Periodic Properties of the Elements

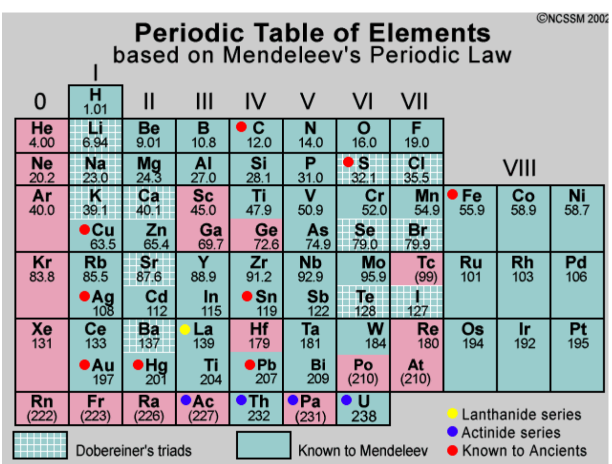
Reading:	Ch 8, sections 6 - 9	Homework:	Chapter 8: 57*, 59, 61*, 63*, 63, 71, 75*, 77

* = ‘important’ homework question

Background Discussion: What do we already know about the origins of today’s modern periodic table? What periodic trends do we already know?

Dmitri Mendeleev
“What was I doing back in 1869?”

Mendeleev’s Periodic Table



Mendeleev’s Predictions (all pretty good!)

Germanium (eka-silicon)

	Mendeleev’s predicted properties	Actual properties
Atomic mass	About 72 amu	72.64 amu
Density	5.5 g/cm^3	5.35 g/cm^3
Formula of oxide	XO_2	GeO_2
Formula of chloride	XCl_4	$GeCl_4$

Overview of Periodic Trends

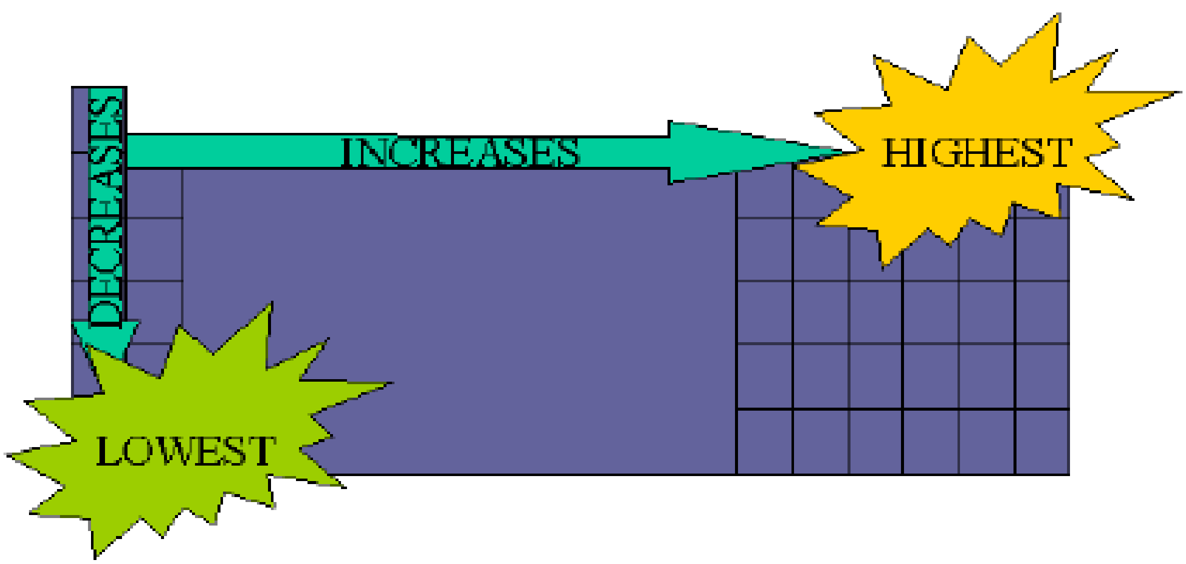
‘Popping the Hood’

Recall: The layout of the Periodic Table is directly correlated to the elements’ electronic structures.

Additional *chemical* and *physical* trends among the table’s constituents can be understood by ‘popping the hood’ on these elements and determining the relationship between atomic properties electronic structures

Essentially all periodic trends follow the same general ‘bottom left to top right’ scheme. See generic diagram the below. The periodic trends examined will be:

