Periodic Properties of the Elements

Chemistry 35

Fall 2000

Beyond Hydrogen

- For atoms with more than one electron, we use the same orbitals (phew!) BUT their energies are not the same.
- Electron energies can be related to the *effective nuclear charge* (Z_{eff}) they experience in an orbital:

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

-electrons in inner shells can *shield* the outer shell electrons from the full positive charge (***Z***) of the nucleus (***S = # of inner shell electrons***)

- In general: for a fixed value of ***n***, energies *increase* with increasing values of ***l***. (i.e., d > p > s)

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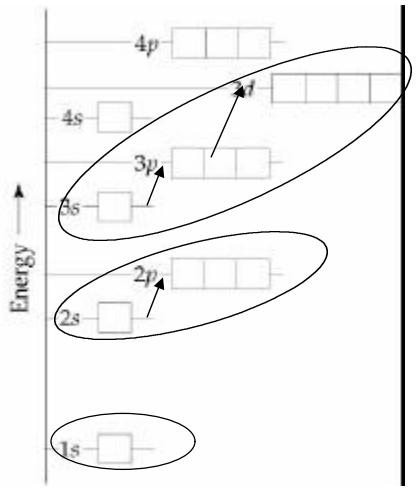
Many-electron Energy Levels

•Energies increase with increasing ***n***:

•Energies within a shell increase with increasing ***l*** of subshell:



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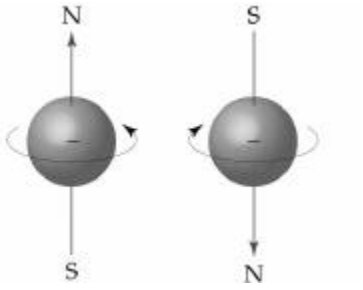
Electron Spin: The 4th Quantum Number

- Electrons also have a property called "spin":



•**<u>The Electron Spin Quantum Number:</u>**

m_s = +½ or -½

-specifies a *specific electron* in an orbital

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Pauli Exclusion Principle

- **"No two electrons in an atom can possess the same set of four quantum numbers."**

  Implications:

  1. Since there are only **two** values of $\mathbf{m_s}$ possible for each orbital, *no more than two electrons (with opposite spins) can "occupy" an orbital*

  2. The four quantum numbers *uniquely identifies* an electron in an atom

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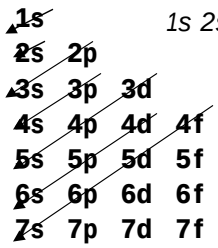
Electron Configurations

- How do we assign electrons in an atom to the various orbitals?

  1. **Fill orbitals so as to give a *minimum energy* for the atom**



1s 2s 2p 3s 3p **4s** *3d 4p* **5s** *4d 5p . . .*

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More Electron Config Rules

2. **Apply Pauli Exclusion Principle**
   - only 2 electrons/orbital
   - each with opposing spin

3. **Hund's Rule**
   - fill *degenerate* orbitals so as to maximize the number of unpaired electrons *with the same spin:*

$3p^3$: ↑ ↑ ↑ ***NOT*** ↑↓ ↑ _

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The Aufbau Process

TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram (1s 2s 2p 3s)	Electron Configuration
Li	3	↑↓ ↑	$1s^2 2s^1$
Be	4	↑↓ ↑↓	$1s^2 2s^2$
B	5	↑↓ ↑↓ ↑	$1s^2 2s^2 2p^1$
C	6	↑↓ ↑↓ ↑ ↑	$1s^2 2s^2 2p^2$
N	7	↑↓ ↑↓ ↑ ↑ ↑	$1s^2 2s^2 2p^3$
Ne	10	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	$1s^2 2s^2 2p^6$
Na	11	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑	$1s^2 2s^2 2p^6 3s^1$

One electron in each p-orbital, before pairing

Use shorthand notation:

[Ne]$3s^1$

core e⁻ *valence e⁻*

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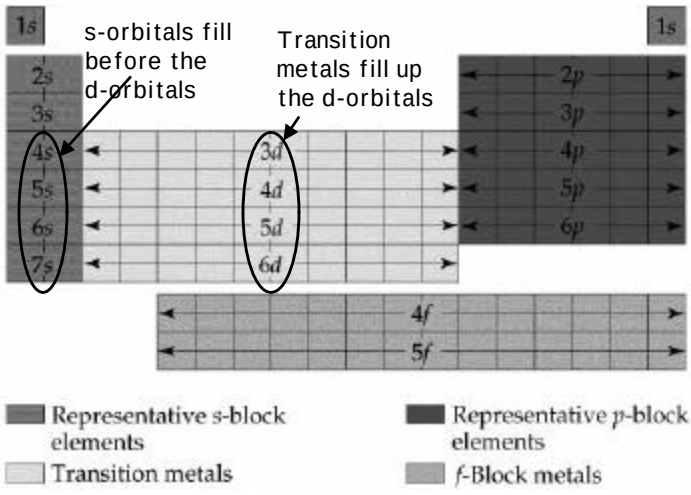
Electron Configurations and the Periodic Table



