

REVIEW ARTICLE

A Simple Approach to the Ionic-Covalent Bond Based on the Electronegativity and Acid Strength of Cations. Part One: Calculation of the Electronegativity and Acid Strength

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ABSTRACT. A simple relation exists between electronegativities of cations and their oxidation states and ionic radii. An empirical law is proposed: $\chi \approx 0.274 z - 0.15 z r - 0.01 r + 1 + \alpha$, z being oxidation number, r ionic radius in Å and α a term related to the atomic number. This relation permits to calculate an electronegativity scale covering a large set of electronic and crystallographic situations. An application to the calculation of acid strengths of cations is presented.

KNOWLEDGE AND CREATION

"Anticipate discovery by thought," wrote Merleau-Ponty. Applied to the domain of the chemistry or physics of solids, this deliberately Cartesian approach should be manifested by the following process of innovation: the engineer wishing to utilize a material with certain functions in a component addresses his request to the chemist of solids; the chemist, utilizing rigorous physical models, determines the ideal chemical composition that satisfies the desired criteria and synthesizes the new material. In practice, it is not that way at all; knowledge rarely precedes creation. The discovery of new materials results more or less from chance, chance sometimes disguised as "intuition of the chemist".

The conceptual background of materials chemistry nevertheless seems sufficiently developed. Quantum mechanics and different models of describing the chemical bond deriving from it, such as the model of the strong bond in the case of ionic-covalent materials, should lead to a band structure describing the new energetics and electron densities involved based on a chemical formula. This scheme should allow predicting the properties of the invented solid. In practice, the route is reversed: a solid is synthesized, its structure is determined, its electronic properties (optical, magnetic, tran-

sport properties) are characterized. Finally, an approximate band model is proposed that takes into account the experimental reality. Quantum mechanics in its current state thus does not seem to be an initial tool for creation, but instead an instrument for phenomenological description. Of course, there is not doubt that in the near future, modeling tools useful for creation will be produced by theoreticians.

While awaiting the time when thought will really anticipate discovery, the chemist who creates materials needs simpler, undoubtedly less rigorous, but more predictive concepts. Two can be cited here: the electronegativity and strength of Lewis acids.

In the following lines, we will study these two concepts. We will attempt to give a version adapted to the reality of ionic-covalent materials. Finally, in a second part, based on some examples, we will demonstrate their utility for interpreting the properties of solids and the creation of new materials.

ELECTRONEGATIVITY AND IONIC RADIUS

The electronegativity is undoubtedly the concept most widely used by chemists. Proposed by Pauling in 1932¹ as "the power of an atom in a molec-

ule to attract electrons," this idea has undergone numerous developments.² It has evolved from the notion of atomic electronegativity (a numerical datum per element) to a more general concept that takes into account the electronegativity of the elements in their different states of oxidation to finally end in orbital electronegativity characteristic of an environment (degree of oxidation, symmetry of the occupied site which determines the hybridization of the orbitals involved).

The physical meaning of electronegativity nevertheless is still very vague. As Mullay reported,² the different scales proposed correspond to different concepts:

Pauling ¹	(energy) ³
Mulliken ³	energy
Allred-Rochow ⁴	force
Gordy ⁵	energy/electron
Sanderson ⁶	dimensionless

Given this theoretical fuzziness, it seemed interesting to make up a new empirical scale based on incontestable experimental data and accounting for the properties of ionic-covalent materials.

In practice, the difference in electronegativity between anion and cation is used as a criterion of covalence: The smaller the difference is, the more covalent the bond is. For a given anion (O^{2-} , for example) whose electronegativity is much higher than the electronegativity of cations ($\chi_0=3.5$ in Pauling's scale), we only take the electronegativity of the cation into consideration. For example, it is believed that the covalence of the cation-anion bond increases with the degree of oxidation of the cation; this statement implies that the electronegativity of the cation increases with its charge. It is also assumed that the covalence, and thus implicitly the electronegativity, increases when the coordination decreases. The same is true for the spin state: a cation with low spin establishes a more covalent bond with opposing anions than the same cation with high spin.

In addition, crystallography shows that the cation-anion interatomic distances are also a function

of the coordination, degree of oxidation, and spin state. This observation led to tables of ionic radii such as Shannon's⁶ by arbitrarily assigning a constant anionic radius ($R_{O^{2-}}=1.40 \text{ \AA}$, for example). These tables correspond to the different electronic (degree of oxidation, spin state, ...) or crystallographic (coordination) situations observed. It should thus be possible, given the previously mentioned relations between covalence and electronegativity, to compile an electronegativity table corresponding to all "cases" of cations encountered in practice.

The correlation between electronegativity, charge number, and ionic radius is shown in Fig. 1. It shows the variation of χ/r as a function of z/r for ions with charges of 1^+ , 2^+ , and 3^+ (χ is the electronegativity expressed in Pauling units, r is the ionic radius in \AA , and z is the charge number). The ionic radii used are those proposed by Shannon for $R_{O^{2-}}=1.40 \text{ \AA}$.⁶ The electronegativity scale is the one proposed by Zhang for ions in their different valence states.⁷ We derive from this:

$$\chi_0/r \gg A_{(z)}z/r + B_{(z)}$$

$A_{(z)}$ and $B_{(z)}$, terms dependent on the charge number, can be determined by linear regression:

$$A_{(z)} \approx 1/z + 0.274 \text{ and } B_{(z)} \approx 0.15z + 0.01.$$

Finally, an approximate value of the electronegativity is obtained:

$$\chi_0 \approx 0.274z - 0.15zr - 0.01r + 1 \quad (1)$$

On average, a satisfactory correlation is obtained with the Zhang electronegativity. However, differences exist in the case of d transition elements in particular. In the case of iron, for example, it has been noted that the values obtained are much lower than those proposed by Zhang for the degree of oxidation of 3^+ and coordination of 6:

$$\chi_0=1.53, \chi_{\text{Zhang}}=1.687$$

Note that the difference ($\chi_0 - \chi_{\text{Zhang}}$) varies as a function of the atomic number of the element, like most periodic properties (atomic or ionic radius, ionization potential, etc.).⁸ It thus seemed neces-