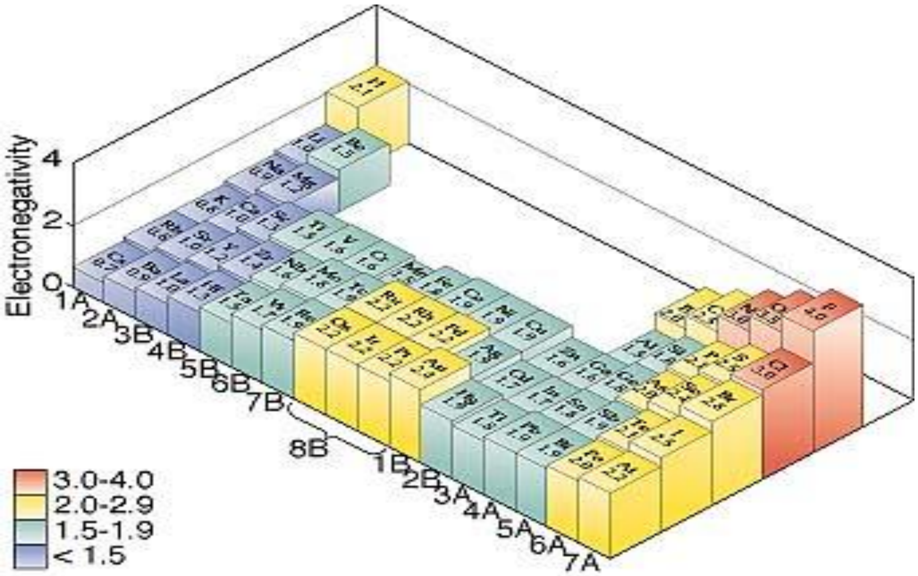
Electronegativity	**Ionization Energy**
Atomic Size (radius)*	**Electron Affinity**



Question: Which ‘bottom left → top right trend’, mentioned above, have we already encountered? Is this a ‘real’ chemical trend?

Answer:

Trends in Electronegativity:



Note: Electronegativity is not a pure atomic property – it is a derived mathematically from *electron affinity* and *ionization energy* values

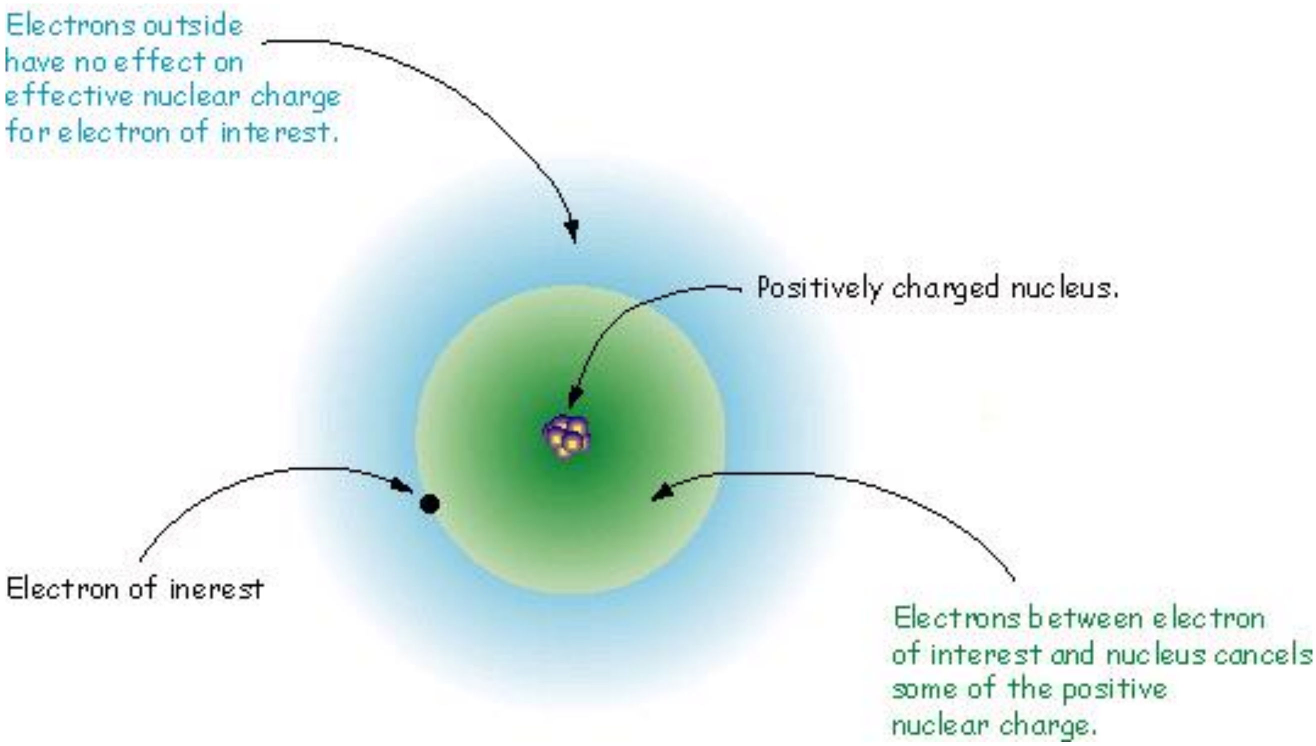
Discussion: What atomic scale factors do you think effect how strongly the nucleus ‘pulls’ on its ‘orbiting’ electrons (so, in turn, effecting each atomic property)? *Hint: consider the analogy of the Earth and its satellites.*

1.
2.
3.

