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Atomic solid state energy scale: Universality and periodic trends in oxidation state

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ABSTRACT

The atomic solid state energy (SSE) scale originates from a plot of the electron affinity (EA) and ionization potential (IP) versus band gap (E_G). SSE is estimated for a given atom by assessing an average EA (for a cation) or an average IP (for an anion) for binary inorganic compounds having that specific atom as a constituent. Physically, SSE is an experimentally-derived average frontier orbital energy referenced to the vacuum level. In its original formulation, 69 binary closed-shell inorganic semiconductors and insulators were employed as a database, providing SSE estimates for 40 elements. In this contribution, EA and IP versus E_G are plotted for an additional 92 compounds, thus yielding SSE estimates for a total of 64 elements from the *s*-, *p*-, *d*-, and *f*-blocks of the periodic table. Additionally, SSE is refined to account for its dependence on oxidation state. Although most cations within the SSE database are found to occur in a single oxidation state, data are available for nine *d*-block transition metals and one *p*-block main group metal in more than one oxidation state. SSE is deeper in energy for a higher cation oxidation state. Two *p*-block main group non-metals within the SSE database are found to exist in both positive and negative oxidation states so that they can function as a cation or anion. SSEs for most cations are positioned above −4.5 eV with respect to the vacuum level, and SSEs for all anions are positioned below. Hence, the energy −4.5 eV, equal to the hydrogen donor/acceptor ionization energy $\varepsilon(+/-)$ or equivalently the standard hydrogen electrode energy, is considered to be an absolute energy reference for chemical bonding in the solid state.

1. Introduction

In this contribution, we report atomic solid-state energy (SSE) values for 94 elements in the periodic table and describe periodic trends in SSEs on the basis of oxidation state. Although the absolute energy of highest occupied and lowest unoccupied states is the first-order consideration in chemistry related to bonding, catalysis, electrochemistry, and electronic and optical devices, only recently has an absolute atomic SSE scale been established [1]. In many ways, the SSE approach is a frontier-orbital-based formulation of electronegativity [2–4]. SSE values are derived from an empirical database of binary inorganic compounds and their ionization potentials (IP), band gaps (E_G), and derived electron affinities (EA) that have been measured with respect to the vacuum level. For a given binary compound, EA is associated with the energy of the cation, and IP defines the energy of the anion. Thus, the average frontier-orbital energy or equivalently the SSE of a given cation is estimated by averaging EAs of all of the binary compounds containing that cation. Likewise, the SSE of a given anion is estimated by averaging IPs. Relative to electronegativity, SSE provides a universal advantage in describing the physical origin of the "power of an atom to attract electrons to itself in a chemical bond." Since SSE represents the average absolute frontier-orbital energy of an atom and electrons occupy the lowest possible energy levels, the "power of attraction" is simply related to the relative energy positioning of the SSEs. Atoms with SSE values deep in energy will strongly attract electrons and function as anions. Atoms with SSE values shallow in energy will tend to release electrons and function as cations. Atoms with similar SSEs will share electrons and thus form polar covalent bonds with the electrons polarized toward the atom with the deeper SSE.

In our original formulation of SSE [1], EA and IP were plotted versus band gap (E_G) for 69 closed-shell binary inorganic

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semiconductors and insulators, yielding SSE estimates for 40 elements. Here, the database of IP, E_G, and EA values is expanded by an additional 92 binary inorganic compounds. This expansion leads to SSE estimates for each block – *s*, *p*, *d*, and *f* – of the periodic table. A periodic table is presented with SSE estimates for 94 elements. 64 of these values have been directly derived from the empirical database, while 30 are estimated via a regression assessment of the correlation between SSE and Pauling electronegativity. SSE is also specified as a function of oxidation state. Cations and anions have SSEs that are consistently above and below −4.5 eV, respectively, as measured with respect to the vacuum level. Atoms exhibiting both positive and negative oxidation states, e.g., As^{3+} and As^{3-}, usually have SSEs positioned quite close to −4.5 eV with the cation SSE positioned above −4.5 eV and the anion SSE below. These observations suggest that the hydrogen donor/acceptor ionization energy $\varepsilon(+/-)$ at −4.5 eV, i.e., the standard hydrogen electrode energy, constitutes an absolute energy reference.