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Transition Metals

- Generally: *fill d-orbitals after filling* ***s-orbitals***

  Sc: $[Ar]4s^2 3d^1$
  Ti: $[Ar]4s^2 3d^2$

  and on to

  Zn: $[Ar]4s^2 3d^{10}$

- Of course, there are exceptions:

  Cr: $[Ar]4s^1 3d^5$ - *not* $[Ar]4s^2 3d^4$
  Cu: $[Ar]4s^1 3d^{10}$ - *not* $[Ar]4s^2 3d^9$

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Lanthanides and Actinides

- Generally: *fill* ***f-orbitals***

Lanthanides:

-fill f-orbitals *after* Lanthanum:

La [Xe]$6s^2$ ***$5d^1$*** ← one electron in d-orbital

Ce [Xe]$6s^2$ ***$4f^1$*** $5d^1$ ← next, fill f-orbitals, until

Hf [Xe]$6s^2 4f^{14}$ ***$5d^2$*** ← resume filling d-orbitals

Actinides:

-fill f-orbitals *after* Actinium (do same as Lanthanides)

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Illustrative Example

- What is the *electron configuration* for **Se**?

Se: *34 electrons*

Se $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

Se $[Ar] 3d^{10} 4s^2 4p^4$

4p ↑↓ ↑ ↑

n = 4, l = 1 p_x p_y p_z

m_s = +½, -½ +½ +½

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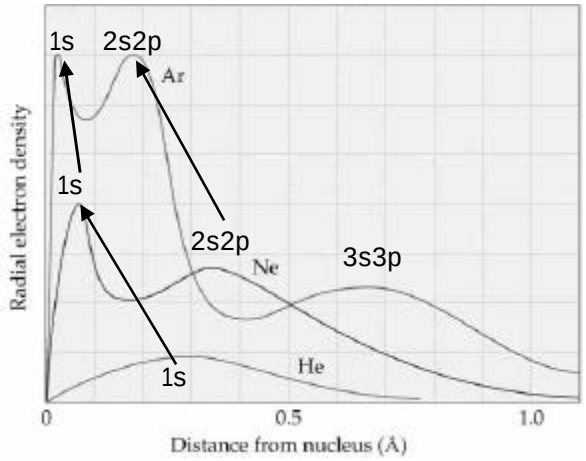
Electron Configuration and Atomic Size

- We need to look at the *radial distribution* of electrons:



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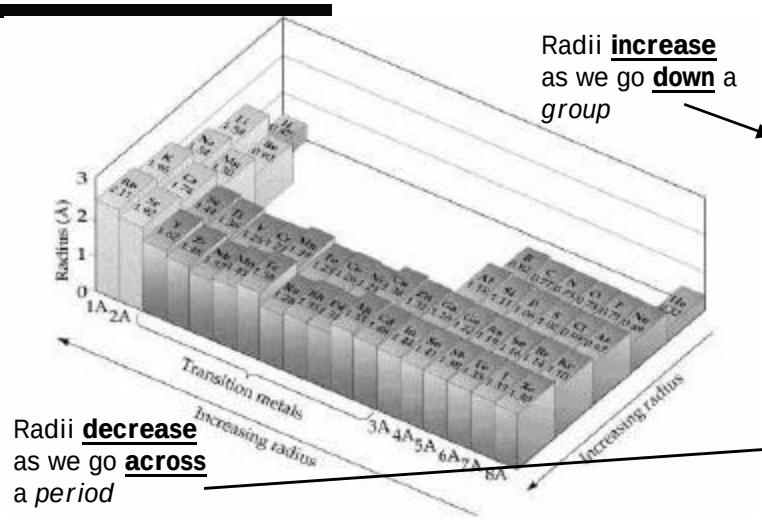
Atomic Size: Perodic Trends



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Effect of Ionization on Size

- **Removal of an electron**

  -makes a *positive* ion

  -cation is *smaller* than the neutral atom . . . WHY?

  - -removing an electron *increases* Z_{eff} remaining e^-
  - -thus, greater *coulombic attraction* giving a smaller radius

- **Addition of an electron**

  -makes a *negative* ion

  -anion is *larger* than the neutral atom . . . WHY?

  - -added electron experiences *less* of positive charge of nucleus and *increases* mutual repulsion of electrons

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Ion Electron Configurations

- Usually add or remove electrons to reach nearest Noble Gas configuration: Na^+ [Ne]
  Cl^- [Ar]

- What about ***Transition Metal Ions***?

