Chapter 8 Periodicity (Ch8 Chang, Chs7 and 8 in Jespersen)

Periodic Relationships Among the Elements (Periodic Trends)

Classification of the elements

There are *four* categories of elements in the Periodic Table (recall Chapter 2)

1. Noble gases, elements in which the *outer shell* is *complete*, Group 8A.

2. Representative elements (main group) Groups 1A, 2A, 2B, 3A, 4A, 5A, 6A, and 7A.

These are elements in which the last electron added enters the *outermost* shell, but the outermost shell is *incomplete*. The outermost shell for these elements is the valence shell. (*Filling the **s** and **p** subshells*).

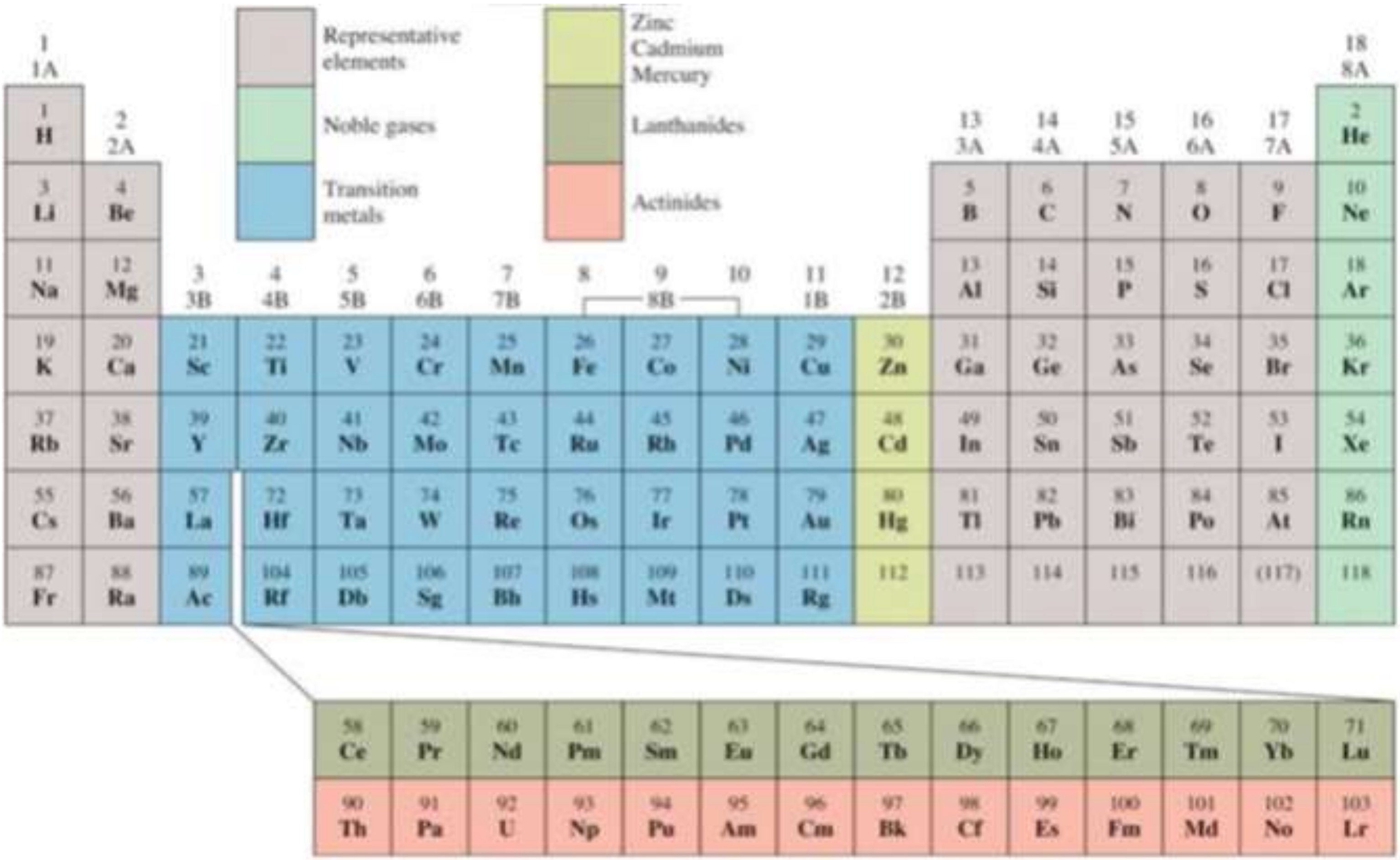
3. The Transition elements. These are elements in which the *second shell* counting in from the outside is building from 8 to 18 electrons.

The outermost **s** subshell and **d** subshell of the second shell from the outside contain the *valence electrons* in these elements. (*Filling the **d** subshell*).

The first transition series runs from scandium (Sc) to copper (Cu).

Elements in group 2B (Zn, Cd, Hg) are often **not** considered transition metals (*d-subshell is **filled***).

4. The inner transition elements. These are elements where we are filling the **f** subshell.

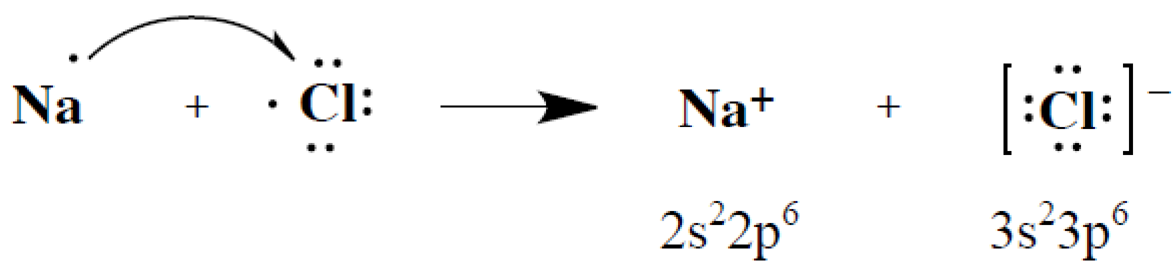


Ions and Their Electron Configurations

Ionic Bonding produces ions.