2. Methods

Literature values for IP and E_G for 161 binary inorganic compounds are used to calculate SSE estimates for 64 elements. IP values from photoemission experiments set the valence-band maximum energy, and optical measurements of E_G are then used to derive EA, setting the conduction-band minimum energy. For a given cation, the available EA values are averaged to calculate SSE. For a given anion, IP values of a compound with that element are averaged to calculate SSE, although *d*-band transition metal compounds, compounds with s^2 cations (i.e., Tl^+, Sn^{2+}, Pb^{2+}, As^{3+}, Sb^{3+}, and Bi^{3+}), and mixed cation oxidation state compounds, i.e., GaSe, InSe, and InTe, are excluded from consideration since IP for such a compound is likely to be at least partially cation-derived. IP, E_G, and EA values for all 161 compounds are collected in Table S1. SSEs, specified as a function of oxidation state for 64 elements, are collected in Table 1. A detailed discussion of SSE-scale fundamentals and relationships to electronegativity, chemical hardness, and ionicity is provided in our previous report [1].

3. Results and discussion

3.1. Solid state energy periodic table

A periodic table specifying an atomic SSE for 94 elements is given in Fig. 1. SSEs for elements color-coded blue (cations) or red (anions) are estimated from experimental data. SSEs color-coded gray are estimated from Pauling electronegativity-SSE trends, as discussed in the section Solid State Energy Database Enhancement (see below).

SSE periodic trends are similar in many respects to those of electronegativity. Electronegativity tends to increase from left to right across a period, and to decrease down a column in the periodic table. Similarly, SSE tends to increase *in magnitude* when going from left to right across a period, and to decrease *in magnitude* when going down a column in the periodic table. Thus, a key difference between electronegativity and SSE is polarity; electronegativity is a positive quantity while SSE is a negative quantity, since it is a measure of energy with respect to a vacuum level reference. Electronegativity and SSE are also distinguished by their respective units, $(eV)^{1/2}$ and eV. In the context of electronegativity, elements to the left (right) of the periodic table tend to be electropositive (electronegative). Likewise, elements to the left (right) of the periodic table tend to have shallow (deep) SSEs; electronic charge transfer occurs from atoms with shallow SSE to

Table 1
Solid State Energy (SSE) values as a function of oxidation number for 64 elements.

Element	Oxidation number	SSE (eV)
F	−1	−9.89
Cl	−1	−8.61
Br	−1	−7.12
I	−1	−6.20
O	−2	−7.98
S	−2	−6.31
Se	−2	−5.86
Te	−2	−6.14
N	−3	−7.00
P	−3	−6.20
As	−3	−5.47
Sb	−3	−4.94
C	−4	−6.48
Li	+1	1.67
Na	+1	0.87
K	+1	0.33
Rb	+1	0.75
Cs	+1	0.60
Be	+2	0.80
Mg	+2	−1.72
Ca	+2	−1.44
Sr	+2	−0.93
Ba	+2	−0.52
B	+3	−2.18
Al	+3	−3.14
Ga	+3	−3.82
In	+3	−4.53
Tl	+1	−3.27
Si	+4	−2.37
Ge	+4	−2.4
Sn	+2	−3.86
Sn	+4	−4.26
Pb	+2	−3.84
As	+3	−3.61
Sb	+3	−4.16
Bi	+3	−4.33
Sc	+3	−0.85
Y	+3	−1.86
Ti	+4	−4.60
La	+3	−2.5
Zr	+4	−3.45
Hf	+4	−3.36
V	+5	−4.26 (−6.46) [7]
V	+4	−2.03
V	+2	−1.23
Nb	+5	−3.49
Ta	+5	−3.69 (−5.00) [7]
Ta	+4	−3.80
Cr	+6	−4.82 (−6.75) [7]
Cr	+3	−3.3
Cr	+2	−1.22
Mo	+6	−4.61 (−6.40) [7]
Mo	+4	−3.94
W	+6	−4.41 (−6.40) [7]
W	+4	−4.00
Mn	+4	−3.02
Mn	+2	0.56
Fe	+3	−4.71
Fe	+2	−2.05
Co	+3	−3.50
Co	+2	−2.80
Rh	+3	−3.6
Ni	+3	−3.50
Pd	+2	−1.67
Pt	+2	−2.17
Cu	+1	−3.46
Cu	+2	−4.30
Ag	+1	−4.10
Zn	+2	−3.73
Cd	+2	−4.31
Hg	+2	−4.55
Ce	+3	−4
Pr	+3	−2.5
Gd	+3	−2.5
Dy	+3	−3.3