Chemistry, McMaster University, for providing the sample of Ag_2S enriched in ^{34}S, Dr. J. Vekris and M. Collins for providing some of the samples, and B. Christian for obtaining preliminary diffuse-reflectance measurements.

Appendix

Although they are not conventionally used, it is possible to describe the vibrational motion (in this case the in-plane motion) of a square-planar D_{4h} system in terms of central force coordinates. Teranishi and Decius[52] treated a planar XY_3 system in this manner, while Cyvin[4,53] has dealt with the nonlinear XY_2, tetrahedral XY_4, and octahedral XY_6 systems. Generally, treatment of the vibrational problem by central force coordinates leads to simpler **G** matrices and simpler expressions for the normal frequencies and may be of use in the study of mean-square amplitudes of vibration because of the mean amplitudes of nonbonded pairs.[4,52]

The internal coordinates used in this case are simply the changes in the directly bonded (Δd_i) and nonbonded (diagonal) distances (ΔD_i). The resulting symmetry coordinates constructed from these internal coordinates are given in Table XIII. For a D_{4h} system, the generalized (central) force field is expressed as

$$2V = f_d\sum^{4}\Delta d_{ij}^2 + f_D\sum^{2}\Delta D_{ij}^2 + 2f_{dd}\sum^{4}\Delta d_{ij}\Delta d_{jk} + 2f_{dd}'\sum^{2}\Delta d_{ij}\Delta d_{kl} + 2f_{DD}\sum^{1}\Delta D_{ij}\Delta D_{kl} + 2f_{dD}\sum^{8}\Delta d_{ij}\Delta D_{jk}$$

where the force constants are defined in ref 54. A simple solution to the vibrational problem may be achieved by restricting f_{DD} and f_{dD} to zero. The resulting values of the force constants and the potential energy distributions are given in Tables XIV and XV, respectively (supplementary material). Of course, the central force constants may be easily obtained from the valence force constants with incorporation of the approximations in the respective potential fields given above with use of the following expressions, which relate the different types of force constants:

$$f_r + 2f_{rr} + f_{rr}' = f_d + f_D + 2f_{dd} + f_{dd}' + f_{DD} + 4(2^{1/2})f_{dD}$$

$$f_r - 2f_{rr} + f_{rr}' = f_d - 2f_{dd} + f_{dd}'$$

$$4f_\alpha - 8f_{\alpha\alpha} + 4f_{\alpha\alpha}' = f_D - f_{DD}$$

$$f_r - f_{rr} - 4f_{r\alpha} + 4f_{r\alpha}' + 2f_\alpha - 2f_{\alpha\alpha}' = f_d - f_{dd}'$$

Registry No. Se_4^{2+}, 12310-32-6; $Se_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$, 82434-40-0; $Se_4(AsF_6)_2$, 53513-64-7; $Se_4(AlCl_4)_2$, 12522-25-7; $Se_4(HS_2O_7)_2$, 35025-26-4; $S_4(S_2O_6F)_2$, 82582-32-9; KS_2O_6F, 14325-72-5; HS_2O_6F, 23754-83-8; $S_4(SO_3F)_2$, 82582-30-7; Te_4^{2+}, 12597-50-1; $Te_4(AsF_6)_2$, 12536-35-5; $Te_4(SbF_6)_2$, 82292-92-0; $Te_4(AlCl_4)_2$, 12522-27-9; $Te_4(Al_2Cl_7)_2$, 36645-21-3; *trans*-$Te_2Se_2^{2+}$, 68652-59-5; *trans*-$Te_2Se_2^{2+}(Sb_3F_{17}^-)(SbF_6^-)$, 68791-83-3.

Supplementary Material Available: Listings of the central force constants (Table XIV) and potential energy distributions (Table XV) for the S_4^{2+}, Se_4^{2+}, and Te_4^{2+} polyatomic cations (2 pages). Ordering information is given on any current masthead page.

