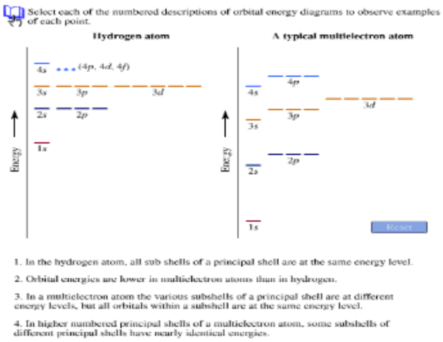
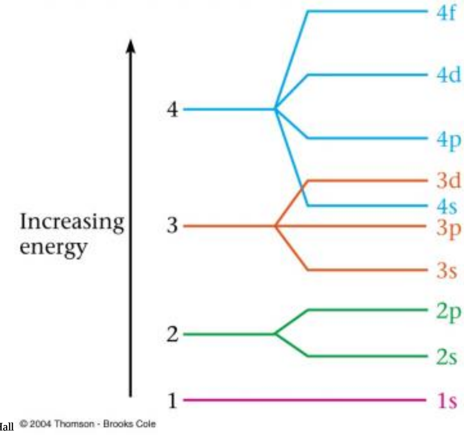
Figure 8.1 Orbital energy diagrams

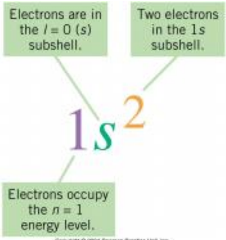




Electron Configurations

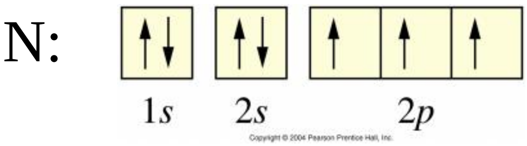
- An ***electron configuration*** describes the distribution of electrons among the various orbitals in the atom.
- Electron configuration is represented in two ways.

The ***spdf notation*** uses numbers to designate a principal shell and letters (*s*, *p*, *d*, *f*) to identify a subshell; a superscript indicates the number of electrons in a designated subshell.



Electron Configurations

In an ***orbital (box) diagram*** a box represents each orbital within subshells, and arrows represent electrons. The arrows' directions represent electron spins; opposing spins are paired.



Rules for Electron Configurations

- Electrons ordinarily occupy orbitals of the lowest energy available.
- No two electrons in the same atom may have all four quantum numbers alike.
- ***Pauli exclusion principle***: one atomic orbital can accommodate no more than ***two*** electrons, and these electrons must have ***opposing*** spins.
- Of a group of orbitals of ***identical*** energy, electrons enter ***empty*** orbitals whenever possible (***Hund's rule***).
- Electrons in half-filled orbitals have ***parallel*** spins (same direction).

Order of Subshell Energies

- Follow the arrows from the top: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, etc.
- Subshells that are far from the nucleus may exhibit exceptions to the filling order.

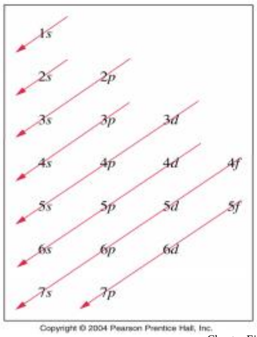
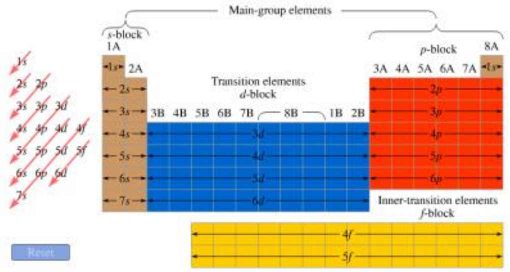


Figure 8.2

Click on each arrow to observe the progression of orbital filling with respect to the layout of the periodic table.



The Aufbau Principle

- The ***Aufbau principle*** describes a hypothetical "building-up" of an atom from the one that precedes it in atomic number.

  (Z = 1) H $1s^1$
  (Z = 2) He $1s^2$
  (Z = 3) Li $1s^2\,2s^1$

  To get He, add one electron to H.
  To get Li, add one electron to He.