$Na(s) \quad + \quad \frac{1}{2} Cl_2(g) \quad \rightarrow \quad NaCl(s) \qquad \Delta H^o_f = -\,410.9$ kJ/mol

Lewis Symbols: use atomic symbol and one dot for each of the *valence* electrons.



Electron Configurations of Ions of Representative Elements

Ions derived from representative elements will usually have noble gas *outer electron configurations*.

Na $\quad 1s^2\ 2s^2 2p^6\ 3s^1 \quad = [Ne]\ 3s^1$

$Na^+ \quad 1s^2\ 2s^2 2p^6 \quad = [Ne]$

Cl $\quad 1s^2\ 2s^2 2p^6\ 3s^2 3p^5 \quad = [Ne]\ 3s^2 3p^5$

$Cl^- \quad 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 \quad = [Ne]\ 3s^2 3p^6 \quad = [Ar]$

Transition metals

In forming ions, transition metals lose the *valence shell* **s** electrons first (***first in, first out!***), and then as many **d** electrons as are required to reach the charge on the ion.

(Notice that for TM's the order of filling does **not** have to match the order of removal. This has to do with *electron-electron* and *electron-nucleus* interactions that occur, based on the number of *currently present* electrons).

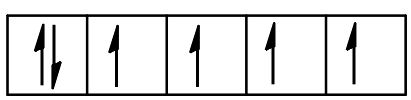
Fe [Ar] $3d^6\ 4s^2$

Fe^{2+} [Ar] $3d^6$

Fe^{3+} [Ar] $3d^5$

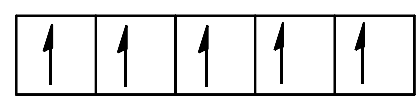
<u>Problem:</u> How many unpaired electrons are in the Fe^{2+} and Fe^{3+} ions ?

Fe^{2+} is [Ar] $3d^6$



4 unpaired electrons

Fe^{3+} is [Ar] $3d^5$



5 unpaired electrons

Periodic Trends in Atomic Size

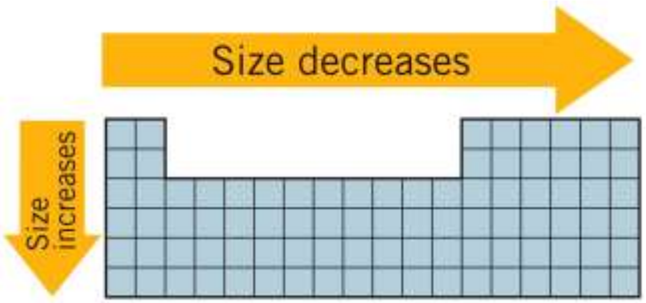
1. Within each vertical column (*group*) the atomic radius tends to *increase* as we proceed from top to bottom. (As go ↓ in periodic table, atoms get bigger).

- $\boldsymbol{Z_{eff}}$ (effective Nuclear charge Ch7) is essentially constant
- ***n*** (principal quantum number) *increases*, outer electrons are *farther away* from nucleus and the radius *increases*.

2. Within each horizontal row (period) the atomic radius tends to decrease as we move from left to right.

(As go → in periodic table, atoms get smaller).

- ***n*** constant
- $\boldsymbol{Z_{eff}}$ *increases*, outer electrons feel a larger $\boldsymbol{Z_{eff}}$ and radius decreases as they are pulled in.



Trends in periodic *properties* depend on several factors including:

(1) The number of *valence electrons*.

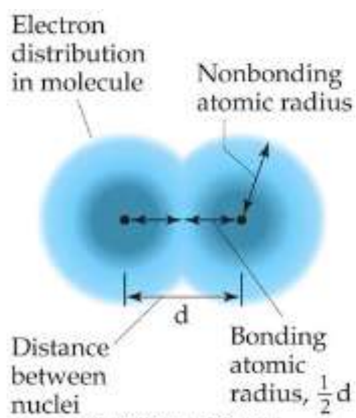
(2) The magnitude of the *nuclear charge* and the *total* number of *electrons* surrounding the nucleus.

(3) The number of **filled** shells lying between the nucleus and the valence shell.

(4) The *distances* of the electrons in the various shells from each other, and from the nucleus.

Variations in Covalent Radii

The bonding atomic radius is half the distance between the centers of neighboring atoms (nuclei).



- For metallic elements it is determined for the solid.
- For nonmetallic elements it is determined for diatomic molecules (covalent bond).

