11.11: Many-Electron Atoms and the Periodic Table

Quantum mechanics can account for the periodic structure of the elements, by any measure a major conceptual accomplishment for any theory. Although accurate computations become increasingly more challenging as the number of electrons increases, the general patterns of atomic behavior can be predicted with remarkable accuracy.

Figure 11.11.1shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

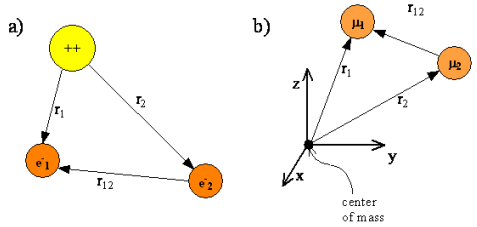


Figure 11.11.1 **:** a) The nucleus (++) and electrons (e-) of the helium atom. b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Schrödinger equation operator for the hydrogen atom serves as a reference point for writing the Schrödinger equation for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$(\hat{T} + \hat{V})\psi = E\psi \tag{11.11.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12})\right)\psi = E\psi \tag{11.11.2}$$

where

$$V(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{11.11.3}$$

$$V(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{11.11.4}$$

$$V(r_{12}) = +\frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{11.11.5}$$

Equation 11.11.2can be extended to any atom or ion by including terms for the additional electrons and replacing the He nuclear charge +2 with a general charge Z; e.g.

$$V(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{11.11.6}$$

Equation 11.11.2then becomes

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i\neq j} V(r_{ij})\right)\psi = E\psi \tag{11.11.7}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the

hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$\Psi(r_1, r_2, \cdots r_i) \tag{11.11.8}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms. The most basic ansatz to the exact solutions involve writing a multi-electron wavefunction as a **simple product of single**-electron wavefunctions

$$\psi(r_1, r_2, \cdots, r_i) = \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i) \tag{11.11.9}$$

Obtaining the energy of the atom in the state described by that wavefunction as the **sum** of the energies of the one-electron components.

By writing the multi-electron wavefunction as a product of single-electron functions in Equation 11.11.9, we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms these single-electron wavefunctions are called atomic orbitals. For molecules, as we will see in the next chapter, they are called molecular orbitals. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Electron Configurations

The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom and is formulated via the *Aufbau* principle, which means "building-up" in German. Aufbau principles determine the order in which atomic orbitals are filled as the atomic number is increased. For the hydrogen atom, the order of increasing orbital energy is given by 1*s* < 2*s* = 2*p* < 3*s* = 3*p* = 3*d*, etc. The dependence of energy on *n* alone leads to extensive degeneracy, which is however removed for orbitals in many-electron atoms. Thus 2*s* lies below 2*p*, as already observed in helium. Similarly, 3*s*, 3*p* and 3*d* increase energy in that order, and so on. The 4*s* is lowered sufficiently that it becomes comparable to 3*d*. The general ordering of atomic orbitals is summarized in the following scheme:

$$\begin{aligned} 1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s \sim 4d \\ < 5p < 6s \sim 5d \sim 4f < 6p < 7s \sim 6d \sim 5f \end{aligned} \tag{11.11.10}$$

and illustrated in Figure 11.11.2 This provides enough orbitals to fill the ground states of all the atoms in the periodic table. For orbitals designated as comparable in energy, e.g., 4*s* ∼ 3*d*, the actual order depends which other orbitals are occupied. The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*. Figure 11.11.2 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

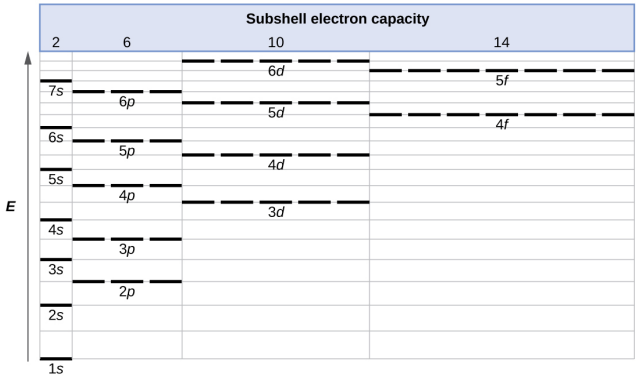


Figure 11.11.2: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 11.11.3):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell (l = 1) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., l = 2) of the principal shell for which n = 3.

