Part I Understanding and Skill in Chemistry

This book follows the California numbering system for labeling all chemistry Subject Matter Requirement (SMR) Domains. Domains 1 through 7 in this section are referred to as Chemistry Domains. Domains 11 and 12 in the following section are referred to as General Chemistry Domains enumerated within the broader scope of general science.

Domain 1.0   Atomic and Molecular Structure

Competency 1.1 Periodic Table and Periodicity

What the ocean was to the child, the Periodic Table is to the chemist.
      —K. Barry Sharpless (Nobel prize in Chemistry, 2001)

Skill 1.1a- Differentiate periodic groups and families of elements and their properties

The construction and organization of the periodic table are described in **Skill 9.1k**.

Groups 1, 2, 17, and 18 are often identified with the group names shown on the table to the right. Groups 3 through 12 are called the **transition metals**. The lanthanoid series is contained in period 6, and the actinoid series is in period 7. The two series together are called the **inner transition metals**. The locations of the transition and inner transition metals in the periodic table are discussed further in **Skill 1.1b**. Elements in the periodic table are also divided into broad categories of metals, nonmetals, and semimetals as discussed in **Skill 9.1l**.

Several elements are found as **diatomic molecules: (H_2, N_2, O_2, and the halogens: F_2, Cl_2, Br_2, and I_2)**. Mnemonic devices to remember the diatomic elements are: "$Br_2I_2N_2Cl_2H_2O_2F_2$" (pronounced "Brinklehof") and "**H**ave **N**o **F**ear **O**f **I**ce **C**old **B**ee**r**." These molecules are attracted to one another using **weak London dispersion forces** (see **Skill 1.3d**).

Note that **hydrogen** is <u>not</u> an alkali metal. Hydrogen is a colorless gas and is the most abundant element in the universe, but H_2 is very rare in the atmosphere because it is light enough to escape gravity and reach outer space. Hydrogen atoms form more compounds than any other element.
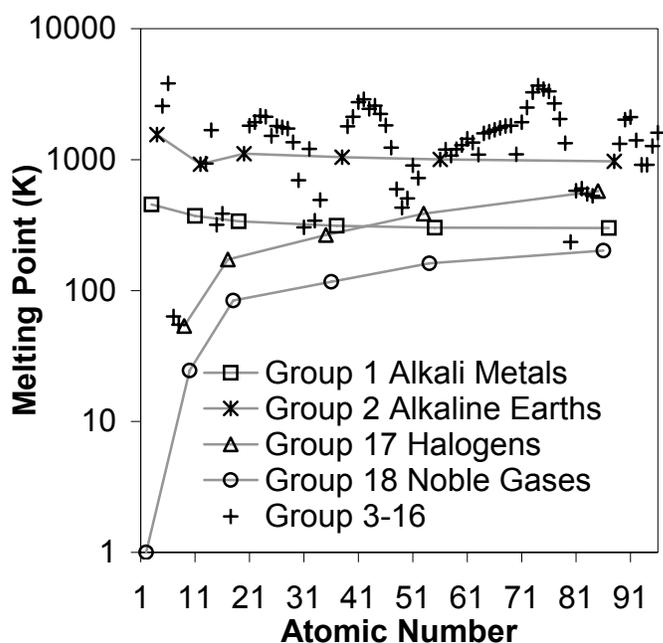
Alkali metals are shiny, soft, metallic solids. They have **low melting points and low densities** compared with other metals because they have a weaker metallic bond (see the square data points in the figures to the left and below). Measures of intermolecular attractions including their **melting points decrease further down the periodic table due to weaker metallic bonds** as the size of atoms increases. See **Skill 1.3d** for a discussion of metallic bonding. Most salts with an alkali metal cation are always soluble (see **Skill 4.1a**).