---

(52) Teranishi, R.; Decius, J. C. *J. Chem. Phys.* **1954**, *22*, 896.

(53) Cyvin, S. *Acta Polytechn. Scand., Phys. Incl. Nucleon. Ser.* **1960**, *6*, 1.

(54) In the central forces potential field the force constants are defined as follows: f_d, chalcogen–chalcogen stretch (directly bonded); f_{dd}, stretch–stretch interaction (adjacent); f_{dd}', stretch–stretch interaction (opposite); f_D, chalcogen–chalcogen stretch (diagonal); f_{DD}, stretch (diagonal)–stretch (diagonal) interaction; f_{dD}, stretch (directly bonded)–stretch (diagonal) interaction.

Contribution from the Shanghai Research Institute of Petrochemistry,
Shanghai 201207, People's Republic of China

Electronegativities of Elements in Valence States and Their Applications. 1. Electronegativities of Elements in Valence States

YONGHE ZHANG

Received January 8, 1982

The electronegativities of the elements in valence states are calculated on the basis of electrostatic force by using observed ionization potentials and covalent radii as main parameters. The ligand field stabilization, the first filling of p orbitals, the transition-metal contraction, and the lanthanide contraction are reflected in the relative values of the electronegativity scale. It is concluded that the electronegativities for the elements situated after the transition series produce the series second period ≫ third period ≈ fourth period > fifth period ≈ sixth period.

Introduction

Electronegativity is a important concept in understanding the chemical bond. It has unique and valuable applications to the interpretation of a vast area of common chemistry.

Pauling first defined electronegativity and suggested methods for its estimation in 1932.[1] Over the years, various other methods have been proposed for evaluating the electronegativity values of the elements. Only one method, proposed by Allred and Rochow,[2] has been widely accepted as an alternative to Pauling's thermochemical scale. Nevertheless, the concept of electronegativity is not precisely perfect and remains largely qualitative. As we shall see, the electronegativity values so determined can only be average ones for an atom's most common valence state and oxidation state cannot be appropriate when applied for quantitative applications. Besides, as the effective nuclear charges adopted in the Allred–Rochow method are from the simplified Slater rule,[3] in which the variations in atomic orbitals with increasing nuclear charges are ignored, this method cannot yet conform itself to some chemical facts; for instance, its electronegativities of the post-scandide elements (from Ga to Kr) are too high and those of the post-lanthanide elements from Tl to Rn) are too low. Although the concept is qualitatively valuable, the attempts to derive a comprehensive quantitative scale of electronegativity have been disappointing because of the lack of correlation between experimental quantities and the scale over a wide front.

---

(1) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(2) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 246 (1958).

(3) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

0020-1669/82/1321-3886$01.25/0

In the present work we have tried to devise a electronegativity scale for elements in valence states in terms of observed ionization potentials. Such a scale is referred to as empirical, meaning "based upon experiment". So a wide range of chemical phenomena such as the ligand field stabilization, the first filling of p orbitals, the transition-metal contraction, and the lanthanide contraction can be reflected. When we come to discuss strengths of Lewis acids in our next paper, it will be seen that such electronegativity values can have considerable predictive value.

Data and Calculations

Pauling originally defined electronegativity as "the power of an atom in a molecule to attract electrons to itself". Actually, when an element possesses different valence states, the electronegativity of the element is a function of their oxidation numbers. The higher the charge number of an element in a compound, the more strongly its atom attracts electrons. Hence, the electron-attracting power of an element is entirely different when it is in different valence states. Cr^{2+} is a rather positive metal, but Cr^{6+} is much like a nonmetal. Thereupon, we can more physically define the electronegativity of the element in valence states as "the electrostatic force exerted by the effective nuclear charges on the valence electrons". According to electrostatics, the force F between the valence electrons and the effective nuclear charges

$$F \propto \frac{Z^*}{r^2} \tag{1}$$

where Z^* is the effective nuclear charge and r is the covalent radius.