- ***Noble-gas-core abbreviation***: we can replace the portion that corresponds to the electron configuration of a noble gas with a bracketed chemical symbol. It's easier to write …

  (Z = 3) Li **[He]**$2s^1$
  (Z = 22) Ti **[Ar]**$4s^2\,3d^2$

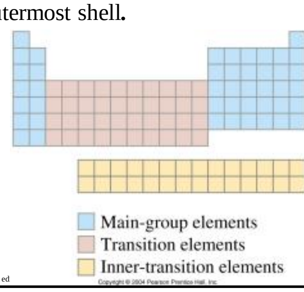
Example 8.1

Write electron configurations for sulfur, using both the *spdf* notation and an orbital diagram.

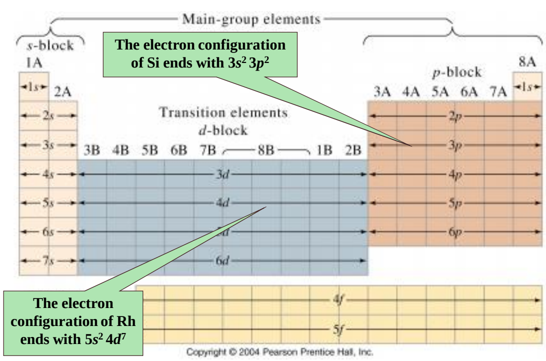
Main Group and Transition Elements

- The ***main group elements*** are those in which the orbital being filled in the aufbau process is an *s* or a *p* orbital of the outermost shell.

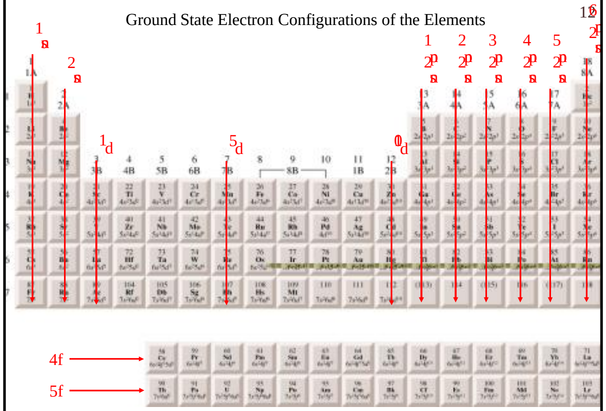
In ***transition elements***, the subshell being filled in the aufbau process is in an ***inner*** principal shell.



Using the Periodic Table to Write Electron Configurations



Ground State Electron Configurations of the Elements



Example 8.2

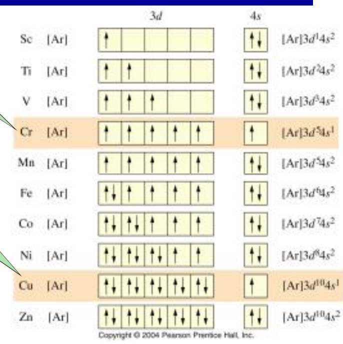
Give the complete ground-state electron configuration of a strontium atom **(a)** in the *spdf* notation and **(b)** in the noble-gas-core abbreviated notation.

Exceptions to the Aufbau Principle

Half-filled *d* subshell plus half-filled *s* subshell has slightly lower in energy than s^2d^4.

Filled *d* subshell plus half-filled *s* subshell has slightly lower in energy than s^2d^9.

More exceptions occur farther down the periodic table. They aren't always predictable, because energy levels get closer together.



Valence Electrons and Core Electrons

- The ***valence shell*** is the outermost occupied principal shell. The valence shell contains the ***valence electrons***.
- For main group elements, the number of valence shell electrons is the same as the periodic table group number (2A elements: two valence electrons, etc.)

  The period number is the same as the principal quantum number *n* of the electrons in the valence shell.
- Electrons in inner shells are called ***core electrons.***

Five valence electrons, for which $n = 4$

Example: As **[Ar]** $4s^2 3d^{10} 4p^3$

28 core electrons

Electron Configurations of Ions

- To obtain the electron configuration of an ***anion*** by the aufbau process, we simply ***add*** the additional electrons to the valence shell of the neutral nonmetal atom.
- The number added usually completes the shell.
- A nonmetal monatomic ion usually attains the electron configuration of a noble gas atom.