Alkaline earth metals (group 2 elements) are grey, metallic solids. They are harder, denser, and have a higher melting point than the alkali metals (see asterisk data points in the figures), but values for these properties are still low compared to most of the transition metals. Measures of metallic bond strength like melting points for alkaline earths do not follow a simple trend down the periodic table.
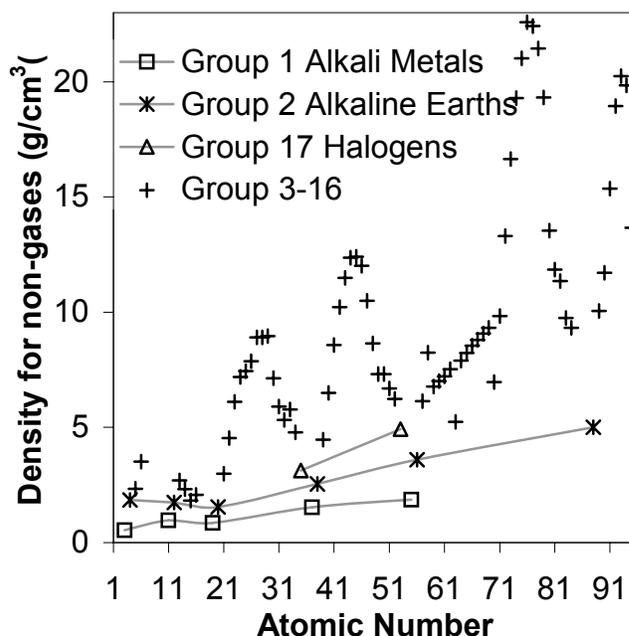
When cut by a knife, the exposed surface of an **alkali metal or alkaline earth metal** quickly turns into an oxide. These elements **do not occur in nature as free metals**. Instead, they react with many other elements to form white or grey water-soluble salts. With some exceptions, the oxides of group 1 elements have the formula M_2O, their hydrides are MH, and their halides are MX (for example, NaCl). The oxides of group 2 elements have the formula MO, their hydrides are MH_2, and their halides are MX_2.

Copper, silver, and gold (group 11) are known as the **noble metals** or **coinage metals** because they are very unreactive.

Halogens (group 17 elements) have an irritating odor. Unlike the metallic bonds between alkali metals, weak **London forces between halogen molecules increase in strength further down the periodic table**, increasing their melting points as shown by the triangular data points in the figures on the previous page. Weak London forces (see **Skill 1.3d**) make Br_2 a liquid and I_2 a solid at 25 °C. The lighter halogens are gases. Halogens form a wide variety of oxides and also combine with other halogens. They combine with hydrogen to form HX gases, and these compounds are also commonly used as acids (hydrofluoric, hydrochloric, etc.) in aqueous solution. Halogens form salts with metals by gaining electrons to become X^- ions. Halogen compounds are called halides. Astatine is an exception to many of these properties because it is an artificial metalloid.

Noble gases (group 18 elements) have no color or odor and exist as **individual gas atoms** that experience London forces. These attractions also increase with period number as shown by the circular data points in the figures on the previous page. Noble gases are **nearly chemically inert**. The heavier noble gases form a number of compounds with oxygen and fluorine such as KrF_2 and XeO_4

Skill 1.1b- Relate valence electrons and the electron shell structures to an element's position in the periodic table

The position of an element in the periodic table may be related to its electron configuration, and this configuration in turn results from the quantum theory describing the filling of a shell of electrons. In this skill, we will take this theory as our starting point. However, it should be remembered that it is the correlation with properties—not with electron arrangements—that have placed the periodic table at the beginning of most chemistry texts.

Quantum numbers
The quantum- mechanical solutions from the Schrödinger Equation (see **Skill 1.2a**) utilize three quantum numbers (n, l, and m_l) to describe an orbital and a fourth (m_s) to describe an electron in an orbital. This model is useful for understanding the frequencies of radiation emitted and absorbed by atoms and chemical properties of atoms.