  -can't accommodate the loss/addition of enough electrons to reach Noble Gas configuration

  -electrons removed from ***ns orbitals*** first, and *then* from ***(n-1)d orbitals:***

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

  Fe^{2+} [Ar]$3d^6$ *electrons removed from 4s*

  Fe^{3+} [Ar]$3d^5$ *electrons removed from 3d*

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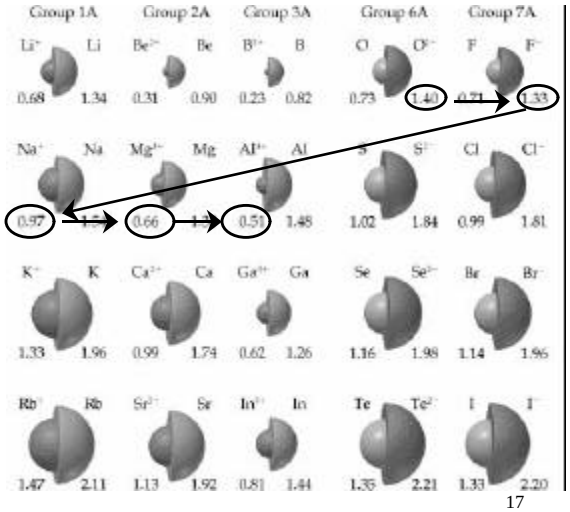
Ionic Sizes

•**Cations:** *smaller*

•**Anions:** *larger*

-**increasing Z** gives ***decreasing size*** for *isoelectronic ions*:

$O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$



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Ionization Energies (again)

- **Ionization Energy** (IE)

  -***Recall:*** IE quantifies the tendency of an electron to leave an atom in the gas phase:

  $X\ (g) \rightarrow X^{+}\ (g) + e^{-} \quad \Delta E = IE_1$

  $X^{+}(g) \rightarrow X^{2+}\ (g) + e^{-} \quad \Delta E = IE_2$

  $IE_2 > IE_1$ (due to greater nuclear charge/e^{-})

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More Ionization Energies

TABLE 7.2 Successive Values of Ionization Energies, *I*, for the Elements Sodium Through Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4560					
Mg	738	1450	7730		(Inner-shell electrons)		
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

Note: IE is always a *positive* value (**endothermic process)**

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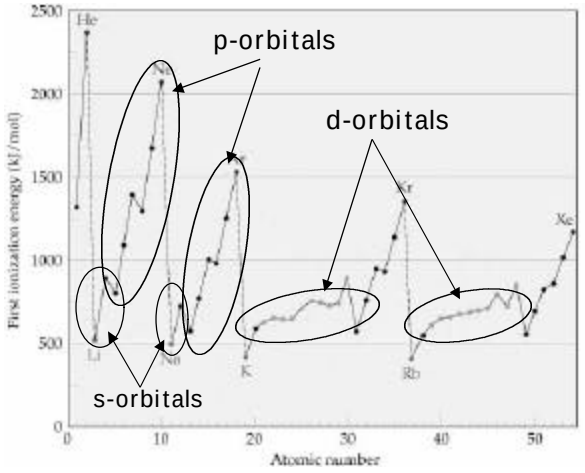
Ionization Energy: Periodic Trends



Generally:

-as **size decr** across a period, the **ionization energy *increases***

-as **size increases** down a group, the **ionization energy *decreases***

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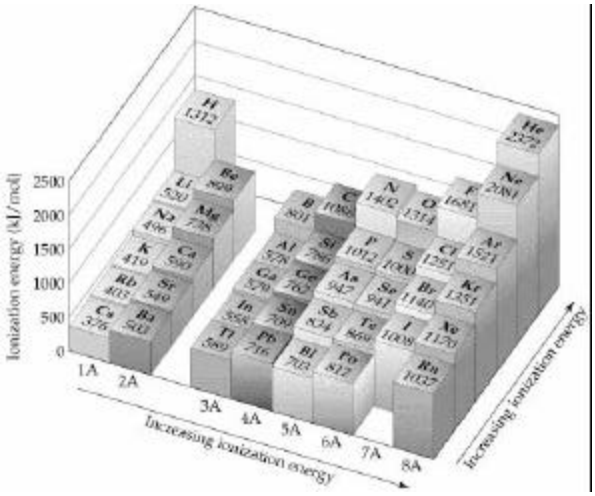
Ionization Energy: Periodic Table



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Electron Affinities: Periodic Trends

Recall: quantifies ability of an atom to *attract* an e^- in the gas phase:

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

$\Delta E = -EA$

H −73							He >0
Li −60	Be >0	B −27	C −122	N >0	O −141	F −328	Ne >0
Na −53	Mg >0	Al −43	Si −134	P −72	S −200	Cl −349	Ar >0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr >0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe >0
1A	2A	3A	4A	5A	6A	7A	8A

Increasing EA

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Magnetic Properties

- Electrons are "natural magnets" due to their spin properties:

Na: $1s^2 2s^2 2p^6 3s^1$ *unpaired* e^- will be ***attracted*** by an external magnetic field (**PARAMAGNETIC)**

Mg: $1s^2 2s^2 2p^6 3s^2$ *paired* e^- will be ***repelled*** by an external magnetic field (**DIAMAGNETIC)**

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