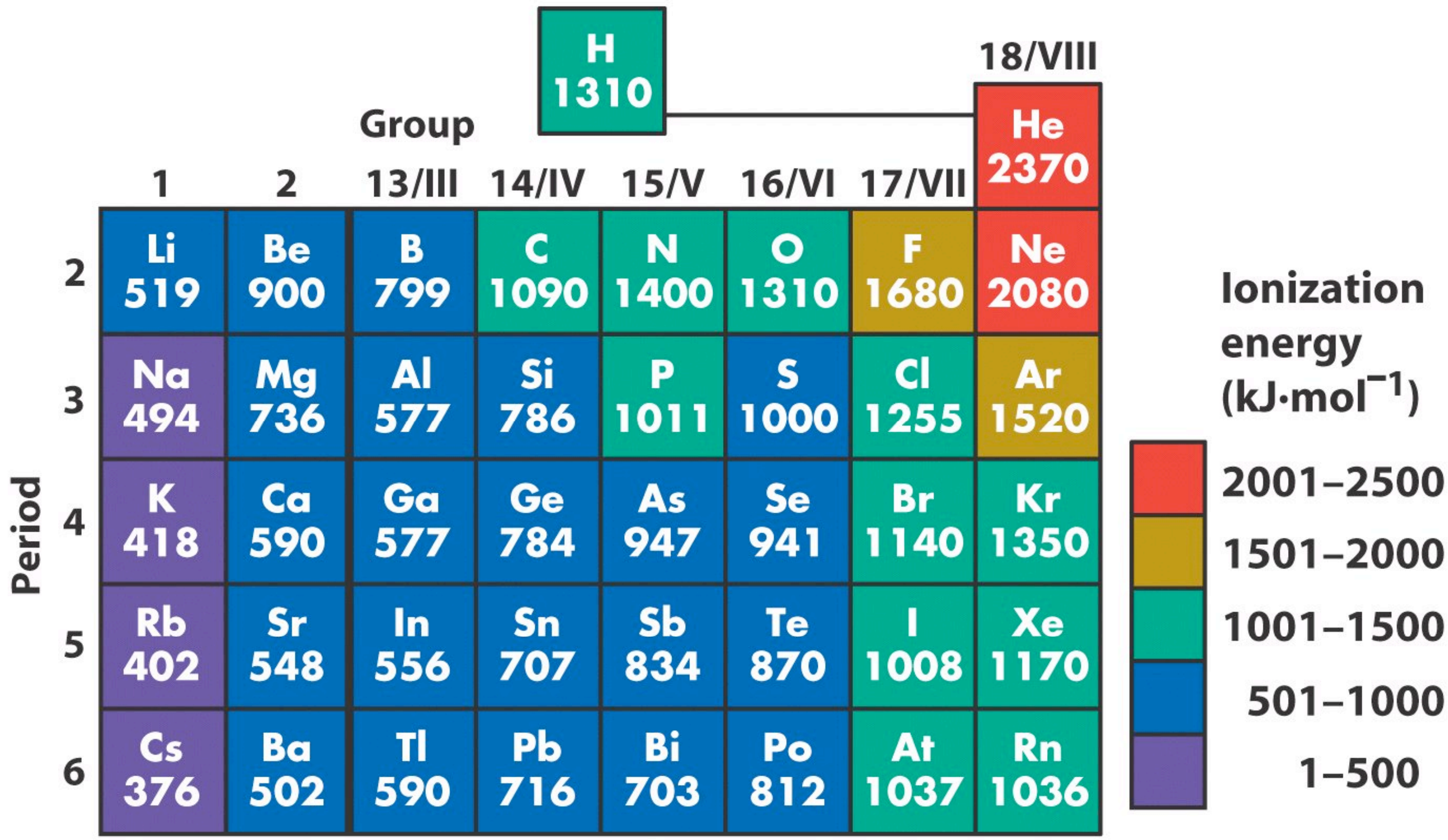
$$X(g) \longrightarrow X^+(g) + e^-$$

The first ionization energy $IE_1$ is the energy required to remove the first electron from the atom.

The second ionization energy $IE_2$, is the energy required to remove the second electron from the +1 positive ion of the atom and so on.

Let's take a look at some experimental data:

# Periodic trends ionization energies of the representative elements: What are the correlations across and down?



## How do we obtain ionization energies?

Photoelectron spectroscopy is an important technique that provides the energies of electrons in different orbitals and provides overwhelming evidence for the existence of shells and subshells.

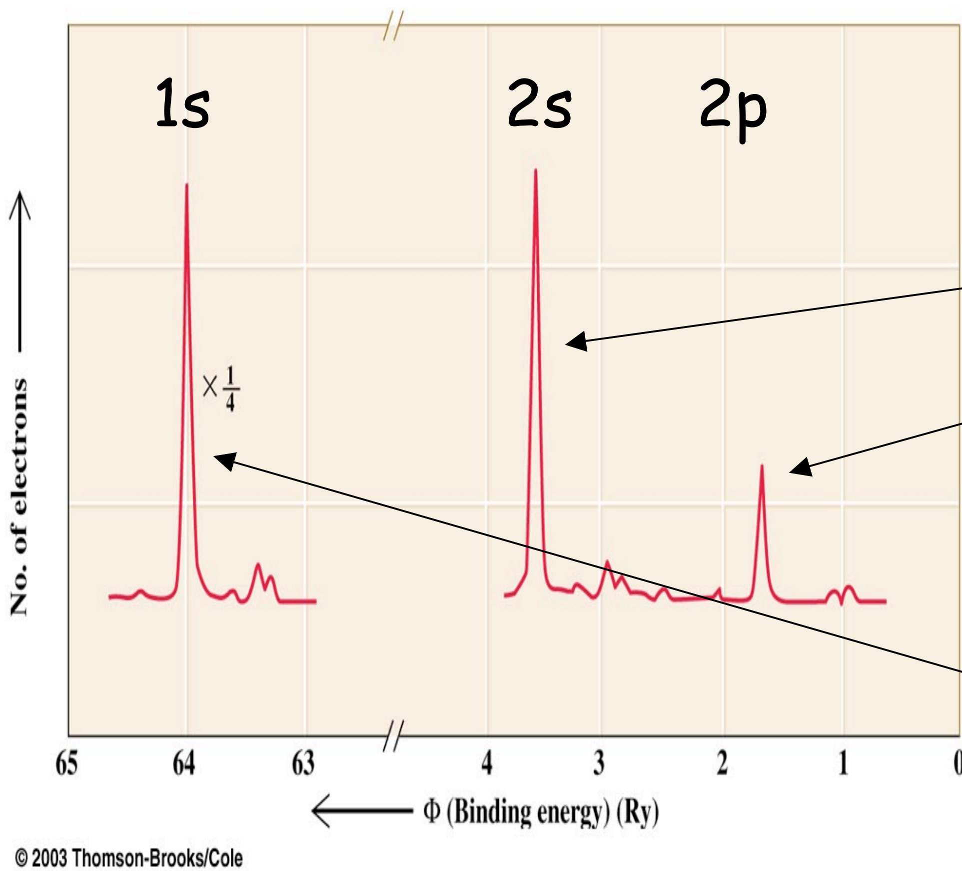
Photoelectron spectroscopy is the photoelectric effect explained by Einstein applied to gases:

A photon $h\nu$ hits an electron and ejects it from the atom; part of the energy of the photon goes into overcoming the attraction of the electron for the nucleus (the ionization energy, IE) and the remainder appears as kinetic energy: $h\nu = \Phi\ (\mathrm{IE}) + (1/2)mv^2$

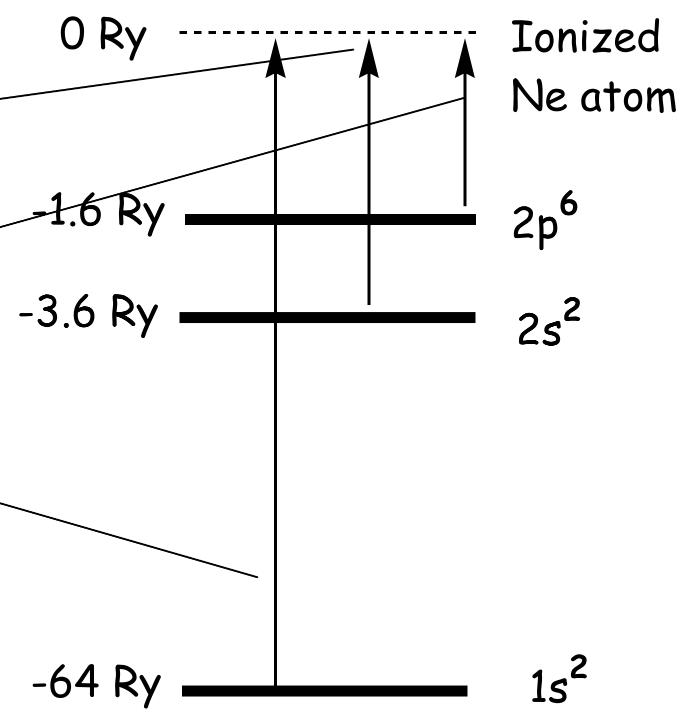
Or: $\Phi\ (\mathrm{IE}) = h\nu - (1/2)mv^2$ (total photon energy - KE)

