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 -Al₂O₃ and β -Al₂O₃; 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 SnH₄ and PbH₄. 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. 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 in-

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

stance, 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 ns² 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 Pb2+ and Bi3+ 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 Si⁴⁺ (1.769) \leq Ge⁴⁺ (1.799) $>$ Sn⁴⁺ (1.583) \geq Pb⁴⁺ (1.557)

Generally, it is concluded that the electronegativities for the elements situated after the transition series produce the series second period \gg third period \approx fourth period >

fifth period ≈ 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.

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

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Received January 8, 1982

A scale for the Lewis acid strengths has been calculated from the dual parameter equation $Z = Z/r_k^2 - 7.7X_z + 8.0$. 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 Davies¹ 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"

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

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

Table I. Strengths of Lewis Acids

acids	$Z/r_{\mathbf{k}^2}$	Xz	Z	α/β^{7}	Y ⁸	$E_n^{\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	σ _A 10	f^{11}	SH _A ¹²	hardnes
Pt ²⁺	2.264	1.513	-1.386		4.82	· · · · · · ·		-1.60	-13.34	S
·u+	0.439	1.257	-1.240		5.95	-4.35		-3.97	-10.25	S
t ⁴⁺	5.285	1.880	-1.191							S
d ²⁺	2.000	1.452	-1.180	40=	4.27			-1.30	-8.61	S
g2+	1.486	1.370	-1.063	187	4.25	-4.64	4.6	-1.38	-5.33	S
.2+	2.525	1.499	-1.017							
u ³⁺	4.152	1.706	-0.984		3.90			-1.17		_
g ⁺	0.565	1.219	-0.821					-2.41	-8.88	S
)s ²⁺	2.841	1.509	-0.778	20.4	2.45	• • •				В
Cu+	0.857	1.233	-0.637	28.4	3.45	-2.30		-2.16	-6.72	S
[r ³⁺	4.462	1.698	-0.613		2.22	2.25	4.0	0.24	1 40	В
Tl ³⁺	2.855	1.485	-0.580		3.23	-3.37	4.3	-0.34	-1.42	S
Rh ²⁺	2.704	1.460	-0.538							
Os ³⁺	4.573	1.681	-0.371	165	2.00	2.02	4.3	2.41	5.00	c
Ag ⁺	0.601	1.161	-0.339	16.5	3.99	-2.82	4.2	-2.41	-5.92	S
Cd+	0.770	1.171	-0.247							
Ag ²⁺	2.742	1.425	-0.231	16.1	2 50		4.1	1.02	1.63	n
Pb ²⁺	1.389	1.241	-0.167	16.1	3.58		4.1	-1.03	-1.62	В
Te ⁴⁺	4.340	1.619	-0.126	12.5	2.04	2.04	2.5	0.39	2.19	S
Cd ²⁺	2.041	1.318	-0.108	12.5	3.04	-2.04	3.5	-0.24	-1.65	S
