[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Correlation of Relative Rates and Equilibria with a Double Basicity Scale

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A new equation, which is a combination of a nucleophilic scale and a basicity scale, is presented for the correlation of the reactions of electron donors. A new nucleophilic scale for donors, based on electrode potentials, is devised. Data used to test the equation and the scale include rates of displacement reactions of carbon, oxygen, hydrogen and sulfur, and equilibrium constants for complex ion associations, solubility products and iodine and sulfur displacements. The results are good for most of the correlations, and are especially encouraging for those cases, such as complex ion constants, which have been treated heretofore only qualitatively. Advantages and consequences of a double basicity scale for electron donors are discussed briefly.

It has been known for some time that rates of nucleophilic displacements on alkyl carbon atoms do not follow the normal basicities (to protons) of the entering electron donors.[1] Recently, a linear free energy relationship, based on the displacement rates of methyl bromide as standard substrate, was employed by Swain and Scott[2] (hereafter S.S.) to correlate many rate data. The rates of nucleophilic displacements in aromatic compounds follow similar patterns as those in aliphatic compounds but there appears to be a greater dependence on the basicity of the entering donor.[3] Similar difficulties involving lack of correlation of basicity to protons with basicity to Lewis acids (such as aqueous cations[4,5]) and to formally positive sulfur compounds[6,7] are also well established. Although there has been no quantitative treatment of these data to date, Foss[6,7] pointed out that there appears to be a relationship between nucleophilic character and electrode potentials.

In this study, the correlation of many rate data (of the nucleophilic displacement type) and equilibrium data (involving some degree of covalent bond formation) has been attempted. The equation

$$\log\left(\frac{K}{K_0}\right) = \alpha E_n + \beta H \qquad (1)$$

where K/K_0 is a relative (to water) rate or equilibrium constant,[8] E_n is a nucleophilic constant characteristic of an electron donor, H is the relative basicity of the donor to protons, and α and β are substrate constants, has been used for these correlations. The calculations have been made by using a least squares analysis of the observed data to determine α and β. In many cases, K_0 is known, but in others it is necessary to treat K_0 as an additional parameter.

The H Scale.—For one standard reaction of donors, the basicity to protons is used. The normal pK_a values of the conjugate acids in aqueous solution are employed; they are changed, however, by the addition of the constant 1.74 which is the correction for the pK_a of H_3O^+. By definition

$$H = pKa + 1.74$$

Many of the needed pK_a values are either unknown or poorly known. This is true for HCl, HBr, HI, HSCN and others; estimated values are employed in these cases. In Table I, H values for the donors (for which the symbol N is used) are presented; those values which are estimates are placed in parentheses.

TABLE I

ELECTRODE POTENTIALS AND DONOR CONSTANTS

N	E^{0a}	E_n	H
NO_3^-	......	0.29^e	(0.40)
$SO_4^=$	−2.01	.59	3.74
$ClCH_2COO^-$	......	$.79^f$	4.54
CH_3COO^-	......	$.95^g$	6.46
C_5H_5N	......	1.20^h	7.04
Cl^-	−1.3595	1.24	(−3.00)
$C_6H_5O^-$	......	1.46^i	11.74
Br^-	−1.087	1.51	(−6.00)
N_3^-	......	1.58^j	6.46
OH^-	−0.95	1.65	17.48
NO_2^-	− .87	1.73	5.09
$C_6H_5NH_2$	......	1.78^j	6.28
SCN^-	− .77	1.83	(1.00)
NH_3	− .76	1.84	11.22
$(CH_3O)_2POS^-$	$-\ .56^b$	2.04	(4.00)
$C_2H_5SO_2S^-$	$-\ .54^b$	2.06	(−5.00)
I^-	− .5355	2.06	(−9.00)
$(C_2H_5O)_2POS^-$	$-\ .53^b$	2.07	(4.00)
$CH_3C_6H_4SO_2S^-$	$-\ .49^b$	2.11	(−6.00)
$SC(NH_2)_2$	$-\ .42^c$	2.18	0.80
$S_2O_3^=$	− .08	2.52	3.60
$SO_3^=$	− .03	2.57	9.00
CN^-	$.19^d$	2.79	10.88
$S^=$	.48	3.08	14.66