# Photoelectron spectroscopy: the photoelectric effect for ejecting electrons from gaseous atoms.

$\Phi$ (ionization energy, IE) = $h\nu - (1/2)mv^2$




Energy diagram for Ne: $1s^2 2s^2 2p^6$

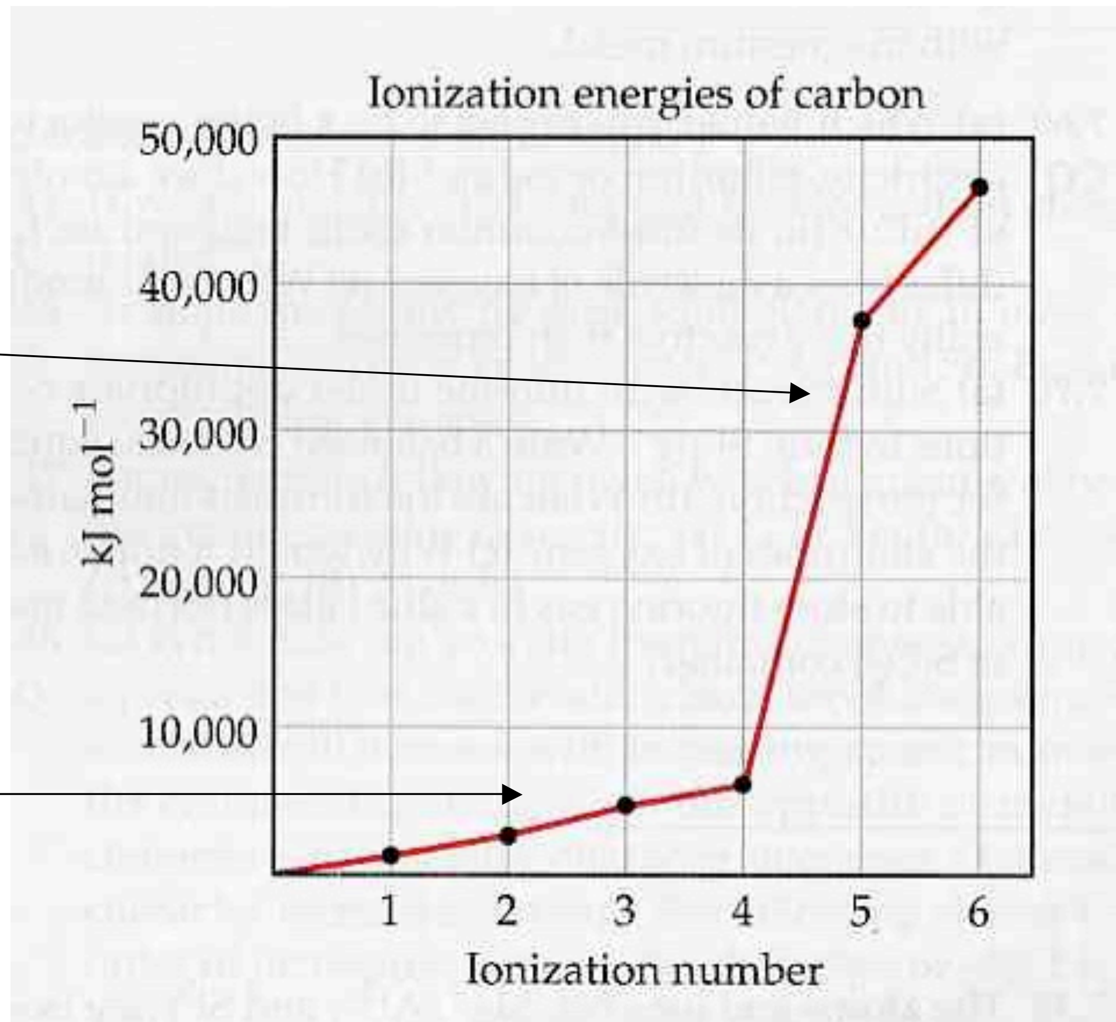


## Experimental data and theoretical ideas

Question: Explain the "two slopes" for the ionization energies of carbon.

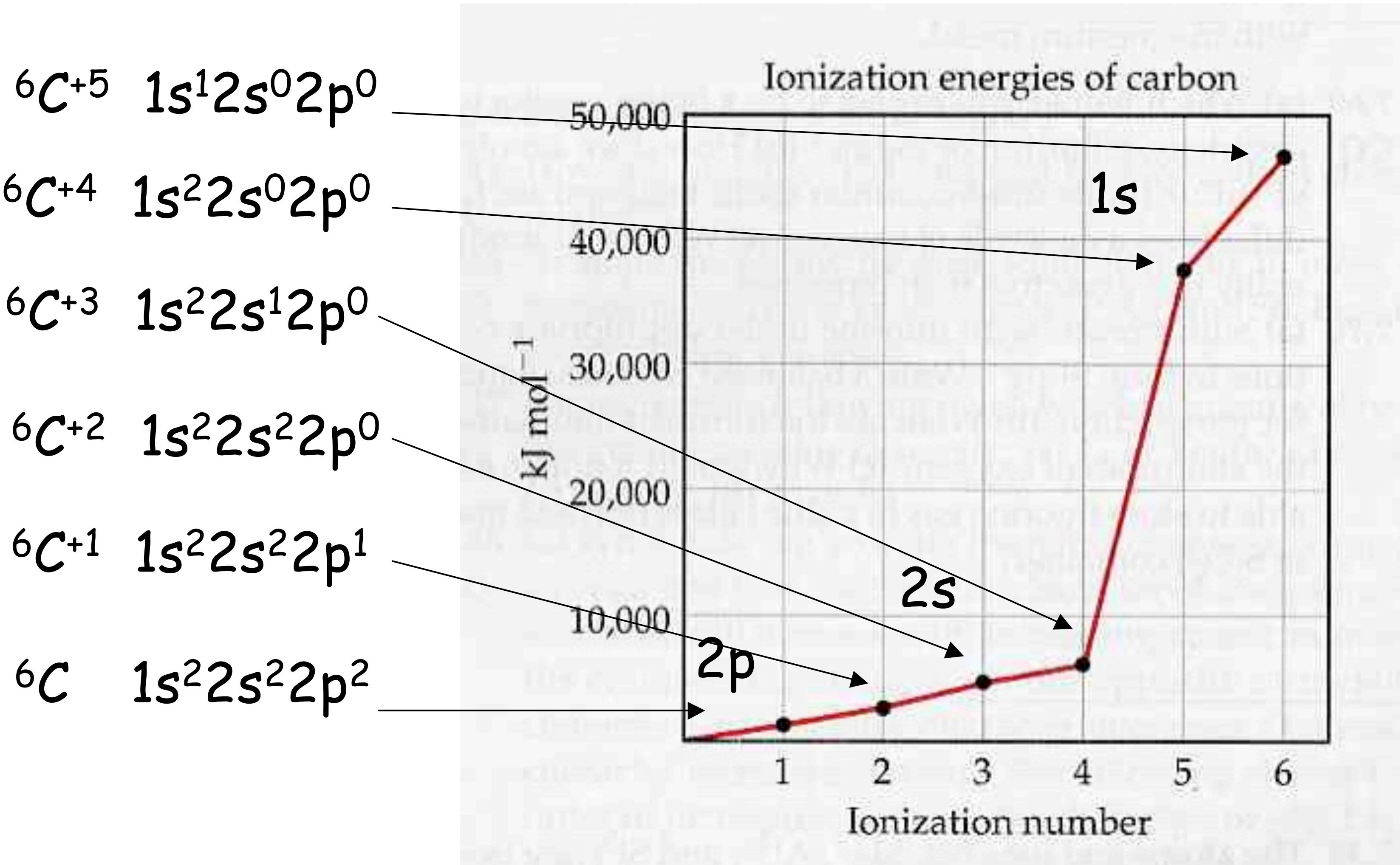
Slope 2

Slope 1



It takes more and more energy to remove an electron from an increasingly positively charged atom.

The first smaller slope is due to removal of n = 2 electrons, the second larger slope is due to removal of n = 1 electrons.



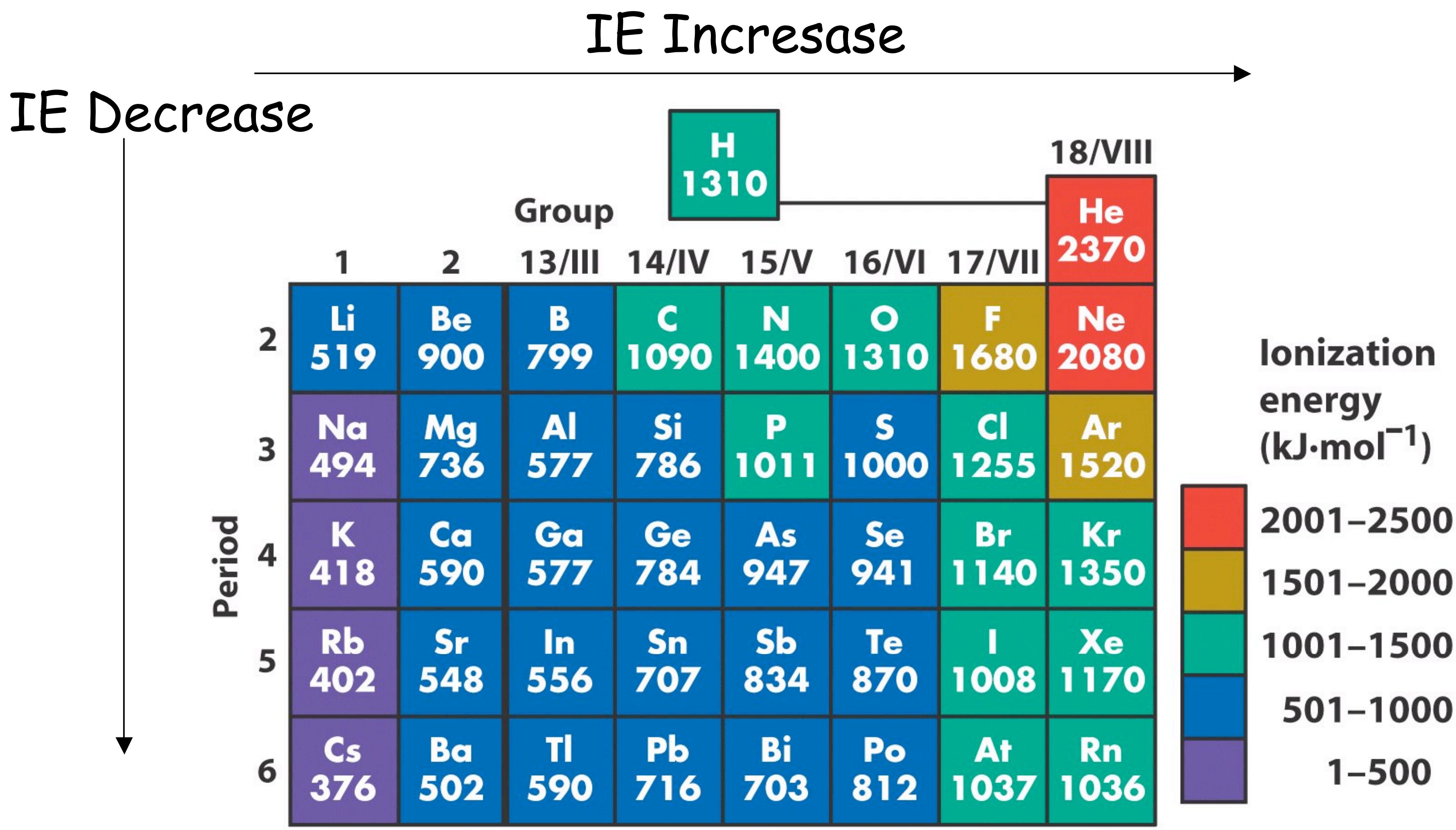
## Looking for trends: Ionization energies in tabular form