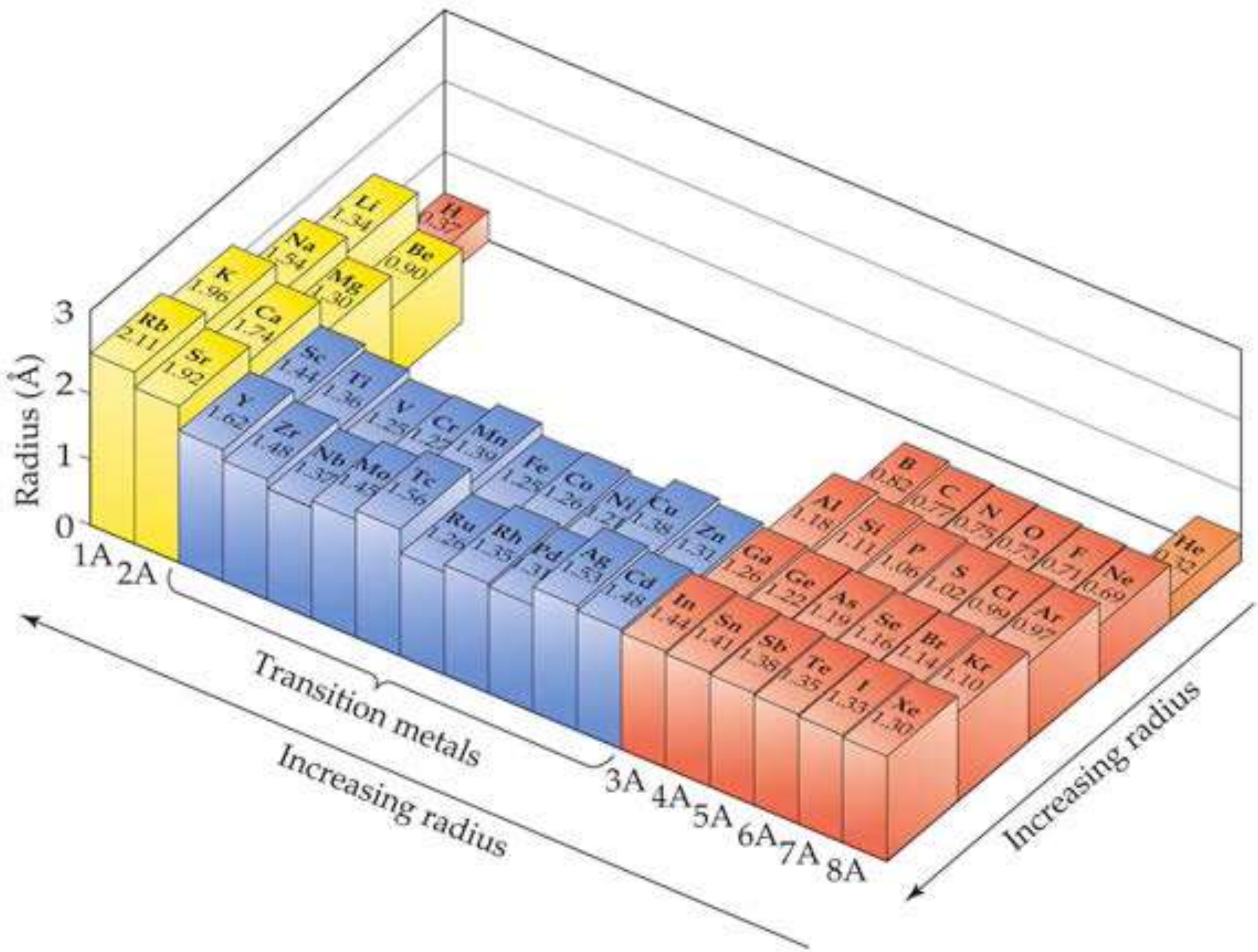
Across a period (gets smaller)

Atom	Covalent Radius, Å	Nuclear Charge	Electron Configuration
Na	1.86	+11	[Ne] $3s^1$
Mg	1.60	+12	[Ne] $3s^2$
Al	1.43	+13	[Ne] $3s^23p^1$
Si	1.17	+14	[Ne] $3s^23p^2$
P	1.10	+15	[Ne] $3s^23p^3$
S	1.04	+16	[Ne] $3s^23p^4$
Cl	0.99	+17	[Ne] $3s^23p^5$

Down a Group (gets larger)

Atom	Covalent Radius, Å	Nuclear Charge	Number of Electrons in Each Shell
F	0.64	+9	2, 7
Cl	0.99	+17	2, 8, 7
Br	1.14	+35	2, 8, 18, 7
I	1.33	+53	2, 8, 18, 18, 7
At	1.40	+85	2, 8, 18, 32, 18, 7

Radii trends in Diagram form



Sizes of Ions, Ionic Radii

• Cations are *smaller* than their parent atoms, and often $\frac{1}{2}$ to $\frac{2}{3}$ times smaller.

(Removal of the outermost electrons results in *fewer* electron-electron repulsions).

Same Z_{eff}, but now less electrons, so the radius contracts.

• Anions are *larger* than their parent atoms. Often 1.5 to 2 times larger.

(There are more electron-electron repulsions).

Same Z_{eff}, but now more electrons, so the radius expands.

