



Empirical Lewis acid strengths for 135 cations bonded to oxygen

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New and updated Lewis acid strengths are listed for 135 cations bonded to oxygen for use with published Lewis base strengths. A strong correlation between Lewis acid strength and ionization energy is shown, and correlation with electronegativity is confirmed.

1. Introduction

The bond-valence model (Brown, 2002, 2016) is a powerful method for the interpretation of atomic arrangements in inorganic solids. The valence-sum rule is a basic axiom of this theory: the sum of the bond valences at each atom is equal to the magnitude of the atomic valence. Bond valences may be calculated from the observed bond distances in a structure using sets of curves that relate bond valence to bond length (*e.g.* Brown & Shannon, 1973; Brown & Altermatt, 1985; Gagné & Hawthorne, 2015).

A key feature of the bond-valence model is the valence-matching principle (Brown, 1981, 2002, 2016), which states that the most stable structures will form when the Lewis acid strength of the cation closely matches the Lewis base strength of the anion. Brown (1988) defined the Lewis acid strength of cations as

$$S_a = \frac{V}{PCN} \quad (1)$$

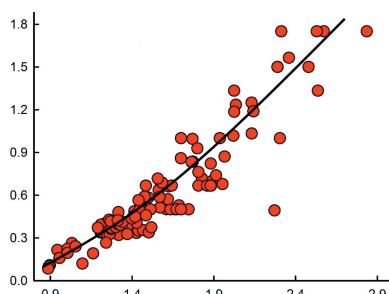
where V is the oxidation state of the cation, and PCN is the predicted coordination number calculated using the ionic radius ratio. The definition was later updated by Brown & Skowron (1990) to

$$S_a = V/N_i \quad (2)$$

where N_i is the average observed coordination number (AOCN) compiled over a large number of crystal structures. The Lewis base strength is defined similarly, and both are expressed in valence units (v.u.).

Values calculated from equation (2) may be interpreted as the mean observed bond valence of the cation (anion) when bonded to a specific anion (cation). It follows from the valence-matching principle that used together, Lewis acid and Lewis base strengths have predictive power with regard to structure stability. This contrasts with the common usage of the bond-valence model, where structural analysis is carried out *a posteriori* (*i.e.* the detailed crystal structure is known prior to making any calculation).

The Lewis base strengths of simple anions show wide variation. For example, bonds to O^{2-} vary from ~ 0.08 v.u. for



Cs—O bonds to 2.00 v.u. for a Cr^{6+} —O bond in the structure of CrO_3 (Stephens & Cruickshank, 1970). This range is not very useful for predicting Lewis basicities for simple anions. However, for many oxide crystal structures, particularly minerals, the formal valence of one or more of the constituent cations exceeds the formal valence of the anion(s). This results in strongly bonded oxyanions, *e.g.* $(\text{SO}_4)^{2-}$, $(\text{CO}_3)^{2-}$, $(\text{SiO}_4)^{4-}$, that strongly affect their structural characteristics and behaviour in natural processes. One may also use equation (2) to derive the Lewis basicity of an oxyanion from the average observed coordination number of that oxyanion. The range of observed Lewis base strengths for an oxyanion is much more restricted than that of its constituent simple anions, and hence one can define a useful Lewis basicity for these complex ions. Thus Lewis acid and Lewis base strengths may be assigned to these groups (*e.g.* Brown, 1981, 1988, 2002) and the stability of compounds they may or may not form may be evaluated *via* the valence-matching principle by comparing the bonding characteristics of the ‘acid’ and ‘base’ constituents. Brown (2002) states that compounds generally occur within $0.5 < S_a / S_b < 2$, where S_a and S_b are the Lewis acid and Lewis base strengths, respectively, of the two constituents and that the closer the ratio is to 1, the more stable the resulting compound.