Lots of data but hard to see trends

| $Z$ | Element | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th |
|---|---|---|---|---|---|---|---|---|---|
| 1 | H | 13.6 | | | | | | | |
| 2 | He | 24.6 | $13.6\times2^2$ → 54.4 | | | | | | |
| 3 | Li | 5.4 | 75.6 | $13.6\times3^2$ → 122 | | | | | |
| 4 | Be | 9.3 | 18.2 | 154 | $13.6\times4^2$ → 218 | | | | |
| 5 | B | 8.3 | 25.1 | 38 | 259 | $13.6\times5^2$ → 340 | | | |
| 6 | C | 11.3 | 24.4 | 48 | 64 | 392 | $13.6\times6^2$ → 490 | | |
| 7 | N | 14.5 | 29.6 | 47 | 77 | 98 | 552 | $13.6\times7^2$ → 667 | |
| 8 | O | 13.6 | 35.1 | 55 | 77 | 114 | 138 | 739 | $13.6\times8^2$ → 871 |
| 9 | F | 17.4 | 35.0 | 63 | 87 | 114 | 157 | 185 | 954 |
| 10 | Ne | 21.6 | 41.1 | 64 | 97 | 126 | 158 | 207 | 238 |
| 11 | Na | 5.1 | 47.3 | 72 | 99 | 138 | 172 | 208 | 264 |
| 12 | Mg | 7.6 | 15.0 | 80 | 109 | 141 | 186 | 225 | 266 |
| 13 | Al | 6.0 | 18.8 | 28 | 120 | 154 | 190 | 241 | 285 |
| 14 | Si | 8.1 | 16.3 | 33 | 45 | 167 | 205 | 246 | 303 |
| 15 | P | 10.5 | 19.7 | 30 | 51 | 65 | 220 | 263 | 309 |
| 16 | S | 10.4 | 23.4 | 35 | 47 | 72 | 88 | 281 | 329 |
| 17 | Cl | 13.0 | 23.8 | 40 | 54 | 68 | 97 | 114 | 348 |
| 18 | Ar | 15.8 | 27.6 | 41 | 60 | 75 | 91 | 124 | 143 |

Periodic trends of the first ionization energies of the representative elements mapped on the periodic table.

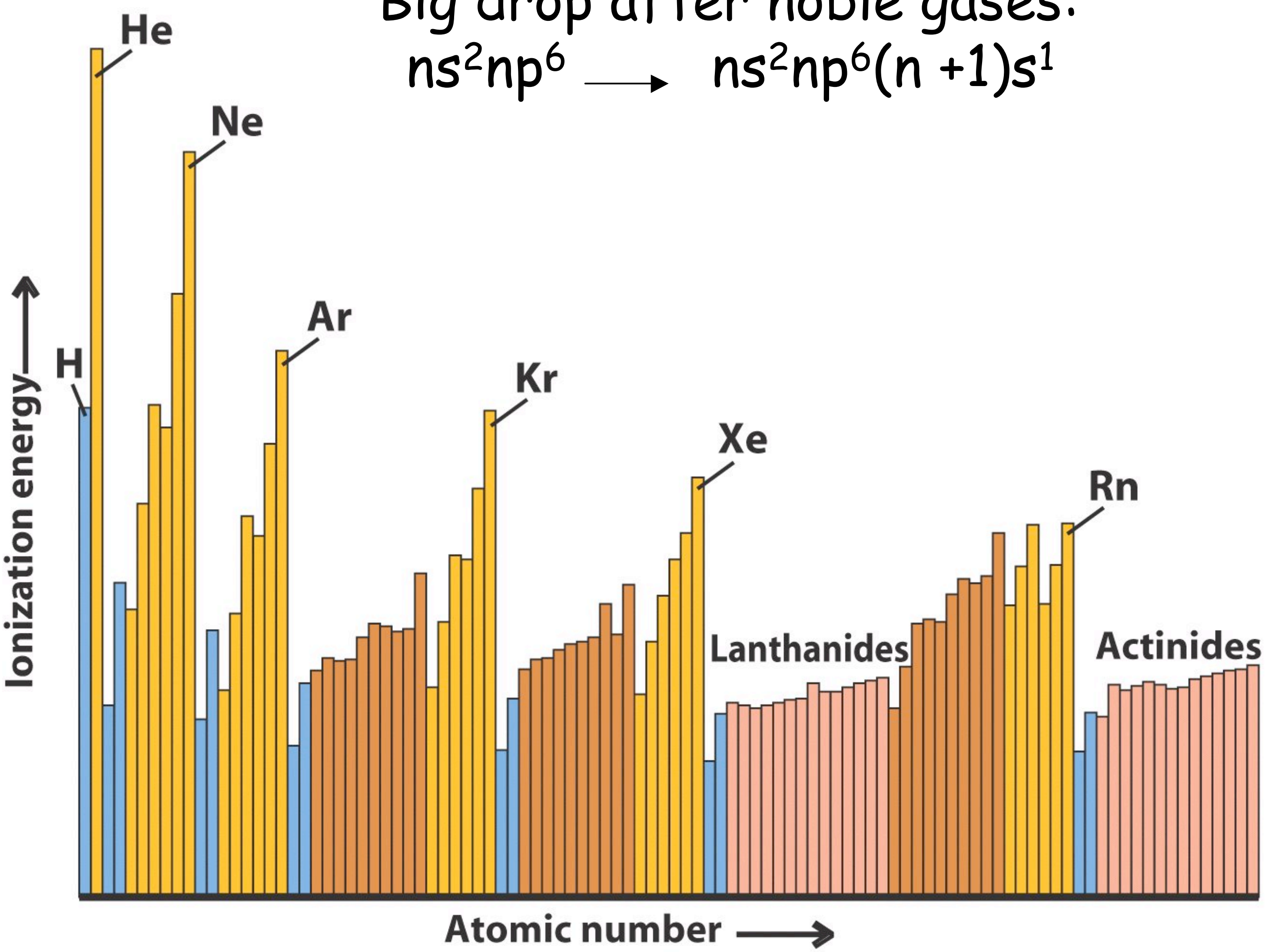
Are correlations more apparent? What are they?



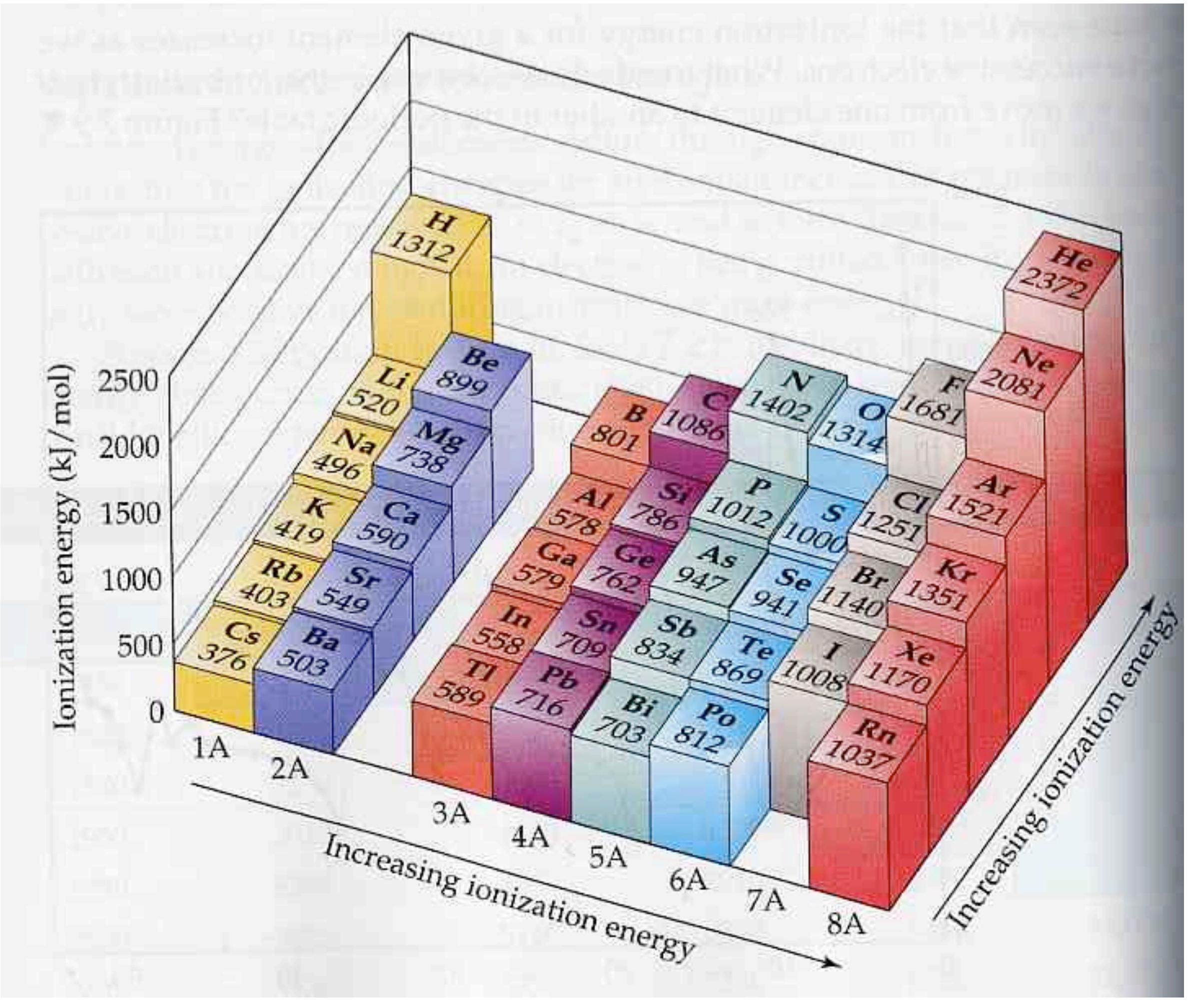
# Looking for trends. Ionization energies as a graph: Periodic trends