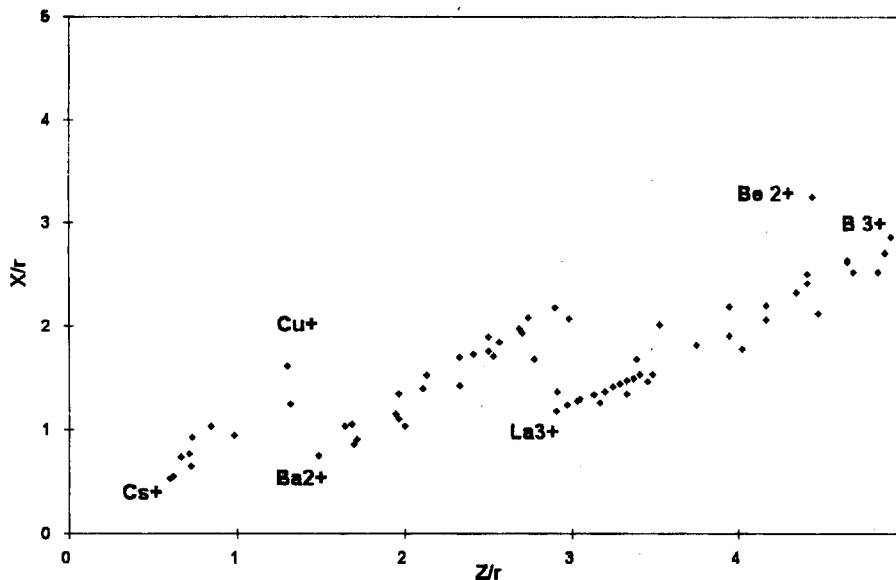


Fig. 1. Variation in χ_{Zhang}/r as a function of z/r for ions with formal charges of 1⁺, 2⁺, 3⁺.

sary to add a correcting term α such that:

$$\chi = \chi_0 + \alpha$$

We first estimated α for a given element as the difference $(\chi_0 - \chi_{Zhang})$, then graphically adjusted it with the graph $\alpha = f(Z_A)$ (Z_A =atomic number) so

(2)

Table 1. Values of α Used for Calculation of χ

Element	α	Element	α	Element	α	Element	α
H	0.830	Cu	0.300	Ba	-0.048	Hg	0.060
Li	-0.160	Zn	0.160	La	-0.047	Tl	0.050
Be	0.000	Ga	-0.015	Ce	0.000	Pb	-0.008
B	0.150	Ge	-0.010	Pr	0.030	Bi	-0.050
C	0.290	As	0.000	Nd	0.030	Po	-0.060
N	0.45	Se	0.005	Pm	0.015	At	-0.070
F	0.720	Br	0.008	Sm	0.000	Fr	-0.050
Na	-0.132	Rb	-0.103	Eu	-0.040	Ra	-0.009
Mg	-0.101	Sr	-0.069	Gd	0.000	Ac	0.000
Al	-0.061	Y	-0.086	Tb	0.015	Th	-0.010
Si	-0.030	Zr	-0.103	Dy	0.030	Pa	0.000
P	0.018	Nb	0.050	Ho	0.030	U	-0.002
S	0.060	Mo	0.130	Er	0.000	Np	0.000
Cl	0.117	Ru	0.180	Tm	-0.020	Pu	-0.005
K	-0.123	Rh	0.190	Yb	-0.030	Am	-0.015
Ca	-0.091	Pd	0.222	Lu	-0.045	Cm	-0.005
Sc	-0.110	Ag	0.240	Hf	-0.045	Bk	-0.002
Ti	-0.136	Cd	0.090	Ta	0.102	Cf	0.000
V	0.030	In	0.000	W	0.145	Es	-0.002
Cr	0.120	Sn	-0.050	Re	0.200	Fm	-0.003
Mn	0.150	Sb	-0.070	Os	0.230	Md	-0.005
Fe	0.180	Te	-0.090	Ir	0.230	No	-0.010
Co	0.220	I	-0.102	Pt	0.240		
Ni	0.240	Cs	-0.082	Au	0.250		

that it varies monotonically within different blocks (blocks *s*, *p*, *d*, *f*) as well as within different periods (Table 1).

Satisfactory agreement was finally obtained with the Zhang scale. In addition, good coherence was found with the ideas concerning the ionic-covalent bond. As an illustration, consider nickel:

– with a given coordination, the electronegativity increases with the degree of oxidation:

$$\chi_{\text{Ni}^{2+}}=1.57, \chi_{\text{Ni}^{3+}}=1.80, \chi_{\text{Ni}^{4+}}=2.04 \text{ (CN=VI)}$$

Table 2. El: element; z: Charge number; CN: Coordination number; r: ionic radius according to [6] ($r_{\text{O}^{2-}}=1.40 \text{ \AA}$); c: electronegativity; ICP: Ionic-Covalent Parameter (acid strength); est: estimated; SQ: square plot; PYR: pyramidal; HS: High Spin; LS: Low Spin