<u>Effective Nuclear Charge (Z_{eff})</u>: The *real* 'Man behind the Curtain'

Basic definition of Z_{eff}: The 'pull' orbiting *valence* electron(s) 'feel' from their respective positively charged nucleus, as modified by screening (*core*) electrons

<u>Diagram</u>



<u>Equation</u>:

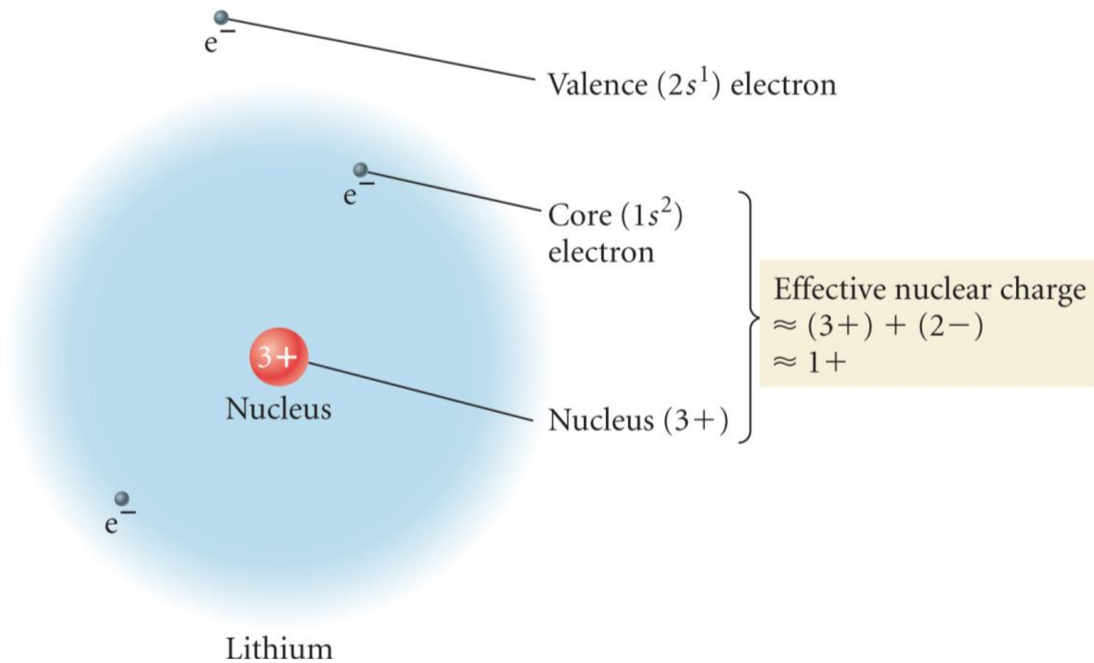
$$Z_{eff} = Z - S$$

Effective nuclear charge (Z_{eff})

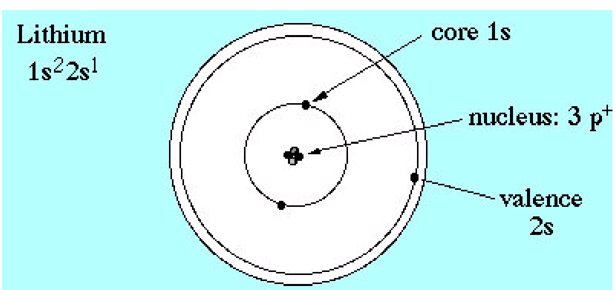
Actual nuclear charge (Z)

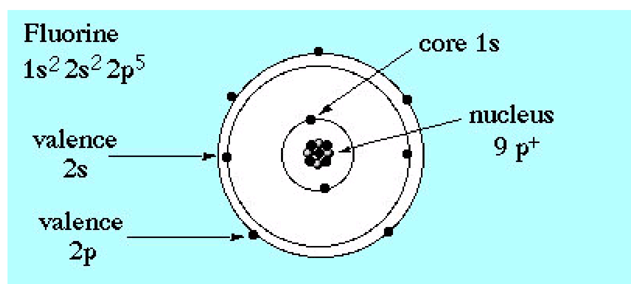
Charge screened by other electrons (S)

Example: Lithium



Lithium and Fluorine (example of a 'row trend'):





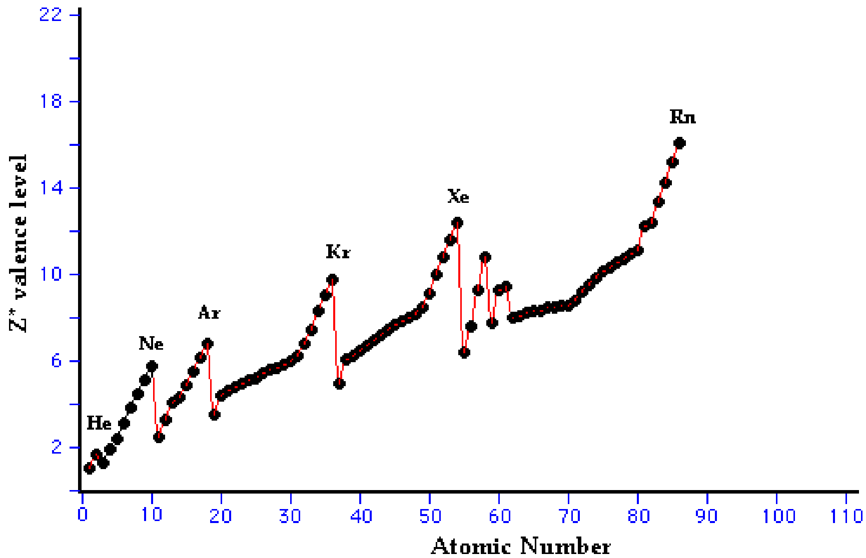
Z_{eff} =

Z_{eff} =

Fact: As Z (atomic number) *increases* 'across a row', the effect of shielding on the valence electrons AND their distance from the nucleus, remains ~*constant*.