Big drop after noble gases:

$ns^2np^6 \longrightarrow ns^2np^6(n+1)s^1$



# Ionization energies of the main group elements in topographical relief form: family relationships.

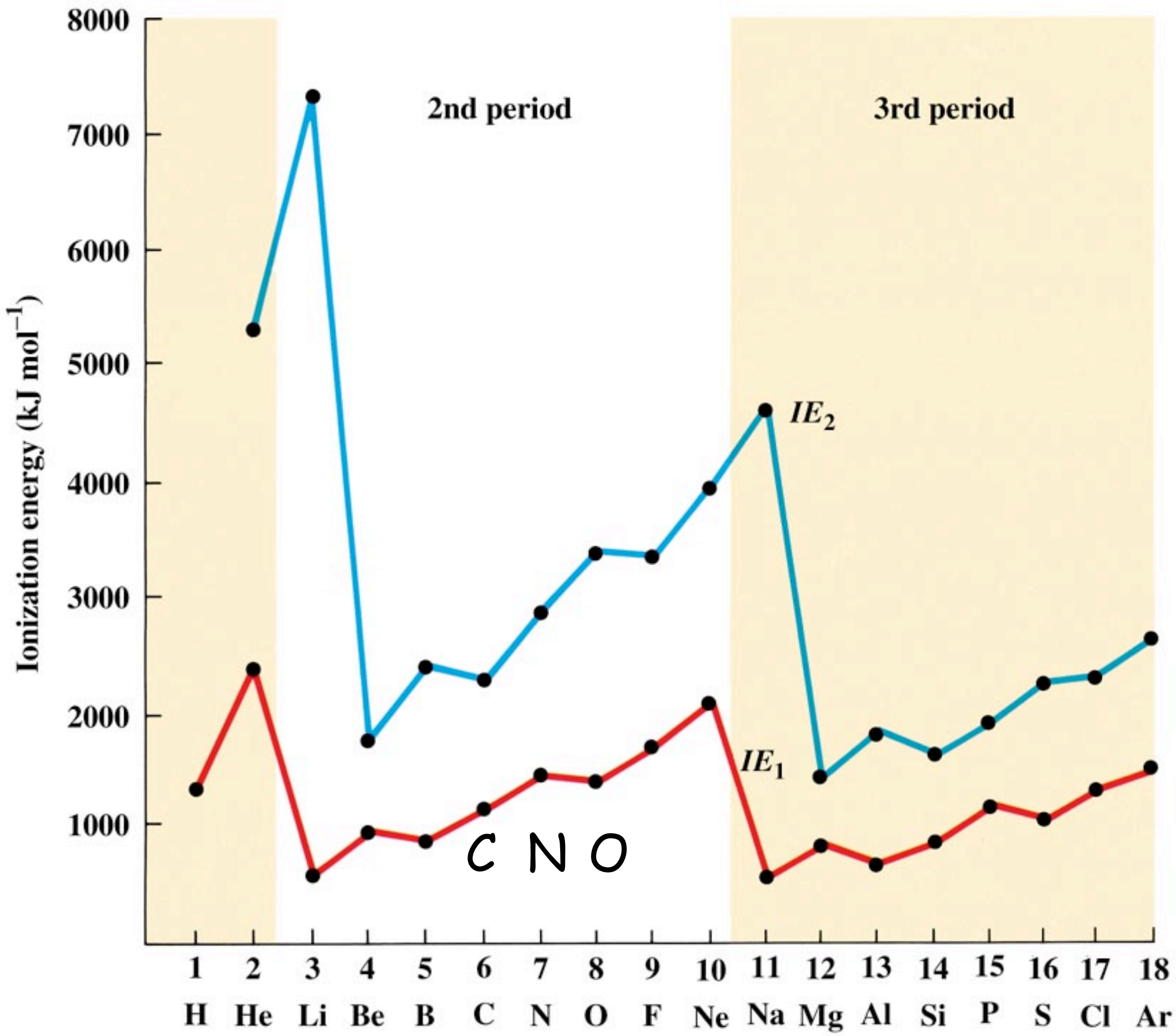



Why is the IE of H so much larger than the IE of Li?

Why are the IEs of the alkali metals so similar?

Why do noble gases have the highest IE?

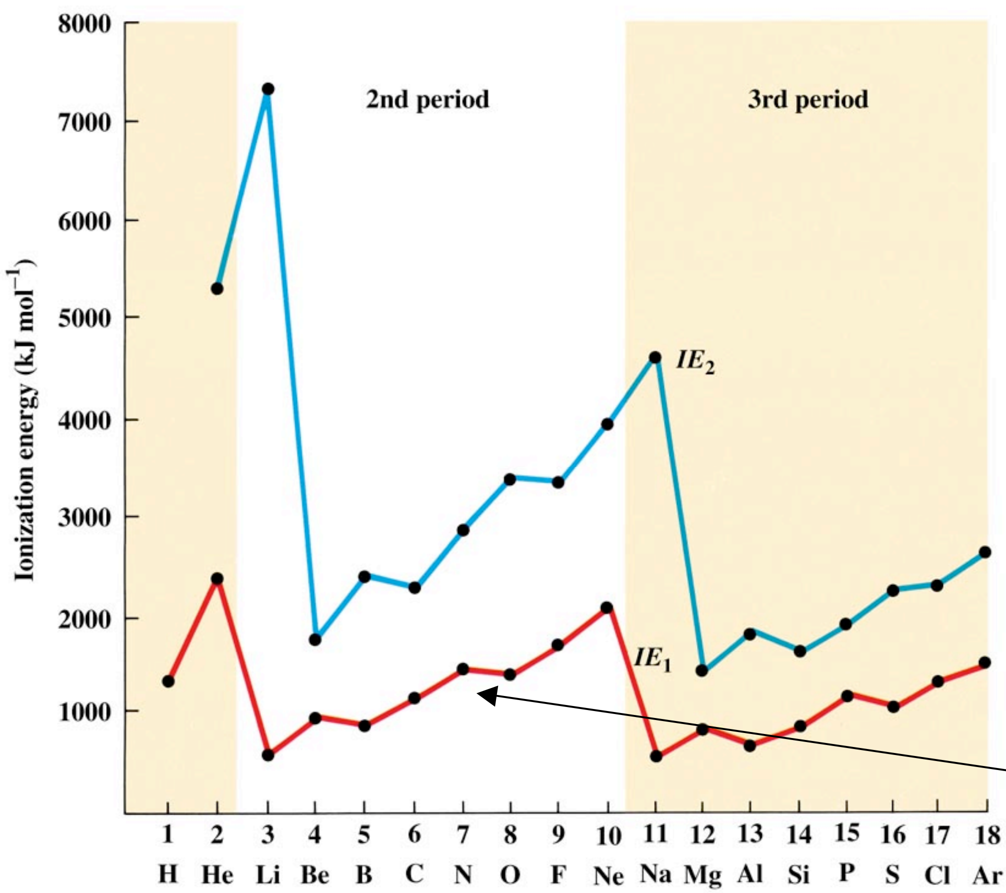
# First and Second ionization energies in graphical form






Why is the IE of N greater than that of C or O?

## Using electron configurations to explain Ionization Energies
## Removal of an electron from a neutral atom: $IE_1$






$Z_{eff}$ increases $\longrightarrow$

$E_n = -(Z_{eff}^2/n^2)$

$E_n = -(Z_{eff}^2)$ if n is fixed

(across a period)