El	z	CN	r(Å)	χ	ICP	Comment
Ac	3	6	1.12	1.307	0.649	IR
Ag	1	2	0.670	1.407	0.480	IR
Ag	1	4	1.020	1.351	0.193	IR
Ag	1	4	1.000	1.354	0.205	IRSQ
Ag	1	5	1.090	1.340	0.150	IR
Ag	1	6	1.150	1.330	0.117	IR
Ag	1	7	1.220	1.319	0.081	IR
Ag	1	8	1.28	1.309	0.053	IR
Ag	2	4	0.790	1.543	0.450	IRSQ
Ag	2	6	0.940	1.497	0.363	IR
Ag	3	4	0.67	1.754	0.479	IRSQ
Ag	3	6	0.75	1.717	0.432	IR
Al	3	4	0.390	1.582	1.187	IR
Al	3	5	0.480	1.540	1.063	IR
Al	3	6	0.535	1.515	1.004	IR
Am	2	7	1.21	1.158	0.612	IR
Am	2	8	1.26	1.142	0.598	IR
Am	2	9	1.31	1.127	0.585	IR
Am	3	6	1.01	1.342	0.690	IR
Am	3	8	1.23	1.241	0.658	IR
Am	4	6	0.85	1.563	0.661	IR
Am	4	8	0.95	1.502	0.649	IR
As	3	6	0.580	1.555	0.878	IR
As	5	4	0.335	2.115	0.804	IR
As	5	6	0.460	2.020	0.659	IR
At	7	6	0.62	2.191	0.311	IR
Au	1	6	1.370	1.305	-0.00	IR
Au	3	4	0.680	1.759	0.458	IRSQ
Au	3	6	0.850	1.681	0.373	IR
Au	5	6	0.57	2.187	0.243	IR
B	3	3	0.010	1.967	3.836	IR
B	3	4	0.110	1.921	1.817	IR
B	3	6	0.270	1.848	1.138	IR

– with a given degree of oxidation, the electronegativity decreases when the coordination increases:

$$\chi_{\text{Ni}^{2+}}(\text{IV})=1.64, \chi_{\text{Ni}^{2+}}(\text{V})=1.59, \chi_{\text{Ni}^{2+}}(\text{VI})=1.57$$

– the spin state is also taken into consideration:

$$\chi_{\text{Ni}^{3+}}(\text{HS})=1.79, \chi_{\text{Ni}^{3+}}(\text{LS})=1.80.$$

We thus have an electronegativity scale corresponding to all cases encountered in the chemistry of solids (Table 2).