According to Slater, the ultimate ionization potential for outer electrons is

$$I_z = R\frac{Z^{*2}}{n^{*2}} \tag{2}$$

where R is the Rydberg constant, $R = 2\pi^2\mu e^4/h^2 = 13.6$ eV, and n^* is the effective principal quantum number. We now have

$$Z^* = n^*(I_z/R)^{1/2} \tag{3}$$

Substituting (3) into (1), we then obtain

$$F \propto \frac{n^*(I_z/R)^{1/2}}{r^2} \tag{4}$$

where $n^*(I_x/R)^{1/2}$ is the effective nuclear charge exerted on the outermost electrons at the covalent boundary, r, of the atom. We plotted Pauling values of X_p against $n^*(I_z/R)^{1/2}/r^2$ in Figure 1. The best straight line is obtained by the method of least-squares

$$X_z = 0.241\frac{n^*(I_z/R)^{1/2}}{r^2} + 0.775 \tag{5}$$

where r is mainly from Pauling[4] and Dean,[5] I_z is from Huheey[6] and the remainder is calculated from the improved Slater method by Zhen Nengwu:[7] $I = R(Z - \sigma)^2/n'^2 + b(Z - Z°)$ (where I is the ionization potential, $R = 2\pi^2\mu e^4/h^2 = 13.6$ eV, n' is the effective principal quantum number, σ is a screening constant, b is a relative increase factor, Z is the atomic number, and $Z°$ is the atomic number of the first element of each electron configuration specified in the periodic table). For the effective principal quantum number n^*, we adopted the following average values based on ref 7 (n^* values 0.85 and 4.99 were obtained by the extension method):

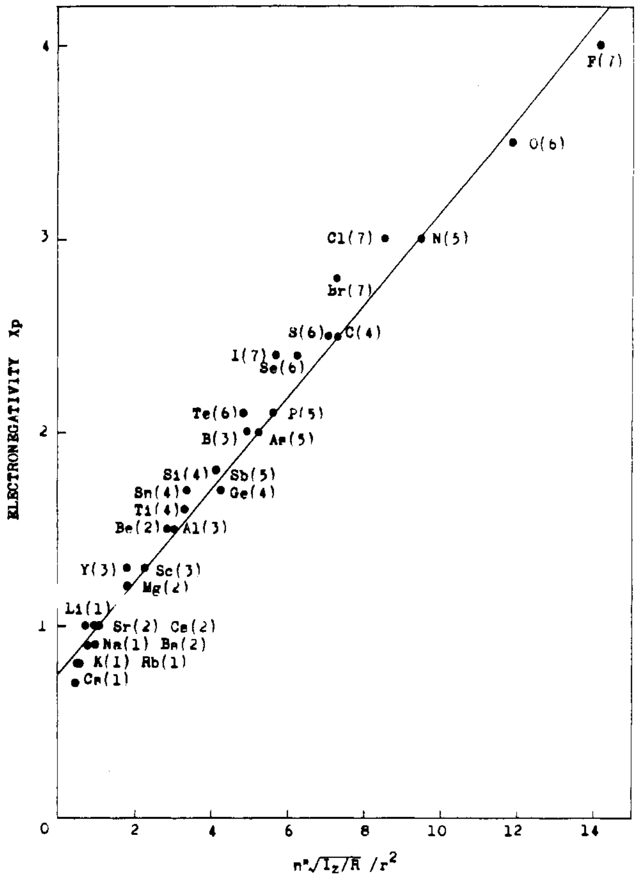

Figure 1. Correlation of electronegativity, X_p, with $n^*(I_z/R)^{1/2}/r^2$. (The numbers in parentheses are oxidation states.)

n	1	2	3	4	5	6	7
n^*	0.85	1.99	2.89	3.45	3.85	4.36	4.99

The electronegativity values calculated from eq 5 are listed in Table I.