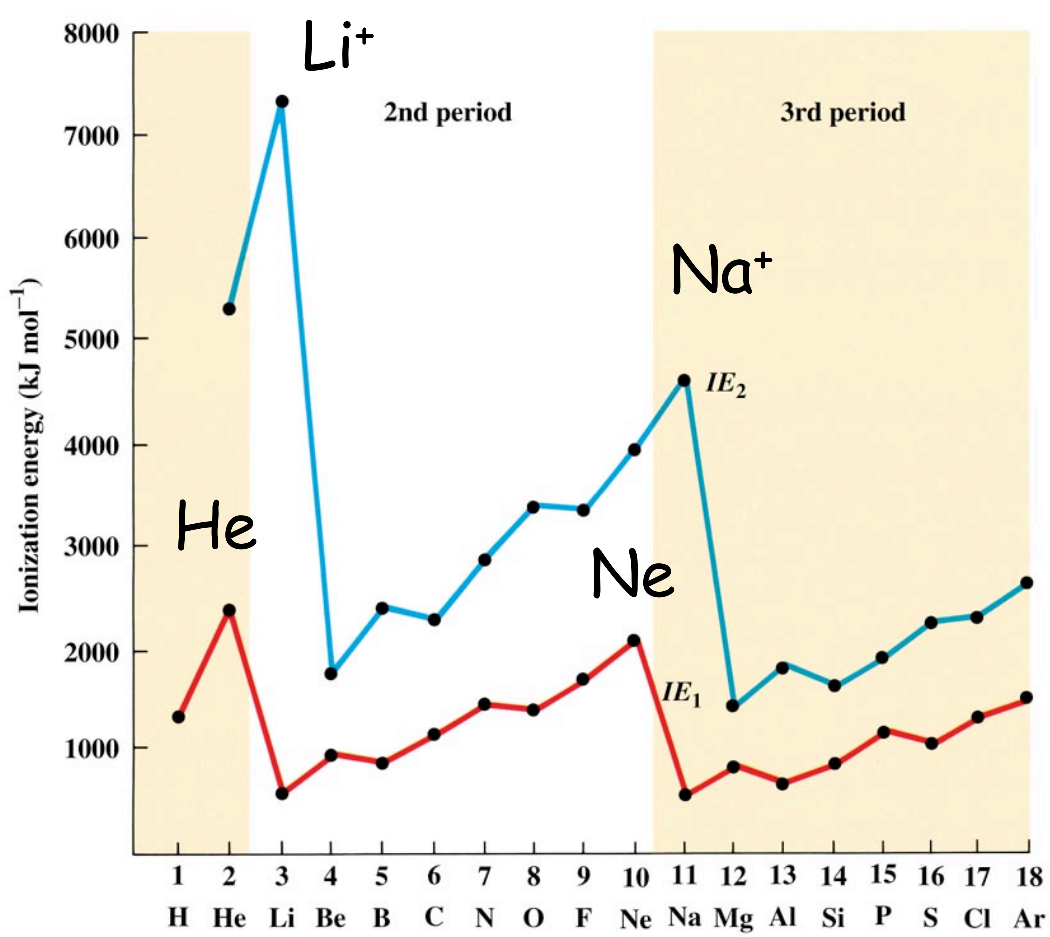
$E_n = -(1/n^2)$ if $Z_{eff}$ is fixed

(down a column)

**$IE_1$**

| | |
|---|---|
| $^{3}$Li | [He]2s (↑) |
| $^{4}$Be | [He]2s$^2$ (↑↓) |
| $^{5}$B | [He]2s$^2$2p$^1$ (↑) |
| $^{6}$C | [He]2s$^2$2p$^2$ (↑↑) |
| $^{7}$N | [He]2s$^2$2p$^3$ (↑↑↑) |
| $^{8}$O | [He]2s$^2$2p$^4$ (↑↓↑↑) |
| $^{9}$F | [He]2s$^2$2p$^5$ (↑↓↑↓↑) |
| $^{10}$Ne | [He]2s$^2$2p$^6$ (↑↓↑↓↑↓) |
| $^{11}$Na | [Ne]3s$^1$ |

# Using electron configurations to explain Ionization Energies
# Removal of the second electron from the atomic cation: $IE_2$






**$IE_2$ (removal from $E^+$)**

| | |
|---|---|
| $^{3}Li^{+}$ | $[He]^{+}$ |
| $^{4}Be^{+}$ | $[He]\ 2s^1$ (↑) |
| $^{5}B^{+}$ | $[He]\ 2s^2$ (↑↓) |
| $^{6}C^{+}$ | $[He]\ 2s^22p^2$ (↑) |
| $^{7}N^{+}$ | $[He]\ 2s^22p^3$ (↑↑) |
| $^{8}O^{+}$ | $[He]\ 2s^22p^4$ (↑↑↑) |
| $^{9}F^{+}$ | $[He]\ 2s^22p^5$ (↑↓↑↑) |
| $^{10}Ne^{+}$ | $[He]\ 2s^22p^6$ (↑↓↑↓↑) |
| $^{11}Na^{+}$ | $[Ne]^{+}$ |

Periodic trends for the representative elements.

Within a row (period) $IE_1$ general increases with increasing Z.

Within each column (family or group) the $IE_1$ generally decreases with increasing Z.

The energy needed to remove an electron from the outermost occupied shell depends on both $E_{eff}$ and $r_{eff}$.

$E_{eff}$ increases and $r_{eff}$ decreases (both increase IE) as one goes across a period. Exceptions are due to special stability of subshells.

# Ionization Energy (IE) and chemical reactivity

Reactivity increases with the number of shells shielding the electrons in the outer (valence) shell.

| IA Family | IE, Volts | Valence Shell |
|---|---|---|
| Li | 5.39 | $2s^1$ |
| Na | 5.14 | $3s^1$ |
| K | 4.34 | $4s^1$ |
| Rb | 4.18 | $5s^1$ |
| Cs | 3.89 | $6s^1$ |

Increasing Reactivity (easier to lose electron)

**The electron affinity (EA) of an atom is the (negative of the) energy change which occurs when an atom gains an electron.**

$$X(g) + e^- \longrightarrow Xe^-(g)$$

A positive value of EA means the system is more stable after adding an electron

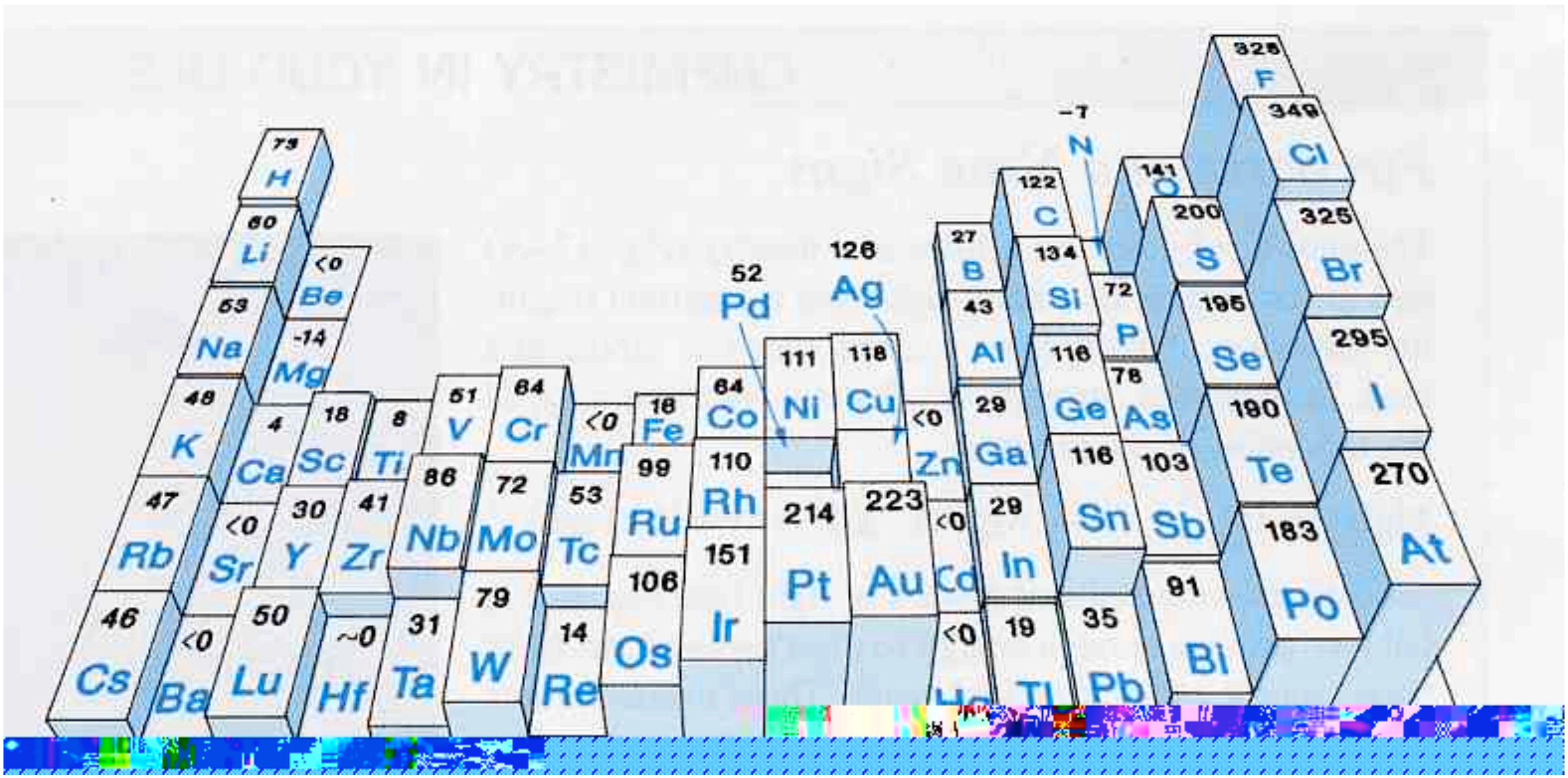
| Period | 1 | 2 | 13/III | 14/IV | 15/V | 16/VI | 17/VII | 18/VIII |
|---|---|---|---|---|---|---|---|---|
| 1 | H +73 | | | | | | | He <0 |
| 2 | Li +60 | Be ≤0 | B +27 | C +122 | N −7 | O +141 −844 | F +328 | Ne <0 |
| 3 | Na +53 | Mg ≤0 | Al +43 | Si +134 | P +72 | S +200 −532 | Cl +349 | Ar <0 |
| 4 | K +48 | Ca +2 | Ga +29 | Ge +116 | As +78 | Se +195 | Br +325 | Kr <0 |
| 5 | Rb +47 | Sr +5 | In +29 | Sn +116 | Sb +103 | Te +190 | I +295 | Xe <0 |
| 6 | Cs +46 | Ba +14 | Tl +19 | Pb +35 | Bi +91 | Po +174 | At +270 | Rn <0 |

Electron affinity ($kJ \cdot mol^{-1}$)

- >300
- 200–300
- 100–200
- 0–100
- <0

# Electron affinities of the elements: relief graph

The periodic trends in the electron affinity parallel to those in the ionization energy of the elements.



# 17.3 Sizes of Atoms and Ions

The radii of atoms and ions

Covalent radius, atomic radius and ionic radius

Periodic trends in the radius of atoms and ions

Radii generally increase down a group (n of outer shell increases) and decrease ($Z_{eff}$ increases for same shell) from left to right across a period.

