CHEM 103

Quantum Mechanics and Periodic Trends

Lecture Notes
April 11, 2006
Prof. Sevian

Agenda

- Predicting electronic configurations using the QM model
- Group similarities
- Interpreting measured properties of elements in light of their electronic configurations
  - Ionization energy
  - Other properties…

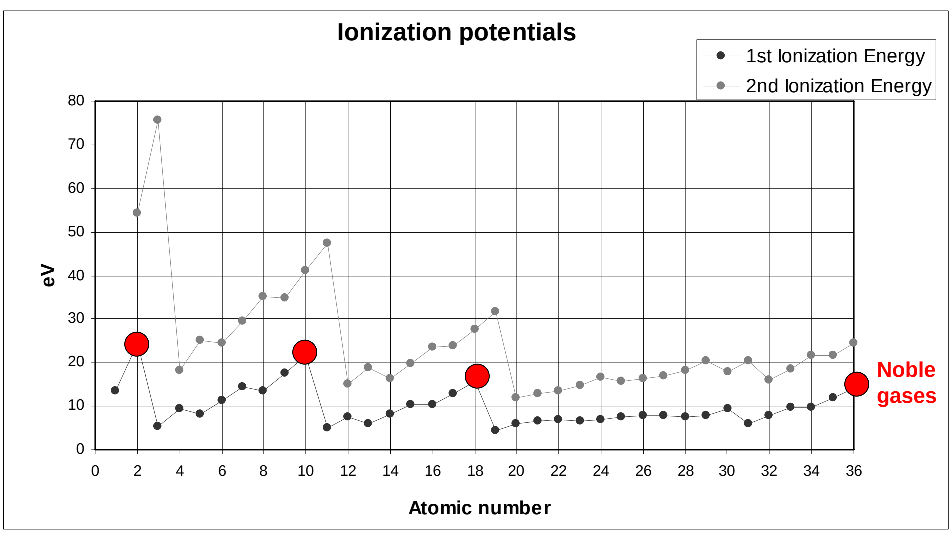
Periodicity

The notion that the elements have properties that repeat periodically according to how the Periodic Table is organized. This periodic repetition of properties is explained by the electronic structures of elements.

Don't memorize this idea! Let's "derive" it.

Ionization Energies of Elements

The energy required to remove the most weakly bound electron from an atom or ion.



Data from H. Sevian et al, Active Chemistry
or see Table 7.2, p. 271 of text

Comparing Noble Gas Group Elements

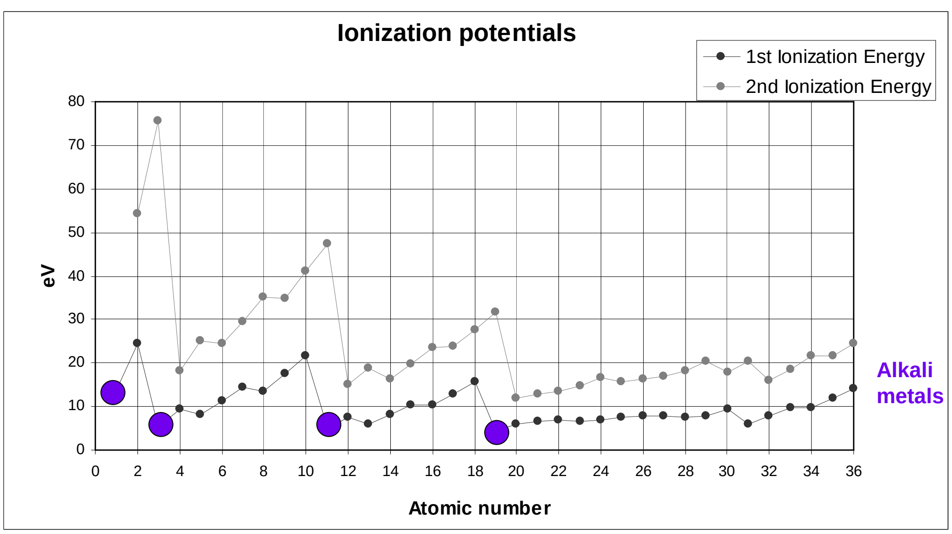
Pd	Elem	Electron Configuration
1	He	$1s^2$
2	Ne	$1s^2\ 2s^2\ 2p^6$
3	Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
4	Kr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$
5	Xe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$

How are they the same?