Consider the compounds Na_2SO_4 , Na_4SiO_4 and Mg_2SiO_4 (Hawthorne, 1994), taking the Lewis acidities and basicities from Brown (1988). The Lewis acidity of Na^+ is 0.17 v.u. (valence units) and the Lewis basicity of $(\text{SO}_4)^{2-}$ is 0.17 v.u.; here, the valence-matching principle is precisely satisfied and Na_2SO_4 forms a stable compound with several polymorphs (*e.g.* Eysel *et al.*, 1985; Rasmussen *et al.*, 1996) and the mineral thenardite (Hawthorne & Ferguson, 1975). The Lewis basicity of $(\text{SiO}_4)^{4-}$ is 0.33 v.u.; for Na_4SiO_4 , the valence-matching principle is not satisfied, Na_4SiO_4 is not a stable mineral and the synthetic compound shows only restricted stability, *i.e.* it is hygroscopic at atmospheric conditions (Barker & Gadd, 1981); for Mg_2SiO_4 , the Lewis basicity of $(\text{SiO}_4)^{4-}$ is 0.33 v.u. and the Lewis acidity of Mg^{2+} is 0.33 v.u., the valence-matching principle is satisfied and Mg_2SiO_4 forms a stable compound with several polymorphs (*e.g.* Eysel *et al.*, 1985; Rasmussen *et al.*, 1996) and the minerals forsterite and wadsleyite.

In natural systems, oxyanions have access to a wide variety of cationic, neutral and anionic species with which to form crystals, and the valence-matching principle implies that a specific oxyanion will select from the wide variety of available constituents the interstitial species that most closely satisfy the valence-matching principle. This simple but very powerful argument has been used to explain the distribution of mineral stoichiometries in nature (Hawthorne, 2012, 2015) and to predict the weakly bonded constituents (the interstitial complex) that link strongly bonded oxyanions to form the crystal structures of minerals (Hawthorne & Schindler, 2008).

Here, we provide an extensive list of Lewis acid strengths for cations bonded to O^{2-} following a large bond length dispersion analysis.

2. Method

We use the results of a large bond-length dispersion analysis described in Gagné & Hawthorne (2016, 2017*a,b,c*) for our analysis. We extracted bond lengths from the Inorganic Crystal Structure Database (ICSD, 2017) for all atoms of the periodic table of elements bonded to O^{2-} , as a function of oxidation state and coordination number. The following selection criteria were used for crystal structures before collection of the bond-length data: (1) publication date ≥ 1975 ; (2) $R_1 \leq 6\%$; (3) the site of interest must be fully occupied by the cation of interest; (4) all bonds involve ions at fully occupied sites; (5) the cation and anion sites of interest show no positional disorder; (6) crystallographic data were measured at ambient conditions; (7) no data from powder, electron or synchrotron diffraction were included; (8) where there was severe ambiguity as to the correct coordination number, the data were not included to avoid error; (9) for H, only neutron diffraction data were collected.

Bond lengths were then collected using the following criteria/considerations: (1) In general, we assumed that all cation–anion bonds are shorter than the shortest cation–cation distance for the coordination number of interest. (2) The ordered list of distances was examined for a hiatus in the increasing distances. (3) We examined the effect of different cation–coordination numbers on the anion coordination. (4) We compared the bond lengths with and without potential bonds to the data already gathered for that cation to see if the behavior resembled that of one coordination number more than other. (5) After $\sim 10\%$ of the structures had been processed for a specific ion pair, we examined the different coordination numbers of the same cation for potential trends and inconsistencies. (6) We examined the chemical formula for the presence of unrefined hydrogen atoms. This was mainly relevant in locating weak bonds between the cation of interest and the O atom of an (H_2O) group. Where hydrogen atoms were not located in the refinement, and such bonds seemed plausible, the data were discarded. (7) We plotted the structure to get a visual sense of any ambiguity. (8) Very sparingly, we used bond-valence curves to determine whether the inclusion or omission of bonds gave better bond-valence sums.

Bond-length distributions were then plotted on the basis of oxidation state and coordination number and thoroughly examined for outliers. Where outliers were identified, the original publications were consulted to validate the distances or identify errors. The above criteria resulted in the collection of 180 369 bond lengths from 31 521 coordination polyhedra, for 135 ions bonded to oxygen from 9367 crystal structure refinements.

These criteria resulted in the inclusion of bonds of the coordination shell that were typically considered ‘insignificant’ in the past, resulting in their exclusion in typical crystal-chemical analysis. Vetting of these longer bonds is particularly important here due to their effect on coordination number which directly influences Lewis acid/base strengths *via* equation (2). We have shown for cations bonded to O^{2-} that better agreement to the valence-sum rule (Brown, 2002) is obtained

Table 1

Empirical Lewis acid strength for 135 cations bonded to O²⁻.