Cations are generally smaller than their parent atoms and anions are larger than their parent atoms

## From the Bohr atom to all atoms: a model for the size of atoms.

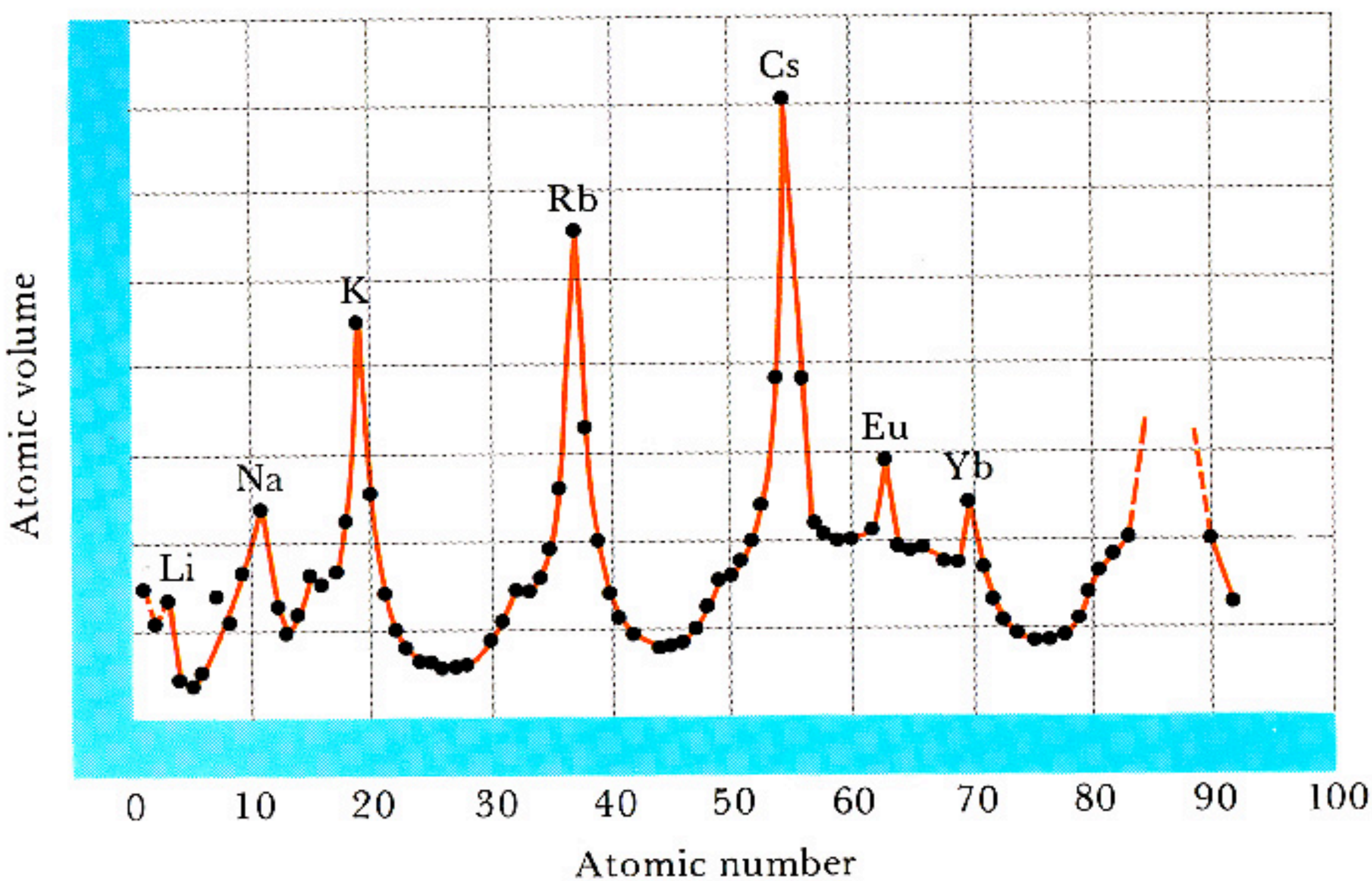
$R \alpha (n^2/Z)$ so that for the same value of n for a multielectron atom

$$r_{eff} \ \alpha \ (1/Z_{eff})$$

When electrons are added to the same shell (same value of n) they are about the same distance from the nucleus as the other electrons in the shell. The electrons in a shell with the same n are spread out and do not shield each other from the positive charge of the nucleus very well. Thus, the effective nuclear charge, $Z_{eff}$, increases as Z increases across the periodic table. The increasing value of $Z_{eff}$ draws the electrons in closer to the nucleus, and the atom becomes more compact and smaller.

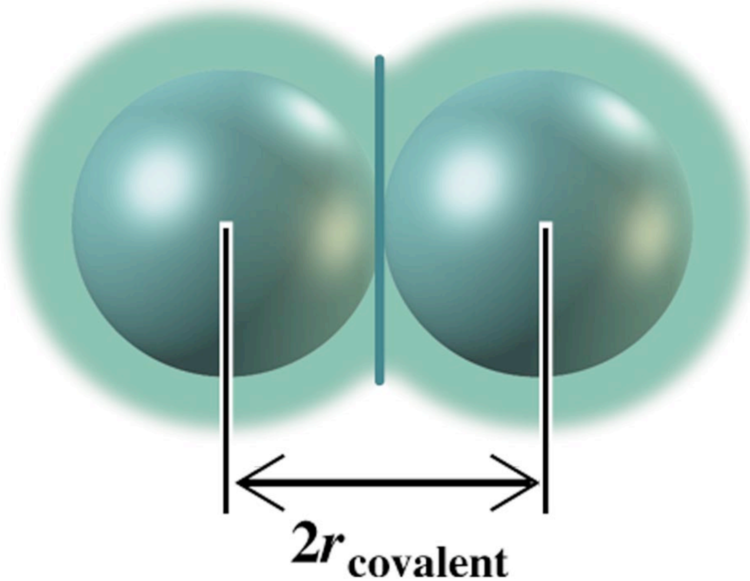
Conclusion: The atomic radius of an atom decreases as one goes across a period for atoms of the same value of n since $E_{eff}$ increases.

# Atomic Volumes



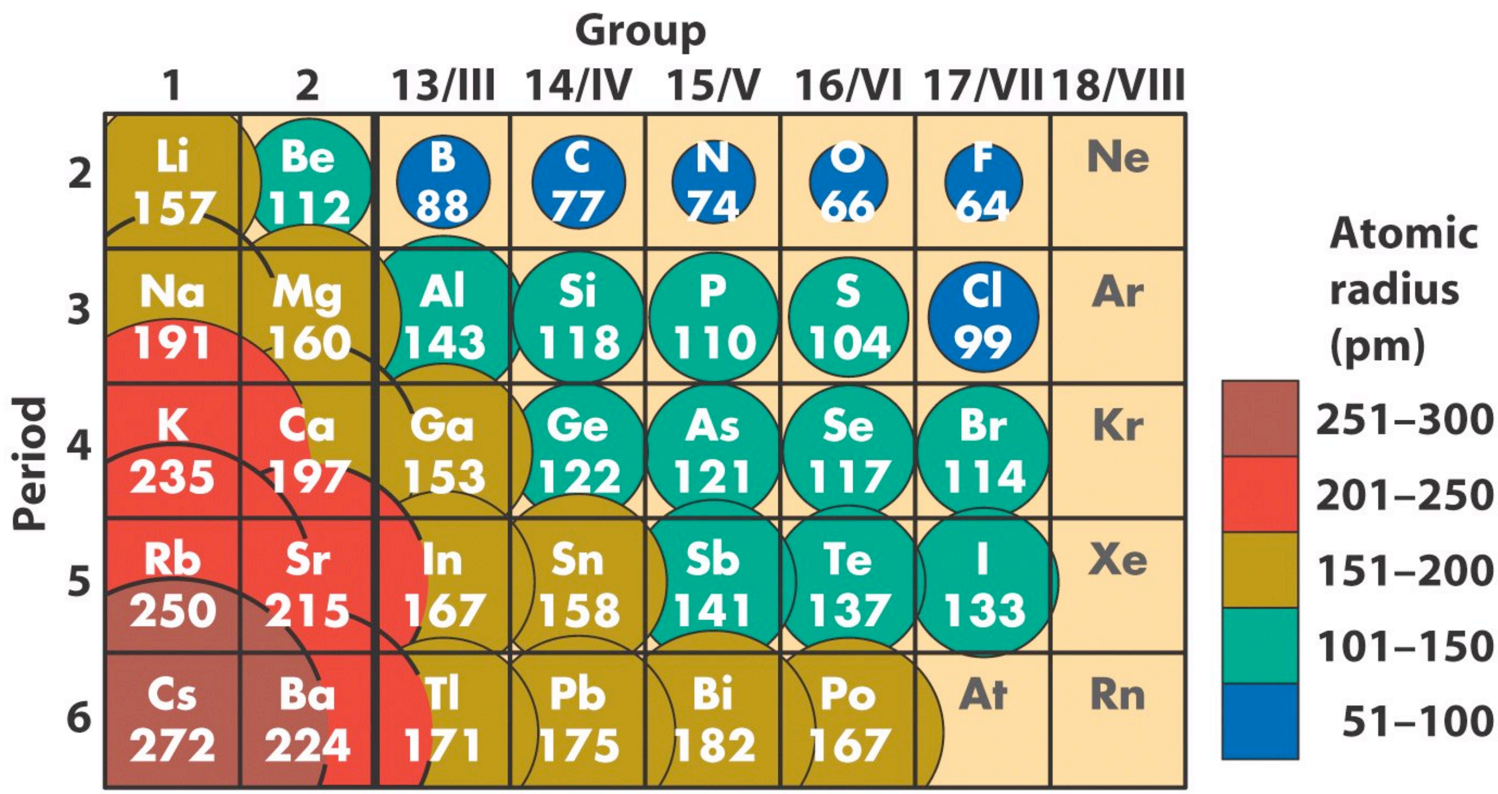
# Covalent Radii from Experiment

- The covalent radius is defined as half the distance between two atoms bound by a single bond in a molecule.