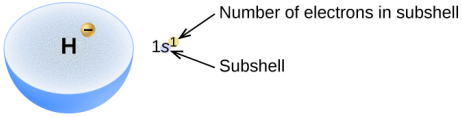


Figure 11.11.3: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 11.11.4), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 11.11.3illustrates the traditional way to remember the filling order for atomic orbitals.

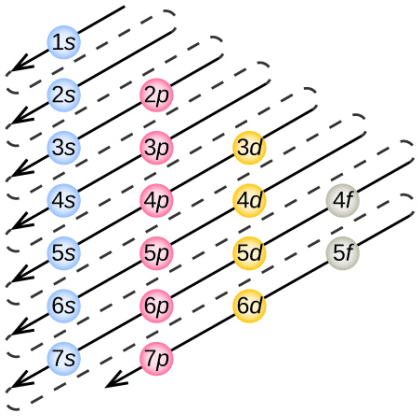


Figure 11.11.4: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure 11.11.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

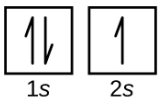
H $1s^1$

Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

In this figure, the element symbol H e is followed by the electron configuration, “1 s superscript 2.” An orbital diagram is provided that consists of a single square. The square is labeled below as “1 s.” It contains a pair of half arrows: one pointing up and the other down.

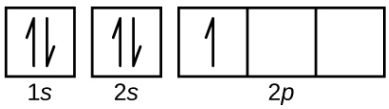
The n = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 11.11.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$ 

An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$ 

Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund’s rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

In this figure, the element symbol C is followed by the electron configuration, “1 s superscript 2 2 s superscript 2 2 p superscript 2.” The orbital diagram consists of two individual squares followed by 3 connected squares in a single row. The first blue square is labeled below as, “1 s.” The second is similarly labeled, “2 s.” The connected squares are labeled below as, “2 p.” All squares not connected to each other contain a pair of half arrows: one pointing up and the other down. The first two squares in the group of 3 each contain a single upward pointing arrow.

Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

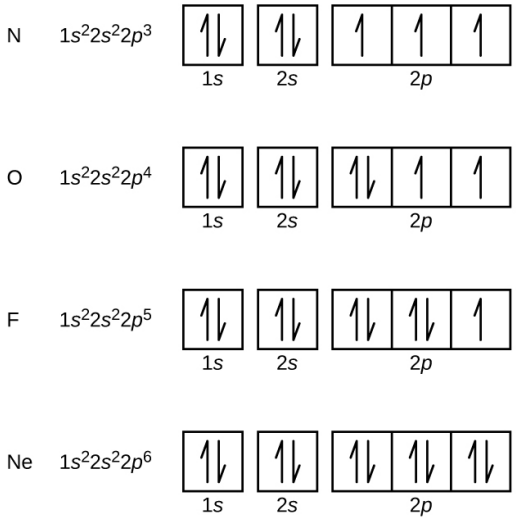


Figure 11.11.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, (1 $s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

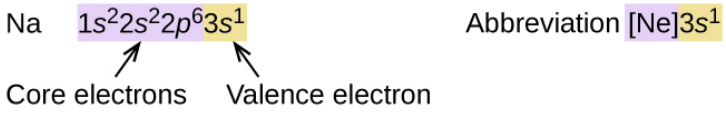


Figure 11.11.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{aligned} \text{Li} &: [\text{He}]\, 2s^1 \\ \text{Na} &: [\text{Ne}]\, 3s^1 \end{aligned} \tag{11.11.11}$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$

m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the (n – 2) shell to bring that shell from 18 electrons to a total of 32 electrons.