The **principal quantum number *n*** may have positive integer values (1, 2, 3, …). *n* is a measure of the **distance** of an orbital from the nucleus, and orbitals with the same value of *n* are said to be in the same **shell**. This is analogous to the Bohr model of the atom (see **Skill 1.2a**). Each shell may contain up to $2n^2$ electrons.

The **azimuthal quantum number *l*** may have integer values from 0 to n- 1. *l* describes the angular momentum of an orbital. This determines the orbital's **shape**. Orbitals with the same value of *n* and *l* are in the same **subshell**, and each subshell may contain up to $4l + 2$ electrons. Subshells are usually referred to by the principle quantum number followed by a letter corresponding to *l* as shown in the following table:

Azimuthal quantum number *l*	0	1	2	3	4
Subshell designation	*s*	*p*	*d*	*f*	*g*

The **magnetic quantum number *m_l* or *m*** may have integer values from $-l$ to l. m_l is a measure of how an individual orbital responds to an external magnetic field, and it often describes an orbital's **orientation**. A subscript—either the value of m_l or a function of the *x*-, *y*-, and *z*-axes—is used to designate a specific orbital. See **Skill 1.2a** for images of electron density regions for a few orbitals of hydrogen. $n=3$, $l=2$, and $m_l=0$ for the $3d_0$ orbital. Each orbital may hold up to two electrons.

The **spin quantum number *m_s* or *s*** has one of two possible values: $-1/2$ or $+1/2$. m_s differentiates between the two possible electrons occupying an orbital. Electrons moving through a magnet behave as if they were tiny magnets themselves spinning on their axis in either a clockwise or counterclockwise direction. These two spins may be described as $m_s = -1/2$ and $+1/2$ or as down and up.

The **Pauli exclusion principle** states that **no two electrons in an atom may have the same set of four quantum numbers**.

The following table summarizes the relationship among *n*, *l*, and m_l through $n=3$:

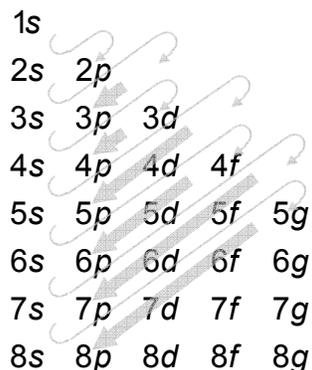| *n*	*l*	Subshell	m_l	Orbitals in subshell	Maximum number of electrons in subshell
1	0	1*s*	0	1	2
2	0	2*s*	0	1	2
	1	2*p*	−1, 0, 1	3	6
3	0	3*s*	0	1	2
	1	3*p*	−1, 0, 1	3	6
	2	3*d*	−2, −1, 0, 1, 2	5	10

<u>Subshell energy levels</u>
In single- electron atoms (H, He^+, and Li^{2+}) above the ground state, subshells within a shell are all at the same energy level, and an orbital's energy level is only determined by n. However, in all other atoms, multiple electrons repel each other. Electrons in orbitals closer to the nucleus create a screening or **shielding effect** on electrons further away from the nucleus, preventing them from receiving the full attractive force of the nucleus. **In multi- electron atoms, both n and l determine the energy level of an orbital**. In the absence of a magnetic field, **orbitals in the same subshell with different m_l all have the same energy** and are said to be **degenerate orbitals**.

The following list orders subshells by increasing energy level:
$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < \ldots$

This list may be constructed by arranging the subshells according to n and l and drawing diagonal arrows as shown below:

$1s$
$2s \quad 2p$
$3s \quad 3p \quad 3d$
$4s \quad 4p \quad 4d \quad 4f$
$5s \quad 5p \quad 5d \quad 5f \quad 5g$
$6s \quad 6p \quad 6d \quad 6f \quad 6g$
$7s \quad 7p \quad 7d \quad 7f \quad 7g$
$8s \quad 8p \quad 8d \quad 8f \quad 8g$

<u>Drawing electron shell structures</u>
Electron shell structures (also called electron arrangements) in an atom may be represented using three methods: an **electron configuration**, an **orbital diagram**, or an **energy level diagram**.