Ion	No. of coordination polyhedra	AOCN†	Standard deviation	Lewis acid strength (S _a)	Standard deviation	Brown (1988, 2002)	% difference‡
H ⁺	224	2.03 (2)	0.22	0.87 (1)§, 0.13 (1)	0.053	0.82, 0.18	–
Li ⁺	690	4.64 (3)	0.88	0.215 (2)	0.041	0.205	4.8
Be ²⁺	169	3.95 (2)	0.21	0.506 (2)	0.027	0.501	1.0
B ³⁺	1572	3.44 (1)	0.50	0.871 (3)	0.126	0.87	0.1
C ⁴⁺	433	3	–	1.333	–	1.35	–1.3
N ⁵⁺	497	3.006 (3)	0.077	1.663 (2)	0.043	1.67	–0.4
Na ⁺	1683	6.31 (3)	1.35	0.159 (1)	0.034	0.156	1.6
Mg ²⁺	469	5.93 (2)	0.46	0.337 (1)	0.026	0.334	1.0
Al ³⁺	856	5.15 (3)	0.97	0.583 (4)	0.109	0.57	2.2
Si ⁴⁺	2530	4.019 (4)	0.194	0.995 (1)	0.048	1	–0.5
P ³⁺	7	3	–	1	–	–	–
P ⁵⁺	3691	4	–	1.25	–	1.247	0.2
S ⁴⁺	30	3	–	1.333	–	–	–
S ⁶⁺	906	4	–	1.5	–	1.5	0.0
Cl ³⁺	5	2.4 (4)	0.8	1.3 (2)	0.4	–	–
Cl ⁵⁺	9	3	–	1.666	–	–	–
Cl ⁷⁺	65	4	–	1.75	–	1.75	0.0
K ⁺	1479	9.23 (6)	2.30	0.108 (1)	0.027	0.126	–16.3
Ca ²⁺	1168	7.58 (3)	1.09	0.264 (1)	0.038	0.274	–3.9
Sc ³⁺	88	6.24 (6)	0.60	0.481 (5)	0.046	0.49	–1.9
Ti ³⁺	24	6.2 (1)	0.5	0.486 (8)	0.037	–	–
Ti ⁴⁺	324	5.91 (2)	0.33	0.676 (2)	0.038	0.67	0.9
V ³⁺	70	5.99 (1)	0.12	0.501 (1)	0.010	0.5	0.2
V ⁴⁺	226	5.58 (3)	0.49	0.717 (4)	0.063	0.71	1.0
V ⁵⁺	714	4.91 (4)	0.95	1.018 (7)	0.197	1.08	–6.1
Cr ²⁺	17	5.2 (2)	0.9	0.39 (2)	0.07	–	–
Cr ³⁺	104	6	–	0.5	–	0.5	0.0
Cr ⁴⁺	7	5.7 (3)	0.7	0.71 (3)	0.09	–	–
Cr ⁵⁺	1	4	–	1.25	–	–	–
Cr ⁶⁺	169	4	–	1.5	–	1.5	0.0
Mn ²⁺	392	5.98 (3)	0.59	0.334 (2)	0.033	0.344	–2.9
Mn ³⁺	94	5.85 (4)	0.41	0.513 (4)	0.036	0.52	–1.4