Example 11.11.1

Quantum Numbers and Electron Configurations What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

The last electron added is a 3*p* electron. Therefore, n = 3 and, for a *p*-type orbital, l = 1. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 11.11.1

Identify the atoms from the electron configurations given:

a. [Ar]$4s^2 3d^5$
b. [Kr]$5s^2 4d^{10} 5p^6$

Answer

(a) Mn (b) Xe

Effective Charge, Shielding and Penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z (Figure 11.11.6). This effect is called electron shielding.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other (Z − 1) electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.1 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

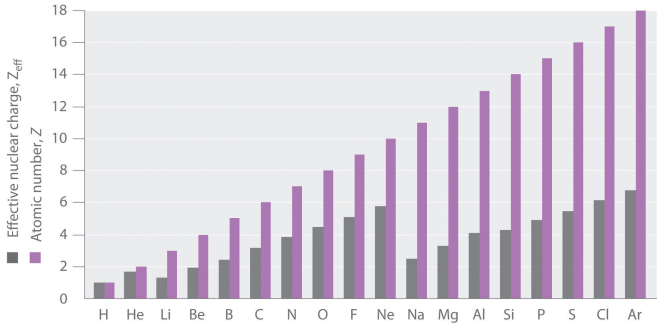


Figure 11.11.6: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row.

Because of the effects of shielding and the different radial distributions of orbitals with the same value of n but different values of l, the different subshells are not degenerate in a multielectron atom. For a given value of n, the ns orbital is always lower in energy than the np orbitals, which are lower in energy than the nd orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of n; for example, the 4s orbital is lower in energy than the 3d orbitals for most atoms.

Note

Except for the single electron containing hydrogen atom, in every other element Z_{eff} is always less than Z.

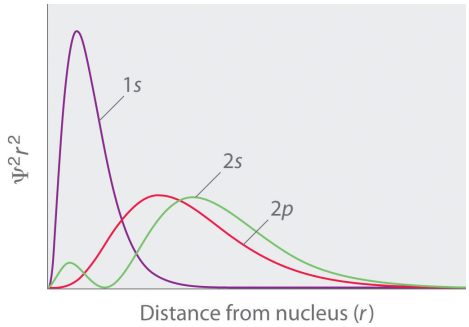


Figure 11.11.7: Orbital Penetration. A comparison of the radial probability distribution of the 2 s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.

Ionization Energy

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Conceptually, ionization energy is the opposite of electronegativity. The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation. Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled. Elements on the left side of the periodic table have low ionization energies because of their willingness to lose electrons and become cations. Thus, ionization energy increases from left to right on the periodic table.

Another factor that affects ionization energy is *electron shielding*. Electron shielding describes the ability of an atom's inner electrons to shield its positively-charged nucleus from its valence electrons. When moving to the right of a period, the number of electrons increases and the strength of shielding increases. As a result, it is easier for valence shell electrons to ionize, and thus the ionization energy decreases down a group. Electron shielding is also known as *screening*.

Note

- The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.
- The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.
- The noble gases possess very high ionization energies because of their full valence shells as indicated in the graph. Note that helium has the highest ionization energy of all the elements.

Some elements have several ionization energies; these varying energies are referred to as the first ionization energy, the second ionization energy, third ionization energy, etc. The first ionization energy is the energy requiredto remove the outermost, or highest, energy electron, the second ionization energy is the energy required to remove any subsequent high-energy electron from a gaseous cation, etc. Below are the chemical equations describing the first and second ionization energies:

First Ionization Energy:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-} \tag{11.11.12}$$

Second Ionization Energy:

$$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-} \tag{11.11.13}$$

Generally, any subsequent ionization energies (2nd, 3rd, etc.) follow the same periodic trend as the first ionization energy.

Ionization energies decrease as atomic radii increase. This observation is affected by n (the principal quantum number) and Z_{eff} (based on the atomic number and shows how many protons are seen in the atom) on the ionization energy (I). The relationship is given by the following equation:

$$I = \frac{R_H Z^2_{eff}}{n^2} \tag{11.11.14}$$

- Across a period, Z_{eff} *increases* and n (principal quantum number) *remains the same*, so the ionization energy *increases*.
- Down a group, n *increases* and Z_{eff} *increases slightly;* the ionization energy *decreases*.

Figure 11.11.8: Periodic trends in ionization energy.