  O^{2-} : [Ne]

  Br^- : [Kr]

Electron Configurations of Ions (cont'd)

- A metal atom loses electrons to form a ***cation***.
- Electrons are ***removed*** from the configuration of the atom.
- The first electrons lost are those of the ***highest principal*** quantum number.
- If there are two subshells with the same highest principal quantum number, electrons are lost from the subshell with the higher *l*.

Electron Configurations of Ions (cont'd)

Atom	Ion	(or)
F $1s^2 2s^2 2p^5$	F^- $1s^2 2s^2 2p^6$	[Ne]
S [Ne] $3s^2 3p^4$	S^{2-} [Ne] $3s^2 3p^6$	[Ar]
Sr [Kr] $5s^2$	Sr^{2+} [Kr] ~~$5s^2$~~	[Kr]
Ti [Ar] $4s^2 3d^2$	Ti^{4+} [Ar] ~~$4s^2 3d^2$~~	[Ar]
Fe [Ar] $4s^2 3d^6$	Fe^{2+} [Ar] ~~$4s^2$~~ $3d^6$	[Ar] $3d^6$

***Valence* electrons are lost first.**

What would be the configuration of Fe^{3+}? Of Sn^{2+}?

Table 8.3 Electron Configurations of Some Metal Ions

Noble Gas			Pseudo–Noble Gas[a]		18 + 2[b]	Various	
Li^+	Be^{2+}	Al^{3+}	Cu^+	Zn^{2+}	In^+	Cr^{2+}:	$[Ar]3d^4$
Na^+	Mg^{2+}		Ag^+	Cd^{2+}	Tl^+	Cr^{3+}:	$[Ar]3d^3$
K^+	Ca^{2+}		Au^+	Hg^{2+}	Sn^{2+}	Mn^{2+}:	$[Ar]3d^5$
Rb^+	Sr^{2+}				Pb^{2+}	Mn^{3+}:	$[Ar]3d^4$
Cs^+	Ba^{2+}				Sb^{3+}	Fe^{2+}:	$[Ar]3d^6$
					Bi^{3+}	Fe^{3+}:	$[Ar]3d^5$
						Co^{2+}:	$[Ar]3d^7$
						Co^{3+}:	$[Ar]3d^6$
						Ni^{2+}:	$[Ar]3d^8$

[a] In the pseudo–noble gas configuration, all valence electrons are lost and the remaining $(n-1)$ shell has 18 electrons in the configuration $(n-1)s^2(n-1)p^6(n-1)d^{10}$.

[b] In the 18 + 2 configuration, $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^2$, two valence electrons remain.

Example 8.3

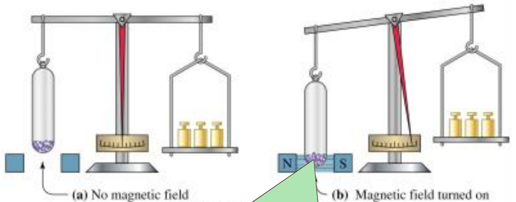
Write the electron configuration of the Co^{3+} ion in a noble-gas-core abbreviated *spdf* notation.

Magnetic Properties

- ***Diamagnetism*** ***(逆磁性)*** is the weak repulsion associated with ***paired*** electrons.
- ***Paramagnetism*** ***(順磁性)*** is the attraction associated with ***unpaired*** electrons.
  – This produces a much stronger effect than the weak diamagnetism of paired electrons.
- ***Ferromagnetism(鐵磁性)*** is the exceptionally strong attractions of a magnetic field for iron and a few other substances.

Magnetic Properties (cont'd)

- The magnetic properties of a substance can be determined by weighing the substance in the absence and in the presence of a magnetic field.



The mass appears to have increased, so this substance must be ___________ and must have (paired, unpaired) electrons.

Example 8.4

A sample of chlorine gas is found to be diamagnetic. Can this gaseous sample be composed of individual Cl atoms?