How are they different?

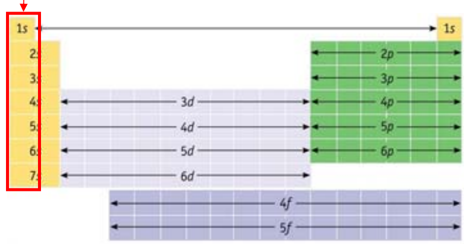
Ionization Energies of Elements

The energy required to remove the most weakly bound electron from an atom or ion.



Comparing Alkali Metal Group Elements

Pd	Elem	Electron Configuration
1	H	$1s^1$
2	Li	$1s^2\ 2s^1$
3	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
4	K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
5	Rb	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1$

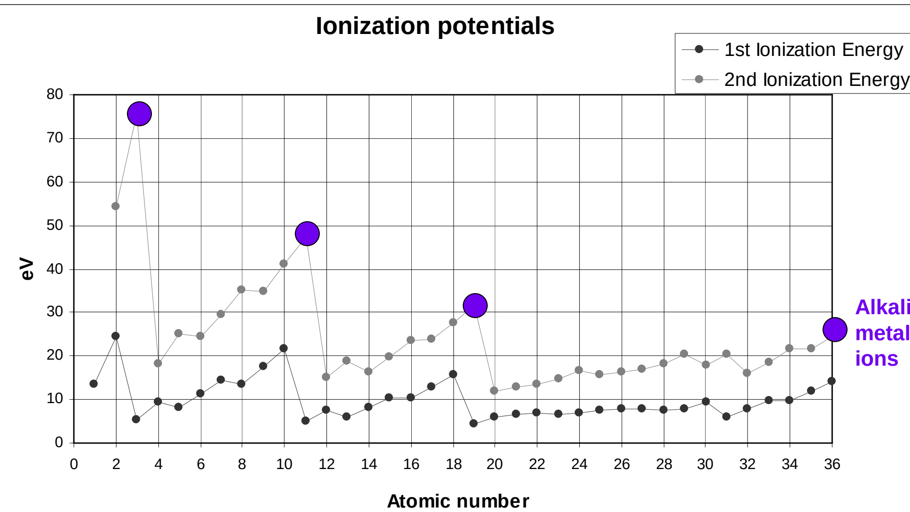


How are they the same?

How are they different?

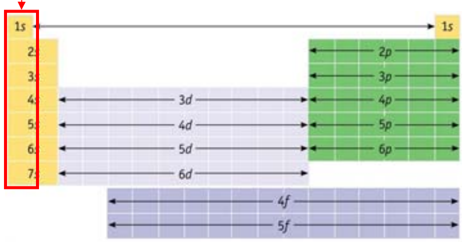
Ionization Energies of Elements

The energy required to remove the most weakly bound electron from an atom or ion.



Comparing Alkali Metal Group Ions

Pd	Ion	Electron Configuration
2	Li^+	$1s^2$
3	Na^+	$1s^2\ 2s^2\ 2p^6$
4	K^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
5	Rb^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$



How are they the same?

How are they different?

What We've Observed So Far

- Noble gases (Group VIIIA)
  - High ionization energies compared to other Groups
  - Within same group, ionization energy is smaller as atomic number increases
  - All elements in group have complete shell electron configurations (outermost *s*- and *p*-subshells are completely filled)
- Alkali metals (Group IA)
  - Low ionization energies compared to other Groups
  - Within same group, ionization energy is smaller as atomic number increases
  - All elements in group have one electron in outermost *s*-subshell
- +1 charged ions of Alkali metals (Group IA)
  - Same ionization energy behavior as noble gases
  - Electron configurations same as noble gases

Core vs. Valence

One way to view an atom or ion
(Note: not drawn to scale!)