Result: Effective Nuclear Charge (Z_{eff}) *increases* for each atom across every row in the Periodic table.

Graph of Z_{eff} vs Atomic Number



Features of the Graph:


'Mesh shirt'

Main

Subtle

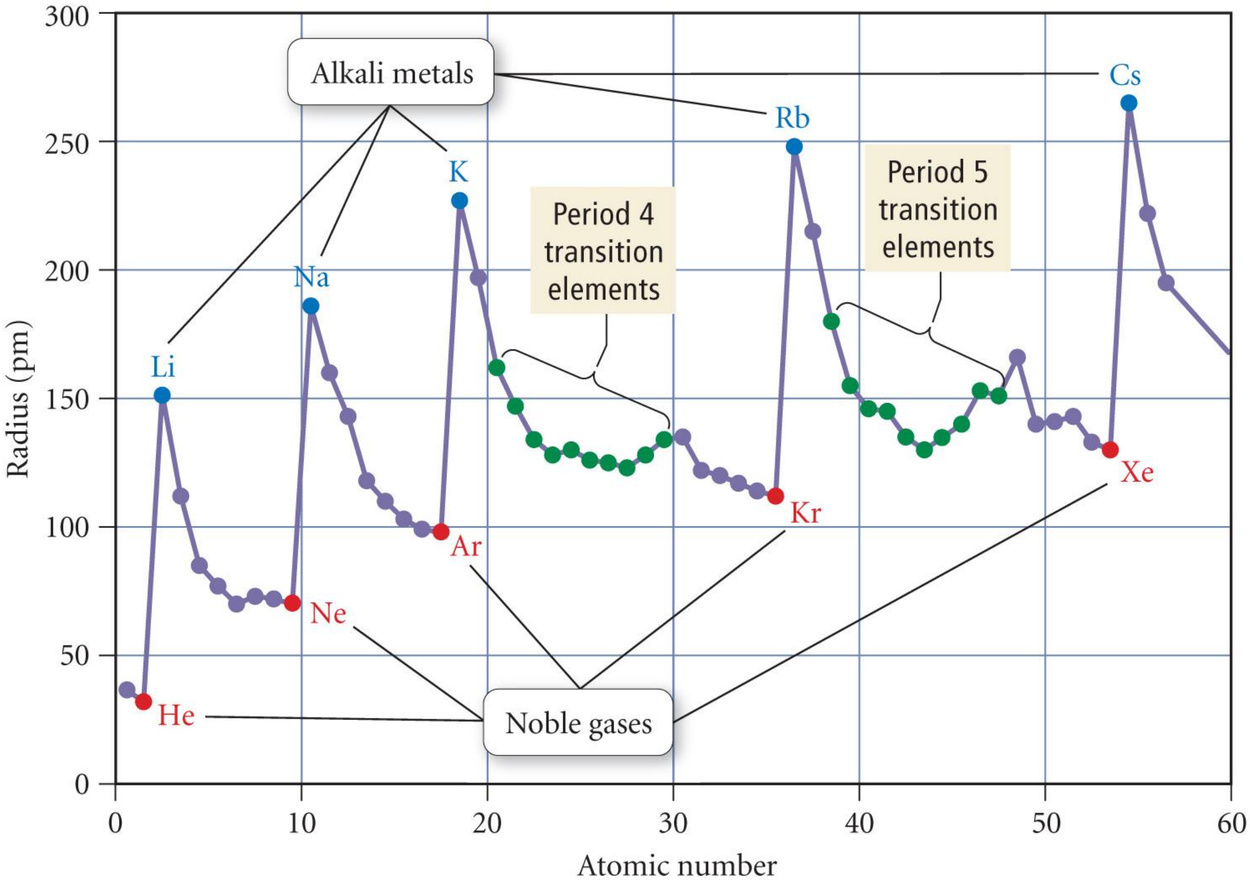
Atomic Radius

Discussion: How and why do trends in Z_{eff} effect the size (radius) of atoms 'across a row' and 'down a column' in the periodic table.