Periodic Properties

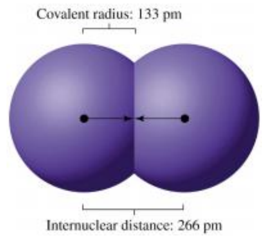
- Certain physical and chemical properties recur at regular intervals, and/or vary in regular fashion, when the elements are arranged according to increasing atomic number.
- Melting point, boiling point, hardness, density, physical state, and chemical reactivity are periodic properties.
- We will examine several periodic properties that are readily explained using electron configurations.

Periodic Properties: Atomic Radius

- Half the distance between the nuclei of two atoms is the ***atomic radius.***

  Covalent radius: half the distance between the nuclei of two identical atoms joined in a *molecule*.

  Metallic radius: half the distance between the nuclei of adjacent atoms in a *solid metal*.

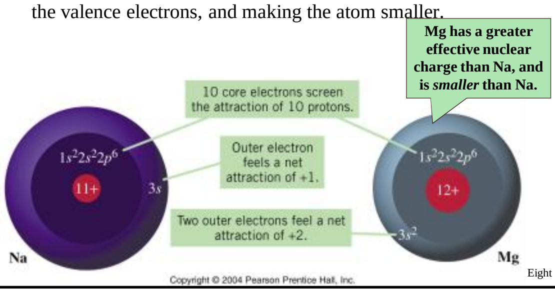


Periodic Properties: Atomic Radius

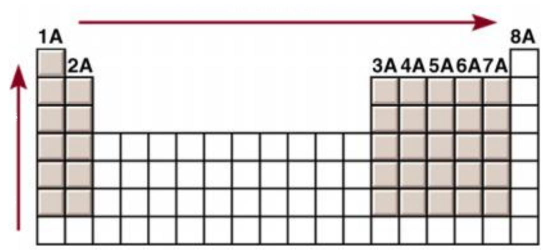
- Atomic radius ***increases*** from top to bottom within a group.
- The value of *n* increases, moving down the periodic table.
- The value of *n* relates to the ***distance*** of an electron from the nucleus.

Periodic Properties: Atomic Radius

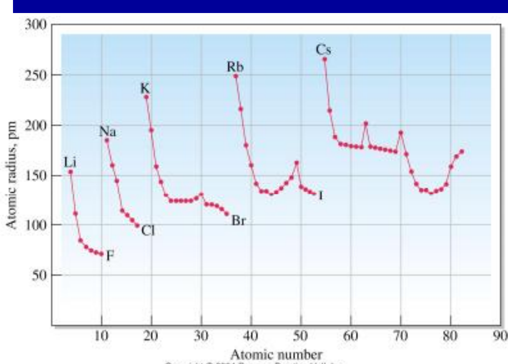
- Atomic radius ***decreases*** from left to right within a period.
- Why? The ***effective nuclear charge(有效核電荷)*** increases from left to right, increasing the attraction of the nucleus for the valence electrons, and making the atom smaller.



Effective Nuclear Charge (Z_{eff})



Atomic Radii of the Elements



Example 8.5

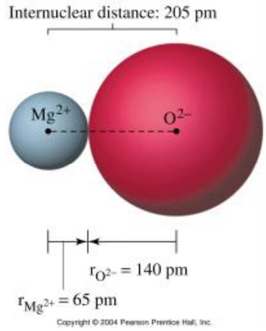
With reference only to a periodic table, arrange each set of elements in order of increasing atomic radius:

(a) Mg, S, Si **(b)** As, N, P **(c)** As, Sb, Se

31

Ionic Radii

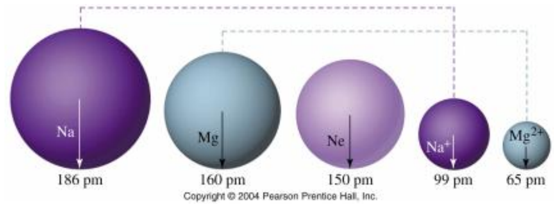
The ***ionic radius*** of each ion is the portion of the distance between the nuclei occupied by that ion.



32

Ionic Radii

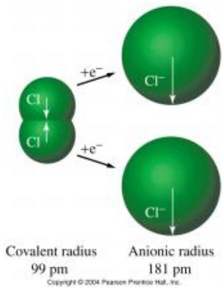
- ***Cations*** are **smaller** than the atoms from which they are formed; the value of *n* usually decreases. Also, there is less electron–electron repulsion.



