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Electron affinities for highly charged groups 15 and 16 anions

Savaş KAYA [1,*], *Robson Fernandes De FARIAS* [2]

[1] *Sivas Cumhuriyet University, Health Services Vocational School, Department of Pharmacy, 58140, Sivas/TURKEY*

[2] *Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal, RN, BRAZIL*

Abstract

Electron affinity, electronegativity, and electrophilicity are chemical concepts that have been related to electron accepting power of chemical species. In the literature, although there are many theoretical approaches proposed to calculate the electronegativity and electrophilicity of atoms, ions, and molecules, just a few approaches suggested are related to the prediction of sequential electron affinities of atoms. In the present work, the electron affinities for highly charged groups 15 and 16 anions are calculated by the semi-empirical (PM6) method. The obtained values are compared with those from literature. So far, the authors are concerned, the third and fourth electron affinities for S, P, As and Sb are calculated for the first time. It is well-known that in the calculation of the lattice energy of any inorganic ionic crystal via Born-Haber thermochemical cycle, many parameters regarding any crystal the atoms forming the crystal are considered. One of these parameters is electron affinity. It should be noted that our electron affinity values calculated are in good agreement with both experimental data, other theoretical approaches, and the data obtained in the light of the Born- Haber cycle.

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1. Introduction

As is known, atoms are the simplest chemical systems; electron affinity of an atom A is equal to the difference of ground state total energies (Etot) of A and its negative ion A-, and can be given as: [1]. In the Conceptual Density Functional Theory [2], chemical concepts such as hardness, electronegativity, chemical potential, and softness have been associated with ionization energy and electron affinity values of chemical species via the following equations. For that reason, the methodologies proposed for the accurate prediction of electron affinities of atoms, ions, and molecules are quite noteworthy for theoretical chemists.

$$\chi = -\mu = (IE + EA)/2 \quad (1)$$

$$\eta = IE - EA \quad (2)$$

Electron affinity is a quantity that can be physically observed and can be experimentally determined although the same is not the case for electronegativity and electrophilicity. Atomic electronegativities have been defined by chemists and physicists from different perspectives. For instance, some researchers noted the electron affinity as the energy required to remove an electron from the negative ion of an A atom, some authors reported this quantity as the energy released when atom A receives an electron. It can be said that both definitions are widely used in the literature [3].

Computational chemistry tools are widely used in the prediction of atomic and molecular properties like electron affinity, ionization energy, proton affinity vs. Pople and co-workers [4] investigated the performances of B-LYP functional with the help of basis sets such as 6-31G(d), 6-3111G (3df,2p) in the prediction of the mentioned properties. Proft and Geerlings [5] calculated electron affinity, ionization energy, electronegativity, and hardness values of some atoms in the light of Dunning's correlation consistent basis sets and analyzed the performances of B3LYP and B3PW91 exchange-correlation functionals.

Chemical hardness is reported as the resistance against electron cloud polarization of chemical species (atoms, ions, and molecules) [6]. This concept has been widely considered in the understanding of the logic of many chemical events. According to Hard and Soft acid-base principle [7] that is an approach introduced based on the chemical hardness concept, "Hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases." Another principle about the concept is the Maximum Hardness Principle [8] states that soft molecules are more reactive compared to hard ones. HSAB Principle has been successful in explaining the geochemistry in nature of the elements.

*Corresponding author. *e-mail address: savaskaya@cumhuriyet.edu.tr*

For instance, hard acids like Fe3+ and Al3+ are found as oxides and fluorides in nature while soft acids such as Hg2+and Cd2+ prefer to bond to the sulphide ion (S2-). Some double-charged negative ions like N2-, S2-, Se2- and O2- exist in the structure of inorganic ionic solids. In the light of this information, Baughan [9] calculated electron affinities of some negative ions situated in the structure of crystals. Considering Electronegativity Equalization Process in a molecule, Orsky and Whitehead [10] defined the chemical hardness for acid and a base as:

$$\eta_A = 1/4(\mathrm{IE}_{A^+} - EA_{A^0})$$
$$\eta_B = 1/4(\mathrm{IE}_{B^0} - EA_{B^-}) \quad (3)$$

It is apparent from the equation given above that to calculate the chemical hardness of a base via the Orsky-Whitehead definition, we need to sequential electron affinity values of atoms or ions. For that reason, the methodologies developed for the calculation of electron affinities of negative ions are quite remarkable for chemists and physicists.