All three methods require knowledge of the subshells occupied by electrons in a certain atom. The **Aufbau principle** or **building- up rule** states that **electrons at ground state fill orbitals starting at the lowest available energy levels**.

An **electron configuration** is a **list of subshells** with superscripts representing the **number of electrons** in each subshell. For example, an atom of boron has 5 electrons. According to the Aufbau principle, two will fill the $1s$ subshell, two will fill the higher energy $2s$ subshell, and one will occupy the $2p$ subshell which has an even higher energy. The electron configuration of boron is $1s^2 2s^2 2p^1$. Similarly, the electron configuration of a vanadium atom with 23 electrons is:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3.$$
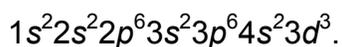
Configurations are also written with their principle quantum numbers together:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2.$$
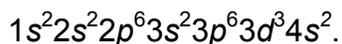
Electron configurations are often written to emphasize the outermost electrons. This is done by writing the symbol in brackets for the element with a full p subshell from the previous shell and adding the **outer electron configuration** onto that configuration. The element with the last full p subshell will always be a noble gas from the right-most column of the periodic table (see **Skill 1.1a** and **Skill 9.1l**). For the vanadium example, the element with the last full p subshell has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. This is $_{18}$Ar. The configuration of vanadium may then be written as [Ar]$4s^2 3d^3$ where $4s^2 3d^3$ is the outer electron configuration.

Electron shell structures may also be written by noting the number of electrons in each shell. For vanadium, this would be:

2, 8, 11, 2.

Orbital diagrams assign electrons to individual orbitals so the energy state of individual electrons may be found. This requires knowledge of how electrons occupy orbitals within a subshell. **Hund's rule** states that **before any two electrons occupy the same orbital, other orbitals in that subshell must first contain one electron each with parallel spins**. Electrons with up and down spins are shown by half- arrows, and these are placed in lines of orbitals (represented as boxes or dashes) according to Hund's rule, the Aufbau principle, and the Pauli exclusion principle. Below is the orbital diagram for vanadium:

1s   2s   2p   3s   3p   4s   3d
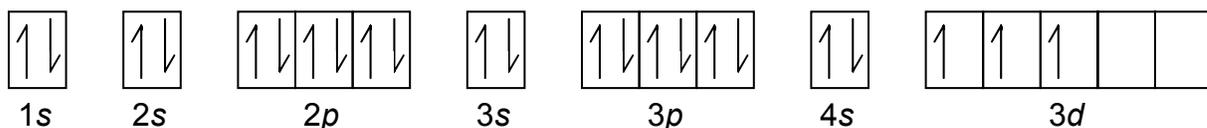
An **energy level diagram** is an orbital diagram that shows subshells with higher energy levels higher up on the page. The energy level diagram of vanadium is:
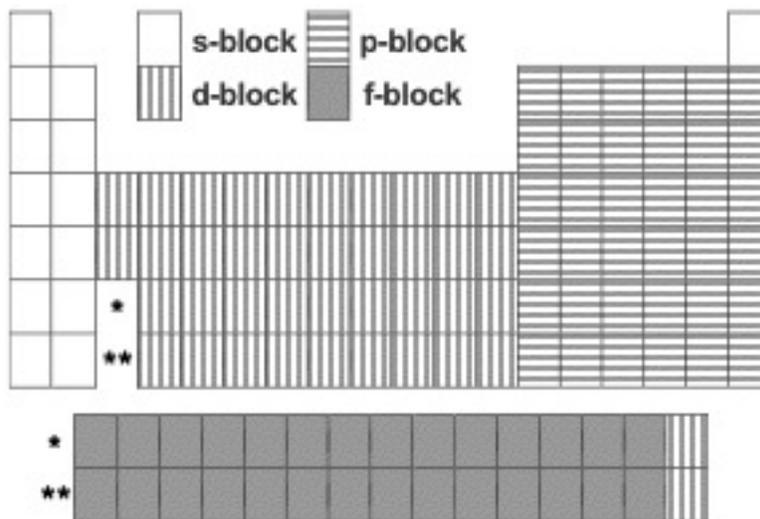
ENERGY