Mn ⁴⁺	21	5.90 (9)	0.43	0.68 (1)	0.05	0.67	1.1
Mn ⁵⁺	8	4	–	1.25	–	–	–
Mn ⁶⁺	2	4	–	1.5	–	1	33.3
Mn ⁷⁺	7	4	–	1.75	–	–	–
Fe ²⁺	192	5.68 (6)	0.88	0.352 (4)	0.054	0.34	3.4
Fe ³⁺	466	5.68 (3)	0.72	0.528 (3)	0.067	0.527	0.1
Co ²⁺	304	5.64 (5)	0.84	0.355 (3)	0.053	0.351	1.1
Co ³⁺	15	6	–	0.5	–	0.51	–2.0
Co ⁴⁺	1	6	–	0.666	–	–	–
Ni ²⁺	255	5.91 (3)	0.44	0.338 (2)	0.025	0.339	–0.2
Ni ⁴⁺	5	6	–	0.666	–	–	–
Cu ⁺	57	2.5 (1)	0.8	0.40 (2)	0.14	0.45	–12.1
Cu ²⁺	716	5.35 (3)	0.79	0.374 (2)	0.055	0.392	–4.8
Cu ³⁺	11	4	–	0.75	–	–	–
Zn ²⁺	461	4.93 (5)	0.96	0.405 (4)	0.079	0.402	0.9
Ga ³⁺	228	4.72 (6)	0.92	0.636 (8)	0.124	0.65	–2.3
Ge ⁴⁺	350	4.31 (4)	0.70	0.928 (8)	0.150	0.89	4.1
As ³⁺	28	4.5 (3)	1.3	0.66 (4)	0.19	0.98	–48.2
As ⁵⁺	526	4.05 (1)	0.31	1.235 (4)	0.095	1.13	8.5
Se ⁴⁺	202	5.85 (8)	1.17	0.68 (1)	0.14	1.2	–75.5
Se ⁶⁺	191	4	–	1.5	–	1.5	0.0
Br ⁵⁺	9	6.3 (2)	0.7	0.79 (3)	0.08	–	–
Br ⁷⁺	2	4	–	1.75	–	–	–
Rb ⁺	464	10.1 (1)	2.4	0.099 (1)	0.024	0.124	–24.9
Sr ²⁺	376	8.99 (8)	1.58	0.222 (6)	0.039	0.233	–4.8
Y ³⁺	178	7.63 (7)	0.91	0.393 (4)	0.047	0.43	–9.4
Zr ⁴⁺	117	6.8 (1)	1.2	0.589 (9)	0.103	0.6	–1.8
Nb ⁴⁺	3	6	–	0.666	–	–	–
Nb ⁵⁺	251	5.99 (2)	0.27	0.835 (2)	0.038	0.823	1.4
Mo ³⁺	5	6	–	0.5	–	–	–
Mo ⁴⁺	9	6	–	0.666	–	–	–
Mo ⁵⁺	76	5.99 (1)	0.11	0.835 (2)	0.016	–	–
Mo ⁶⁺	970	5.06 (3)	0.99	1.185 (7)	0.232	1.23	–3.8
Tc ⁷⁺	6	4	–	1.75	–	–	–
Ru ³⁺	3	6	–	0.5	–	–	–
Ru ⁴⁺	8	6	–	0.666	–	–	–
Ru ⁵⁺	23	6	–	0.833	–	0.83	0.4
Rh ³⁺	11	6	–	0.5	–	0.5	0.0