CORE (+ charged)
- **Nucleus (protons and neutrons)**
- **All complete inner shells of electrons**

VALENCE SHELL (– charged)
- **Outer electrons beyond all complete inner shells**

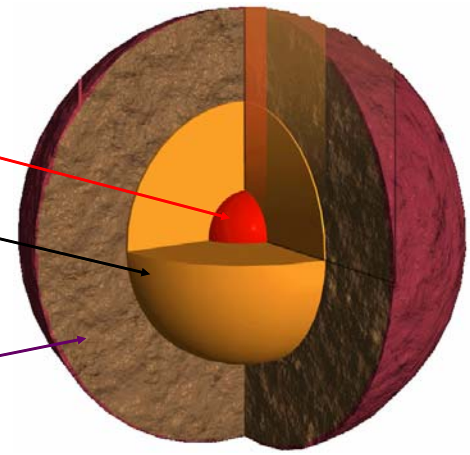


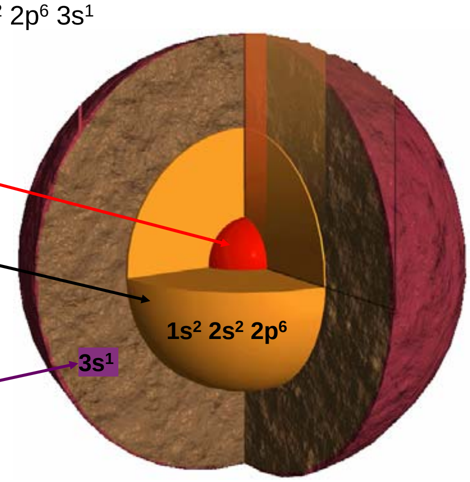
Image modified from http://www.badastronomy.com/bad/movies/thecore_review.html

Example: Sodium Atom

A neutral sodium atom has 11 protons and 11 electrons
Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$
(Note: not drawn to scale!)

CORE (Net +1 charge)
- **11 protons and some neutrons (charge: +11)**
- **All complete inner shells of electrons (charge: -10)**

VALENCE SHELL (Net -1 charge)
- **Outer electrons beyond all complete inner shells (charge: -1)**



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Recall Coulomb's Law

Force of attraction (or repulsion):

- Increases when magnitudes of charges increase
- Decreases as distance between charges increases

$$F = \frac{k\,Q_+\,Q_-}{r^2}$$

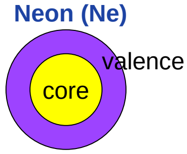
- proportionality constant (k)
- Charge on positive part (Q_+)
- Charge on negative part (Q_-)
- Force of attraction (F)
- distance between parts (r)

Building a Chemical Explanation

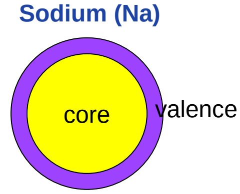
Why do noble gas atoms always have larger ionization energies than their nearest neighbor alkali metal atoms?

- Example: Why does Ne have a larger first ionization energy than Na?

Neon (Ne)



Sodium (Na)



It requires less energy to remove the outermost electron from Na than from Ne

↑

Na's outermost electron is further away from its core, and therefore is less tightly bound than Ne's outermost electron

↑

Ne has 1 shell in core
Core of +8: 10 protons + $1s^2$ electrons
Valence of - 8: $2s^2\ 2p^6$ electrons

↑

Ne has 10 protons, 10 electrons, and 2 shells (which are complete)

Na has 2 shells in core
Core of +1:
11 protons + $1s^2\ 2s^2\ 2p^6$ electrons
Valence of - 1: $3s^1$ electron