↑	↑	↑		

3*d*

↑↓

4*s*

↑↓

3*s*

↑↓	↑↓	↑↓

3*p*

↑↓	↑↓	↑↓

2*p*

↑↓

2*s*

↑↓

1*s*
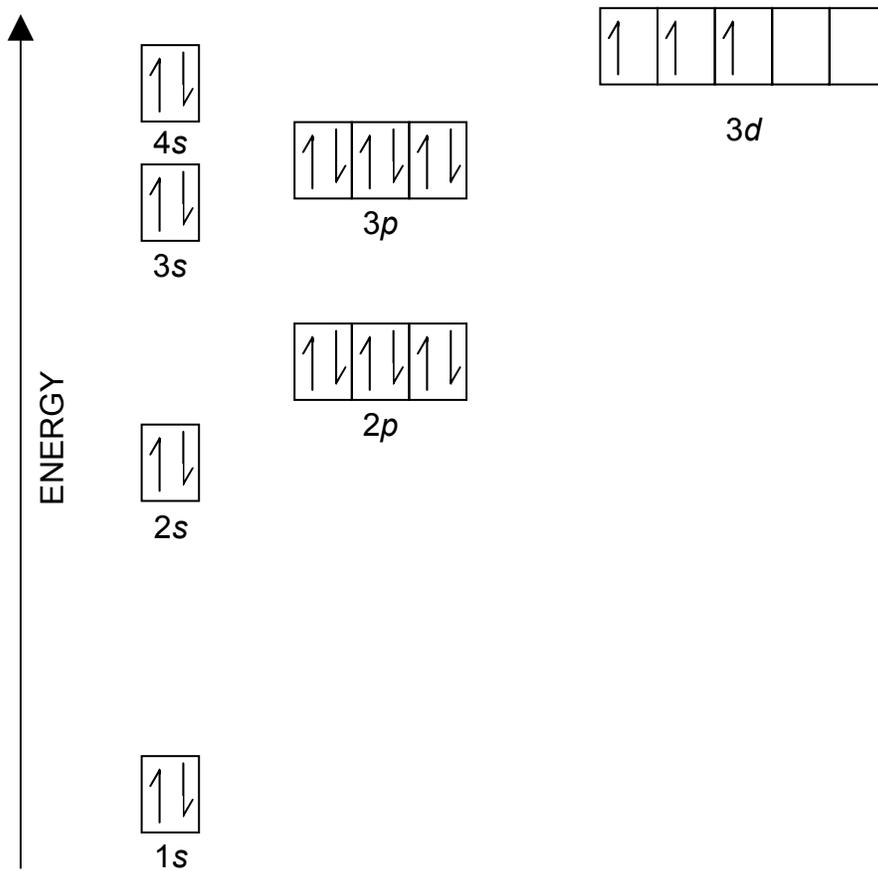
<u>Valence shell electrons and the periodic table</u>
Electrons in the **outermost shell** are called **valence shell electrons**. For example, the electron configuration of Se is $[Ar]4s^23d^{10}4p^4$, and its valence shell electron configuration is $4s^24p^4$.

The **periodic table** may be related to the electron shell structure of any element. The table may be divided up into **blocks corresponding to the subshell**
designation of the most recent orbital to be filled by the building- up rule.

Elements in the s- and p-blocks are known as **main- group elements**. The d- block elements are called **transition metals.** The f- block elements are called **inner transition metals**.