Table 1 (continued)

Ion	No. of coordination polyhedra	AOCN†	Standard deviation	Lewis acid strength (S_a)	Standard deviation	Brown (1988, 2002)	% difference‡
Rh ⁴⁺	3	6	—	0.666	—		
Pd ²⁺	29	4	—	0.5	—	0.46	8.0
Pd ⁴⁺	2	6	—	0.666	—		
Ag ⁺	196	5.2 (1)	1.4	0.191 (4)	0.052	0.2	−4.5
Cd ²⁺	164	6.25 (6)	0.70	0.320 (3)	0.036	0.326	−1.9
In ³⁺	125	6.06 (3)	0.30	0.495 (2)	0.025	0.5	−1.1
Sn ²⁺	50	4.7 (3)	1.8	0.43 (2)	0.16	0.45	−5.3
Sn ⁴⁺	38	5.8 (1)	0.6	0.69 (1)	0.08	0.68	1.1
Sb ³⁺	54	5.3 (2)	1.5	0.56 (2)	0.16	0.62	−9.8
Sb ⁵⁺	183	6	—	0.833	—	0.83	0.4
Te ⁴⁺	212	7.0 (1)	1.6	0.571 (9)	0.130	0.98	−71.6
Te ⁶⁺	155	6	—	1	—	1	0.0
I ⁵⁺	134	6.56 (7)	0.75	0.762 (8)	0.087	1.3	−70.6
I ⁷⁺	36	5.89 (8)	0.46	1.19 (2)	0.09	1.2	−1.0
Cs ⁺	544	11.9 (1)	2.9	0.084 (1)	0.020	0.109	−29.5
Ba ²⁺	856	10.28 (6)	1.64	0.194 (1)	0.031	0.195	−0.3
La ³⁺	182	8.7 (1)	1.3	0.343 (4)	0.053	0.35	−2.1
Ce ³⁺	76	9.4 (2)	1.4	0.320 (5)	0.047		
Ce ⁴⁺	28	8.8 (3)	1.6	0.45 (2)	0.08		
Pr ³⁺	99	9.2 (1)	1.4	0.326 (5)	0.051		
Nd ³⁺	203	8.3 (1)	1.4	0.363 (4)	0.059		
Sm ³⁺	97	7.9 (1)	1.1	0.380 (6)	0.055		
Eu ²⁺	3	8.3 (3)	0.5	0.240 (8)	0.014		
Eu ³⁺	49	8.1 (1)	0.8	0.371 (5)	0.035		
Gd ³⁺	107	8.1 (1)	1.1	0.371 (5)	0.051		
Tb ³⁺	48	8.0 (1)	1.0	0.375 (7)	0.048		
Tb ⁴⁺	7	6	—	0.666	—		
Dy ³⁺	70	7.6 (1)	1.0	0.396 (6)	0.053		
Ho ³⁺	81	7.4 (1)	0.9	0.403 (6)	0.050		
Er ³⁺	102	7.66 (8)	0.83	0.392 (4)	0.043		
Tm ³⁺	44	7.3 (2)	1.0	0.413 (9)	0.06		
Yb ³⁺	82	7.2 (1)	1.0	0.416 (7)	0.0596		
Lu ³⁺	53	7.1 (1)	1.1	0.423 (9)	0.064		
Hf ⁴⁺	22	6.8 (2)	0.9	0.59 (2)	0.08		
Ta ⁵⁺	162	6.09 (2)	0.28	0.822 (3)	0.038	0.822	−0.1
W ⁵⁺	4	6	—	0.833	—		
W ⁶⁺	436	5.81 (3)	0.56	1.033 (5)	0.100	1.07	−3.6
Re ⁵⁺	3	6	—	0.833	—	0.83	0.4
Re ⁷⁺	59	4.5 (1)	0.8	1.56 (4)	0.27	1.51	3.5
Os ⁵⁺	4	6	—	0.833	—		
Os ⁶⁺	1	6	—	1	—		
Os ⁷⁺	7	5.9 (1)	0.3	1.20 (3)	0.07		
Os ⁸⁺	8	5.4 (2)	0.7	1.49 (7)	0.19		
Ir ³⁺	1	6	—	0.5	—		
Ir ⁴⁺	17	5.4 (2)	0.9	0.74 (3)	0.12		
Ir ⁵⁺	6	6	—	0.833	—		
Pt ²⁺	3	4	—	0.5	—		
Pt ⁴⁺	33	6	—	0.666	—	0.67	−0.5
Au ³⁺	24	4	—	0.75	—		
Hg ²⁺	52	6.1 (2)	1.3	0.327 (9)	0.068	0.36	−10.1
Tl ⁺	74	8.4 (3)	2.4	0.119 (4)	0.035	0.14	−17.3
Tl ³⁺	9	6.6 (3)	0.8	0.46 (2)	0.06	0.49	−7.1
Pb ²⁺	276	7.5 (1)	2.1	0.266 (4)	0.072	0.29	−9.2
Pb ⁴⁺	12	5.6 (2)	0.8	0.72 (3)	0.10	0.7	2.3
Bi ³⁺	231	6.9 (1)	1.7	0.436 (7)	0.109	0.48	−10.1
Bi ⁵⁺	11	5.8 (2)	0.6	0.86 (3)	0.08		
Th ⁴⁺	27	8.9 (2)	1.2	0.45 (1)	0.06		
U ⁴⁺	18	9.8 (5)	1.9	0.41 (2)	0.08		
U ⁵⁺	4	6.8 (2)	0.4	0.74 (2)	0.05		
U ⁶⁺	585	6.91 (2)	0.48	0.868 (2)	0.060		
Np ⁵⁺	33	7.0 (8)	0.5	0.711 (8)	0.046		
Np ⁶⁺	7	7.1 (1)	0.3	0.84 (2)	0.04		
Np ⁷⁺	2	6	—	1.166	—		
Am ³⁺	1	9	—	0.333	—		
Cm ³⁺	1	9	—	0.333	—		
Absolute mean deviation							7.7
Weighted absolute mean deviation							5.1