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Ba	2	6	1.350	1.082	0.622	IR
Ba	2	7	1.380	1.072	0.615	IR
Ba	2	8	1.420	1.060	0.608	IR
Ba	2	9	1.480	1.041	0.597	IR
Ba	2	10	1.520	1.029	0.591	IR
Ba	2	11	1.570	1.014	0.585	IR
Ba	2	12	1.610	1.001	0.580	IR
Be	2	3	0.160	1.498	1.899	IR
Be	2	4	0.270	1.464	1.492	IR
Be	2	6	0.450	1.409	1.125	IR
Bi	3	5	0.960	1.330	0.751	IR
Bi	3	6	1.030	1.298	0.734	IR
Bi	3	8	1.170	1.234	0.712	IR
Bi	5	6	0.760	1.742	0.607	IR
Bk	3	6	0.96	1.378	0.684	IR
Bk	4	6	0.83	1.588	0.647	IR
Bk	4	8	0.93	1.527	0.632	IR
Br	3	4	0.590	1.559	0.859	IRSQ
Br	5	3	0.310	2.142	0.834	IRPY
Br	7	4	0.250	2.661	0.452	IR
Br	7	6	0.390	2.512	0.270	IR
C	4	3	0.001	2.386	7.383	est,
C	4	4	0.150	2.295	1.157	IR
C	4	6	0.160	2.288	1.110	IR
Ca	2	6	1.000	1.147	0.792	IR
Ca	2	7	1.060	1.128	0.767	IR
Ca	2	8	1.120	1.110	0.745	IR
Ca	2	9	1.180	1.091	0.725	IR
Ca	2	10	1.230	1.076	0.711	IR
Ca	2	11	1.340	1.042	0.683	IR
Cd	2	4	0.780	1.396	0.664	IR
Cd	2	5	0.870	1.368	0.608	IR
Cd	2	6	0.950	1.344	0.566	IR
Cd	2	7	1.030	1.319	0.530	IR
Cd	2	8	1.100	1.297	0.502	IR
Cd	2	9	0.980	1.334	0.551	IR
Cd	2	12	1.310	1.232	0.440	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Ce	3	6	1.010	1.357	0.669	IR
Ce	3	7	1.070	1.330	0.657	IR
Ce	3	8	1.143	1.296	0.646	IR
Ce	3	9	1.196	1.272	0.641	IR
Ce	3	10	1.250	1.247	0.636	IR
Ce	3	12	1.340	1.206	0.633	IR
Ce	4	6	0.870	1.565	0.637	IR
Ce	4	8	0.970	1.504	0.627	IR
Ce	4	10	1.070	1.443	0.626	IR
Ce	4	12	1.140	1.401	0.629	IR
Cf	3	6	0.95	1.385	0.684	IR
Cf	4	6	0.821	1.595	0.646	IR
Cf	4	8	0.92	1.535	0.630	IR
Cl	5	3	0.120	2.396	1.308	IRPY
Cl	7	4	0.080	2.951	1.041	IR
Cl	7	6	0.270	2.749	0.263	IR
Cm	3	6	0.98	1.366	0.683	IR
Cm	4	6	0.85	1.573	0.647	IR
Cm	4	8	0.95	1.512	0.635	IR
Co	2	4	0.580	1.588	0.656	IRHS
Co	2	5	0.670	1.560	0.570	IR
Co	2	6	0.745	1.537	0.510	IRHS
Co	2	6	0.650	1.567	0.587	IRLS
Co	3	6	0.610	1.761	0.550	IRLS
Co	3	6	0.545	1.791	0.606	IRHS
Cr	2	6	0.730	1.442	0.659	IRHS
Cr	2	6	0.800	1.420	0.609	IRLS
Cr	3	6	0.615	1.659	0.684	IR
Cr	4	4	0.410	1.966	0.738	IR
Cr	4	6	0.550	1.881	0.600	IR
Cr	5	4	0.345	2.228	0.623	IR
Cr	5	6	0.490	2.118	0.470	IR
Cr	5	8	0.570	2.057	0.423	IR
Cr	6	4	0.260	2.527	0.534	IR
Cr	6	6	0.440	2.364	0.303	IR
Cs	1	6	1.670	0.925	0.353	IR
Cs	1	8	1.740	0.913	0.333	IR
Cs	1	9	1.780	0.907	0.322	IR
Cs	1	10	1.810	0.902	0.314	IR
Cs	1	11	1.850	0.896	0.304	IR
Cs	1	12	1.880	0.891	0.296	IR
Cu	1	2	0.460	1.500	0.678	IR
Cu	1	4	0.600	1.478	0.478	IR
Cu	1	6	0.770	1.451	0.299	IR
Cu	2	4	0.570	1.671	0.557	IR
Cu	2	4	0.570	1.671	0.557	IRSQ
Cu	2	5	0.650	1.647	0.477	IR
Cu	2	6	0.730	1.622	0.410	IR
Cu	3	6	0.540	1.874	0.501	IRLS
Dy	2	6	1.070	1.246	0.596	IR
Dy	2	7	1.130	1.228	0.575	IR
Dy	2	8	1.190	1.209	0.555	IR
Dy	3	6	0.912	1.432	0.654	IR
Dy	3	7	0.970	1.406	0.638	IR
Dy	3	8	1.027	1.380	0.624	IR
Dy	3	9	1.083	1.354	0.614	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Er	3	6	0.890	1.413	0.703	IR
Er	3	7	0.945	1.387	0.686	IR
Er	3	8	1.004	1.360	0.671	IR
Er	3	9	1.062	1.333	0.659	IR
Es	3	6	0.94	1.388	0.690	est
Eu	2	6	1.170	1.145	0.658	IR
Eu	2	7	1.200	1.136	0.649	IR
Eu	2	8	1.250	1.121	0.635	IR
Eu	2	9	1.300	1.105	0.622	IR
Eu	2	10	1.350	1.090	0.611	IR
Eu	3	6	0.947	1.346	0.740	IR
Eu	3	7	1.010	1.317	0.724	IR
Eu	3	8	1.066	1.292	0.713	IR
Eu	3	9	1.120	1.267	0.705	IR
F	7	6	0.08	3.553	0.210	IR
Fe	2	4	0.630	1.533	0.661	IRHS
Fe	2	4	0.640	1.530	0.652	IRHSSQ
Fe	2	6	0.610	1.539	0.681	IRLS
Fe	2	6	0.780	1.486	0.540	IRHS
Fe	2	8	0.920	1.443	0.456	IRHS
Fe	3	4	0.490	1.777	0.719	IRHS
Fe	3	5	0.580	1.735	0.630	IR
Fe	3	6	0.550	1.749	0.657	IRLS
Fe	3	6	0.645	1.705	0.579	IRHS
Fe	3	8	0.780	1.643	0.499	IRHS
Fe	4	6	0.585	1.919	0.493	IR
Fe	6	4	0.250	2.597	0.473	IR
Fm	3	6	0.93	1.391	0.694	est
Fr	1	6	1.8	0.936	0.272	IR
Ga	3	4	0.470	1.591	1.011	IR
Ga	3	5	0.550	1.554	0.926	IR
Ga	3	6	0.620	1.522	0.866	IR
Gd	3	6	0.938	1.391	0.688	IR
Gd	3	7	1.000	1.362	0.672	IR
Gd	3	8	1.053	1.338	0.660	IR
Gd	3	9	1.107	1.313	0.651	IR
Ge	2	6	0.730	1.312	0.838	IR
Ge	4	4	0.390	1.848	0.944	IR
Ge	4	6	0.530	1.763	0.795	IR
H	1	2	0.001	2.104	7.171	est
Hf	4	4	0.580	1.697	0.807	IR
Hf	4	6	0.710	1.618	0.741	IR