33

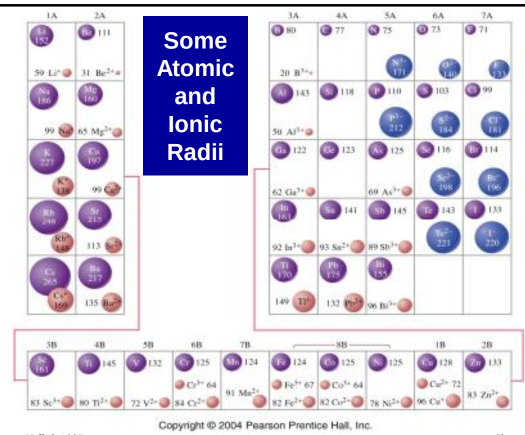
Ionic Radii

- ***Anions*** are ***larger*** than the atoms from which they are formed.
- Effective nuclear charge is unchanged, but additional electron(s) increase electron–electron repulsion.
- ***Isoelectronic(等電子)*** species have the same electron configuration; size decreases with effective nuclear charge.



34

Some Atomic and Ionic Radii



35

Example 8.6

Refer to a periodic table but not to Figure 8.14, and arrange the following species in the expected order of increasing radius:

Ca^{2+}, Fe^{3+}, K^+, S^{2-}, Se^{2-}

36

Ionization Energy(游離能)

- ***Ionization energy*** (*I*) is the energy required to remove an electron from a ground-state gaseous atom.
- *I* is usually expressed in kJ per mole of atoms.

$$M(g) \rightarrow M^+(g) + e^- \quad \Delta H = I_1$$
$$M^+(g) \rightarrow M^{2+}(g) + e^- \quad \Delta H = I_2$$
$$M^{2+}(g) \rightarrow M^{3+}(g) + e^- \quad \Delta H = I_3$$

37

Ionization Energy Trends

- $I_1 < I_2 < I_3$
  - Removing an electron from a *positive ion* is more difficult than removing it from a *neutral atom*.
- A large jump in I occurs after valence electrons are completely removed (why?).
- I_1 ***decreases*** from top to bottom on the periodic table.
  - n increases; valence electron is farther from nucleus.
- I_1 generally ***increases*** from left to right, with exceptions.
  - Greater effective nuclear charge from left to right holds electrons more tightly.

38

Selected Ionization Energies

Compare I_2 to I_1 for a 2A element, then for the corresponding 1A element.

Why is I_2 for each 1A element so *much* greater than I_1?

Why don't we see the *same* trend for each 2A *element*? $I_2 > I_1$ … but only about twice as great …

Table 8.4 Ionization Energies of Group 1A and Group 2A Elements, kJ/mol

	1A	2A
	Li	Be
I_1	520	900
I_2	7298	1757
	Na	Mg
I_1	496	738
I_2	4562	1451
	K	Ca
I_1	419	590
I_2	3051	1145
	Rb	Sr
I_1	403	550
I_2	2633	1064
	Cs	Ba
I_1	376	503
I_2	2230	965

39

Selected Ionization Energies

General trend in I_1: An increase from left to right, but …

…I_1 drops, moving from 2A to 3A.

The electron being removed is now a *p* electron (higher energy, easier to remove than an *s*).

Table 8.5 Ionization Energies of the Second- and Third-Period Elements, kJ/mol

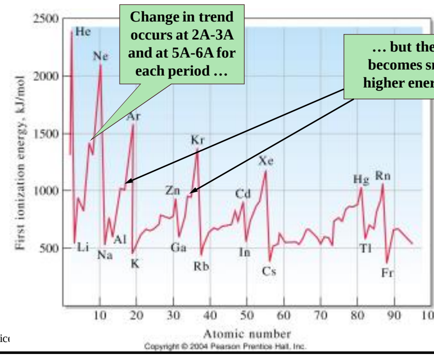
	1A	2A	3A	4A	5A	6A	7A	8A
	Li	Be	B	C	N	O	F	Ne
I_1	520	900	801	1086	1402	1314	1681	2081
I_2	7298	1757	2427	2352	2856	3388	3374	3952
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1	496	738	578	787	1012	999	1251	1521
I_2	4562	1461	1817	1577	[illegible]	2251	2298	2666

I_1 drops again between 5A and 6A.