Laszlo von Szentpaly known with his studies regarding chemical reactivity of chemical species imparted a useful equation to science to calculate the second electron affinities of atoms [11]. The equation is given as follows.

$$EA_{2,cal} = EA_1 - (7/6)\eta^0 \quad (4)$$

Where in, IE2, IE1, and η0 are second electron affinity, first electron affinity, and chemical hardness value of the neutral form of chemical species. It should be noted that this methodology proposed by Szentpaly is very useful in the calculation of second electron affinities.

2. Materials and Methods

The employed reference data were taken from the literature [12,13]. All computations were performed using Spartan [14]. Thermochemical calculations were performed by semi-empirical (PM6) method. The SE-PM6 approach was chosen to take into account its minor computation time consuming and its reliability for inorganic species, as verified for PtF6 [15]. To verify the reliability of the employed theoretical approach, besides the anions (P-3, S-3), etc., investigated here for the first time, the electron affinities for the neutral atoms (first electron affinity) and the respective monoanionic (second electron affinities) were also calculated and the results compared with reference values.

Also, in order to verify such reliability, the second electron affinity for oxygen was calculated through a Born-Haber cycle:

Mg(s) + ½ O2(g) → MgO (s) ΔHf (MgO) = -601.6

MgO(s) → Mg2+(g) + O-2(g) ΔHlatt (MgO) = 3791

Mg(g) → Mg(s) ΔH = -147.1

O(g) → ½ O2(g) ΔH = -249.3

Mg+(g) + e- → Mg(g) ΔH = -737.8

Mg2+(g) + e- → Mg+(g) ΔH = - 1450.7

O(g) + 2e- → O2- (g) ΔH = 604.5

With the help of the obtained result above, the following statements can be written.

O-(g) → O(g) + e- ΔH= 150

O(g) + 2e- → O2- (g) ΔH = 604.5

O-(g) + e- → O2- (g) ΔH = 754.5 kJmol-1 = 7.82 eV

The same procedure was repeated for sulphur

Mg(s) + ½ S(g) → MgS (s) ΔH_f (MgS) = -345.7

MgS(s) → Mg^{2+}(g) + S^{-2}(g) ΔH_{latt} (MgS) = 3238

Mg(g) → Mg(s) ΔH = -147.1

S(g) → ½ S_2(g) ΔH = -215

M^+(g) + e^- → Mg(g) ΔH = -737.8

Mg^{2+}(g) + e^- → Mg^+(g) ΔH = - 1450.7

S(g) + 2e^- → S^{2-} (g) ΔH = 314.4

With the help of the obtained result above for sulphur, the following statements can be written.

S^-(g) → S(g) + e^- ΔH = 200.7

S(g) + 2e^- → S^{2-} (g) ΔH = 314.4

S^-(g) + e^- → S^{2-} (g) ΔH = 515.1 kJmol^{-1} = 5.61eV

3. Results and Discussion

The obtained results are summarized in Table 1. When available, reference values are provided. As can be verified by Table 1 data, the values to the electron affinity for O^- (that is, the second electron affinity for oxygen, forming O^{2-}) obtained by the Born-Haber cycle and the SE-PM6 method are in exceptional agreement, testifying the reliability of the chose theoretical approach. For sulphur, the agreement between the calculated (SE-PM6) and Born-Haber cycle values are not so good. However, it is necessary to remember that the SE calculated value is for a modelled gas phase specie, whereas the Born-Haber cycle employs values for condensed phase species. Furthermore, since sulphur is more polarizable than oxygen, the superimposition of orbitals (condensed phase compounds) must be taken into account.

In Table 2 are summarized the electron affinity values calculated in the presented work and previous ones, from literature. Guo and Whitehead [16] have calculated second electron affinities for atoms from helium to krypton using the self-interaction corrected generalized exchange local-spin-density functional theory with the correlation energy functional. The dependence of the second electron affinities of the elements O, S, and Se on the Watson sphere radius was considered. As can be seen in Table 2, there is a really good agreement between those values calculated for the second electron affinity for oxygen, especially taking into account the significant differences between the employed theoretical approaches (present work and Ref. 4). Nevertheless, we think that the value calculated here is most reliable, taking into account, for example, the exceptional agreement between our value and those obtained through a Born-Haber cycle for the second electron affinity to oxygen.