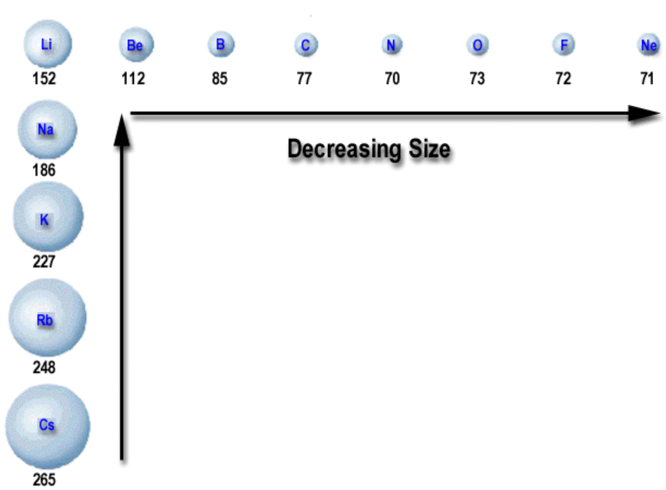
1. 'Across a Row'

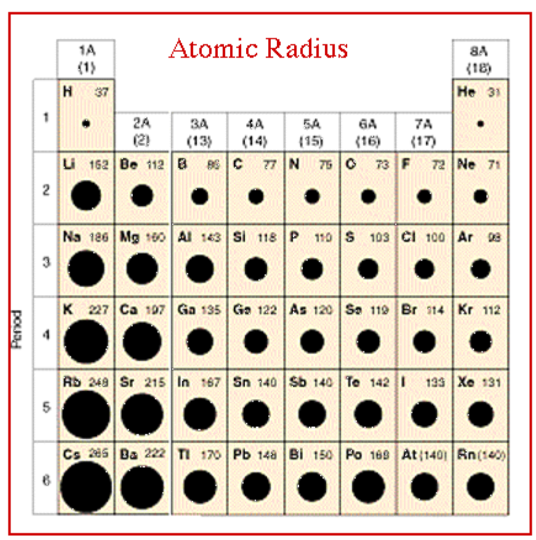
2. 'Down a Column'

<u>Atomic Radius Trends</u>

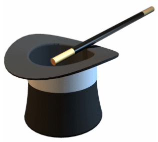


The atomic radii of the *main group elements* follow the classic 'bottom left → top right' periodic trend





<u>Typical Question</u>: Arrange the following atoms in order of increasing atomic radii: Na, Be, Mg.



	Be
Na	Mg

Questions of this type (as well as for other periodic trends) often select three elements from the periodic table that have a 'triangular' relationship.

Understanding the classic 'bottom left → top right' periodic trend allows for the answer to be determined.

<u>Answer</u>:

Ionization Energy

<u>Discussion</u>: What is *ionization*? What then is *1st ionization energy*?

<u>1st Ionization Energy</u>: Energy *required* to remove the first electron from a gaseous atom or ion.

<u>Example</u>: Sodium

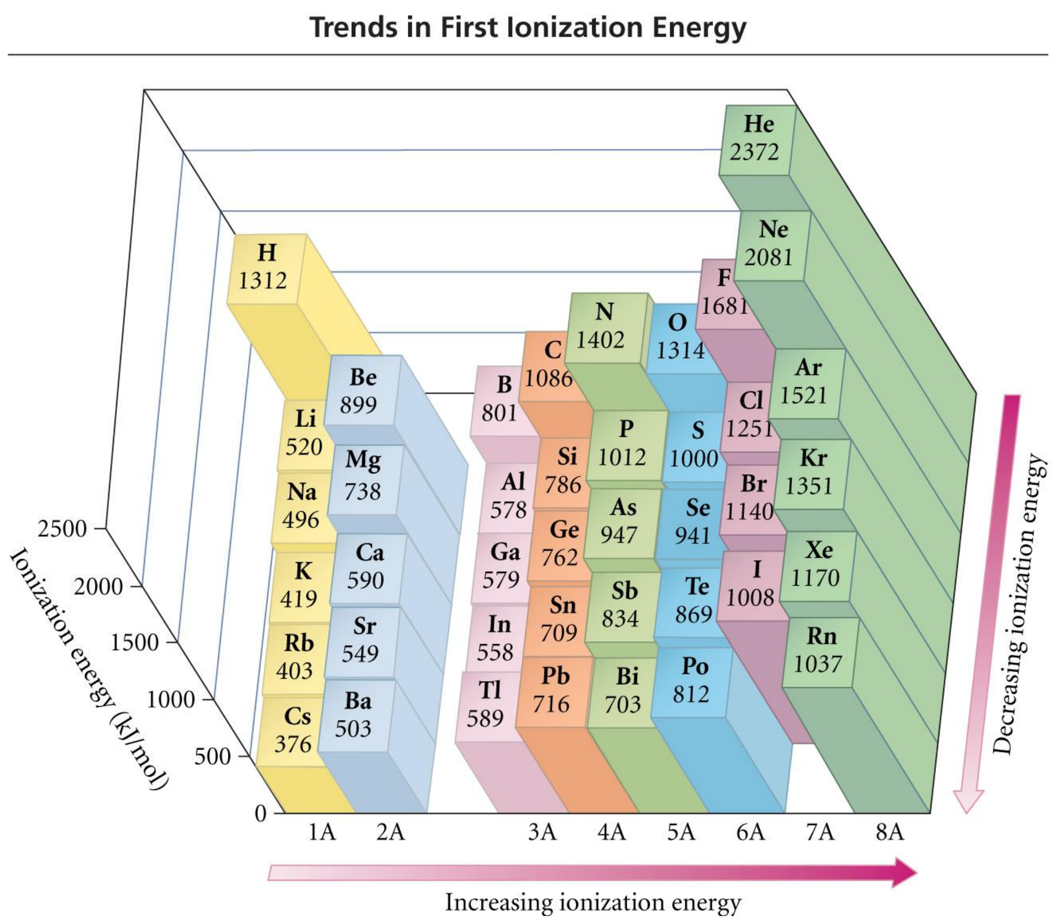
$$Na\,(g) \rightarrow Na^{+}\,(g) + e^{-}\ ;\ I_1 = 496\ kJ/mol$$