The maximum number of electrons in each subshell (2, 6, 10, or 14) determines the number of elements in each block, and the order of energy levels for subshells create the pattern of blocks. These blocks also usually correspond to the value of l for the **outermost electron** of the atom. This has important consequences for the physical and chemical properties of the elements as shown in **Skill 1.1c**. The outermost shell or valence shell principle quantum number (for example, 4 for Se) is also the period number for the element in the table.

Atoms in the d- and f- blocks often have unexpected electron shell structures that cannot be explained using simple rules. Some heavy atoms have unknown electron configurations because the number of different frequencies of radiation emitted and absorbed by these atoms is very large.

http://www.cowtownproductions.com/cowtown/genchem/08_07T1.htm contains a brief tutorial on energy level diagrams.

http://www.colorado.edu/physics/2000/applets/a2.html contains (among other things) energy level diagrams and animations of electron shells and nuclei.

http://intro.chem.okstate.edu/WorkshopFolder/Electronconfnew.html animates the building up of energy level diagrams.

Skill 1.1c- Predict periodic trends including electronegativity, ionization energy, and the relative sizes of ions and atoms
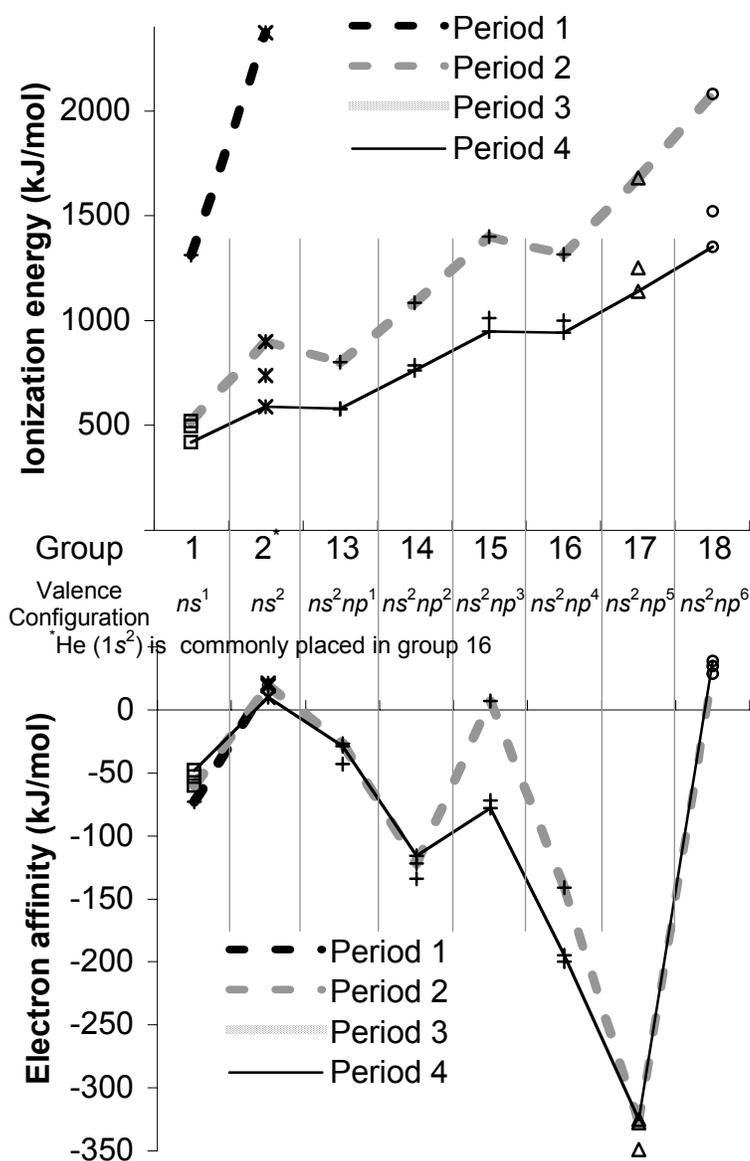
Electronegativity
Electronegativity measures the ability of an atom to attract electrons in a chemical bond. The most metallic elements (see **Skill 9.1l**) at the lower left of the periodic table have the lowest electronegativity. The most nonmetallic have the highest electronegativity. Fluorine is the most electronegative element. Electronegativity decreases to the left and down from fluorine. The impact of electronegativity on chemical bonding is discussed in **Skill 1.3a**.