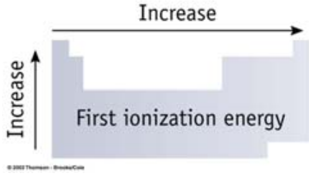
↑

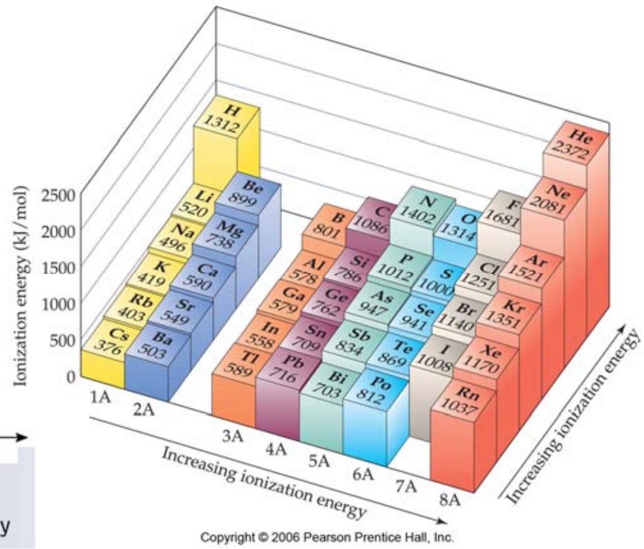
Na has 11 protons, 11 electrons, and 3 shells (2 of which are complete)

Summary of Ionization Energy Trends

Ionization energy generally:

- Increases across a period (row)
- Decreases down a group (column)





From Chemistry & Chemical Reactivity 5th edition by Kotz / Treichel. C 2003.
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Chemical Explanations

In general, there are only a few basic concepts on which the logical steps of chemical explanations are built.

The importance of size and charge (Coulomb's law)

1. Core vs. valence in a single atom or ion

   The core is always positively charged and consists of all the protons plus the electrons that don't participate in any action. All the electrons that participate in any action are in the valence shell. Comparisons are made based on magnitude of charges and distance separating the charges. (Note: it is possible to have competing effects.)

2. Charge density of an ion

   If two particles have equal charge but are different in size, the smaller one has greater charge density (more charge packed into a smaller space). Generally, something with greater charge density can have a stronger effect (e.g., it can get closer to oppositely charged particles, so the force of attraction will be greater)

3. Partial (polarizable) charge (next semester…)

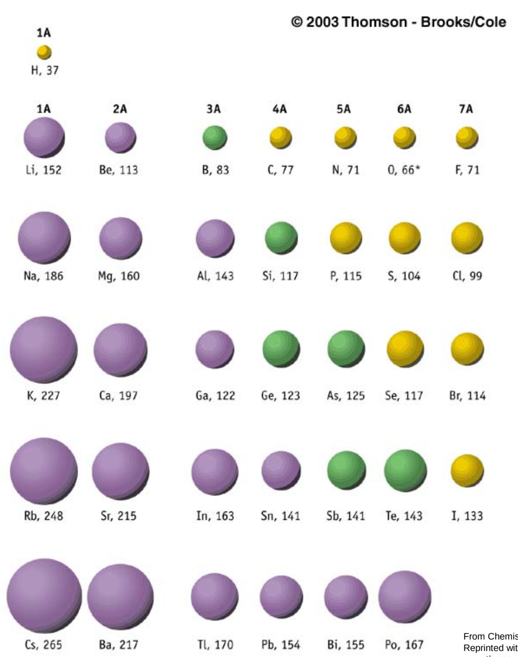
Periods vs. Groups

Comparing two elements in the same period:

- Same number of complete shells, so size (radius) of cores is the same
- Different charges in nucleus, but same number of core electrons, leads to different core charge
- Different numbers of electrons in valence
- Arguments are usually based on Q_+ (core charge) and Q_- (valence charge) being different while distance between core and valence (r) is nearly the same

Comparing two elements in the same group:

- Different number of complete shells, so size (radius) of cores is different
- Core charges are the same because valence electrons same
- Arguments are usually based on distance between core and valence (r) being different while Q_+ and Q_- are the same