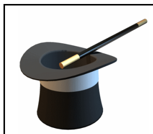
<u>Task</u>: Draw electron dot diagrams illustrating this process

Discussion: How do you think trends in Z_{eff} and atomic radius effect trends in 1st ionization energy 'across a row' and 'down a column' in the periodic table. ***Who wins!?***

1. 'Across a Row'

2. 'Down a Column'





The 1st I.E. of the atoms ***generally*** follow the classic 'bottom left → top right' periodic trend*

Subtle Trends in 1st I.E.: How can subtle deviations ('peaks') from the general trend across any row be rationalized for the group II, III and group V, VI elements?

Task: Draw out ground state orbital 'box' diagrams for Be and B, as well as N and O. What differences do you notice between the two diagrams? How do these features correlate with the unexpected 'peaks'.

'Box' Diagram for Be

Be:					
	1s	2s	2p		

'Box' Diagram for B

B:					
	1s	2s	2p		

'Box' Diagram for N

N:					
	1s	2s	2p		

'Box' Diagram for O

O:					
	1s	2s	2p		

Notes:

Removing electrons from *full* or *half full* (p or d) SUBSHELLS requires more energy than that required to remove electrons from 'adjacent' atom's *incomplete* SUBSHELLS

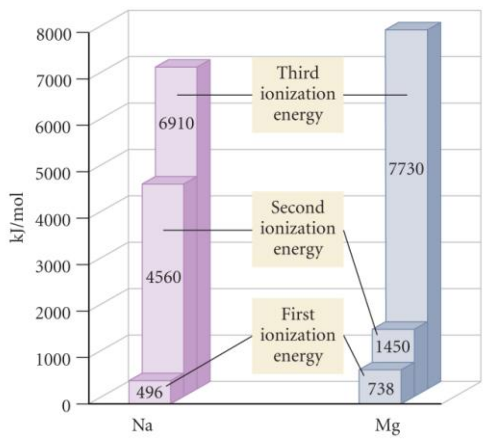
Typical Question: Using only the periodic table as a guide, list the following atoms in order of increasing 1st ionization energy: O, N, Li, Na. Hint: consider both general and subtle trends.

Subsequent Ionization Energies

Discussion: What is the definition of second ionization energy (I_2)? Would you expect this value to be higher or lower than I_1 for Na? Why?

$$Na^{+}(g) \rightarrow Na^{2+}(g) + e^{-}\ ;\ I_1 = \_\_\_\_\_\_\_\_\_ \text{ kJ/mol}$$

Electron dot diagram:



Notes:

TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_5	IE_4	IE_6	IE_7
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

Core electrons

Electron Affinity

Discussion: What is *electron affinity*?

Electron Affinity: Energy *released* when an electron is added to a gaseous atom or ion.