Hf	4	7	0.760	1.588	0.724	IR
Hf	4	8	0.830	1.545	0.706	IR
Hg	1	3	0.970	1.179	0.474	IR
Hg	1	6	1.190	1.144	0.345	IR
Hg	2	2	0.690	1.394	0.773	IR
Hg	2	4	0.960	1.310	0.602	IR
Hg	2	6	1.020	1.292	0.575	IR
Hg	2	8	1.140	1.255	0.530	IR
Ho	3	6	0.901	1.438	0.658	IR
Ho	3	8	1.015	1.385	0.627	IR
Ho	3	9	1.072	1.359	0.615	IR
Ho	3	9	1.072	1.359	0.615	IR
Ho	3	10	1.120	1.337	0.608	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
I	5	3	0.440	1.933	0.818	IRPY
I	5	6	0.950	1.546	0.684	IR
I	7	4	0.420	2.371	0.401	IR
I	7	6	0.530	2.254	0.360	IR
In	3	4	0.620	1.537	0.846	IR
In	3	6	0.800	1.454	0.738	IR
In	3	8	0.920	1.399	0.693	IR
Ir	3	6	0.680	1.739	0.486	IR
Ir	4	6	0.625	1.945	0.401	IR
Ir	5	6	0.570	2.167	0.271	IR
K	1	4	1.370	0.931	0.515	IR
K	1	6	1.380	0.930	0.511	IR
K	1	7	1.460	0.917	0.480	IR
K	1	8	1.510	0.909	0.462	IR
K	1	9	1.550	0.903	0.448	IR
K	1	10	1.590	0.896	0.434	IR
K	1	12	1.640	0.888	0.419	IR
La	3	6	1.032	1.301	0.729	IR
La	3	7	1.100	1.270	0.716	IR
La	3	8	1.160	1.242	0.708	IR
La	3	9	1.550	1.063	0.704	IR
La	3	10	1.270	1.191	0.700	IR
La	3	12	1.360	1.150	0.697	IR
Li	1	4	0.590	1.020	1.125	IR
Li	1	6	0.760	0.992	0.943	IR
Li	1	8	0.920	0.967	0.812	IR
Lu	3	6	0.861	1.381	0.775	IR
Lu	3	8	0.977	1.328	0.739	IR
Lu	3	9	1.032	1.302	0.727	IR
Lw	2	6	1	1.218	0.694	est
Md	3	6	0.92	1.394	0.700	est
Mg	2	4	0.570	1.271	1.110	IR
Mg	2	5	0.660	1.243	1.021	IR
Mg	2	6	0.720	1.224	0.971	IR
Mg	2	8	0.890	1.172	0.860	IR
Mn	2	4	0.660	1.492	0.677	IRHS
Mn	2	5	0.750	1.466	0.603	IRHS
Mn	2	6	0.670	1.490	0.666	IRLS
Mn	2	6	0.830	1.441	0.549	IRHS
Mn	2	7	0.900	1.419	0.508	IRHS
Mn	2	8	0.960	1.400	0.478	IR
Mn	3	5	0.580	1.705	0.671	IR
Mn	3	6	0.645	1.675	0.620	IRHS
Mn	3	6	0.580	1.705	0.671	IRLS
Mn	4	4	0.390	2.008	0.723	IR
Mn	4	6	0.530	1.923	0.574	IR
Mn	5	4	0.330	2.269	0.604	IR
Mn	6	4	0.255	2.562	0.504	IR
Mn	7	4	0.250	2.803	0.255	IR
Mn	7	6	0.460	2.580	0.033	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Mo	3	6	0.690	1.635	0.618	IR
Mo	4	6	0.650	1.830	0.526	IR
Mo	5	4	0.650	2.006	0.379	IR
Mo	5	6	0.610	2.036	0.392	IR
N	3	6	0.16	2.198	1.109	IR
N	5	3	-0.104	2.899	0.738	IR
Na	1	4	0.990	0.983	0.726	IR
Na	1	5	1.000	0.982	0.719	IR
Na	1	6	1.020	0.978	0.707	IR
Na	1	7	1.120	0.962	0.648	IR
Na	1	8	1.180	0.953	0.615	IR
Na	1	9	1.240	0.943	0.586	IR
Na	1	12	1.390	0.919	0.520	IR
Nb	3	6	0.720	1.541	0.710	IR
Nb	4	6	0.680	1.731	0.622	IR
Nb	4	8	0.790	1.664	0.584	IR
Nb	5	4	0.480	2.055	0.574	IR
Nb	5	6	0.640	1.934	0.492	IR
Nb	5	7	0.690	1.896	0.479	IR
Nb	5	8	0.740	1.858	0.471	IR
Nd	2	8	1.290	1.178	0.528	IR
Nd	2	9	1.350	1.160	0.514	IR
Nd	3	6	0.983	1.400	0.634	IR
Nd	3	8	1.109	1.342	0.609	IR
Nd	3	9	1.163	1.317	0.602	IR
Nd	3	12	1.270	1.268	0.594	IR
Nd	4	6	1.020	1.504	0.584	est
Ni	2	4	0.550	1.618	0.662	IR
Ni	2	4	0.490	1.636	0.737	IRSQ
Ni	2	5	0.630	1.593	0.578	IR
Ni	2	6	0.690	1.574	0.525	IR
Ni	3	6	0.600	1.786	0.530	IRHS
Ni	3	6	0.560	1.804	0.565	IRLS
Ni	4	6	0.480	2.043	0.494	IRLS
No	2	6	1.1	1.197	0.640	IR
Np	2	6	1.24	1.164	0.582	IR
Np	3	6	1.01	1.357	0.669	IR
Np	4	6	0.87	1.565	0.637	IR
Np	4	8	0.98	1.498	0.626	IR
Np	5	6	0.75	1.800	0.539	IR
Np	6	6	0.75	1.962	0.395	IR
Np	7	6	0.71	2.165	0.228	IR
Os	4	6	0.630	1.932	0.412	IR
Os	5	6	0.575	2.153	0.282	IR
Os	6	5	0.490	2.418	0.135	IR
Os	6	6	0.545	2.368	0.111	IR
Os	7	6	0.525	2.582	-0.084	IR
Os	8	4	0.390	2.950	-0.276	IR
P	3	6	0.440	1.638	1.004	IR
P	5	4	0.170	2.259	1.195	IR
P	5	5	0.290	2.168	0.857	IR
P	5	6	0.380	2.099	0.717	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Pa	3	6	1.04	1.344	0.663	IR
Pa	3	6	1	1.357	0.678	est
Pa	4	6	0.9	1.547	0.633	IR
Pa	4	8	1.01	1.480	0.625	IR
Pb	2	4	0.980	1.236	0.687	IRPY
Pb	2	6	1.190	1.171	0.608	IR
Pb	2	7	1.230	1.158	0.597	IR
Pb	2	8	1.290	1.140	0.581	IR
Pb	2	9	1.350	1.121	0.567	IR
Pb	2	10	1.400	1.106	0.557	IR
Pb	2	11	1.450	1.090	0.548	IR
Pb	2	12	1.490	1.078	0.541	IR
Pb	4	4	0.650	1.691	0.717	IR
Pb	4	5	0.730	1.642	0.683	IR
Pb	4	6	0.775	1.615	0.669	IR
Pb	4	8	0.940	1.514	0.640	IR
Pd	1	2	0.590	1.402	0.598	IR
Pd	2	4	0.640	1.572	0.594	IRSQ
Pd	2	6	0.860	1.503	0.431	IR
Pd	3	6	0.760	1.694	0.451	IR
Pd	4	6	0.615	1.943	0.417	IR