Atomic Radius Comparisons

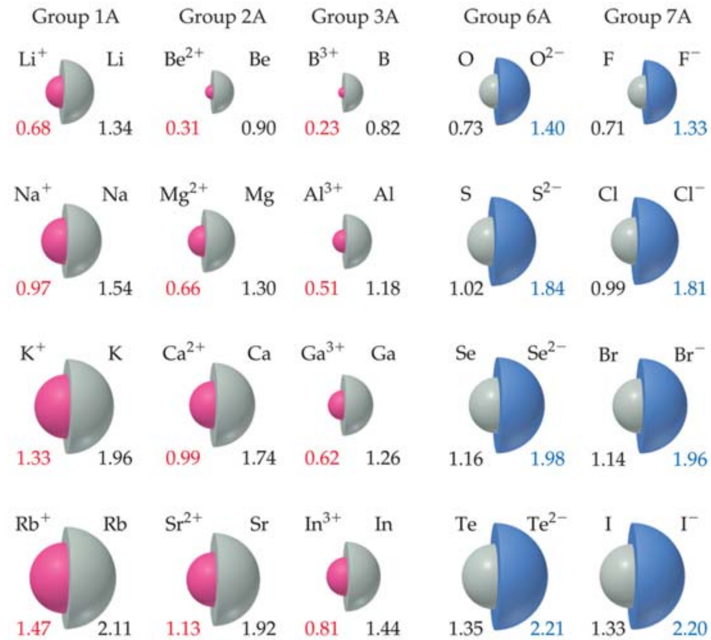
1. Trend down any given group?
2. Trend across any given period?
3. What happens to radii if these atoms become ions?

Radii of Cations and Anions vs. Neutral Atoms

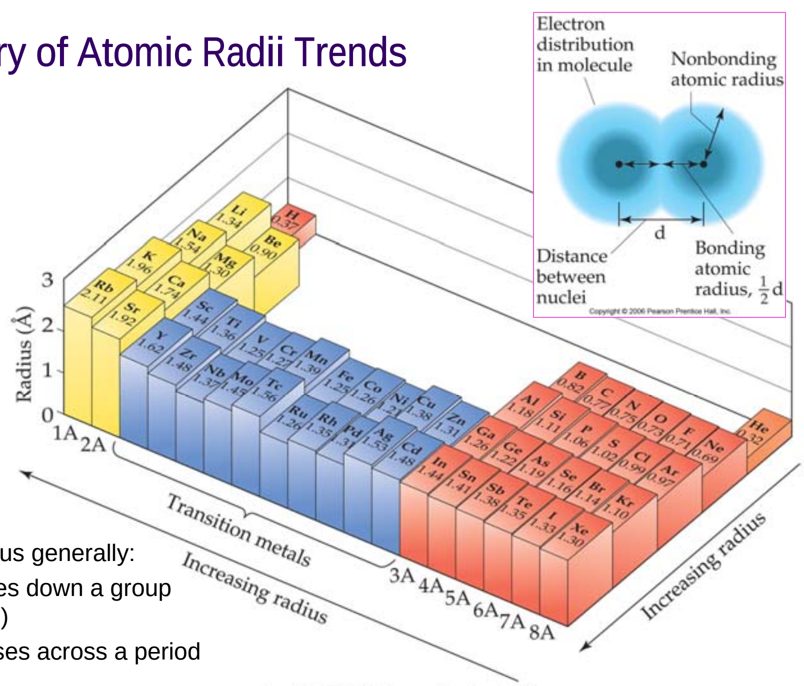
Gray = atoms

Red = cations

Blue = anions



Summary of Atomic Radii Trends



Atomic radius generally:

- Increases down a group (column)
- Decreases across a period (row)