[a] Data from ref. 9, except where indicated otherwise. [b] Ref. 7. [c] P. W. Preisler and L. Berger, THIS JOURNAL 69, 322 (1947). [d] Assuming the free energy change for the reaction $C_2N_2(g) \rightleftarrows C_2N_2(aq)$ is negligible. [e] Calculated from $Hg(NO_3)_2$ complex; ref. 5. [f] Calculated from $Ag(ClCH_2COO)_2^-$ complex. [g] Calculated from epichlorohydrin rate. [h] Calculated from mustard cation rate. [i] Calculated from ICH_2COO^- rate. [j] Calculated from methyl bromide rate.

The E_n Scale.—A search was made for a standard state for the nucleophilic character of a donor which would be more fundamental than rates of reaction with an arbitrary substrate. While nucleophilic character is strongly linked to electron polarizability, it is difficult to relate the measured

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[1] (a) P. D. Bartlett and G. Small, THIS JOURNAL, **72**, 4867 (1950); (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Chapter VII, pp. 306–418; (c) E. D. Hughes, *Quart. Revs.*, **5**, 245 (1951).

[2] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

[3] (a) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951); (b) Ref. 1b, Chapter XV, pp. 797–815.

[4] E. C. Lingafelter, THIS JOURNAL, **63**, 1999 (1941).

[5] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[6] O. Foss, *Kgl. Norske Vid. Selsk. Skrifter*, **2** (1945).

[7] (a) O. Foss, *Acta Chem. Scand.*, **1**, 8 (1947); (b) **1**, 307 (1947); (c) **3**, 1385 (1949).

[8] Wherever possible, data for room temperature (18–25°) and aqueous solution will be used.

polarizability of a donor particle to the nucleophilic strength of a specific part of this donor.

Inspection of electrode potentials given by Latimer[9] for oxidative dimerizations of the type

$$2I^- \rightleftharpoons I_2 + 2e^-$$

showed that these potentials become more positive in the same order as the *n* values of S.S. become larger. That the relationship is a linear one may be seen in Fig. 1; in this figure the data for the six donors for which there are reliable data are presented.

As all of the rate and equilibrium constants correlated in this study are values relative to the water values, the potential for the couple

$$2H_2O \rightleftharpoons H_4O_2^{+2} + 2e^-$$

is needed. However, it is not reported[9] and there does not appear to be any way to calculate it from the present thermodynamic data. It was, therefore, necessary to calculate a value for this couple by means of a least squares correlation of the data shown in Fig. 1. From this calculation the potential value -2.60 is obtained for the above couple.[10]

From the value of the potential of the couple and the values of the oxidation potentials of the donors, a nucleophilic scale defined by the equation

$$E_n = E° + 2.60$$

is set up. In Table I, E_n values for all of the donors to be correlated are presented. In the absence of electrode potential data, E_n values were obtained by secondary standardizations; for example, the E_n value for $ClCH_2COO^-$ was obtained using the known formation constant for the complex $Ag(ClCH_2COO)_2^-$, the known *H* value for $ClCH_2COO^-$ and the values of α and β found for other complexes containing a silver ion and two donors.

Displacement Rates on Carbon.—S.S. correlated the rates of nucleophilic displacements on carbon with eight substrates. For six of these substrates, the experimental data can be reasonably well correlated using only the αE_n term. For mustard cation and β-propiolactone, however, the results show a skewness which can best be interpreted as the need for the βH term. For example, with OH^- attacking the mustard cation, the former calculated rate[2] was over forty-fold lower than the observed rate.

For comparison of the present correlation with that of S.S., log (K/K_0) data are presented in Table II. The deviations of the calculated from the observed values using equation 1 are all less than 0.30, *i.e.*, a factor of 2, and the average deviation for the 13 pieces of data calculated using equation 1 is 0.14. Concerning the need for the βH term in these correlations, it is pertinent to point out that the calculated values using the equation of S.S. are low for OH^-, CH_3COO^-, $C_6H_5NH_2$ and $S_2O_3^=$, are high for Br^- and I^-, and are close to the observed values for SCN^- and Cl^-. Only in one case (Cl^- with mustard cation) is the deviation significantly inverted to the direction one would expect because of the lack of a βH term.