Pm	3	6	0.99	1.382	0.653	IR
Pm	3	8	1.093	1.334	0.633	IR
Pm	3	9	1.144	1.311	0.625	IR
Po	4	6	0.94	1.463	0.711	IR
Po	4	8	1.08	1.377	0.709	IR
Po	6	6	0.67	1.974	0.475	IR
Pr	3	6	0.990	1.397	0.633	IR
Pr	3	8	1.126	1.334	0.607	IR
Pr	3	9	1.179	1.310	0.601	IR
Pr	4	6	0.850	1.608	0.599	IR
Pr	4	8	1.126	1.439	0.587	IR
Pr	4	9	1.179	1.407	0.592	IR
Pt	2	4	0.600	1.602	0.608	IRSQ
Pt	2	6	0.800	1.540	0.444	IR
Pt	3	6	0.700	1.740	0.460	est
Pt	4	6	0.625	1.955	0.387	IR
Pt	5	6	0.570	2.177	0.257	IR
Pu	3	6	1	1.357	0.678	IR
Pu	4	6	0.86	1.566	0.645	IR
Pu	4	8	0.96	1.505	0.634	IR
Ra	2	7	1.7	1.012	0.518	IR
Ra	2	8	1.48	1.080	0.544	IR
Rb	1	6	1.520	0.928	0.430	IR
Rb	1	7	1.560	0.922	0.416	IR
Rb	1	8	1.610	0.914	0.400	IR
Rb	1	9	1.630	0.910	0.393	IR
Rb	1	10	1.660	0.906	0.384	IR
Rb	1	11	1.690	0.901	0.375	IR
Rb	1	12	1.720	0.896	0.366	IR
Rb	1	14	1.830	0.878	0.337	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Re	4	6	0.630	1.912	0.439	IR
Re	5	6	0.580	2.129	0.308	IR
Re	6	6	0.550	2.344	0.137	IR
Re	7	4	0.380	2.715	0.013	IR
Rh	3	6	0.665	1.706	0.551	IR
Rh	4	6	0.6	1.920	0.470	IR
Rh	5	4	0.55	2.142	0.336	IR
Ru	3	6	0.680	1.689	0.555	IR
Ru	4	6	0.620	1.898	0.472	IR
Ru	5	6	0.565	2.121	0.342	IR
Ru	7	4	0.380	2.695	0.040	IR
Ru	8	4	0.360	2.936	-0.188	IR
S	4	6	0.370	1.930	0.876	IR
S	6	4	0.120	2.595	1.113	IR
S	6	6	0.290	2.440	0.560	IR
Sb	3	4	0.760	1.402	0.854	IRPY
Sb	3	5	0.800	1.384	0.835	IR
Sb	3	6	0.760	1.402	0.854	IR
Sb	5	6	0.600	1.844	0.672	IR
Sc	3	6	0.745	1.369	0.917	IR
Sc	3	8	0.870	1.312	0.862	IR
Se	4	6	0.500	1.796	0.800	IR
Se	6	4	0.280	2.394	0.654	IR
Se	6	6	0.420	2.267	0.477	IR
Si	2	6	0.500	1.363	1.096	est
Si	4	4	0.260	1.907	1.214	IR
Si	4	6	0.400	1.822	0.958	IR
Sm	2	7	1.220	1.170	0.588	IR
Sm	2	8	1.270	1.154	0.574	IR
Sm	2	9	1.320	1.139	0.562	IR
Sm	3	6	0.958	1.381	0.682	IR
Sm	3	7	1.020	1.353	0.667	IR
Sm	3	8	1.079	1.326	0.656	IR
Sm	3	9	1.132	1.301	0.648	IR
Sm	3	12	1.240	1.252	0.637	IR
Sn	2	6	0.850	1.235	0.813	est
Sn	4	4	0.550	1.711	0.835	IR
Sn	4	5	0.620	1.668	0.790	IR
Sn	4	6	0.690	1.625	0.756	IR
Sn	4	7	0.750	1.589	0.734	IR
Sn	4	8	0.810	1.552	0.717	IR
Sr	2	6	1.180	1.113	0.696	IR
Sr	2	7	0.980	1.175	0.771	IR
Sr	2	8	1.260	1.088	0.673	IR
Sr	2	9	1.310	1.073	0.660	IR
Sr	2	10	1.360	1.057	0.649	IR
Sr	2	12	1.440	1.032	0.634	IR
Ta	3	6	0.720	1.593	0.638	IR
Ta	4	6	0.680	1.783	0.550	IR
Ta	5	6	0.640	1.986	0.420	IR
Ta	5	7	0.690	1.948	0.408	IR
Ta	5	8	0.740	1.910	0.399	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
Tb	3	6	0.923	1.412	0.672	IR
Tb	3	7	0.980	1.386	0.656	IR
Tb	3	8	1.040	1.359	0.642	IR
Tb	3	9	1.095	1.333	0.632	IR
Tb	4	6	0.760	1.647	0.641	IR
Tb	4	8	0.880	1.574	0.615	IR
Tc	4	6	0.645	1.853	0.500	IR
Tc	5	6	0.6	2.064	0.368	IR
Tc	7	4	0.37	2.676	0.090	IR
Tc	7	6	0.56	2.474	0.008	IR
Te	4	3	0.520	1.689	0.914	IR
Te	4	4	0.660	1.603	0.824	IR
Te	4	6	0.970	1.414	0.751	IR
Te	6	4	0.430	2.163	0.601	IR
Te	6	6	0.560	2.044	0.535	IR
Th	4	6	0.940	1.513	0.642	IR
Th	4	8	1.050	1.446	0.639	IR
Th	4	9	1.090	1.421	0.640	IR
Th	4	10	1.130	1.397	0.642	IR
Th	4	11	1.180	1.366	0.647	IR
Th	4	12	1.210	1.348	0.650	IR
Ti	2	6	0.860	1.145	0.926	IR
Ti	3	6	0.670	1.377	0.998	IR
Ti	4	4	0.420	1.703	1.079	IR
Ti	4	5	0.510	1.649	0.986	IR
Ti	4	6	0.605	1.591	0.918	IR
Ti	4	8	0.740	1.508	0.856	IR
Tl	1	6	1.500	1.084	0.226	IR
Tl	1	8	1.590	1.070	0.195	IR
Tl	1	12	1.700	1.052	0.161	IR
Tl	3	4	0.750	1.527	0.694	IR
Tl	3	6	0.885	1.465	0.636	IR
Tl	3	8	0.980	1.421	0.607	IR
Tm	2	6	1.030	1.209	0.681	IR
Tm	2	7	1.090	1.190	0.658	IR
Tm	3	6	0.880	1.397	0.734	IR
Tm	3	8	0.994	1.345	0.701	IR
Tm	3	9	1.052	1.318	0.688	IR
U	3	6	1.025	1.349	0.669	IR
U	4	6	0.89	1.551	0.637	IR
U	4	7	0.95	1.515	0.631	IR
U	4	8	1	1.484	0.628	IR
U	4	9	1.05	1.454	0.628	IR
U	5	6	0.76	1.790	0.541	IR
U	5	7	0.84	1.730	0.538	IR
U	6	2	0.45	2.233	0.465	IR
U	6	4	0.52	2.169	0.427	IR
U	6	6	0.73	1.978	0.396	IR
U	6	7	0.81	1.905	0.406	IR
V	2	6	0.790	1.333	0.740	IR
V	3	6	0.640	1.558	0.789	IR
V	4	5	0.530	1.803	0.740	IR
V	4	6	0.580	1.772	0.704	IR
V	4	8	0.720	1.687	0.634	IR
V	5	4	0.355	2.130	0.733	IR
V	5	5	0.460	2.050	0.618	IR
V	5	6	0.540	1.990	0.563	IR