The periodic structure of the elements is evident for many physical and chemical properties, including chemical valence, atomic radius, electronegativity, melting point, density, and hardness. The classic prototype for periodic behavior is the variation of the first ionization energy with atomic number, which is plotted in Figure 11.11.8

Electron Affinity

The electron affinity (EA) of an element E is defined as minus the internal energy change associated with the gain of an electron by a gaseous atom, at 0 K :

$$E_{(g)} + e^{-} \rightarrow E^{-}_{(g)} \tag{11.11.15}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be positive (energy is released when an electron is added), negative (energy must be added to the system to produce an anion), or zero (the process is energetically neutral).

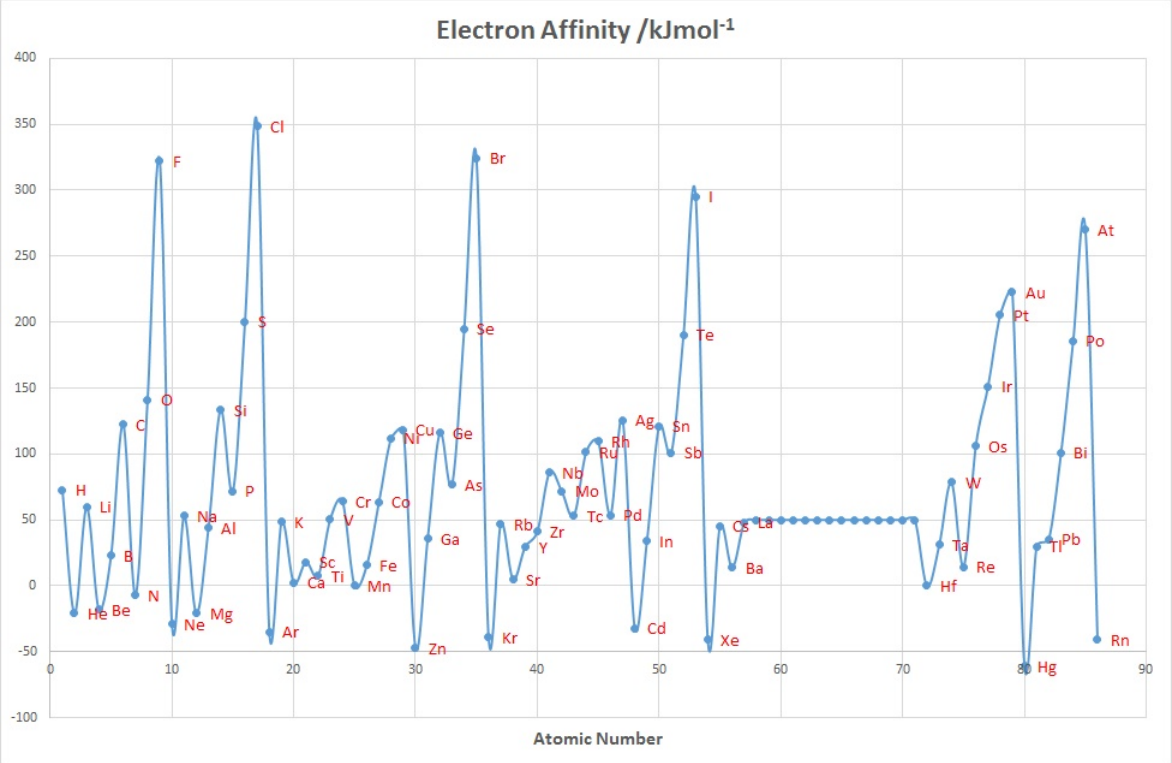


Figure* 11.11.9*: *Periodic trends in electron affinities.*

The periodic trends of electron affinity (Figure 11.11.9) shows that chlorine has the most positive electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element, EA= 348.6 kJmol^{-1} and the Group 17 elements have the largest values overall. The addition of a second electron to an element is expected to be much less favored since there will be repulsion between the negatively charged electron and the overall negatively charged anion. For example, for O the values are:

$$O_{(g)} + e^{\rightarrow} O^{-}_{(g)} \quad EA = +141\ kJmol^{-1} \tag{11.11.16}$$

$$O^{-}_{(g)} + e^{-} \rightarrow O^{2-})(g) \quad EA = -798\ kJmol^{-1} \tag{11.11.17}$$

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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