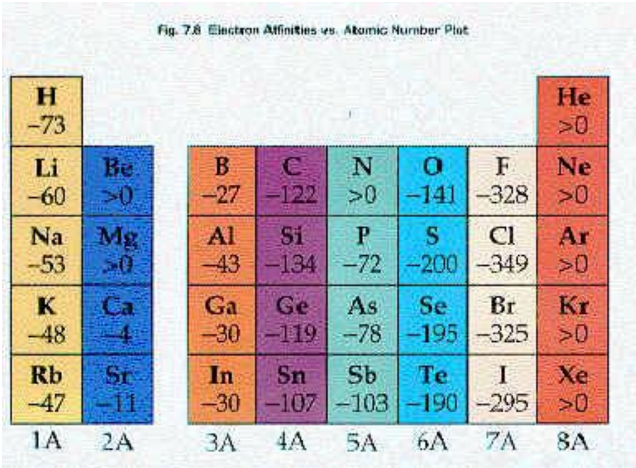
Example: Chlorine

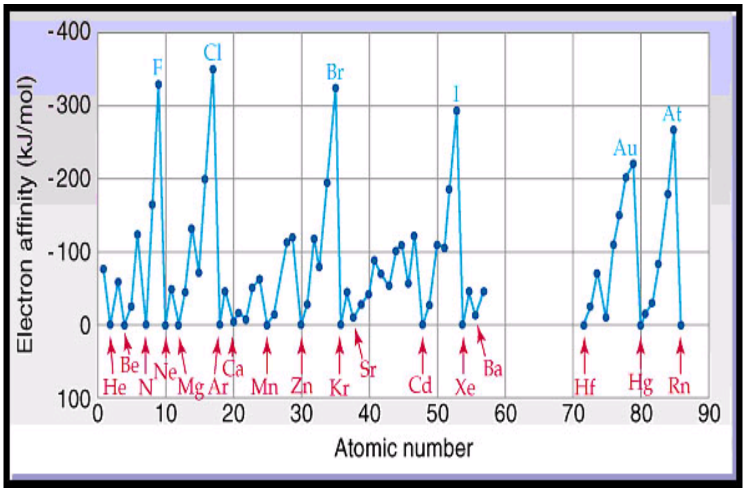
$$Cl\ (g) + e^- \rightarrow Cl^-\ (g) \quad ; \ \Delta E = -349\ kJ/mol$$

Task: Draw electron dot diagrams illustrating this process

Trends in Electron Affinity

Electron affinity and *electronegativity* are similar, except that electron affinity is measured experimentally, while electronegativity is determined mathematically.





Periodic style representations of atomic electron affinity trends. Note both the general and subtle features 'across each row'

Discussion: Why do certain elements, such as Be, N, He and Ne, have negligible electron affinity values? Hint: draw out their respective 'box' diagrams

Be:	1s	2s	2p	N:	1s	2s	2p
He:	1s	2s	2p	Ne:	1s	2s	2p

Answer:

While *electron affinity* and *electronegativity* share a similar general periodic trend, 'subtle' subshell factors must also be taken into account with electron affinity

"Trends"

The following question was taken from your 3rd practice midterm:

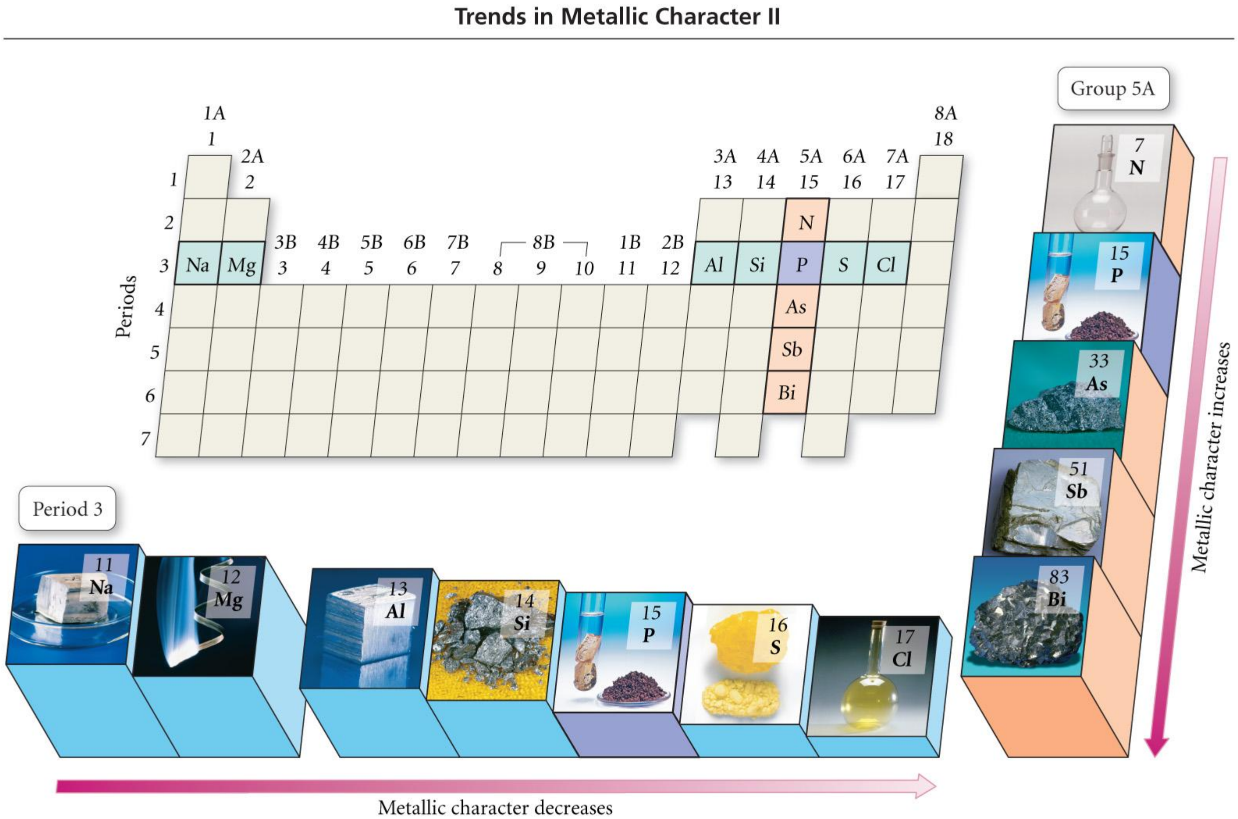
List the following properties of Li, K and Ne in order of:

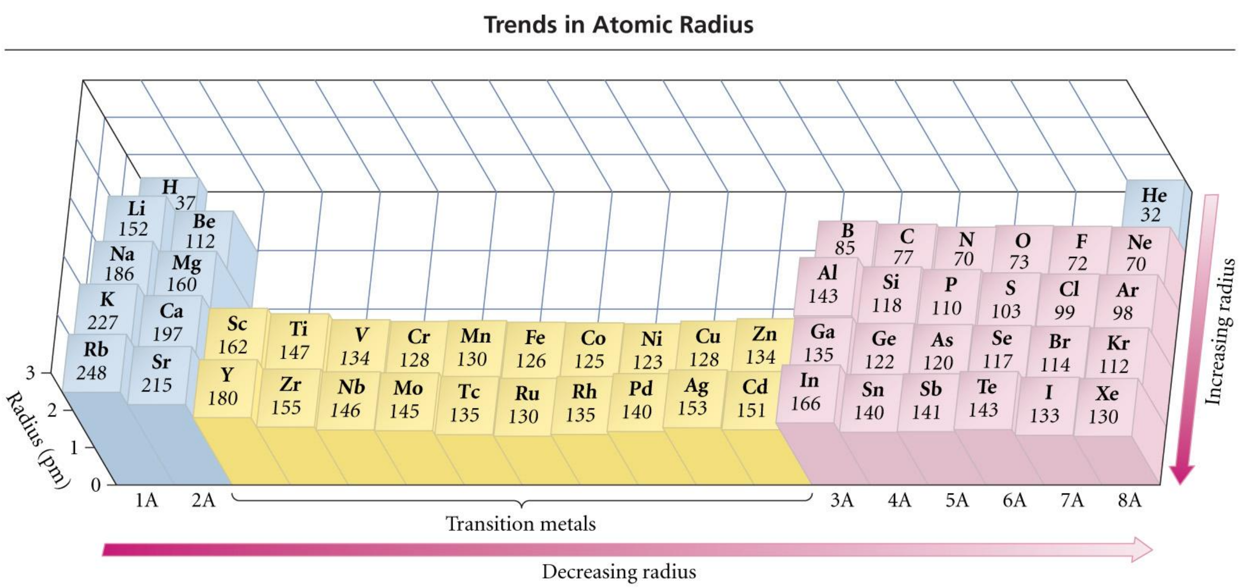
Increasing atomic radius (smallest first)

Increasing effective nuclear charge, Z_{eff}, (smallest first)

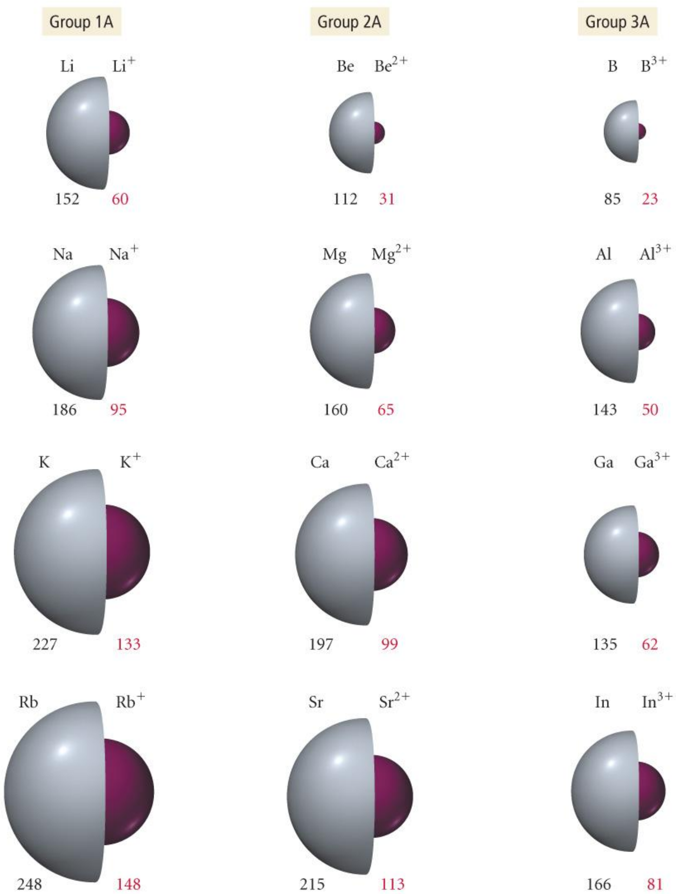
Decreasing 1st ionization energy (largest first)

Appendix:


Trends in Metallic Character II
Group 5A
Period 3
Periods
Metallic character increases
Metallic character decreases
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
7 N
15 P
33 As
51 Sb
83 Bi


Trends in Atomic Radius
Radius (pm)
Transition metals
Increasing radius
Decreasing radius
1A
2A
3A
4A
5A
6A
7A
8A

Radii of Atoms and Their Cations (pm)



Radii of Atoms and Their Anions (pm)