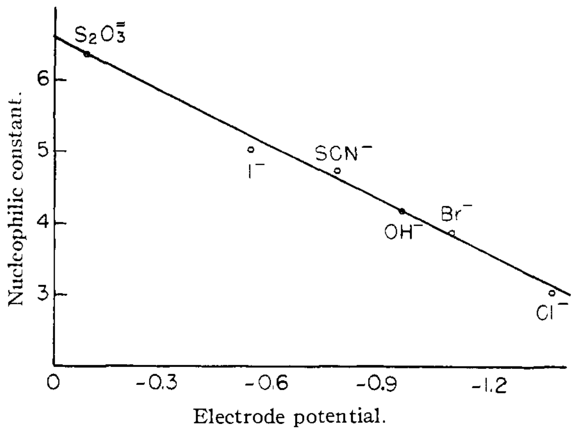

Fig. 1.—The linear relation between the nucleophilic constant of Swain and Scott and the electrode potential.

TABLE II

CORRELATIONS OF TWO DISPLACEMENTS ON CARBON

	β-Propiolactone			Mustard cation		
N	Obsd.[a]	Calcd.[b]	S.S.[c]	Obsd.[d]	Calcd.[e]	S.S.[c]
CH_3COO^-	2.49	2.35	2.10	2.72	2.80	2.58
Cl^-	2.26	2.27	2.34	3.04	2.81	2.89
Br^-	2.77	2.60	3.00	..	..	..
OH^-	6.08[f]	..	..	5.62	5.33	3.99
$C_6H_5NH_2$	..	..	..	4.60	4.82	4.26
SCN^-	3.58	3.74	3.67	4.54	4.54	4.53
I^-	3.48	3.51	3.87	4.54	4.37	4.79
$S_2O_3^=$	5.28	5.30	4.90	6.15	6.43	6.04

[a] Data of ref. 1a. [b] Calculated using α = 2.00 and β = 0.069. [c] Calculated by S.S. [d] Data of ref. 11 and 2. [e] Calculated using α = 2.45 and β = 0.074. [f] This rate is not comparable with the others since OH^- reacts with β-lactones in a manner different from that of other donors.

There are other pieces of data from the studies on mustard cation[11] which can be correlated by equation 1. These are presented in Table III. The results are poorer, especially for thiourea. Since thiourea is about twenty times more nucleophilic to alkyl bromides than is pyridine,[12] it is difficult to understand why the two donors should show quite similar reactivities to mustard cation.

TABLE III

OTHER DISPLACEMENTS ON MUSTARD CATION

N	Obsd.[a]	Calcd.[b]
$SO_4^=$	2.41	1.72
C_5H_5N	3.45[c]	..
$SC(NH_2)_2$	3.90	5.39
$CH_3C_6H_4SO_2S^-$	4.43	4.73
$(C_2H_5O)_2POS^-$	5.34	5.36

[a] Ref. 11. [b] Calculated using α = 2.446 and β = 0.0741. [c] Used as secondary standard.

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[9] W. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

[10] This value is quite reasonable for it is more negative than -1.77 which is the potential for the couple

$$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e^-$$

and the equilibrium constant for the reaction

$$H_4O_2^{+2} \rightleftharpoons H_2O_2 + 2H^+$$

is overwhelmingly in favor of the right side.

[11] A. G. Ogston, E. R. Holiday, J. St. L. Philpot and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948).

[12] R. G. Pearson, S. H. Langer, F. V. Williams and W. J. McGuire, THIS JOURNAL, **74**, 5130 (1952).

In Table IV, the results for ten series of displacements on carbon are presented. Of the 59 pieces of data, four were used for secondary standards and for only two did the calculated rate differ from the observed rate by more than an order of magnitude. One of these two cases is shown in Table III; the other is with CN^- replacing I^- in ICH_2COO^- with the calculated rate being high by almost two orders of magnitude.