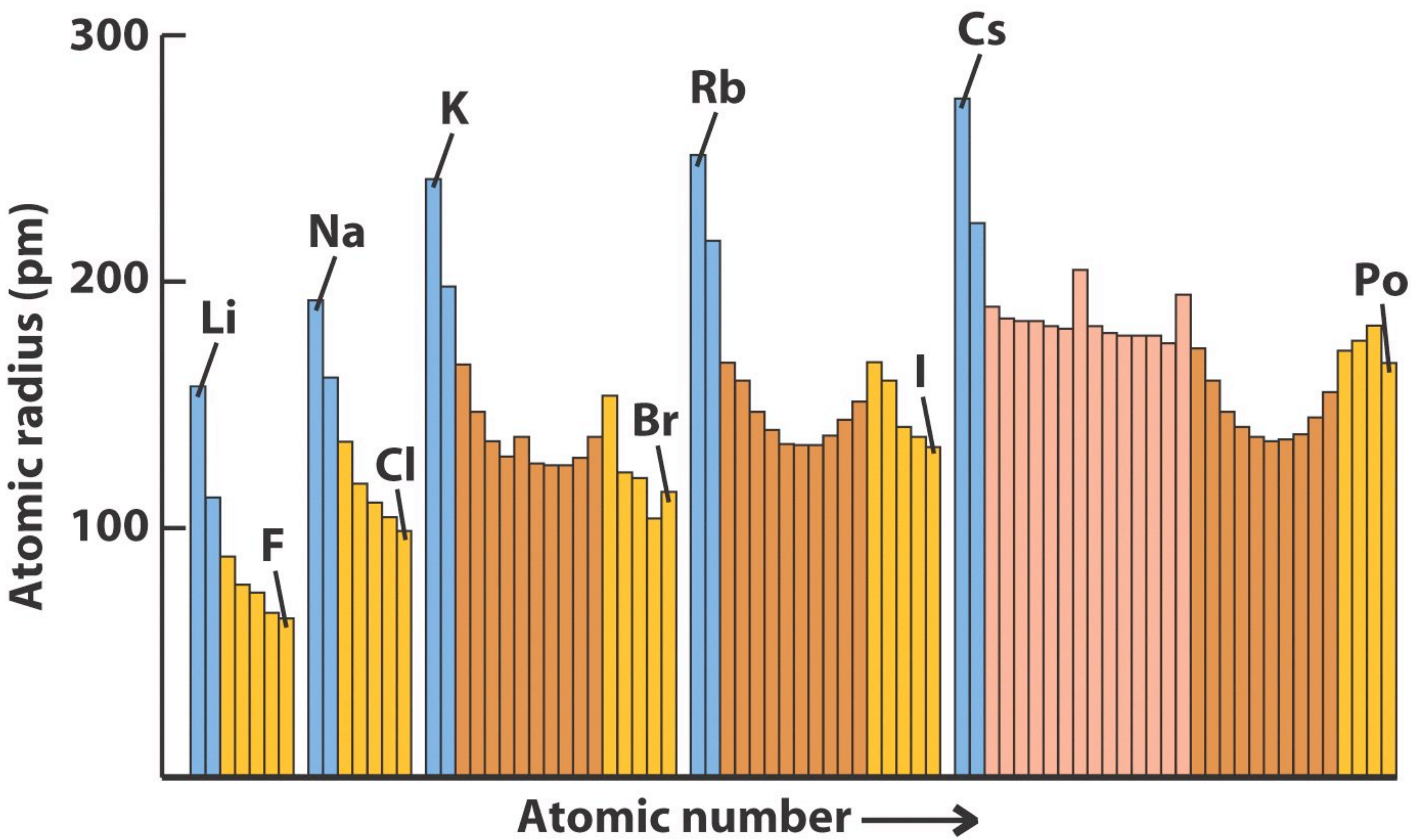


## Periodic properties of atomic radius: What are the correlations?

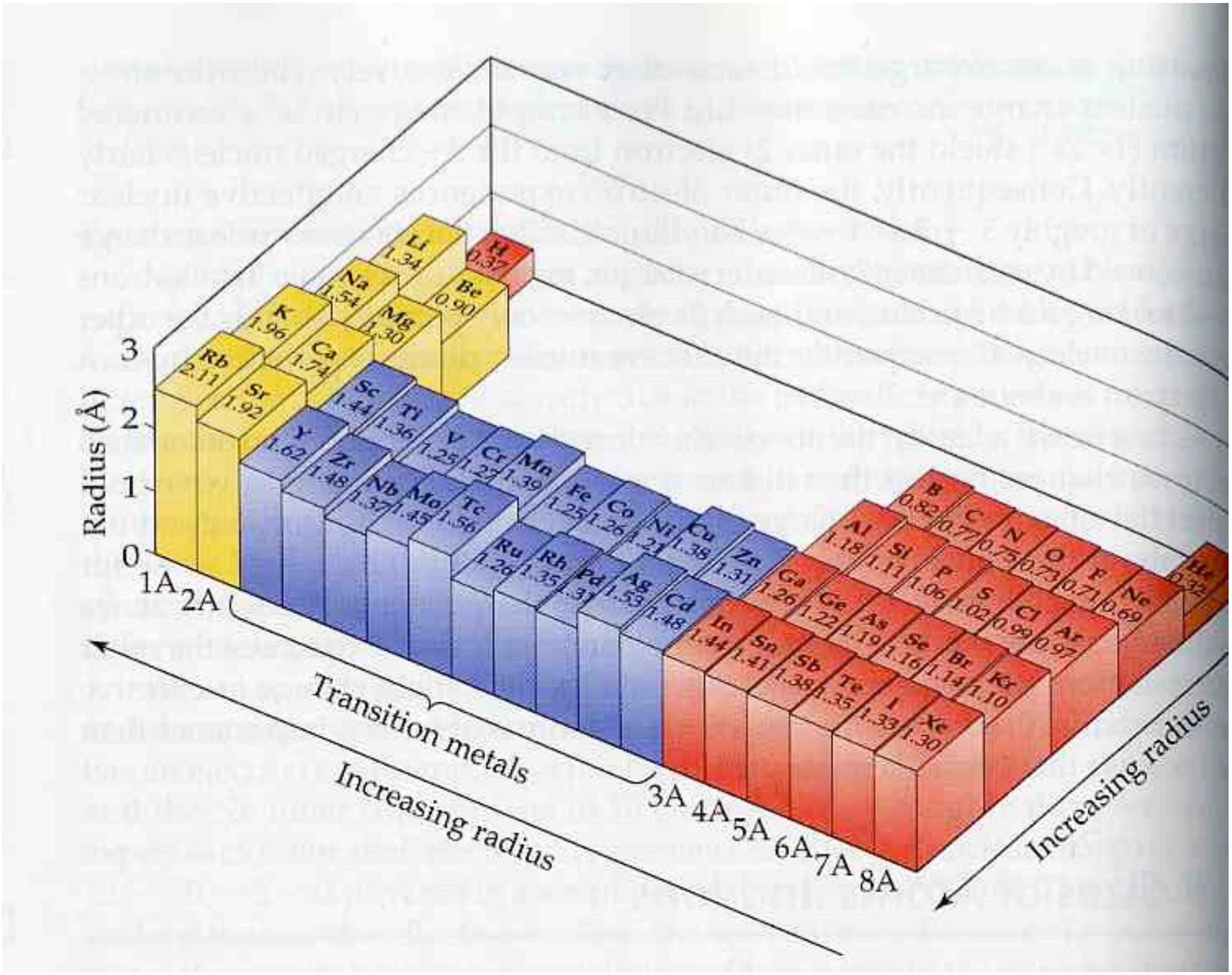
General Rule: The size of an atom decreases in a row as the nuclear charge increases and the size of an atom increases in a column as the nuclear charge increases



Graph of the radii of atoms as a function of atomic number: Periodic trends.



# Radii of the elements in relief form



## 17.4 Properties of the Chemical Bond

Bond length: The distance between the nuclei of two bonded atoms.

Bond enthalpy: The energy required to break a bond between two atoms.

Bond order: The number of shared electron pairs (not electrons) in a covalent bond.

# Bond Lengths (Å)
# $H_2$ = 0.74Å

| | |
|---|---|
| $F_2$ | 1.42 |
| $Cl_2$ | 1.99 |
| $Br_2$ | 2.28 |
| $I_2$ | 2.67 |
| ClF | 1.09 |
| BrCl | 2.14 |
| BrF | 1.76 |
| ICl | 2.32 |

| | |
|---|---|
| HF | 0.92 |
| HCl | 1.27 |
| HBr | 1.41 |
| HI | 1.61 |
| $N_2$ | 1.09 |
| $O_2$ | 1.21 |
| NO | 1.15 |
| CO | 1.13 |

# The Nature of the Chemical Bond

- Pose the question:“Why do atoms sometimes form stable molecules and compounds…. and sometimes not?”

- Or perhaps reducing the general question to more limited questions for which there is a higher probability of getting answers:
  - “What is the energy in bonds?”
  - “What is the distance between atoms?”
  - “What is the shape and geometry that results?”