Tl ⁺	0.372	1.096	-0.067		3.78	-1.88		-1.67	-5.04	S
Ru ²⁺	3.048	1.434	0.006					-1.33	-0.83	В
Ge ²⁺	2.642	1.380	0.016					1.70		
Ir ⁴⁺	6.835	1.913	0.105					1.79		
W ⁴⁺ Cu ²⁺	6.250	1.832	0.144	0.7	3.00	0.55	2.1	1.00	1 7/	т.
	3.858	1.517	0.177	9.7	2.89	-0.55	3.1	-1.02	-1.74	В
Sn ²⁺	1.922	1.259	0.228		3.17			-1.08	2.44	В
[n ⁺	0.574	1.079	0.266		202	0.30	3.0	-1.59	2.22	n
Ni ²⁺ Mn ²⁺	3.858 3.287	1.502	0.293 0.307	07	2.82	0.29	2.0 2.0	0.46 0.56	-2.22	В
Cr ²⁺	3.287	1.426		8.7	3.03	0.01	2.0		-0.69	H
		1.402	0.330		2.06	0.91	1.0	0.56	1 6 1	В
Co²+ Tm²+	3.652	1.467	0.356		2.96		1.8	-0.20	-1.61	В
Fe ²⁺	1.461 3.463	1.180	0.375 0.390		3.09	0.69		-0.27	-0.09	В
Rh³+	5.333	1.438	0.390		3.09	0.09		0.07		В
Cr ³⁺		1.672			2.70	2.06			1.27	В
Ru³+	5.263 5.060	1.661	0.473		2.70	2.06		1.95	5.17	
Ru Bi ³⁺	3.255	1.634	0.478					0.42	1 02	D
Mo ⁴⁺	5.233 6.409	1.398	0.490					0.42	1.83	В
Tm ³⁺	2.884	1.805	0.511 0.543					2.03		
Tc ⁴⁺	6.491	1.343 1.810	0.554					2.03		
Pm ³⁺	2.435	1.281	0.571					1.38		
Ti ²⁺	2.000	1.224	0.575					1.50		
Nd ³⁺	2.379	1.272	0.585					1.33		
Dy ³⁺	2.711	1.314	0.593					1.60		
Er³+	2.828	1.328	0.602					1.66		
Ho ³⁺	2.768	1.320	0.604					1.63		
V^{2+}	2.974	1.346	0.610					1.03		
v Pr ³⁺	2.349	1.263	0.624					1.58		
Sb ³⁺	3.704	1.439	0.624					0.06	-1.91	В
Tb ³⁺	2.655	1.301	0.637					1.57	1.71	D
Zn ²⁺	3.652	1.428	0.656	5.4	2.34		3.1	0.40	-1.94	В
Ce ³⁺	2.268	1.428	0.658	٠.٦	2.57		3.1	1.53	4.65	Н
Sm ³⁺	2.488	1.248	0.638					1.70	₩.03	п
Pd ⁴⁺	7.017	1.858	0.710					1.61		
Gd³+	2.582	1.272	0.710					1.51		
Pb ⁴⁺	4.778	1.557	0.789					1.57		
La ³⁺	2.184	1.212	0.852			4.51	0.5	1.51	4.74	Н
Yb ²⁺	1.486	1.119	0.832			7.51	0.5	1.51	7./4	11
Lu³+	2.994	1.313	0.884					1.83		Н
Lu I ⁵⁺	6.840	1.805	0.884					0.02		H
In³+	4.152	1.445	1.026	6.9	2.24			1.40	2.06	Н
Ce ⁴⁺	3.921	1.412	1.028	0.7	- +≥ ¬			2.86	2.00	11
Eu²+	1.165	1.054	1.049					2.00		
Pr ⁴⁺	4.081	1.430	1.070							
V ³⁺	5.479	1.609	1.070							
Bi ^{s+}	6.173	1.698	1.098					3.56		
Th ⁴⁺	4.081	1.418	1.162					2.04	7.76	Н
Ba ²⁺	0.901	1.005	1.162	4.4	2.62	1.89	0.5	0.98	0.16	11
Ga ³⁺	5.194	1.562	1.167	5.0	2.04	1.45	0.5	2.54	3.38	Н
Yb³+	2.953	1.269	1.182	5.0		1.45		2.06	٠.٥٥	11
Co ³⁺	6.683	1.745	1.247		2.56			1.72	13.86	Н
As ³⁺	5.787	1.623	1.290		2.00			0.55	13.00	H
Nb ⁴⁺	5.949	1.642	1.306					0.55		11
Fe ³⁺	6.301	1.687	1.311	3.7	2.37	2.22	3.1	1.48	9.25	Н
		1.190	1.376	5.1	2.5 (J.1	1.46	7.23	**
Eu³+	2.539	1.170								