Variations in Ionic Radii

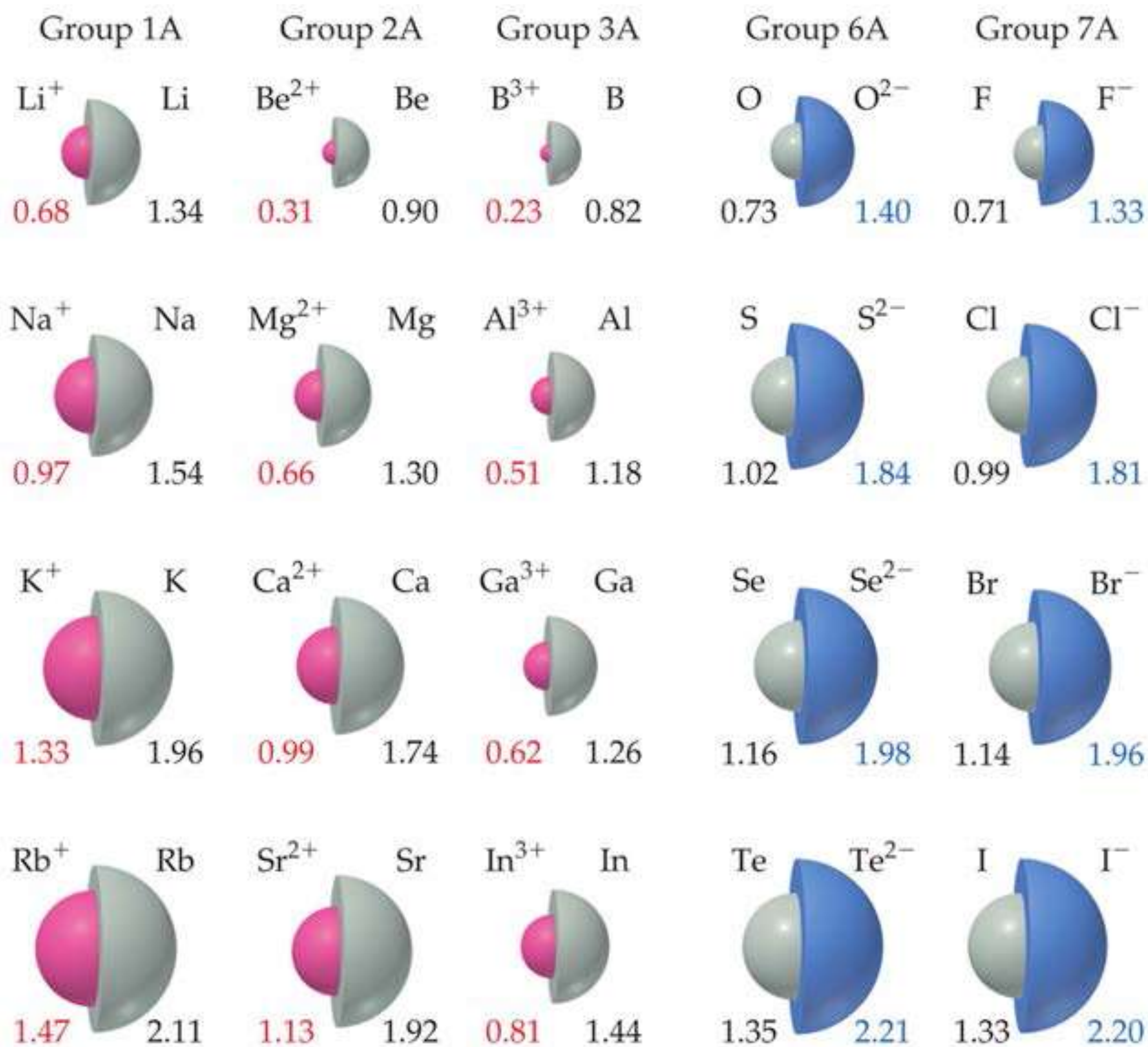
Species	**N^{3-}**	**O^{2-}**	**F^{-}**	**Ne**	**Na^{+}**	**Mg^{2+}**	**Al^{3+}**
Radius, Å	1.71	1.40	1.33	1.12	0.97	0.66	0.50
Nuclear Charge	+7	+8	+9	+10	+11	+12	+13

The above ions all have the **same** electron configuration: $1s^2\ 2s^2 2p^6$

(Isoelectronic means "same number of electrons").

The increasing nuclear charge L → R pulls the electrons in *closer* (so the ionic radius *decreases*).

Figure showing **sizes** of selected Atoms and their *corresponding* Ions



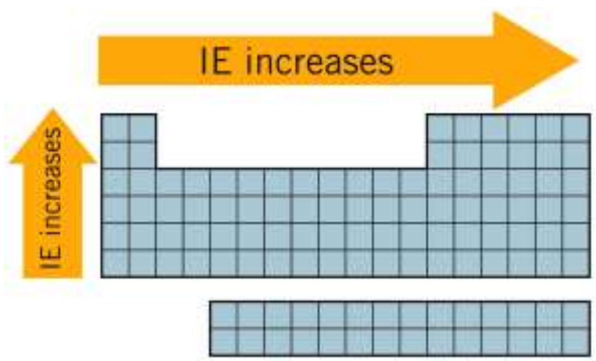
Ionization energy

The ionization energy is the minimum amount of energy required to *remove* an *electron* from the *ground state* of an *isolated gaseous atom* or *ion*.

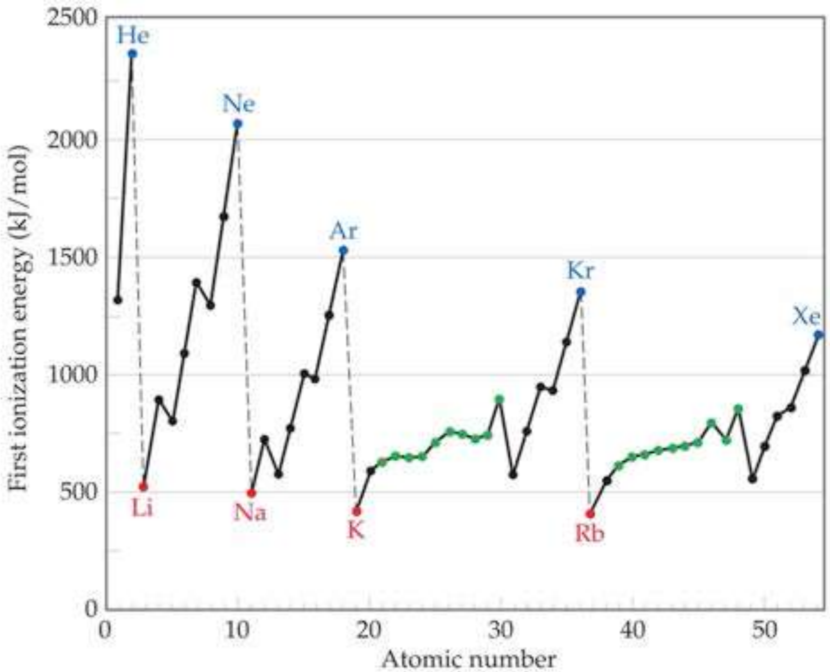
I_1	**$Na(g)$**	$\rightarrow$	**$Na^+(g)$**	+	**e^-**	496 kJ/mol
I_2	**$Na^+(g)$**	$\rightarrow$	**$Na^{2+}(g)$**	+	**e^-**	4560 kJ/mol