† AOCN is the average observed coordination number. ‡ Calculated as $[S_a - S_{a(\text{Brown})}]/S_a \times 100\%$. § Due to the unusual behaviour of H⁺, the values of Lewis acid strength given here are those of the mean bond valence observed for the O—H and O···H bonds, respectively.

when including the longer bonds for configurations involving lone pair stereoactive cations (Gagné & Hawthorne, 2015) and alkali and alkaline-earth metals (Gagné & Hawthorne, 2015, 2016) leading to maximum observed coordination numbers greater than 12 for K^+ , Rb^+ , Cs^+ and Ba^{2+} . Hence, the longer interatomic distances are retained in our analysis.

3. Lewis acid strengths for ions bonded to O^{2-}

Table 1 gives the average observed coordination number (AOCN) and resulting Lewis acid strengths for 135 cations bonded to O^{2-} along with a comparison with the values of Brown (1988, 2002). The standard deviations associated with the AOCN are given as a measure of the spread of observed coordination numbers, *i.e.* the ability of the cation to adjust to a range of Lewis base strengths *via* the valence-matching principle. For example, Cs^+ with a standard deviation of 2.869, is more flexible in adjusting to different Lewis base-strength than Na^+ with a standard deviation of 1.346, which is in turn much more flexible than Be^{2+} with standard deviation of 0.212.

Of the 135 values given in Table 1, 61 values are new, and 74 values update those of Brown (1988, 2002) with an average absolute difference of 7.7%, and 5.1% when we weighted the percentage difference with the number of coordination polyhedra. Gagné & Hawthorne (2016) showed that for small sample sizes (~ 1 –100 data points), values derived for structural parameters can be significantly in error (*i.e.* different from the values derived for the same parameters from large sample sizes). The closer agreement when taking into account the number of coordination polyhedra is in accord with this result.

Aside from the larger sample size, these deviations are largely due to the inclusion of the longer bonds in the determination of the coordination polyhedra, as discuss above. The agreement is otherwise good for ions not prone to large and distorted coordination polyhedra.

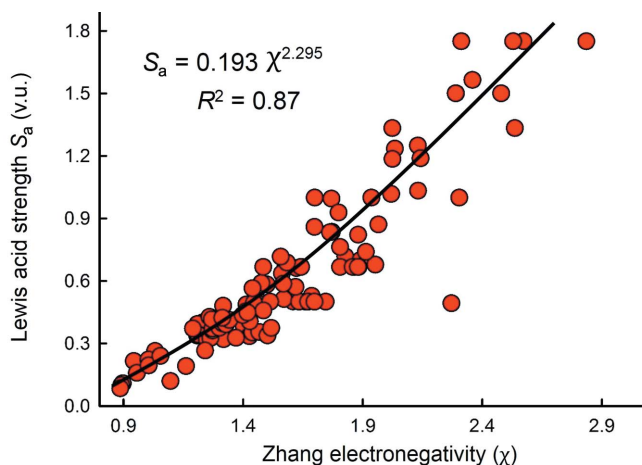


Figure 1
Correlation between Lewis acid strength and Zhang (1982) electronegativity ($n = 106$).

4. Correlation with electronegativity

Zhang (1982) derived a scale for electronegativity based on oxidation state, which he used to derive a scale for Lewis acid strengths to quantify Pearson's 'hard/soft/borderline' classification (Pearson, 1963, 1968). After setting the Lewis acid or Lewis base scale onto the scale of bond valences *via* equation (1), Brown (1988) also showed a strong correlation between Lewis acid strength and electronegativity for the scale of Zhang. Brown & Skowron (1990) later correlated Lewis acid strength values *via* equation (2) to the Allen electronegativity (Allen, 1989) for the main-group elements in their highest oxidation state. Bickmore *et al.* (2017) recently correlated Lewis acid strength to bond character (calculated using the Pauling electronegativity) (Pauling, 1960) for a handful of cations taken from Brown (2002), also in their highest oxidation states.