Results and Discussion

The stability of a metal complex (the strength of the metal–ligand bond) should be the function of the electron-attracting power of the metal. Consequently, we may identify the electronegativities for dipositive metal ions by the Irving–Williams order,[8] according to which the stability of complexes increases in the order

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The electronegativity values from eq 5 are

$$Mn^{2+}\ (1.426) < Fe^{2+}\ (1.438) < Co^{2+}\ (1.467) < Ni^{2+}\ (1.502) < Cu^{2+}\ (1.517) > Zn^{2+}\ (1.428)$$

which follow the order.

Table I indicates that the electronegativities from eq 5 for the post-scandide elements are close to those of the elements in the corresponding group in the third period but not as high as those from the Allred–Rochow method.[2] In order to prove this, the author has compiled the following evidence. The post-scandide elements in the fourth period that follow after the first filling of a set of d levels are affected by increased effective nuclear charge and exhibit higher ionization potentials. In addition, for the elements in the third period that follow after the first filling of a set of p orbitals the same effects

---

(4) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(5) J. A. Dean, "Lange's Handbook of Chemistry", 11th ed., McGraw-Hill, New York, 1973, pp 3–118.

(6) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", Harper & Row, New York, 1972, p 40.

(7) Zhen Nengwu, *K'o Hsueh T'ung Pao*, **22** (12), 531 (1977).

(8) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

Table I. Electronegativities of the Elements[a]

		1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
1		H																
	X_z	(1)2.271																
	X_p	2.1																
	X_a	2.1																
2		Li	Be											B	C	N	O	F
	X_z	(1)0.943	(2)1.460											(3)1.966	(4)2.536 (2)1.858	(5)3.062 (4)2.809	(6)3.642 (2)2.221	(7)4.188
	X_p	1.0	1.5											2.0	2.5	3.0	3.5	4.0
	X_a	0.97	1.47											2.01	2.5	3.07	3.5	4.1
3		Na	Mg											Al	Si	P	S	Cl
	X_z	(1)0.956	(2)1.208											(3)1.499 (1)1.107	(4)1.709 (2)1.373	(5)2.131 (3)1.699	(6)2.479 (4)2.024	(7)2.835 (5)2.362
	X_p	0.9	1.2											1.5	1.8	2.1	2.5	3.0
	X_a	1.01	1.23											1.47	1.74	2.06	2.44	2.83
4		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	X_z	(1)0.897	(2)1.032	(3)1.316 (1)1.164	(4)1.577 (3)1.414 (2)1.224	(5)2.019 (4)1.827 (3)1.609 (2)1.346	(6)2.290 (4)1.891 (3)1.661 (2)1.402	(7)2.573 (6)2.383 (4)1.953 (2)1.426	(8)2.799 (6)2.418 (3)1.687 (2)1.438	(3)1.745 (2)1.467	(3)1.786 (2)1.502	(2)1.517 (1)1.233	(2)1.428 (1)1.247	(3)1.562 (1)1.123	(4)1.799 (2)1.380	(5)2.035 (3)1.623	(6)2.289 (4)1.873	(7)2.529 (5)2.110
	X_p	0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
	X_a	0.91	1.04	1.2	1.32	1.45	1.56	1.6	1.64	1.7	1.75	1.75	1.66	1.82	2.02	2.20	2.48	2.74
5		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
	X_z	(1)0.891	(2)1.004	(3)1.209	(4)1.476 (3)1.349 (2)1.209	(5)1.771 (4)1.642 (3)1.476	(6)2.025 (4)1.805 (2)1.383	(7)2.312 (4)1.810 (2)1.384	(4)1.882 (3)1.634 (2)1.434	(4)1.864 (3)1.672 (2)1.460	(4)1.858 (3)1.656 (2)1.452	(2)1.425 (1)1.161	(2)1.318 (1)1.171	(3)1.445 (1)1.079	(4)1.583 (2)1.259	(5)1.763 (3)1.439	(6)1.936 (4)1.619	(7)2.142 (5)1.805
	X_p	0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
	X_a	0.89	0.99	1.11	1.22	1.23	1.30	1.36	1.42	1.45	1.35	1.42	1.46	1.49	1.72	1.82	2.01	2.21
6		Cs	Ba	La$^{\Delta}$	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
	X_z	(1)0.886	(2)1.005	(3)1.212	(4)1.568 (3)1.439 (2)1.306	(5)1.881 (4)1.736 (3)1.576	(6)2.132 (5)1.988 (4)1.832	(7)2.359 (6)2.216 (4)1.886	(8)2.596 (6)2.304 (4)1.959	(4)1.913 (3)1.698 (2)1.499	(4)1.880 (3)1.689 (2)1.513	(3)1.706 (1)1.257	(2)1.370 (1)1.219	(3)1.485 (1)1.096	(4)1.557 (2)1.241	(5)1.698 (3)1.398	(6)1.905 (4)1.593	(7)2.048 (5)1.740
	X_p	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2
	X_a	0.86	0.97	1.08	1.23	1.33	1.40	1.46	1.52	1.55	1.44	1.42	1.44	1.44	1.55	1.67	1.76	1.90
7		Fr	Ra	Ac	Δ Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	X_z	(1)0.883	(2)0.963	(3)1.230	(4)1.412 (3)1.248	(4)1.430 (3)1.263	(4)1.447 (3)1.272	(3)1.281	(3)1.275	(3)1.190 (2)1.054	(3)1.272	(4)1.484 (3)1.301	(3)1.314	(3)1.320	(3)1.328	(3)1.343 (2)1.180	(3)1.269 (2)1.119	(3)1.313
	X_p	0.7	0.9	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.2
	X_a	0.86	0.97	1.00	1.06	1.07	1.07	1.07	1.07	1.01	1.11	1.10	1.10	1.10	1.11	1.11	1.06	1.14