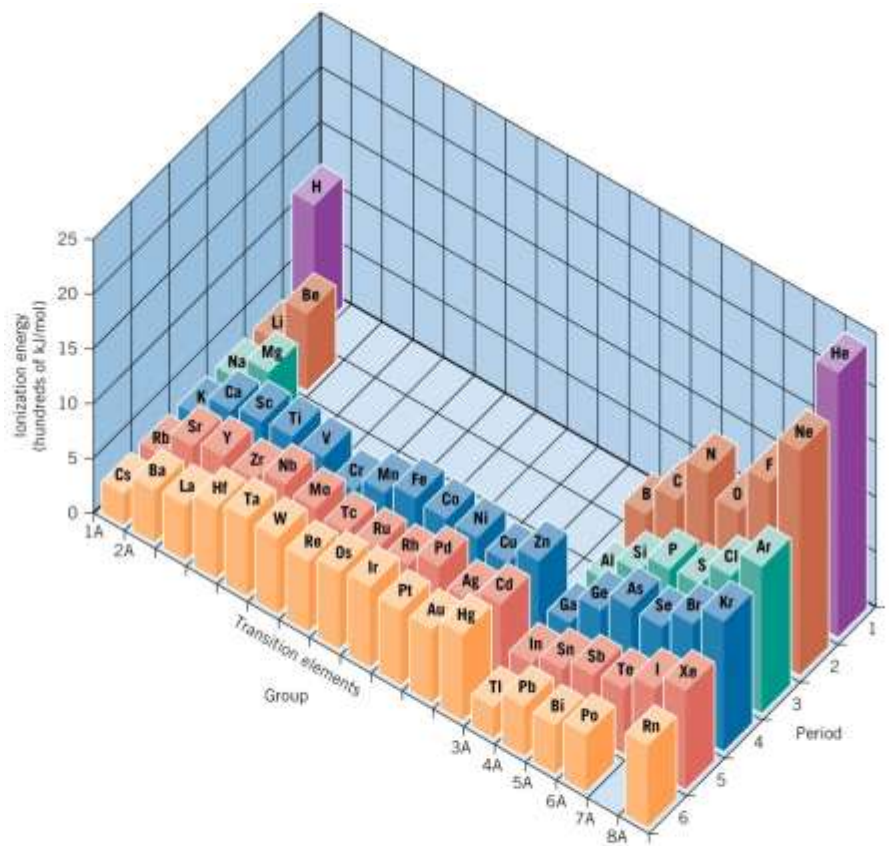
General Trends:

- Ionization energy *decreases* down a vertical column / group (as ***n*** increases).
- Ionization energy *increases* across a horizontal row / period (as $\boldsymbol{Z}_{\mathbf{eff}}$ increases).



Notice the general trends of IE *increasing* as you go → and ↑ the periodic table.

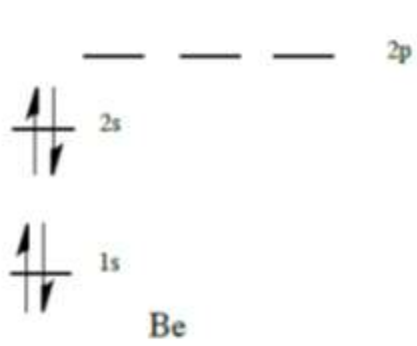


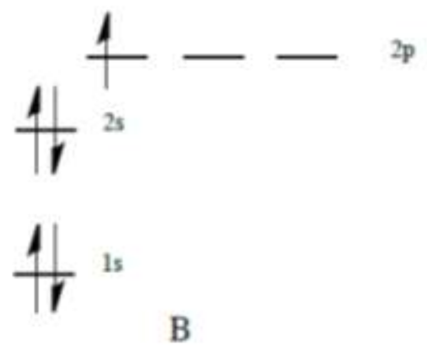


On *closer* inspection of the 2nd row, there is the trend of increasing IE as →, but the *specific* values for **B** and **O** seem off…

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

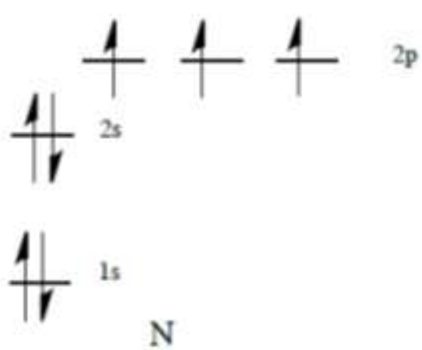
<u>Explanation for the **B** and **O** values</u>

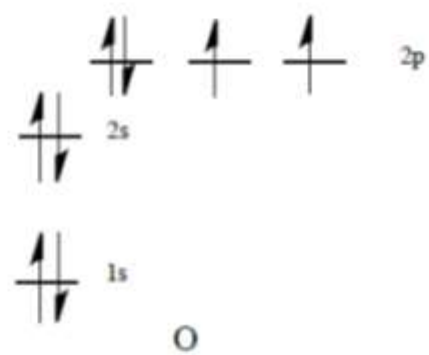




The electron *removed* for **B** is from the *higher* energy 2p orbital.

EASIER TO REMOVE.
Lower IE for **Boron**.





The electron *removed* for **O** is one of the paired electrons.

This electron has electron/electron repulsions, and also its *removal* generates a half filled subshell (extra stability).

EASIER TO REMOVE.
Lower IE for **Oxygen**.

Higher Ionization Energies:

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312					
2	He	2,373	5,251				
3	Li	520	7,300	11,815			
4	Be	899	1,757	14,850	21,005		
5	B	801	2,430	3,660	25,000	32,820	
6	C	1,086	2,350	4,620	6,220	38,000	47,261
7	N	1,400	2,860	4,580	7,500	9,400	53,000
8	O	1,314	3,390	5,300	7,470	11,000	13,000
9	F	1,680	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

$I_1 < I_2 < I_3 <$ etc.