Fig. 1 gives the values of Lewis acid strength derived in this work as a function of Zhang's oxidation-state-based electronegativity for which electronegativity values were available ($n = 106$ ions). We found Zhang's electronegativity scale to give significantly better results than the scales of Pauling and Allen with $R^2 = 0.87$ ($R^2 = 0.47$ for Pauling electronegativity on the same sample of ions, and $R^2 = 0.41$ for Allen electronegativity on a slightly different sample). Correlating our values to bond character gives $R^2 = 0.42$ for the set of 106 cations.

5. Correlation with ionization energy

We observe a correlation between Lewis acid strength and the n th ionization energy for cations bonded to O^{2-} , where n is the oxidation state of the ion. This is shown in Fig. 2. Agreement for this correlation ($R^2 = 0.90$) is very similar to that involving Zhang's oxidation-state-based electronegativity, but more importantly, this relation is able to cover the 135 cations for which we derived Lewis acid strength values due to the wider availability of ionization energy values. The same

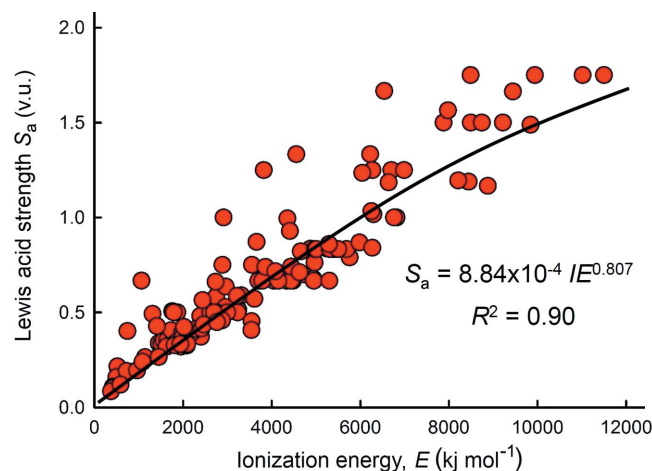


Figure 2
Correlation between Lewis acid strength and ionization energy ($n = 135$).

correlation to the *sum* of the ionization energies (1 to *n*) yields $R^2 = 0.87$.

5.1. Correlation between ionization energy and electronegativity

We observe a correlation between ionization energy and electronegativity. Running a student *t*-test for the Zhang electronegativity and ionization energy values ($n = 106$) yields a *p*-value of 1.6×10^{-40} with $R^2 = 0.82$. This is to a certain extent expected from the work of Mulliken (1934, 1935) who proposed a conceptually simple scale of electronegativity based on the arithmetic mean of ionization energy and electron affinity. Mulliken's scale was shown to correlate highly to the scale of Pauling (Bratsch, 1988).

Ionization energy and electronegativity yield individual *p*-values of 4.4×10^{-55} and 6.2×10^{-43} when correlated to Lewis acid strength. By including ionization energy in the first step of a stepwise regression analysis, the *p*-value for electronegativity changes to 1.2×10^{-5} and $R^2 = 0.91$ ($n = 106$). By then adding electronegativity, R^2 changes to 0.92, showing that although both variables correlate to Lewis acid strength to 99% confidence intervals, the sole consideration of ionization energy is adequate.

5.2. Correlation to ionization energy versus electronegativity

Electronegativity is a measure of the ability of an atom/ion to draw bonding electrons to itself, which accords well with Lewis acidity, *i.e.* the ability to accept electron pairs. On the other hand, ionization energy is a measure of the energy required to remove an outer electron from the atom or cation, and the *n*th ionization energy is the energy required to remove an electron from the cation from oxidation state $n - 1$ to n . Thus, the impetus for the cation to return to its $n - 1$ state, *i.e.* by gaining an electron, is measured by the *n*th ionization energy. The higher the ionization energy, the greater is the affinity of the cation for surrounding electrons. Therefore, the two concepts are not exclusive. However, use of ionization energy may be preferable to the use of electronegativity in certain situations as (1) there are more values available, and (2) ionization energy shows stronger correlation than electronegativity to certain parameters (*e.g.* bond-valence parameter R_o , Gagné & Hawthorne, 2015; Lewis acid strength, this work). The usual correlation of physical parameters to electronegativity should also be made with ionization energy.

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