Table 2. Continued

El	z	CN	r(Å)	χ	ICP	Comment
W	4	6	0.660	1.838	0.500	IR
W	5	6	0.620	2.044	0.368	IR
W	6	4	0.420	2.407	0.284	IR
W	6	5	0.510	2.325	0.229	IR
W	6	6	0.600	2.243	0.201	IR
Y	3	6	0.900	1.322	0.818	IR
Y	3	7	0.960	1.294	0.800	IR
Y	3	8	1.019	1.267	0.786	IR
Y	3	9	1.075	1.242	0.775	IR
Yb	2	6	1.020	1.202	0.699	IR
Yb	2	7	1.080	1.183	0.675	IR
Yb	2	8	1.140	1.165	0.654	IR
Yb	3	6	0.868	1.393	0.752	IR
Yb	3	7	0.925	1.367	0.733	IR
Yb	3	8	0.985	1.339	0.717	IR
Yb	3	9	1.042	1.313	0.704	IR
Zn	1	6	1.000	1.274	0.316	est
Zn	2	4	0.600	1.522	0.718	IR
Zn	2	5	0.680	1.497	0.644	IR
Zn	2	6	0.740	1.479	0.596	IR
Zn	2	8	0.900	1.429	0.495	IR
Zr	3	6	0.960	1.277	0.824	est
Zr	4	4	0.590	1.633	0.881	IR
Zr	4	5	0.660	1.590	0.843	IR
Zr	4	6	0.720	1.553	0.818	IR
Zr	4	7	0.780	1.517	0.799	IR
Zr	4	8	0.840	1.480	0.785	IR
Zr	4	9	0.890	1.450	0.777	IR

ACID STRENGTH OF CATIONS BASE STRENGTH OF ANIONS

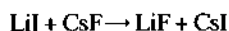
The electronegativity is not a sufficient parameter for describing an ionic-covalent solid. There is no evident correlation, for example, between the electronegativity and a fundamental property such as the forbidden band width of an oxide. It is thus necessary to investigate other parameters. We suggest using the acid strength of cations considered as Lewis acids.

Pearson proposed an empirical classification of Lewis acids and bases (HSAB principle, Hard and Soft Acids and Bases) (Table 3).⁹ Cations and anions can be divided into "hard," "soft," or "borderline." As an example, the O⁻ ion is a strong base, Al³⁺ and Li⁺ are strong acids, Cs⁺ and Ba²⁺ are weak acids. "Hard" cations tend to give stable combinations with "hard" anions and vice versa.

Table 3. Comparison of Acid Strengths (H=hard, B=borderline, S=soft) of Some Cations Proposed by Pearson, Zhang, and Those Calculated in the Present Study (ICP). The Cations Are Classified by Decreasing ICP

Cation	Pearson	Zhang	ICP	Cation	Pearson	Zhang	ICP
Be ²⁺	H	2.504	1.899	Fe ²⁺	B	0.39	0.681
Si ⁴⁺	H	1.769	1.214	Mn ²⁺	H	0.307	0.666
Al ³⁺	H	3.042	1.004	Ti ³⁺	S	-0.58	0.636
Mg ²⁺	H	1.402	0.971	Hg ²⁺	S	-1.063	0.602
Li ⁺	H	1.974	0.943	Cd ²⁺	S	-0.108	0.566
Ti ⁴⁺	H	3.064	0.918	Ni ²⁺	B	0.293	0.525
Sc ³⁺	H	1.697	0.917	K ⁺	H	1.526	0.511
Ga ³⁺	H	1.167	0.866	Co ²⁺	B	0.356	0.510
Zr ⁴⁺	H	2.043	0.818	Pd ²⁺	S	-1.18	0.431
Ca ²⁺	H	1.593	0.792	Cu ²⁺	B	0.177	0.410
In ³⁺	H	1.026	0.738	Pt ⁴⁺	S	-1.191	0.387
Zn ²⁺	B	0.656	0.718	Hg ⁺	S	-0.821	0.345
Na ⁺	H	1.382	0.707	Cu ⁺	S	-0.637	0.299
La ³⁺	H	0.852	0.704	Ti ⁺	S	-0.067	0.226
Sr ²⁺	H	1.417	0.696	Ag ⁺	S	-0.339	0.193
				Au ⁺	S	-1.24	0.00