On the other hand, the agreement observed for oxygen is not verified for sulphur and selenium. Indeed, as can be verified, the agreement between the values calculated in the previous work and those obtained by Guo and Whitehead decreases down the group, that is, for the heavier and more polarizable elements (S and Se) the agreement is poor, whereas is good for the lighter (and less polarizable) element (oxygen). Based on the results obtained for oxygen, we believe that our values are more reliable. As can be verified, the second electron affinity decreases down the group: 7.81, 4.20, and 3.87 eV for O, S, and Se, respectively. Such results are compatible with the fact that the heavier and more polarizable elements require a minor amount of energy to "accept" a second "extra" electron in their electro sphere.

Table 1. Electron affinities (EA) for several species as calculated by SE-PM6 method.

Species	$EA/eV_{ref.value}$	$EA/eV_{calc.}$
O	-1.46[a]	-0.88
O^-	7.82[b]	7.81
S	-2.08[a]	-2.67
S^-	5.61[b]	4.20
S^{-2}	_	17.25
S^{-3}	_	49.74
Se	-2.02[a]	-2.21
Se^-	_	3.87
Te	-1.97[a]	-1.55/-1.67[c]
Te^-	_	4.97/6.31[c]
N	(not stable)[a]	0.23
N^-	_	9.81
N^{-2}	_	19.39
P	-0.75[a]	-0.14
P^-	_	7.14
P^{-2}	_	14.41
P^{-3}	_	205.58
As	-0.80[a]	-0.40
As^-	_	8.85
As^{-2}	_	17.28
As^{-3}	_	113.07
Sb	-1.05[a]	1.34
Sb^-	_	10.30
Sb^{-2}	_	19.20
Sb^{-3}	_	190.59

[a] CRC Handbook, 2016; [b]Through a Born-Haber cycle; Calc.= through SE-PM6 method; [c]With a relativistic correction (multiplied by γ).

Table 2. Electron affinities (EA) for several species as calculated by SE-PM6 method (present work) and those previously obtained by another theoretical approach.

Species	$EA/eV_{calc.}$	$EA/eV_{Ref.\ 5}$
O	-0.88	
O^-	7.81	8.22/8.89[a]
S	-2.67	
S^-	4.20	5.83/6.49[a]
S^{-2}	17.25	
S^{-3}	49.74	
Se	2.21	
Se^-	3.87	5.53/6.19[a]
Te	-1.55/-1.67[c]	
Te^-	4.97/6.31[c]	
N	0.23	
N^-	8.81	8.68/9.51[a]
N^{-2}	19.39	
P		
P^-	7.14	6.56/7.37[a]
P^{-2}	14.41	
P^{-3}	205.58	
As	_	
As^-	8.58	6.35/7.14[a]
As^{-2}	17.28	
As^{-3}	113.07	
Sb	1.34	
Sb^-	10.30	
Sb^{-2}	19.20	
Sb^{-3}	190.59	_

Calc.= present work; [a]With and without VWN (Vosko, Wilk and Nusair) correlation energy functional.

In Figure 1, the calculated second electron affinities for oxygen, sulphur, and selenium are plotted as a function of their polarizabilities: 0.802, 2.90, and 3.77 for O, S, and Se, respectively. The obtained curve (r= 0.9773) provides the equation:

$$EA = -1.40\,p + 8.78 \qquad (5)$$

where EA is the second electron affinity and p is the polarizability (in units of 10-24 cm3).

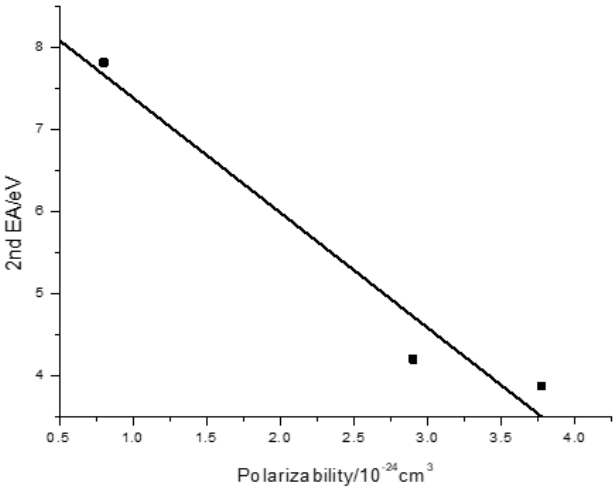

Figure 1. Second electron affinity (eV) as a function of the polarizability (10^{-24} cm^3) for O, S, and Se.

