The Periodicity of Electron Affinity

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It is common in textbooks to see graphs showing ionization energy, *IE*, as a function of atomic number. One does not see such graphs for electron affinity, *EA*, even though this is necessary to understand the chemical behavior of the elements. This may be because it is not realized how extensive the data are (*1–3*). The data are given in periodic table form in Figure 1, and graphed in Figure 2, which shows that, in general, *EA* has about the same periodic behavior as does *IE*. There are some deviations from strict periodicity, most of them having interesting and instructive explanations. Some of the divergences from periodic behavior are unexplained.

All electron affinities are in eV, and are shown as positive values, meaning exoergic processes. It used to be common to see large negative electron affinities for many elements, when all we had to depend on were extrapolation processes. I assume that no *EA* is (much) below zero, i.e., endoergic to a significant extent. The logic is that the screening constant for an atom cannot be (much) larger than the atomic number. No set of screening constants has ever suggested such extremely high values. I will use the screening constants of Slater (*4*), because they are convenient and suffice for explaining most of the trends in a qualitative fashion.

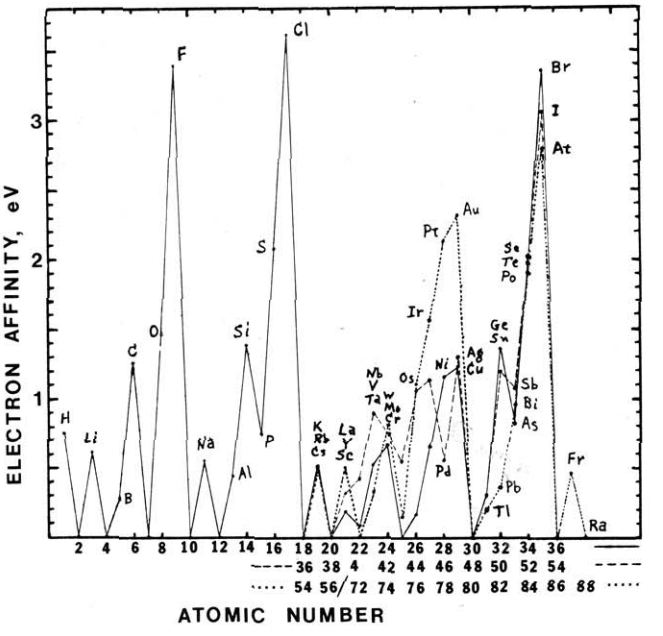

Figure 1. Electron affinities of elements as function of atomic number; data from refs *1–3*.

Interpretation of the Data

The very low values of *EA* (~0) for the noble gases are expected, because there will be effective screening of the added electron outside an octet (or closed shell, for He). This corresponds to very low values of *IE* for Group 1 elements (*2*).

One would expect low values of *EA* for the alkaline earths (Group 2), and Group 12, due to effective screening, and the low ionization energies of the atoms with atomic number one higher (*2*). The fact that the experimental EA's are near zero is surprising.

The elements of Group 15 have rather low values of *EA*, as expected. This is due to pairing up of the added electron in the p orbitals, and corresponds to the low values (*2*) of *IE* of Group 16. This does not explain why *N* is so extremely low.

The low value of *EA* for Pb (corresponding to a low *IE* for Bi), noted by Chamizo (*5*), is due to spin-orbit coupling (*6*).

In the case of the transition elements, the added electron usually goes to the d orbitals and hence is not screened by the outer s electrons. On the other hand, d electrons are strongly screened by "inner" electrons. Then, as the number of electrons in the d subshell increases, the effective nuclear charge gradually increases. The net result is that the *EA* of these elements is generally fairly low but shows a general increase across a period. There is some tendency for *EA* to increase as one goes down a column. The inconsistencies present interesting aspects.

The low value for Pd arises from its ground state of $4d^{10}$, which means that the added electron must go to the 5s, and is screened much more effectively than for Ni and Pt, for which the added electron goes to the d orbitals (*1*).