Repulsion of the paired electron in 6A makes that electron easier to remove.

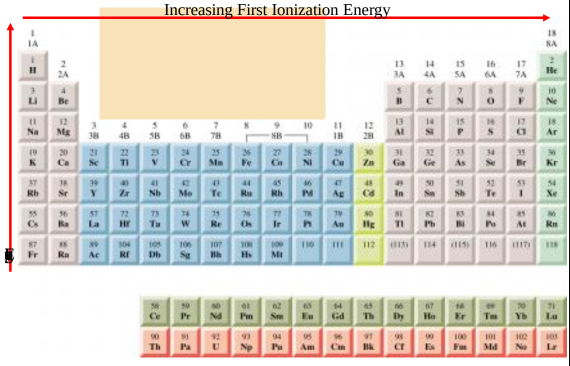
40

First Ionization Energies



41

General Trend in First Ionization Energies



42

Example 8.7

Without reference to Figure 8.15, arrange each set of elements in the expected order of increasing first ionization energy.

(a) Mg, S, Si **(b)** As, N, P **(c)** As, Ge, P

43

Electron Affinity

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

$M(g) + e^- \rightarrow M^-(g) \qquad \Delta H = EA_1$

- A ***negative*** electron affinity means that the process is ***exothermic***.
- Nonmetals generally have more affinity for electrons than metals do. (Nonmetals like to form anions!)
- Electron affinity generally is ***more*** negative or less positive on the right and toward the top of the periodic table.

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44

Selected Electron Affinities

The halogens have a greater affinity for electrons than do the alkali metals, as expected.

Table 8.6 Some Selected First Electron Affinities, kJ/mol

1A	2A	3A	4A	5A	6A	7A	8A
Li −60	Be >0	B −27	C −154	N ≈0	O −141	F −328	Ne >0
Na 53					S 200	Cl 349	
K −48					Se −195	Br −325	
Rb −47					Te −190	I −295	
Cs −46					Po −183	At −270	

Pre... ...ht

45

Example 8.8 A Conceptual Example

Which of the values given is a reasonable estimate of the second electron affinity (EA_2) for sulfur?

$S^-(g) + e^- \rightarrow S^{2-}(g) \qquad EA_2 = ?$

–200 kJ/mol	+450 kJ/mol
+800 kJ/mol	+1200 kJ/mol

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46

Metals

- ***Metals*** have a small number of electrons in their valence shells and tend to form ***positive*** ions.
  - For example, an aluminum atom loses its three valence electrons in forming Al^{3+}.
- All *s*-block elements (except H and He), all *d*- and *f*-block elements, and some *p*-block elements are metals.

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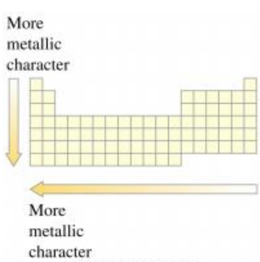
47

Metallic Character

- Metallic character is related to atomic radius and ionization energy.
- Metallic character generally ***increases*** from right to left across a period, and ***increases*** from top to bottom in a group.



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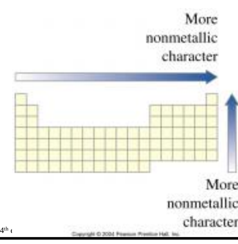
48

Nonmetals

- Atoms of a **nonmetal** generally have larger numbers of electrons in their valence shell than do metals.
- Many nonmetals tend to form negative ions.
- All nonmetals (except H and He) are *p*-block elements.

Nonmetallic character generally ***increases*** right-to-left and ***increases*** bottom-to-top on the periodic table (the opposite of metallic character).