To tellurium (Z = 52) it is necessary to remember that relativistic contributions matter [17]. That is, the higher relativistic contraction/effects must be taken into account.

The relativistic and non-relativistic equations can be related by using γ = 1/[1-(v2/c2)], where v is the velocity of the considered body (in our case, an electron). The velocity of the 1s electron is ≈ Z/137, where Z is the atomic number. Hence, γ = 1/[1-((Z/137)2/c2)]1/2. For tellurium γ= 1.08 and to polonium, γ= 1.27. The relativistic corrected values are also shown in Tables 1 and 2. About the correlation between the second electron affinity and the polarizability, an important observation must be done: the polarizability reference values [1] for O, S, and Se have an estimated accuracy of 2%, whereas for tellurium (5.5) such estimated accuracy is high as 25%, making a possible correlation unreliable.

As can be verified, the second electrons affinities to N and P calculated in the present work agree very well with those values calculated by Guo and Whitehead. As mentioned to oxygen, the verified agreement is really good, especially taking into account the significant differences between the employed theoretical approaches. As verified for group 16 anions, the agreement between SE-PM6 results and Whitehead data decreases as the polarizability increases down the group.

In Figure 2, the calculated second electron affinities for phosphorus, arsenic, and antimony are plotted as a function of their polarizabilities: 3.63, 4.32, and 6.6 for P, As and Sb, respectively [1]. The obtained curve (r= 0.9692) provides the equation:

$$EA = 0.987\,p + 3.889 \qquad (6)$$

where EA is the second electron affinity and p is the polarizability (in units of 10^{-24} cm^3).

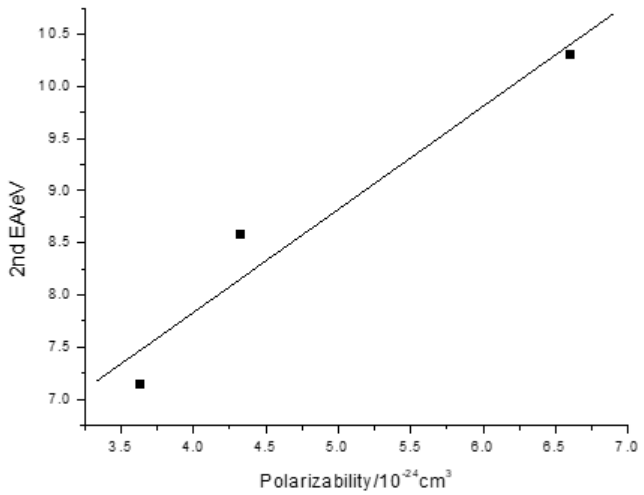

Figure 2. Second electron affinity (eV) as a function of the polarizability (10^{-24} cm^3) for P, As, and Sb.

Nitrogen (the lightest and harder, less polarizable element of the group) deviate from linearity, as predictable. Chattaraj and Duley [18] also investigated the electron affinities for a series of anions, including some studied in the present work, as N^- and O^-. All the calculations were done at the HF/6-311+G(d), B3LYP/6-311+G(d), and MP2/6-311+G(d) levels of theory. However, we have chosen do not to use such values for comparison since they are (a series of sometimes very different values for the same specie) highly dependent on the chose theoretical approach. For example, to gas phase N^-, they had obtained values from -3.28 eV (B3LYP/6-11+G(d) level of theory) to -6.80 eV (Hartree-Fock).

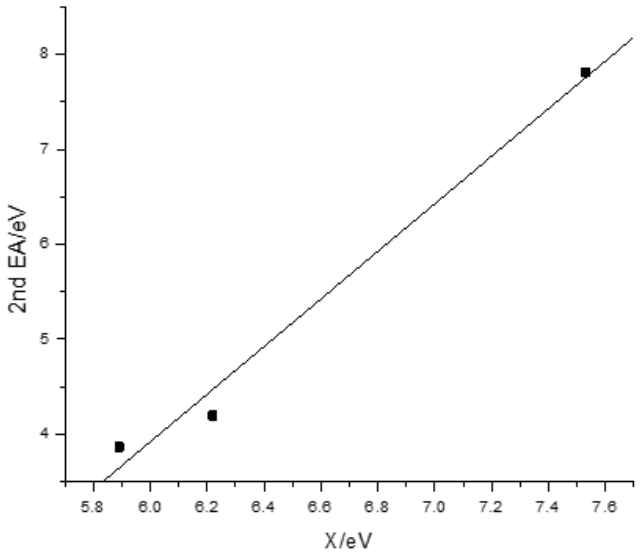

Figure 3. Calculated second electron affinity (eV) as a function of the experimental Mulliken electronegativities (eV) for O, S, and Se.