Notice the "big jumps"

Li = [He] $2s^1$

C = [He] $2s^2 2p^2$

(It is **especially difficult** to remove an electron from a *noble gas configuration*).

Electron affinities

Electron affinity (EA) is the energy change that occurs when an *electron* is *added* to a gaseous atom.

$X(g)$	+	**e^{-}**	$\rightarrow$	**$X^{-}(g)$**		
$Cl(g)$	+	**e^{-}**	$\rightarrow$	**$Cl^{-}(g)$**	$\Delta E = -349$ kJ/mol	(EA = 349 kJ/mol)

Since the addition of one electron to *almost* all the elements is exothermic, sometimes the electron affinity is reported as $-\Delta E$ (*so be careful to know which convention your source is using*).

For some very *unfavorable* cases, ΔE can be +ve :

$Ar(g)$	+	**e^{-}**	$\rightarrow$	**$Ar^{-}(g)$**	$\Delta E > 0$

Notice these **different sign conventions** for Electron Affinity…

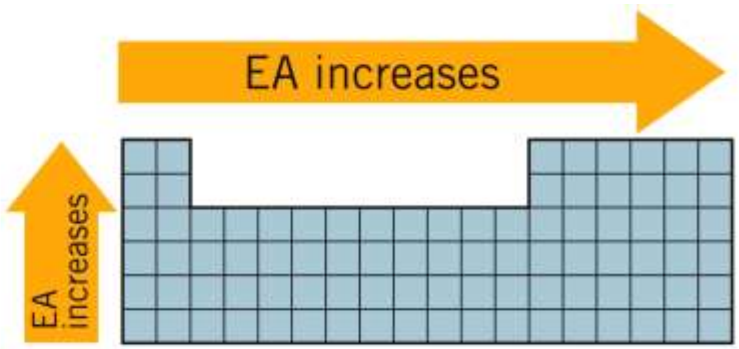
Electron Affinities of the Representative Elements (kJ/mol

1A	2A	3A	4A	5A	6A	7A
H						
−73						
Li	Be	B	C	N	O	F
−60	+238	−27	−122	~+9	−141	−328
Na	Mg	Al	Si	P	S	Cl
−53	+230	−44	−134	−72	−200	−349
K	Ca	Ga	Ge	As	Se	Br
−48	+155	−30	−120	−77	−195	−325
Rb	Sr	In	Sn	Sb	Te	I
−47	+167	−30	−121	−101	−190	−295
Cs	Ba	Tl	Pb	Bi	Po	At
−45	+50	−30	−110	−110	−183	−270

Electron Affinities (kJ/mol) of Some Representative Elements and the Noble Gases

1A	2A	3A	4A	5A	6A	7A	8A
H							He
73							< 0
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	0	141	328	< 0
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	44	134	72	200	349	< 0

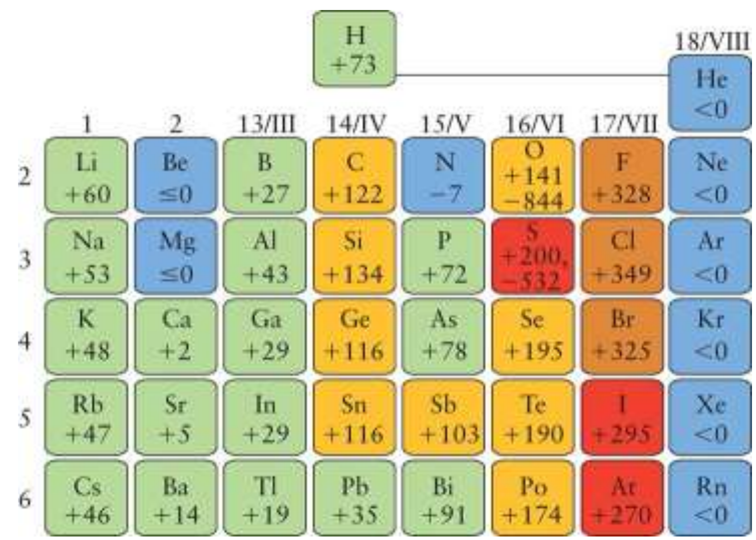
General Trends



Electron affinity becomes less *exothermic* down **column** / **group** as ***n*** increases.
(Electron is harder to add as the orbital is farther from nucleus and feels less positive charge).

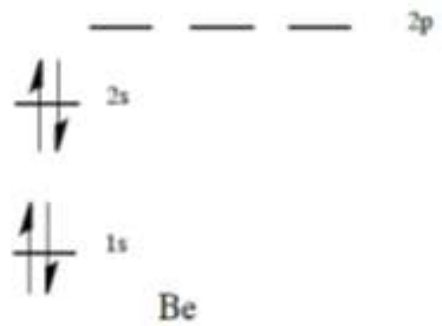
Electron affinity becomes more *exothermic* across **row** / **period** as $\boldsymbol{Z}_{\mathbf{eff}}$ increases.
(Easier to attract electrons as positive charge increases).

In the tables, **Be** and **N** seem off – but again we can explain looking at the *electrons*…

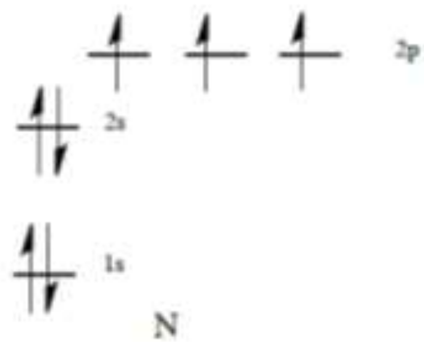


	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H +73				He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200, −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6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

Be has a *filled* subshell (extra stability), which is disrupted on the addition of 1e−.