Table I (Continued)

acids	$Z/r_{\mathbf{k}^2}$	$X_{\mathbf{z}}$	Z	α/β^7	Y ⁸	$E_n^{\dagger 9}$	$\sigma_{\mathbf{A}}^{10}$	f ¹¹	SH _A ¹²	hardne
Mg ²⁺	2.704	1.208	1.402	5.8	0.87	2.42	1.4	1.68	4.47	Н
Sr ²⁺	1.148	1.004	1.417	13.0	2.08	2.21	0.6	0.97	3.19	Н
Ru ⁴⁺	7.935	1.882	1.444					2.16		
Hf4+	5.536	1.568	1.462					2.94	7.32	H
Y ³⁺	2.774	1.209	1.465				0.60	1.83	1.55	
Cs ⁺	0.305	0.886	1.483		2.73			0.69		
Rb ⁺	0.363	0.891	1.502					0.83		
Tb ⁴⁺	4.938	1.484	1.511							
K ⁺	0.433	0.897	1.526		0.92			0.55	0.61	Н
Rh4+	7.305	1.864	1.582					2.06		
Ca ²⁺	1.539	1.032	1.593	3.5	1.62	2.33	0.9	1.22	3.39	Н
Sn ⁴⁺	5.806	1.583	1.617					2.44	5.05	Н
H ⁺	11.111	2.271	1.624	0		0.42	2.28		5.87	H
Ti ³⁺	4.573	1.414	1.685	·				2.09		
Sc ³⁺	3.830	1.316	1.697					2.00	6.40	Н
Mn ³⁺	5.787	1.570	1.698					2.25	•	
Ta ⁵⁺	8.218	1.881	1.734					4.14		
Cr ⁴⁺	8.402	1.891	1.841							
Mn ⁴⁺	8.912	1.953	1.874							
Li ⁺	1.235	0.943	1.974		0.36	0.49		0.87	0.72	Н
Zr ⁴⁺	5.408	1.476	2.043		0.50	0.15		2.70	9.36	H
Be ²⁺	5.746	1.460	2.504			3.75		4.15	6.32	H
Nb ⁵⁺	8.218	1.771	2.581			3.75		4.24	0.52	**
Al ³⁺	6.584	1.499	3.042	0.6	0.70	6.01		3.70	8.35	Н
Os ⁶⁺	12.787	2.304	3.046	0.0	0.70	0.01		3.70	0.55	**
Ge ⁴⁺	8.911	1.799	3.059					4.35		
Ti ⁴⁺	7.207	1.577	3.064			4.35		3.30	12.13	Н
W ⁶⁺	11.574	2.132	3.158			4.55		4.90	12.13	**
Sb ⁵⁺	9.131	1.763	3.559					3.97		
Mo ⁶⁺	11.259	2.025	3.667					5.58		
P3+	8.918	1.699	3.836					5.50		
V ⁴⁺	10.078	1.827	4.010							
Tc ⁷⁺	14.286	2.312	4.484							
Te ⁶⁺	12.245	1.936	5.338					6.6		Н
Re ⁷⁺	15.594	2.359	5.403					7.9		**
V ⁵⁺	13.007	2.019	5.461					4.98		
As ⁵⁺	13.889	2.035	6.220					6.80		
I7+	15.594	2.142	7.101					8.7		Н
Mn ⁷⁺	19.444	2.573	7.632					12.9		H
S ⁴⁺	15.379	2.024	7.794					12.7		-11
Si ⁴⁺	13.717	1.769	8.096					6.57	13.68	Н
Cr ⁶⁺	17.836	2.290	8.203					7.1	27.48	Н
Se ⁶⁺	19.133	2.289	9.508					9.30	27.70	11
P5+	18.491	2.131	10.082					7.50		
B ³⁺	17.847	1.966	10.709					11.2		
Br ⁷⁺	24.920	2.529	13.447					11.4		
S ⁶⁺	32.450	2.479	21.362							
Cl7+	41.642	2.835	27.813					20.1	36.7	Н
\sim 1	71.072	2.536	32.917					21.4	30.7	n

^a Pearson classification: S, soft; H, hard; B, borderline.