In the case of Mn, Tc, and Re, the added electron pairs up with one in half-filled d orbitals, and the resultant Coulomb repulsion causes rather low values for *EA* as compared with the preceding elements, Cr, Mo, and W. The near-zero value for Mn is unexpected but is reminiscent of the extremely low value for *N*, in which the electron pairs up in half-filled p orbitals. Hotop and Lineberger were unable to assign an outer electron configuration to Mn^-. It is also possible that the added electron goes to an outer orbital, and the configuration is $3d^5 4s^2 4p$, which would give higher screening, and lower *EA*, for this ion.

The high value of *EA* for Nb is no doubt connected with its divergent electron configuration, $4d^4 5s$, as compared with V, $3d^3 4s^2$, and Ta, $5d^3 6s^2$. However, whether the electron added

																1 H 0.754	2 He ~0
3 Li 0.618	4 Be ~0											5 B 0.277	6 C 1.263	7 N 0	8 O 1.461	9 F 3.399	10 Ne ~0
11 Na 0.548	12 Mg ~0											13 Al 0.441	14 Si 1.385	15 P 0.746	16 S 2.077	17 Cl 3.617	18 Ar ~0
19 K 0.501	20 Ca ~0	21 Sc 0.188	22 Ti 0.079	23 V 0.525	24 Cr 0.666	25 Mn ~0	26 Fe 0.163	27 Co 0.661	28 Ni 1.156	29 Cu 1.228	30 Zn ~0	31 Ga 0.3	32 Ge 1.35	33 As 0.81	34 Se 2.021	35 Br 3.365	36 Kr ~0
37 Rb 0.486	38 Sr ~0	39 Y 0.307	40 Zr 0.426	41 Nb 0.893	42 Mo 0.746	43 Tc 0.55	44 Ru 1.05	45 Rh 1.137	46 Pd 0.557	47 Ag 1.302	48 Cd ~0	49 In 0.3	50 Sn 1.2	51 Sb 1.07	52 Te 1.971	53 I 3.059	54 Xe ~0
55 Cs 0.472	56 Ba ~0	57 La 0.5	72 Hf ~0	73 Ta 0.322	74 W 0.815	75 Re 0.15	76 Os 1.1	77 Ir 1.565	78 Pt 2.128	79 Au 2.309	80 Hg ~0	81 Tl 0.2	82 Pb 0.36	83 Bi 0.946	84 Po 1.9	85 At 2.8	86 Rn ~0
87 Fr 0.470	88 Ra ~0	89 Ac	104	105	106												

58 Ce 0.5	59 Pr (est.)	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu →
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 2. Electron affinities of elements; data from refs *1–3*.

to Nb goes to the 4d or the 5s, it should be screened better than an electron added to the other two congeners, giving it a *lower EA*. Consequently, the high value for Nb is puzzling and may be in error.

The extremely low value for Hf is completely inexplicable; the ground state electron configuration for the elements in this group is completely parallel, and the added electron goes into the d orbitals. Perhaps this is also an error in measurement.

In the case of the inner transition elements (rare earths, lanthanides) the added electron most likely does not go to the 4f subshell, because this would mean no screening by the 5s and 5p electrons and consequently a high effective nuclear charge. The added electron probably goes to the 5d except for Sm and Tm (*7*). The effective nuclear charge for all these elements is 2.00, with the exception of Ce and Gd, where it is 3.65. The low effective nuclear charge explains the low and constant values of *EA*, 0.5 eV, assumed (*1*) for these elements. (The *EA* of Ce and Gd should be a little higher, because there is already an electron in the 5d, which, being in the same subshell as the added electron, screens less.) The *EA* of Sm and Tm are not high, because the number of 4f electrons changes (*7*), and this has considerable effect on energies of electrons.

Finally, we note the high values for Os, Ir, Pt, and Au, resulting from the lanthanide contraction, in addition to the normal decrease in size, and increase in effective atomic number, which occurs across a row of transition elements.

Conclusion

In general, the values of electron affinity for the elements can be understood in terms of their ground state electron configuration, and the screening (effective nuclear charge) exerted on the added electron by the electrons already present in the neutral atom. There are some cases where an explanation is not possible, and this may mean erroneous data, which need to be reexamined.

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