Hence, although some of their calculated values agree well with those obtained in the present work (e.g. 7.24 eV for O^-, by B3LYP method), we do not consider such values as really conclusive and useful (reliable) for comparison. If the calculated electron affinity values for O^-, S^- and Se^- (that is, the second electron affinities for O, S, and Se) are plotted as a function of the experimental values for Mulliken electronegativities [19,20] for those elements (7.53, 6.22 and 5.89, respectively), the curve shown in Figure 3 (r= 0.9933) is obtained. Providing the equation:

$$EA = 2.503\chi - 11.092 \quad (7)$$

where EA is the second electron affinity and χ is the Mulliken electronegativity (eV).

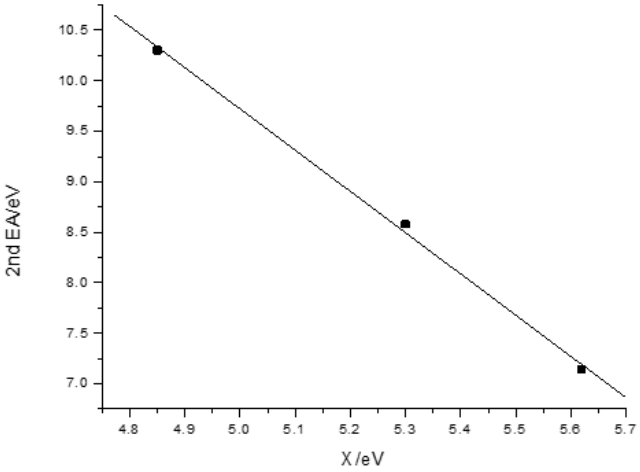

Figure 4. Calculated second electron affinity (eV) as a function of the experimental Mulliken electronegativities (eV) for P, As, and Sb.

If the calculated electron affinity values for P^-, As^- and Sb^- (that is, the second electron affinities for P, As and Sd) are plotted as a function of the experimental values for Mulliken electronegativities for those elements (5.62, 5.30 and 4.85, respectively), the curve shown in Figure 4 (r= 0.9989) is obtained. Providing the equation:

$$EA = -4.086\chi + 30.150 \quad (8)$$

where EA is the second electron affinity and χ is the Mulliken electronegativity (eV).

Of course, analogous relationships can be obtained employing the third and fourth electron affinities.

To S, S^-, S^{-2}, and S^{-3}, if the calculated SE-PM6 electron affinities are plotted as a function of the nuclear

effective charges (Z_{eff}, using Slater rules: 5.45, 5.10, 4.75 and 0.8, respectively), the curve shown in Figure 5 (r = 0.9727) is obtained, providing the equation:

$$EA = -10.43Z_{eff} + 59.11 \quad (9)$$

Of course, analogous curves and equations can be obtained to P, As and Sb.

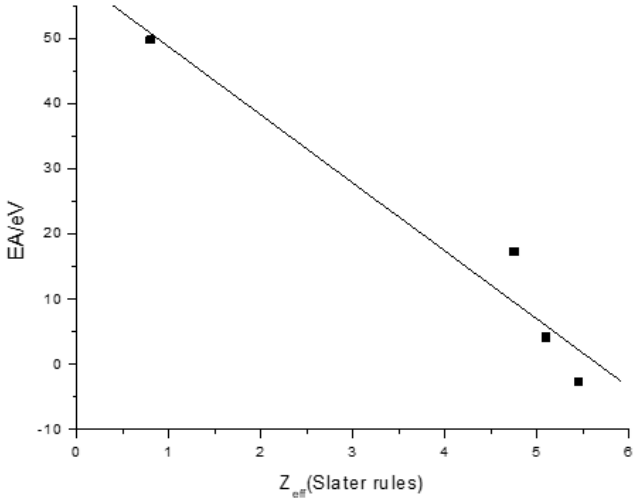

Figure 5. Calculated (SE-PM6) electron affinities for S, S^-, S^{-2}, and S^{-3} as a function of nuclear effective charges (Slater rules).

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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