to describe the species of class a and b. The hard species, both acids and bases, tend to be small, slightly polarizable species and soft acids and bases tend to be larger and more polarizable. Pearson then formulates a general principle (HSAB principle) according to which hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. Pearson has suggested that at least two factors are involved in acid-base interactions. One is the inherent strength. The other is the hardness or softness of the species involved. He has reported a four-parameter equation

$$\log K = S_{A}S_{B} + \sigma_{A}\sigma_{B} \tag{1}$$

where S is the strength factor and σ is the softness factor. The subscripts A and B indicate acid and base. This concept, however, enables the user to predict qualitatively the relative stability of acid-base adducts only in the case where the strength factor has been ignored. The weakness of the concept has been noted by Drago and Kabler⁴ and Myers.⁵

Drago and Wayland⁶ have proposed a quantitative equation for correlating enthalpies of adduct formation in nonpolar solvents. This equation has the form

$$-\Delta H = E_{\rm A} E_{\rm B} + C_{\rm A} C_{\rm B} \tag{2}$$

where E_A and E_B relate to the tendencies of acids and bases, respectively, to undergo electrostatic bonding and C_A and C_B are similar tendencies to undergo covalent bonding. This equation accurately depicts the essence of the strength of bonding and gives excellent agreement with experiment.

Over the years there have been many attempts⁷⁻¹² to find

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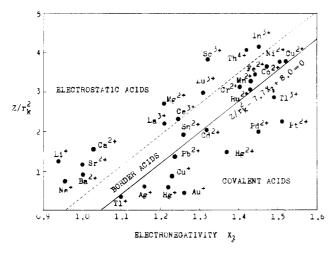


Figure 1. Electrostatic or covalent nature of Lewis acids.

empirical parameters to establish a quantitative scale for metal ion Lewis acids. On the basis of these enlightening works, a new quantitative scale for the strengths of metal ion Lewis acids is given in the present study. Its advantages include useful predictive power, explicit physical meaning, and easy treatment.

Data and Calculations

Mulliken's ionic-covalent model¹³ has indicated that the donor-acceptor bonding molecular orbital is described as a linear combination of covalent (charge-transfer) and electrostatic wave functions. The Drago-Wayland E-C equation has pointed out that the proper combination of electrostatic and covalent factors that can contribute to donor strength and acceptor strength should produce a close approximation to the enthalpy of adduct formation.⁶ The Lewis acid strength could be composed of some electrostatic and some covalent properties. The electrostatic force between a positive charge and a negative charge is approximately proportional to Z/r_k^2 , where Z is the charge number of the atomic core (i.e., the number of valence electrons) and r_k is the ionic radius, which must operate in such a way that the stability of the complex rises with the increase in charge of the metal ion and fall with an increase in its radius. Apart from electrostatic force there appears to be covalent force. Since the σ bond is formed by sharing of an electron pair between the metal ion and the ligand, its strength is found to increase with the tendency of the cation to take electrons, i.e., with increasing electronegativity of the metal ion involved. The electronegativity values we have adopted here are the ones in valence states that we proposed previously. The other electronegativity values, as shown by f values of ref 11 in Table I, could not obtain very good results. The quantity Z/r_k^2 was calculated, with use of ionic radii mainly from Shannon¹⁴ and Dean.¹⁵ Thus the ideal results, as shown in Figure 1, are obtained by plotting Z/r_k^2 against X_z . The equation for classification is derived as

$$Z/r_{\rm k}^2 - 7.7X_{\rm z} + 8.0 = 0 \tag{3}$$

and we define the function Z as the scale for strengths of Lewis acids by

$$Z = Z/r_k^2 - 7.7X_z + 8.0 (4)$$

The values of the scale for the strengths of 126 metal ion Lewis acids are calculated from eq 4 and listed in Table I along with those values proposed by other authors.