[a] X_Z is from eq 5 (the numbers in parentheses are oxidation states), X_p is from Pauling's scale,[1] and X_a is from the Allred–Rochow scale.[2]

of incomplete shielding (though less pronounced to be sure) presumably are operative here as in the post-scandide elements. For example, the effects cause the electronegativity of Na^+ (0.956), following immediately after Ne, to be higher than that of its lighter congener Li^+ (0.943). In both cases the effects of unshielded nuclear charges lead to the electronegativities of two periods to be close with each other. Furthermore, this may be illustrated by the fact that, in many ways such as in chemical structure, the post-scandide elements in the fourth period resemble their lighter congeners in the third period more than their higher congeners in the fifth period. For instance, for group 3, gallium oxide exists in α and β forms corresponding to α-Al_2O_3 and β-Al_2O_3; moreover, like aluminum, gallium forms the hydroxides $Ga(OH)_3$ and $GaO(OH)$. Indium and thallium, however, do not exist in these forms. For group 4, silicon and germanium can form binary hydrogen compounds, which have the general formula M_nH_{2n+2} (M = Si or Ge) and are known as silanes and germanes. Tin and lead, on the other hand, form only the single-metal compounds SnH_4 and PbH_4. For group 5, arsenic trioxide and pentoxide resemble the phosphorus oxides in being entirely acidic, and they give rise to the arsenate(III) and arsenate(V) ions, respectively. Antimony trioxide is amphoteric and will yield not only the antimonate(III) species but also the antimony ion SbO^+.