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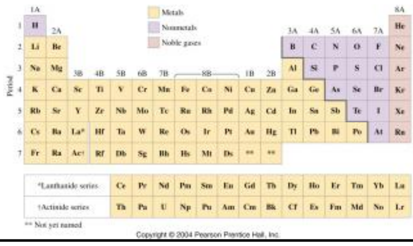
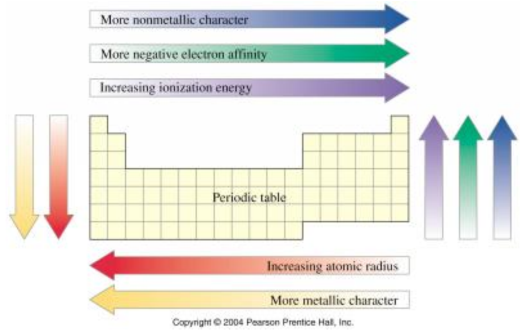
Metalloids

- A heavy stepped diagonal line separates metals from nonmetals; some elements along this line are called **metalloids**.
- Metalloids have properties of both metals and nonmetals.



A Summary of Trends



Example 8.9

In each set, indicate which is the more metallic element.

(a) Ba, Ca **(b)** Sb, Sn **(c)** Ge, S

Example 8.10 A Conceptual Example

Using only a blank periodic table such as the one in Figure 8.17, state the atomic number of **(a)** the element that has the electron configuration $4s^2 4p^6 4d^5 5s^1$ for its fourth and fifth principal shells and **(b)** the most metallic of the fifth-period *p*-block elements.

The Noble Gases

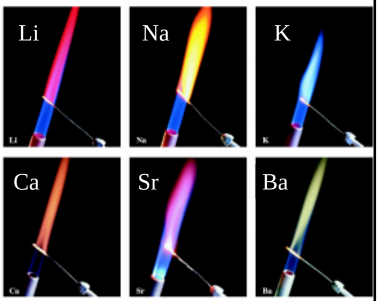
- The **noble gases** are on the far right of the periodic table between the highly active nonmetals of Group 7A and the very reactive alkali metals.
- The noble gases rarely enter into chemical reactions because of their stable electron configurations.
- However, a few compounds of noble gases (except for He and Ne) have been made.

Flame Colors

Atoms emit energy when electrons drop from higher to lower energy states (Ch.7).

Elements with low **first ionization energies** can be excited in a Bunsen burner flame, and often emit in the visible region of the spectrum.

Elements with high values of IE_1 usually require higher temperatures for emission, and the emitted light is in the UV region of the spectrum.

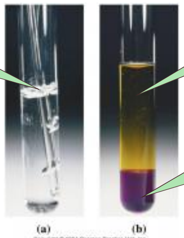


Oxidizing and Reducing Agents Revisited

- The halogens (Group 7A) are good oxidizing agents.
- Halogens have a high affinity for electrons, and their oxidizing power generally varies with electron affinity.

When Cl_2 is bubbled into a solution containing colorless iodide ions …

… the chlorine oxidizes I^- to I_2, because EA_1 for Cl_2 is greater than EA_1 for I_2.



Displaced I_2 is brown in aqueous solution …

… but dissolves in CCl_4 to give a beautiful purple solution.

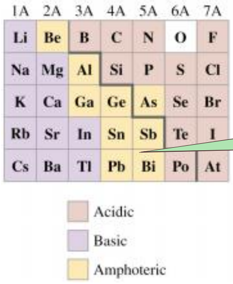
Oxidizing and Reducing Agents Revisited

- The *s*-block elements are very strong reducing agents.
- All the IA metals and the heavier IIA metals will displace H_2 from water, in part because of their low values of IE_1.
- A low IE_1 means that the metal easily gives up its electron(s) to hydrogen in water, forming hydrogen gas.

Acidic, Basic, and Amphoteric Oxides

- An ***acidic oxide*** produces an acid when the oxide reacts with water.
- Acidic oxides are molecular substances and are generally the oxides of ***nonmetals***.
- ***Basic oxides*** produce bases by reacting with water.
- Often, basic oxides are ***metal*** oxides.
- An ***amphoteric oxide*** can react with either an acid or a base.

Properties of the Oxides of the Main-group Elements



The metalloids and some of the heavier metals form amphoteric oxides.

Cumulative Example

Given that the density of solid sodium is 0.968 g/cm^3, estimate the atomic (metallic) radius of a Na atom. Assess the value obtained, indicating why the result is only an estimate and whether the actual radius should be larger or smaller than the estimate.