8.2: The Aufbau Principle

The **aufbau principle**(German for “building up” principle), or building up principle, suggests that we can construct a description of an atom my adding subatomic particles one at a time, moving through the periodic table until we reach the element of interest.

Under this description, a carbon atom (atomic number 6) is similar to a boron (atomic number 5) atom, but with one additional proton and some additional neutrons in the nucleus and one additional electron added to the electron cloud.

Electronic Configurations

Consider carbon, which is atomic number 6. Most chemists advanced to a level to which they are prepared to take a course in physical chemistry can construct an electronic configuration for ${}_6C$.

$$ {}_6C\text{: } [He]2s^2 2p^2$$

Or for ${}_{23}V$, one would write

$$ {}_{23}V\text{: } [Ar]4s^2 3d^3$$

It is a curious thing that that the 4s subshell fills before the 3d subshell, since in atomic hydrogen, the 3d subshell has a lower energy. However, in polyelectronic atoms, (specifically for K and Ca) the 4s subshell is actually lower in energy than the 3d subshell. As such, according to the aufbau principle, it is the 4s subshell that fills first of the two.

However, it is important to note that the relative energies of the subshells change with changing nuclear charge and differing numbers of electrons. For example, in Sc, it is the 4s electrons that are higher in energy than the 3d electron. As such, the 4s electrons are the first to be removed when the atom is ionized.

Shells, Subshells, Orbitals and Spin

It is useful to develop some nomenclature to describe the different combinations of quantum numbers that describe the different wavefunctions for the electrons in an atom. In order to do this, we need ot define a few terms that will come in handy later.

i. **shell**– characterized by the principle quantum number n
ii. **subshell**– characterized by n and the angular momentum quantum number *l*
iii. **orbital**– characterized by n, *l* and the azimuthal quantum number m_l.

In addition to shells, subshells and orbitals, electrons have spin. The spin quantum number of an electron is $\mathbf{s} = \frac{1}{2}$. But generally electrons are described as being “spin up” or “spin down” based on the value of the z-axis component of the spin, m_s. m_s can take values of $+\frac{1}{2}$ and $-\frac{1}{2}$. Each orbital can hold two electrons. If there are two electrons in the orbital, the spins must be pairs such that one is “spin up” and the other is “spin down.”