Physics of electrons and stability of electron configurations
For an isolated atom, the **most stable system of valence electrons is a filled set of orbitals** (see **Skill 1.1b** and **Skill 9.1l**). For the main group elements, this corresponds to group 18 (ns^2np^6 and $1s^2$ for helium), and, to a lesser extent, group 2 (ns^2). The next most stable state is a set of degenerate half-filled orbitals. These occur in group 15 (ns^2np^3). The least stable valence electron configuration is a single electron with no other electrons in similar orbitals. This occurs in group 1 (ns^1) and to a lesser extent in group 13 (ns^2np^1)).

An atom's first **ionization energy** is the energy required to remove one electron by the reaction $M(g) \rightarrow M^+(g) + e^-$. Periodicity is in the opposite direction from the trend for atomic radius. The most metallic atoms have electrons further from the nucleus, and these are easier to remove.

Group	1	2*	13	14	15	16	17	18
Valence Configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6

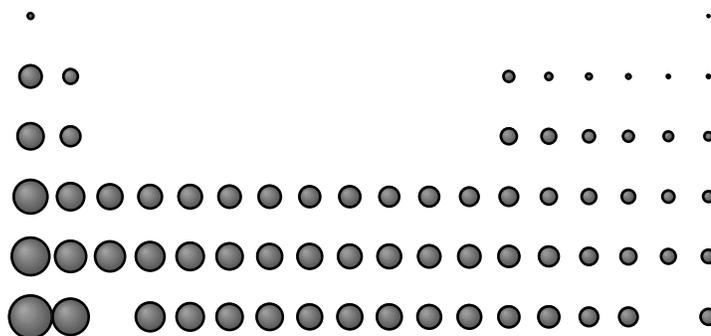*He ($1s^2$) is commonly placed in group 16

An atom's **electron affinity** is the energy released when one electron is added by the reaction $M(g) + e^- \rightarrow M^-(g)$.
A large negative number for the exothermic reaction indicates a high electron affinity. Halogens have the highest electron affinities.

Trends in **ionization energy and electron affinity** within a period reflect the **stability of valence electron configurations**. A stable system requires more energy to change and releases less when changed. Note the peaks in stability for groups 2, 13, and 16
to the right.

The **size of an atom** is not an exact distance due to of the probabilistic nature of electron density (see Skill 1.2a), but we may compare radii among different atoms using some standard. As seen to the right, the sizes of neutral atoms increase with period number and decrease with group number. As period number increases, the outermost electrons are shielded from the positive charge of the nucleus by more electrons in shells further in, so they are held less tightly. As group number increases, electrons are added to the same shell, so they experience little additional shielding, but the increased number of protons holds them in more closely. This trend is similar to the trend for metallic character. The smallest atom is helium.

The **size of an ion** is also not an exact distance due to the probabilistic nature of electron density, but different ion sizes may be compared. The size of different ions with the same number of electrons decreases as the number of protons increases because more protons provide a greater attractive force (e.g., the size of O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+} for ions with 10 electrons). Cations are smaller than the same parent atom (Na^+ < Na) because of decreased repulsion among electrons and anions are larger than the same parent atom (Cl^- > Cl) because of increased electron repulsion. Ions of the same charge show periodic trends identical to the trends for neutral atoms. Sizes increase with period number (F^- < Cl^- < Br^- < I^-) and decrease with group number (Na^+ > Mg^+ > Al^+).