## Bond Energies (Enthalpies in kJ/mol) of homonuclear diatomic molecule

## $H_2$ = 400 kJ/mol (benchmark)

### Diatomic molecules

- $Li_2$ 105
- $Na_2$ 71
- $K_2$ 50
- $Rb_2$ 46
- $Cs_2$ 44

- $F_2$ 154
- $Cl_2$ 247
- $Br_2$ 192
- $I_2$ 151
- $N_2$ 946
- $O_2$ 498

# Bond Energy (Enthalpy): the energy required to break a bond between 2 atoms

| Bond | kJ/mol | Bond | kJ/mol | Bond | kJ/mol |
|---|---|---|---|---|---|
| H—H | 431 | Sn—Sn | 163 | N—Cl | 201 |
| C—C | 345 | Sb—Sb | 121 | O—Cl | 218 |
| C=C | 610 | C—H | 416 | Si—Cl | 381 |
| C≡C | 835 | N—H | 391 | P—Cl | 326 |
| N—N | 163 | O—H | 464 | S—Cl | 339 |
| N≡N | 945 | F—H | 565 | As—Cl | 293 |
| O—O | 146 | Si—H | 318 | Se—Cl | 243 |
| O=O | 494 | P—H | 322 | Sn—Cl | 318 |
| F—F | 155 | S—H | 347 | Sb—Cl | 310 |
| Cl—Cl | 242 | Cl—H | 431 | C—N | 305 |
| Br—Br | 193 | As—H | 247 | C≡N | 890 |
| I—I | 151 | Se—H | 276 | C—O | 358 |
| Si—Si | 222 | Br—H | 366 | C=O | 745 |
| P—P | 201 | Te—H | 239 | C—S | 272 |
| S—S | 226 | I—H | 299 | C=S | 536 |
| Se—Se | 209 | C—Cl | 339 | S=O | 498 |

## 17.5 Ionic and Covalent Bonds

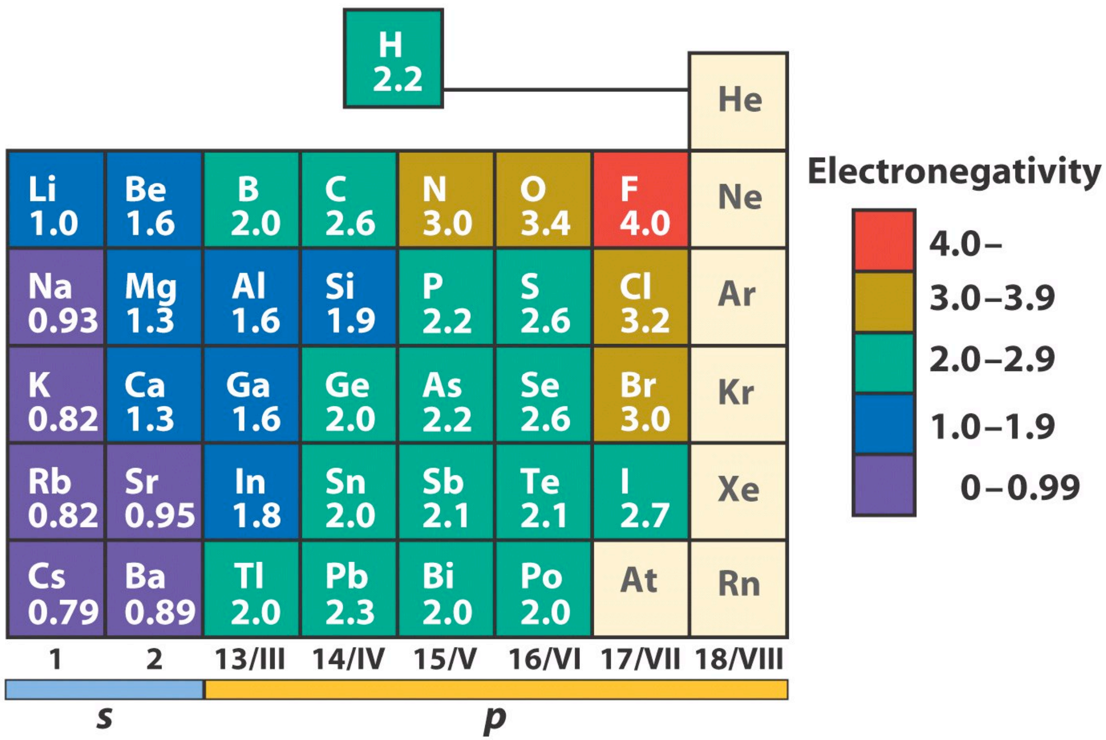
Ionic bonds: Electron density is mainly transferred from one atom to another atom to create a bond between two atoms.

Covalent bonds: Electron density is shared by two bonded atoms.

Electronegativity: A measure of the ability of an atom in a bond to attract electrons from other atoms.

Percent covalent (ionic) character: A measure of the polarity of a bond between two atoms.

# Electronegativity: a measure of the power of an atom to attract electrons to itself in a bond. Most electronegative atoms: F > O > Cl > N ~ Br > I




$E_n = -(Z^2/n^2)$

Across row $Z_{eff}$ increases for similar n (valence electrons see more + as $Z_{eff}$ increases)

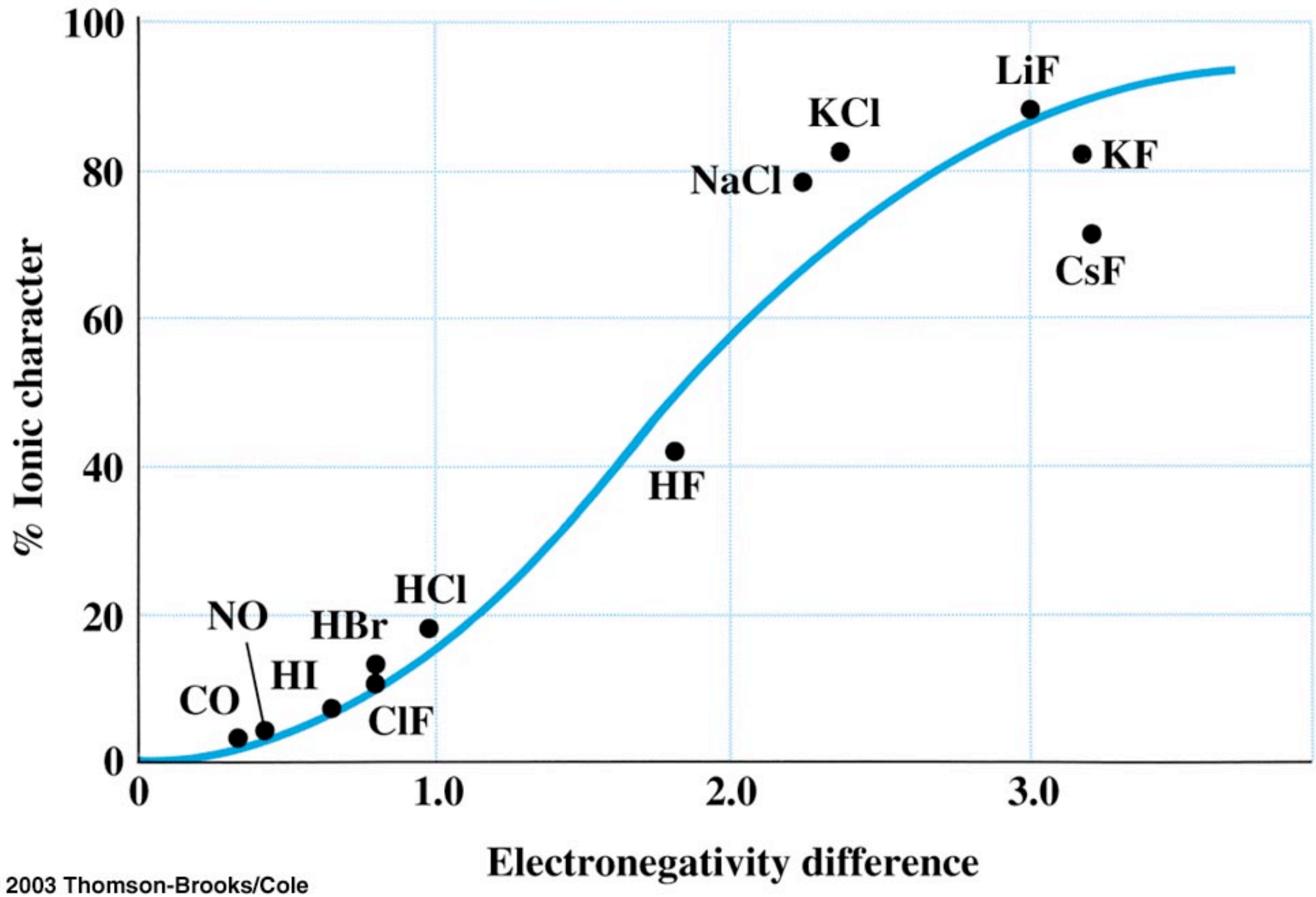
Down column $Z_{eff}$ is similar for increasing n and increasing r (valence electrons further away with same $Z_{eff}$)

% Ionic character from dipole moments: Compare the measured dipole moment to the dipole moment for complete transfer of one electron (=100%).

**TABLE 17–4** Ionic Character of Diatomic Molecules

| Molecule | Percent Ionic Character ($100\,\delta$) | Molecule | Percent Ionic Character ($100\,\delta$) |
|---|---|---|---|
| $H_2$ | 0 | CsF | 70 |
| CO | 2 | LiCl | 73 |
| NO | 3 | LiH | 76 |
| HI | 6 | KBr | 78 |
| ClF | 11 | NaCl | 79 |
| HBr | 12 | KCl | 82 |
| HCl | 18 | KF | 82 |
| HF | 41 | LiF | 84 |
| | | NaF | 88 |

# % Ionic character as a function of electronegativity difference: % IC = $(EN_L - EN_{S)})/ EN_L x100\%$



# Previews of coming attractions

Chapter 18 Molecular orbitals and spectroscopy

Diatomic molecules

Polyatomic molecules

Conjugation of bonds and resonance structures

The interaction of light and matter (spectroscopy)

Buckyballs

## 18.1 Diatomic molecules

Molecular orbitals

Orbital correlation diagrams

Homonuclear diatomic molecules

Heteronuclear diatomic molecules

## 18.2 Polyatomic molecules

Valence bond theory and molecular orbital theory

Hybridization of orbitals

Hybridization and molecular geometry

Hybridization and bond order. Single, double and triple bonds

## 18.3 Conjugation of bonds. Resonance structures

Resonance hybrids

Connection between MO theory and Lewis resonance structures

MOs of conjugated molecules

# The interaction of light and molecules. Molecular spectroscopy

Electronic spectroscopy

Vibrational spectroscopy

Spin spectroscopy (Magnetic resonance)

Absorption of light and color

Photochemistry