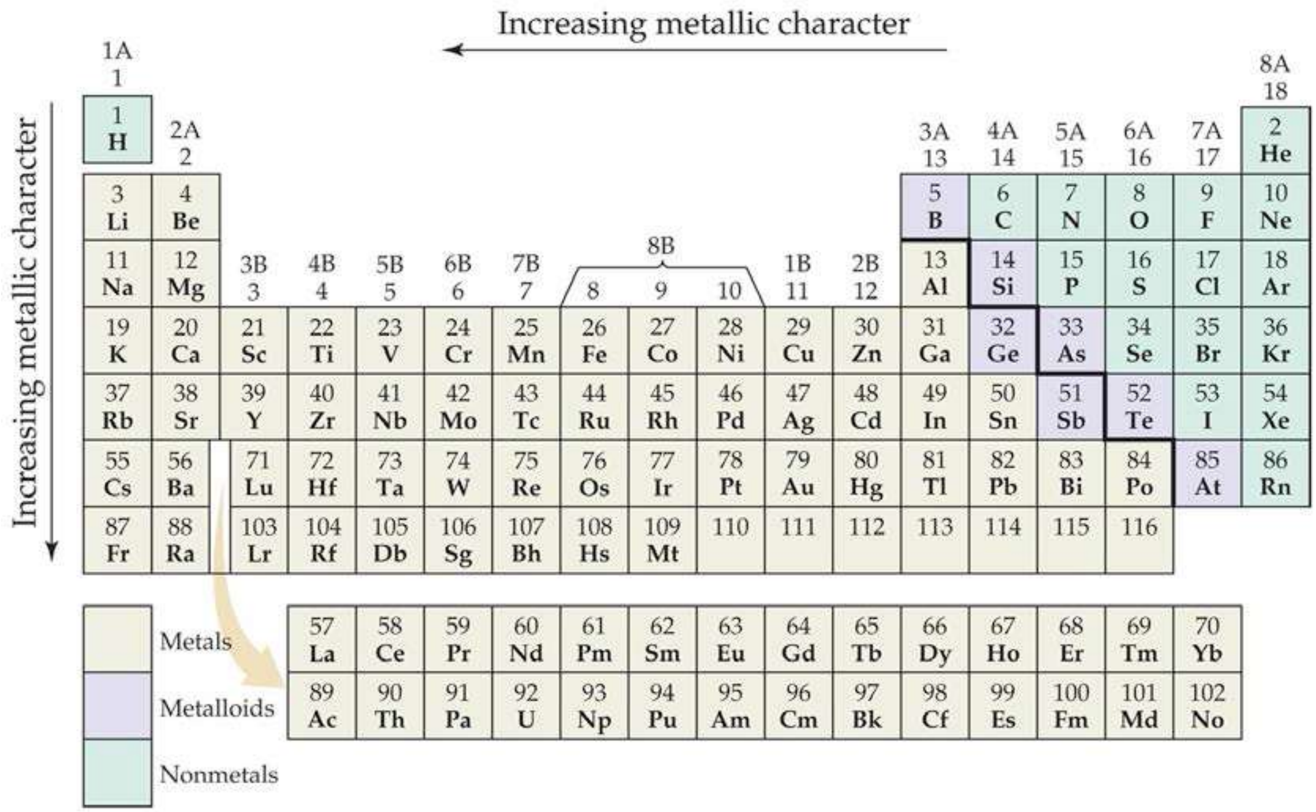
N has a *half filled* subshell (extra stability), which is disrupted on the addition of 1e−.



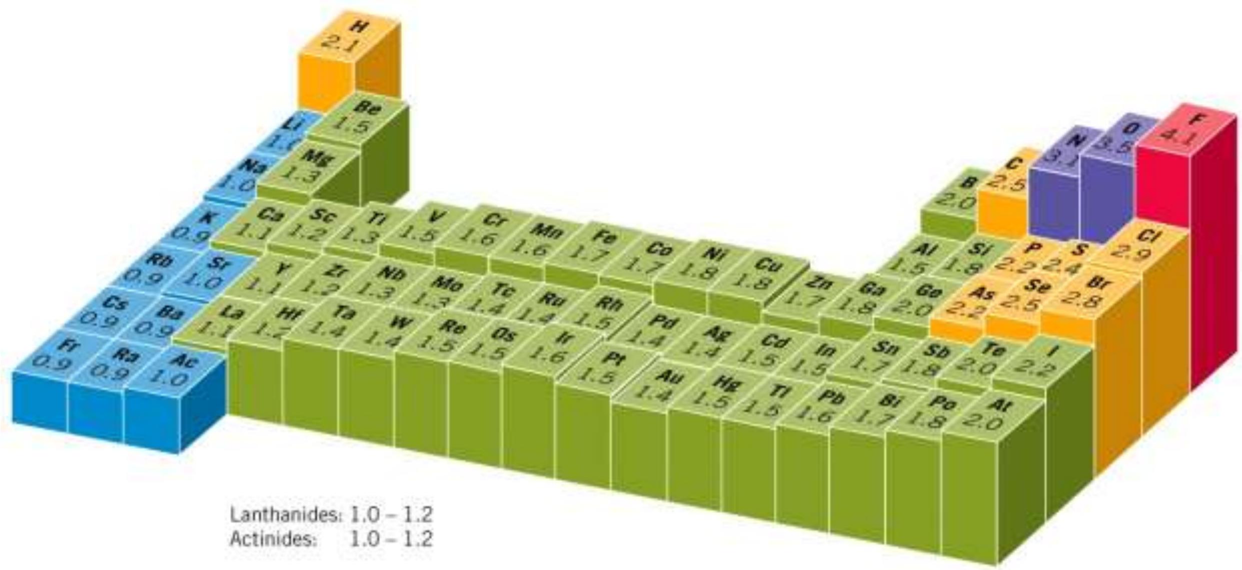
Metallic Character

Metals tend to *lose electrons* in chemical reactions, as indicated by their **low** ionization energies.