The electronegativities calculated from eq 5 for the post-lanthanide elements, as shown in Table I, are approximate to those of the elements in the corresponding group in the fifth period, but they are neither as low as those from the Allred–Rochow method based on electrostatic force nor as high as the values from thermochemical data.[9] This may be explained by the fact that both the ionization potentials and the electron affinities of the post-lanthanide elements are slightly greater than those of their corresponding lighter congeners in the fifth period as might be expected as a result of the addition of 14 poorly shielded protons across the lanthanide series. For instance, for group 3, the chemistry of indium is more similar to that of thallium than to that of aluminum and gallium, because indium and thallium tend to retain the ns^2 shell but aluminum and gallium have a slight tendency to form unipositive compounds. Aluminum and gallium form the amphoteric oxides and hydroxides, but indium and thallium sesquioxides are completely basic. For group 4, the melting point for carbon is extremely high and the values for silicon and germanium are high, resulting from the very stable arrangement of a diamond type of lattice. The melting points for tin and lead are low and indicate that they do not use all four outer electrons for metallic bonding. Generally, small atoms attract electrons more than large ones and are therefore more electronegative. The covalent radii increase down the group, but the difference in size between silicon and germanium and between tin and lead are small, so the difference in electronegativities between silicon and germanium and between tin and lead are also small. In addition, as would be expected from increasing size and decreasing ionization potentials, the basicity of the elements increases on descending through the group. Nevertheless, the basicity of lead and bismuth are not very great, and even of the lead(II) and bismuth(III) compounds, there are few containing discrete Pb^{2+} and Bi^{3+} ions. Hence, the electronegativities of lead and bismuth are not very low. Then the series for group 4 calculated from eq 5 reads

$$C^{4+}\ (2.536) \gg Si^{4+}\ (1.769) \leq Ge^{4+}\ (1.799) > Sn^{4+}\ (1.583) \geq Pb^{4+}\ (1.557)$$

Generally, it is concluded that the electronegativities for the elements situated after the transition series produce the series

$$\text{second period} \gg \text{third period} \approx \text{fourth period} > \text{fifth period} \approx \text{sixth period}$$

Conclusion

Whatever the explanations, it appears that the electronegativities of elements in valence states do describe a wide range of chemical phenomena in a quantitative way. This will become clearer when we discuss specific examples in later papers.

---

[9] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).

Contribution from the Shanghai Research Institute of Petrochemistry,
Shanghai 201207, People's Republic of China

Electronegativities of Elements in Valence States and Their Applications. 2. A Scale for Strengths of Lewis Acids

YONGHE ZHANG

Received January 8, 1982

A scale for the Lewis acid strengths has been calculated from the dual parameter equation $\mathbf{Z} = Z/r_k^2 - 7.7X_z + 8.0$. One parameter, Z/r_k^2, where Z is the charge number of the atomic core and r_k is the ionic radius, is related to electrostatic force. Another parameter, the electronegativity of elements in valence states, X_z, is related to covalent bond strength. Satisfactory agreement with unexpected experimental evidence and several examples of the applications of the scale values are given.

Introduction

Lewis acid–base interactions are involved in chemistry that is very important and relevant to everyday life, e.g., organic and inorganic syntheses, catalytic activity, biological applications, etc. Lewis acid–base interactions also play an important role in understanding chemical bonds, reactions, and equilibria.

Ahrland, Chatt, and Davies[1] deserve credit for the concept of the classification of metals and metal ions into class a, class b, and border region. They stated that class a are those which form their most stable complexes with the first ligand atom of each group, class b are those which form their most stable complexes with the second or subsequent ligand atom, and the border region is around the core of pronounced class b acceptors in the periodic table. It seems that Schwarzenbach invented the concept earlier,[2] but his paper was in German and was published in a journal not widely read.

Pearson has extended these concepts to a wide range of acids and bases.[3] He has introduced the terms "hard" and "soft"

---

[1] S. Ahrland, J. Chatt, and N. Davies, *Q. Rev., Chem. Soc.*, **12**, 265 (1958).

[2] G. Schwarzenbach, *Experientia, Suppl.*, **5**, 162 (1956).

0020-1669/82/1321-3889$01.25/0