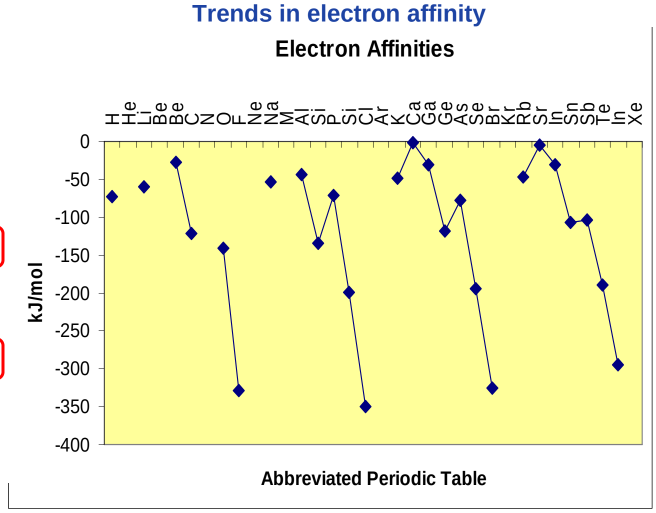
Electron Affinity

The energy associated with an atom gaining an electron → Measures ease with which an atom gains an electron

H	$1s^1$
He	$1s^2$
Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$

Why don't He, Be, N and Ne gain electrons easily?

Trends in electron affinity

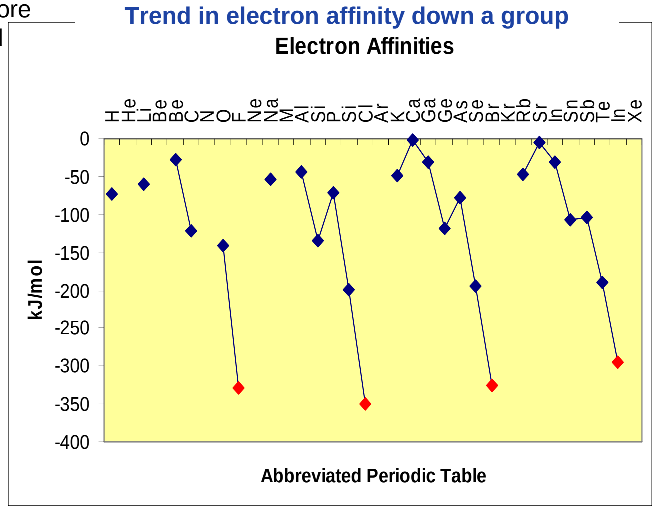


Electron Affinity

Two competing effects:

- Attraction between newly added electron and core to which it is attracted depends on distance between them – as distance increases, attraction decreases
- Repulsion between newly added electron and other electrons already present – when electrons are closer together (as in smaller shells) they repel each other more

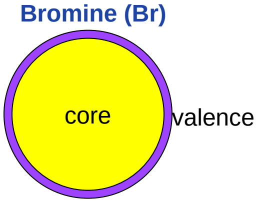
Trend in electron affinity down a group



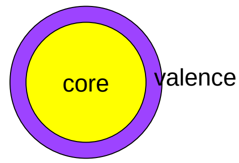
Building a Chemical Explanation

Why does Br have a smaller electron affinity than Cl?

Bromine (Br)



Chlorine (Cl)



Chlorine has greater affinity for electrons than bromine

↑

Newly placed electron in chlorine experiences greater attraction to core in chlorine

↑

Valence electrons of chlorine are closer to the core, while valence electrons of bromine are further from the core

↑

Since charges of core and valence are the same, attraction depends only on distance between core and valence

↑

Both elements have core of +7 and valence of +7 | **Chlorine is in period 3 Bromine is in period 4**

Lattice Energy

The energy associated with forming an ionic crystal from atoms

Why does magnesium chloride ($MgCl_2$) have a larger lattice energy than calcium chloride ($CaCl_2$)?

$MgCl_2$ has a larger lattice energy than $CaCl_2$

↑

More energy is required to disrupt the $MgCl_2$ lattice

↑

Ionic bonding is stronger in $MgCl_2$ than in $CaCl_2$

↑

Cl^- ions get closer to the center of positive charge (core) in $MgCl_2$ than in $CaCl_2$

↑

Mg^{2+} cations have smaller radius than Ca^{2+} cations

↑

Magnesium is in period 3 Calcium is in period 4