Results and Discussion

Classification of Metal Ions. Interestingly, when Figure 1 is compared with Table I, it is clear that all metal ions are divided into three parts. The metal ions in which there is clear dominance by the electrostatic force Z/r_k^2 congregate in the top left-hand corner of the figure and have Z values higher than 0.66. We call these acids large electrostatic acids, or simply E acids. The metal ions in which there is clear dominance by the electronegativity X_z , i.e., with a large covalent property, congregate in the bottom right-hand corner of the figure and have Z values lower than zero. We call these acids large covalent acids, or simply C acids. The metal ions lying between E and C acids and having Z values higher than zero and lower than 0.66 are border acids, or simply B acids.

The Z value gives a quantitative order of relative Pearson hardness or softness for the various Lewis acids and agrees fairly well with the Pearson classification.³ The result also agrees extremely well with previous works, 7-10,12 especially with the works of Yinst and McDaniel, ⁷ Klopman, ⁹ and Ahrland. ¹⁰ It does not agree well with ref 11 as it adopted qualitative electronegativity, which is not appropriate for quantitative applications.

Stability Constants of Metal Ions. Although they are not included within the above classifications, there are some other useful gradations.

For a given ligand, corresponding stability constants of complexes of bivalent metal ions of the first transition series are usually in the Irving-Williams order. 16 The sequence of Z values tend to follow this order as listed below and compared with corresponding stability constants with the ligand SCN⁻:

	Mn ²⁺	Fe ²⁺	Co2+	Ni ²⁺	Cu2+	Zn2+
Z	0.307	0.390	0.356	0.293	0.177	0.656
$\log \beta$,	1.23	1.0	1.01	1.2	1.7	0.5

For non-transition-metal ions complex stability decreases as the order of magnitude of Z decreases. For example, stability constants of the metal ions in group 1A with the ligand P₄O₁₃⁶⁻ decrease in the order

	1A						
	Li ⁺	Na ⁺	K+	Rb+	Cs⁺		
Z	1.974	1.382	1.526	1.502	1.483		

the metal ions in group 2A with the ligand Tiron in the order

		2A							
	Be ²⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺				
Z	2.504	1.402	1.593	1.417	1.163				
$\log \beta_1$	12.88	6.86	5.8	4.55	4.1				

and the metal ions in group 3A with the ligand malonic acid in the order

	3A					
	A13+	Sc ³⁺	Y ³⁺	La ³⁺		
Z	3.042	1.697	1.465	0.852		
$\log \beta_1$	5.24		4.40	3.69		

Both sodium and magnesium form less stable compounds than would be expected on the basis of the behavior of their lighter (Li, Be) and heavier (K, Ca) congeners.¹⁷ These elements are those that follow immediately after the first filling of a

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Table II Correlation of Lawis Acid

Table II. Correlation of Lewis Acid Strengths Z with Electron Configurations^a

	8		1B	2 B	3B	48
Pe	Co	Ni	Cu	Zn	G ₉ .	Ge
a ⁵ (3)1.311	a ⁶ (3)1.247	a ⁷ (3)0.370	a9(2)0~77	d ¹⁰ (2)0.656	a ¹⁰ (3)1.167	g ¹⁰ (4)3.059
a ⁶ (2)0.390	a ⁷ (2)0.356	a ⁸ (2)0.293	a ¹⁰ (1)-0.63%	$s^{1}(1) = 0.311$	s ² (1)0.210	s ² (2)0.016
Ru	Rh	Æd	Ag	Cd	In	Sn
a ⁵ (3)0.478	a ⁶ (3)0.459/	a ⁶ (4)0.710	d ⁹ (2)-0.231	a ¹⁰ (2)-0.108	a ¹⁰ (3)1.026	a ¹⁰ (4)1.617
a ⁶ (2)0.006	a ⁷ (2)-0.538	a ⁸ (2)-1.180	d ¹⁰ (1)-0.339	s ¹ (1)-0.247	In d ¹⁰ (3)1.026 s ² (1)0.266	a ² (2)0.228
0з /	Ir	Pt	Au	Нg	Tl	Pb
a ⁵ (3)=0.371	a ⁶ (3)-0.613	d ⁶ (4)-1.191	d ⁸ (3)-0.984	a ¹⁰ (2)-1.063	$\frac{d^{10}(3)-0.580}{2}$	a ¹⁰ (4)0.789
d ⁶ (2)-0.778	a ⁷ (2)-1.017	a ⁸ (2)-1.386	d ¹⁰ (1)-1.240	s ¹ (1)-0.821	s ² (1)-0.067	s ² (2)-0.167

^a C acids are underlined. The numerals in parentheses are charge numbers.

set of p orbitals (Ne), and the effects of incomplete shielding presumably are operative here. This coincides with Z values.