For example, the following reaction is observed:



hard-soft + soft-hard \rightarrow hard-hard + soft-soft

Zhang proposed a numerical classification of the acid strength of cations.⁷ He correlates the acid strength of cations with parameter Z:

$$Z = P - 7.7\chi + 8 \quad (3)$$

where χ is the electronegativity and P is the polarizing power z/r^2 , where z is the formal charge and r is the ionic radius. In a previous publication,¹⁰ we proposed another parameter called ICP (ionic-covalent parameter), implicitly correlated with the acid strength as:

$$\text{ICP} = \log(P) - 1.38\chi + 2.07 \quad (4)$$

where P is calculated with the ionic radii proposed by Shannon for $r_{\text{O}^{2-}} = 1.40 \text{ \AA}$, χ is the electronegativity, defined previously, and the zero of the scale corresponds to the Au⁺ ion in coordination VI. ICP is a dimensionless number.

ICP is representative of the ionic-covalent bond. In effect, it involves forces of the electrostatic type which tend to attract electrons from the anion to the cation; these forces can be described by the polarizing power z/r^2 . They are combated by forces of the covalent type which on the contrary tend to

distribute valence electrons in the orbitals of the anion and cation. The latter are represented by the electronegativity

It is interesting to compare the results of the three classifications (Table 2). The numerical values proposed by Zhang are in good agreement with Pearson's empirical classification. The values that we propose are also in agreement with the preceding values for the hardest (Be²⁺, Si⁴⁺, Al³⁺, ...) or softest cations (Cu⁺, Ti⁺, Ag⁺, Au⁺, ...). However, there are some differences. As an example, the K⁺ ion, considered as hard by Pearson and Zhang, would tend to be soft in our classification. We will see below that in the case of oxides, our proposition better accounts for effects of polarization of the O²⁻ counterion.

DISCUSSION

Pearson also proposed a classification for Lewis bases as a function of their base strength:

HARD	BORDERLINE	SOFT
F ⁻ , O ²⁻ , OH ⁻ , PO ₄ ³⁻ , Cl ⁻	Br	S ²⁻ , I ⁻ , H ⁻

We could ask whether this classification has any meaning in the case of ionic-covalent solids. In effect, it is logical to think that the basicity of

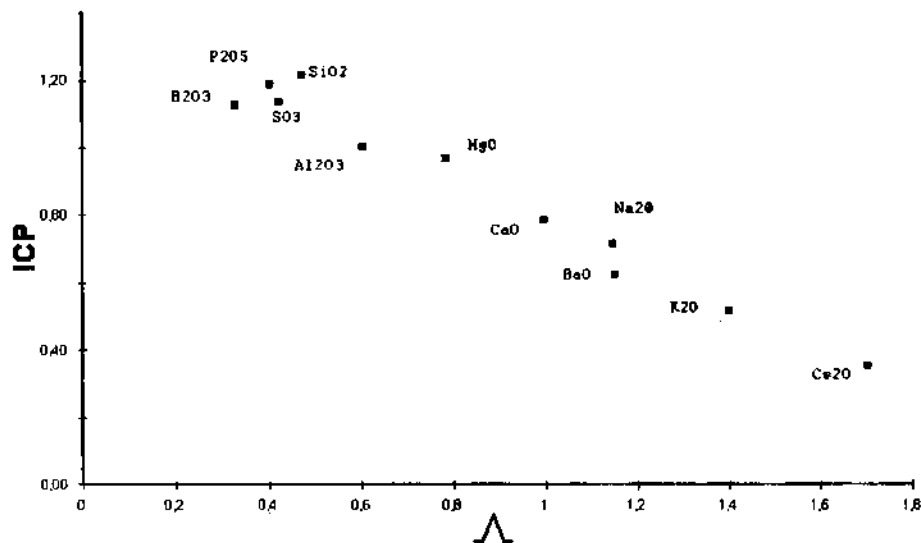


Fig. 2. Variation in the acidity of cations as a function of the optical basicity for some s and p oxides.

a given anion will be a function of the acidity of the counteranion which will induce its polarization. As a consequence, anions should have different base strengths as a function of the opposing cation.

In the case of oxides, this was clearly established by Duffy, who experimentally measured the basicity of the oxides with the chemical shift of the ultraviolet spectrum of a probe such as Pb^{2+} incorporated in an oxide.¹¹

Fig. 2 shows the variation in ICP as a function of the optical basicity A for some s and p oxides. Note that these two parameters are linearly correlated by the relation:

$$\text{ICP} = -0.64 A + 1.42 \quad (5)$$

We find that potassium, classified as hard by Pearson and Zhang, in fact seems to be soft if its optical basicity or the acidity (ICP) of K^+ is taken into consideration. This finding seems to justify the use of ICP [Equation 4] instead of Z [Equation 3] for calculating the acid strength of cations, at least in the case of ionic-covalent compounds.

Equation 5 shows that ICP or A can be used indifferently for describing an oxide. In effect, an oxygen ion of low base strength will correspond to a

cation with high acid strength and vice versa. We will use ICP rather than A in the remainder of this study. The data concerning the last parameter are in effect limited, while we have a complete set of ICP values.

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