(Nonmetals tend to *gain electrons* in chemical reactions, as indicated by their **high** electron affinities, and have a high attraction for electrons within a compound).



Electronegativity – the ability of an atom in a molecule to attract electrons to itself.



Electronegativity *increases* as you go:

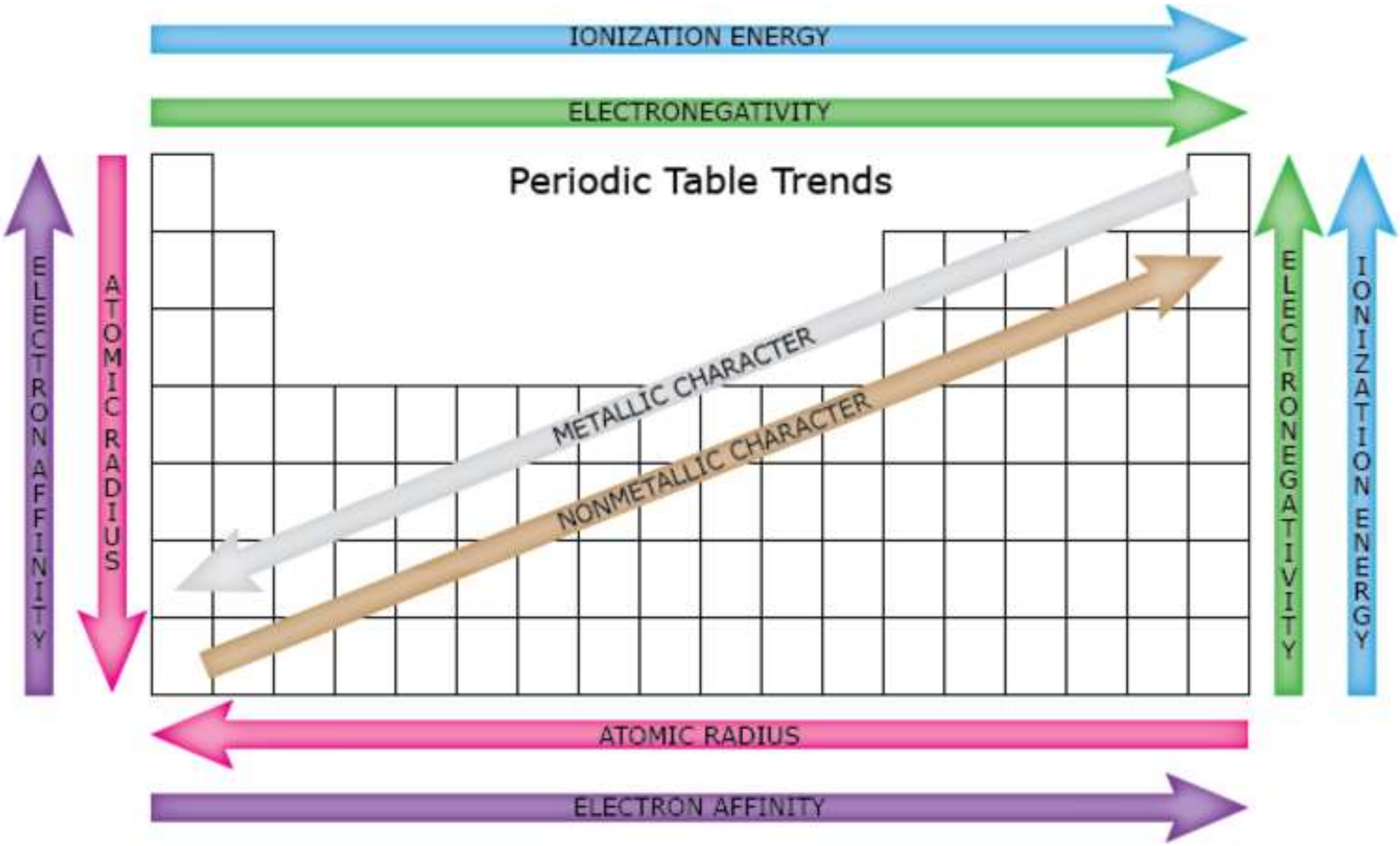
i) Up a Group / column

ii) L → R across a Period / row.

Within a compound, metal atoms have relatively *low* attraction for electrons, as indicated by their *low* electronegativities.

Nonmetals tend have *high* attraction for electrons within a compound.

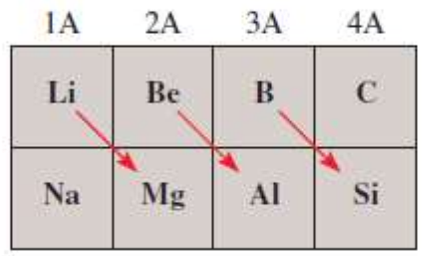
Summary of Periodic Trends



Diagonal Relationships

The up/down and left/right trend in the periodic table give rise to Diagonal Relationships.

These are *similarities* between *pairs* of *elements* in *different groups* and *periods* of the periodic table.



The first three elements of second period (**Li**, **Be**, and **B**) exhibit many similarities to those elements located diagonally below them.

Li→Mg **Be→Al** **B→Si**.

Oxide Trend

Another trend is that the *Oxides* go from basic to acidic moving from L → R in the Periodic table.

In general, group 1A and 2A metal oxides are basic, and nonmetal oxides are acidic. (*Recall Ch4*).

Aluminum oxide is amphoteric. It can display **both** *acidic* and *basic* properties depending on the nature of its environment. (It will be acidic in basic media, and basic in acidic media).