The stability constants of the metal ions within the triangular shape area of the periodic table with the ligands of most C (or soft) bases such as CN⁻ in the order of magnitude of Z

The data of the stability constants we cited above are all from ref 18.

Catalytic Activity of Metal Ions. Germain¹⁹ has proposed that if the deforming power q/r^2 of the cation is taken as a measure of its hardness, the following sequences of decreasing selectivity are expected

(a)
$$V^{5+} > Mo^{6+}$$
, $W^{6+} > Nb^{5+}$, $V^{4+} > Ti^{4+} > Zr^{4+} > Th^{4+}$

(b)
$$Sb^{5+} > Sn^{4+} > Pb^{4+} > Sb^{3+} > Bi^{3+}, Pb^{2+} > Cu^{+} > Ag^{+}$$

and vanadium, molybdenum, and tungsten oxides are in the first ranks of selectivity sequences in allylic or benzylic oxidations. The only notable inconsistency is the position of cuprous oxide; the interaction between the C acid and the C base may not be correctly described by the deforming power of the cation of class b elements. Here if we take Z values as Lewis acid strengths, the correct sequences are obtained:

(a)
$$V^{5+}$$
 (5.461) > Mo^{6+} (3.667), W^{6+} (3.158) > Nb^{5+} (2.581), V^{4+} (4.010) > Ti^{4+} (3.064) > Zr^{4+} (2.043) > Th^{4+} (1.162)

(b)
$$Sb^{5+}$$
 (3.559) > Sn^{4+} (1.617) > Pb^{4+} (0.789) > Sb^{3+} (0.624) > Bi^{3+} (0.490), Pb^{2+} (-0.167) > Ag^+ (-0.339) > Cu^+ (-0.637)

It appears that the position of cuprous oxide in Lewis acid strength Z is different from that in deforming power q/r^2 .

Stability constants of Pb²⁺, Ag⁺, and Cu⁺ with the ligand SCN⁻ were obtained, ¹⁸ which confirmed this expectation:

Pb²⁺ Ag⁺ Cu⁺ log
$$β_2$$
 1.4 8.2 11.0

Influence of the Electron Configuration. It is clear from Table II that all C acids have a large number of d electrons in their outer shell and the C (large covalent) properties increase with the number of d electrons. Many of the most typical C acids even have their outer d shells completely full, i.e., the configuration d¹⁰, but also the configurations d⁸ and d⁶ often result in very strong C properties. Acids with less than six d electrons never exhibit very strong C properties, and less than five means E (large electrostatic) properties.

It is interesting from the survey contained in Table II that all C acids happen to congregate in a triangular shape at the end of the transition series. This expresses the rather natural fact that the mere existence of d electrons is not sufficient to create the covalent bonding involved in C type coordination (C acid-C base). The C acids must further be highly polarizable. The C properties of an acid of a certain type will therefore be more marked, the higher the period it belongs to. This accounts for the well-known triangular shape of the area within the periodic table comprising the most typical C acids. 1,20

In front of the transition series, the acids do not contain any d electrons and do not exhibit any C properties, although some of them are highly polarizable. Beyond the end of the transition series, since further electrons in shells outside the d shell cause a considerable decrease in the shielding of the d shell, the acids no longer possess the typical C properties.

Conclusion

The various applications discussed in this paper demonstrate that both the scale for electronegativities of elements in valence states and the scale for strengths of Lewis acids do describe a wide range of chemical phenomena in a quantitative way. They can have useful predictive power, and the treatment can be handled easily. In this case the two scales can be of value by calling attention to the need for further consideration.

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