6.8: Electron Affinities

Electron affinities are more difficult to measure experimentally than are ionization energies, and far fewer values are available. The relationship of the periodic table with those electron affinities that have been measured or estimated from calculations can be seen on the table of ionization energies and electron affinities (in the red), seen below.

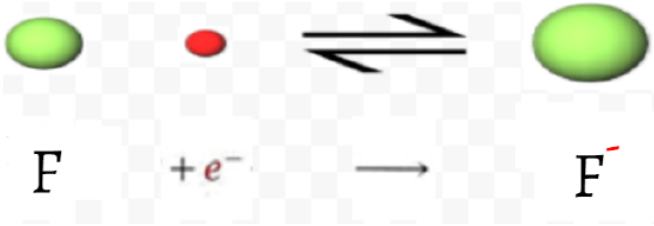
Table 6.8.1 Ionization Energies and Electron Affinities. The electron affinities are the red values above the atomic symbol.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

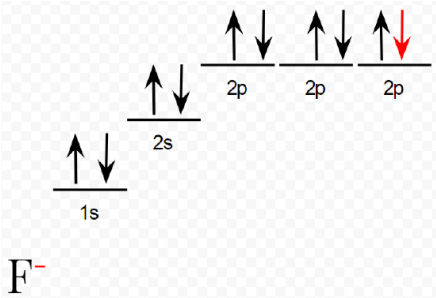
** Electron affinities marked with an asterisk (*) have been obtained from theoretical calculations rather than experimental measurements. The heavy colored line separates metals (ionization energy usually below about 800 kJ mol–1) from nonmetals.*

It is not easy to discern many obvious regularities in this table, especially since some of the electron-affinity values quoted are negative, indicating that energy is sometimes *required* to force an extra electron onto an atom. Nevertheless, it is quite obvious which of the periodic groups correspond to the highest electron affinities. All the halogens have values of about 300 kJ mol^{-1} while the group VI nonmetals have somewhat lower values, in the region of 200 kJ mol^{-1} or less. The high electron affinities of the halogens are a result of their having an almost complete outer shell of electrons.

The element fluorine, for example, has the structure $1s^2 2s^2 2p^5$, in which one of the 2*p* orbitals contains but one electron. If an extra electron (in the red in both diagrams below) is added to this atom to form a fluoride ion, the electron can pair with the electron in the half-filled 2*p* orbital (as seen in the orbital diagram below).



Macroscopic view of a Fluorine atom shown as a green sphere reacting with a single electron represented by a small red sphere. The resulting product is a larger green sphere labeled F superscript negative sign.



The orbital diagram for a fluoride ion has three separate levels. The lowest level, labeled "1 s" has two opposite pointing arrows. The next higher level, labeled "2 s" also has two opposite pointing arrows. The highest level has three identical levels adjacent to one another, each labeled "2 p". The first two levels have two opposite pointing arrows respectively. The last level has one upward pointing arrow with one downward pointing arrow in a different color than the rest of the arrows in the entire orbital.

The added electron will be shielded from the nucleus by the 1*s* electrons, but the 2*s* and 2*p* electrons are in the same shell and will shield it rather poorly. There will thus be quite a large effective nuclear charge (a rough estimate is +5) attracting the added electron. Because of this overall attraction, energy will be *released* when the electron is captured by the fluorine atom. Similar reasoning also explains why oxygen also has a high electron affinity. Here, though, the nuclear charge is smaller, and the attraction for the added electron distinctly less.