TABLE IV

SUBSTRATE CONSTANTS FOR DISPLACEMENT ON CARBON

Substrate	M^a	α	β
Ethyl tosylate[b]	5	1.68	0.014
Benzyl chloride[c]	3	3.53	− .128
β-Propiolactone[d]	7	2.00	.069
Epichlorohydrin[e]	6	2.46	.036
Glycidol[e]	6	2.52	.000
Mustard cation[f]	12	2.45	.074
Methyl bromide[g]	6	2.50	.006
Benzoyl chloride[h]	4	3.56	.008
Diazoacetone[i]	4	2.37	.191
Iodoacetate anion[j]	6[k]	2.59	− .052

[a] Number of bases correlated including H_2O. The relative rates are given along with experimental conditions in Table I of ref. 2, except for diazoacetone and iodoacetate ion. [b] H. R. McCleary and L. P. Hammett, THIS JOURNAL, **63**, 2254 (1941). [c] G. W. Beste and L. P. Hammett, *ibid.*, **62**, 2481 (1940). [d] Ref. 1a. [e] J. N. Brönsted, M. Kilpatrick and M. Kilpatrick, *ibid.*, **51**, 428 (1929). [f] Ref. 2 and 11. [g] Ref. 2; E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **45**, 167 (1949); A. Slator and D. F. Twiss, *J. Chem. Soc.*, **95**, 93 (1909). [h] Ref. 2. [i] C. E. McCauley and C. V. King, THIS JOURNAL, **74**, 6221 (1952), in water at 25°. [j] H. J. Backer and W. H. van Mels, *Rec. trav. chim.*, **49**, 177, 363, 457 (1930); C. Wagner, *Z. physik. Chem.*, **A115**, 121 (1925); in water at 25°. [k] Since the K_0 value is not known, it was necessary to calculate it in the least squares analysis. The calculated log K_0 value is −6.25. The rate with CN^- was not used in the least squares as it is inconsistent with the other data.

In their review, Bunnett and Zahler[3a] point out that there have been no experiments designed to elucidate the order of nucleophilic strength of donors toward aromatic carbon displacements. They do, however, give preliminary data in their Tables 31 and 32 which indicate that the basicity to protons is important in the nucleophilic character of the entering group. The approximate order of strength found (with 1-chloro-2,4-dinitrobenzene as substrate under a variety of conditions; see ref. 3) is

$$SO_3^{=} \sim OH^- > C_6H_5O^- > C_6H_5NH_2 > NH_3 > I^- > Br^-$$

The halogens are much less reactive than are the donors which have higher *H* values. It is apparent that displacements on aromatic carbons cannot be correlated with displacements on aliphatic carbons by means of a single scale of base strength; rather a double scale such as equation 1 will be required.

Displacement Rates on Hydrogen.—In only one case, the mutarotation of glucose, is there an adequate amount of data to test equation 1. These data are presented in Table IVA; the observed relative rates are compared with calculated values from equation 1 in column three and with values calculated by the Brönsted equation[13] (modified to give relative rates) in the last column. The new calculation gives excellent results (average deviation = 0.08).

Although the data on the enolization of acetone do not include as many donors, it is important to note that the deviations from Brönsted's equation are in the opposite direction to those for the mutarotation of glucose. Acetate ion is high relative to H_2O and OH^- [14] which indicates the need for a positive value of α. For this reason, poor results are obtained if the acetone and glucose data are plotted in accordance with the ideas of Pfluger.[15] Further, the fact that deviations are in both directions from the proton basicity scale indicates that statistical factors, and perhaps steric factors, are secondary in comparison to some more fundamental cause of deviation with these two substrates.

TABLE IVA

RELATIVE RATES IN MUTAROTATION OF GLUCOSE

N	Obsd.[a]	Calcd. (1)[b]	Brönsted[c]
$SO_4^{=}$	1.61	1.52	1.56
$ClCH_2COO^-$	1.74	1.75	1.90
CH_3COO^-	2.43	2.60	2.70
C_5H_5N	2.92	2.82	2.94
NH_3	4.47	4.53	4.69
OH^-	7.60	7.56	7.31

[a] J. N. Brönsted and E. A. Guggenheim, THIS JOURNAL, **49**, 2554 (1927); and G. Kilde and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **49**, 243 (1953). [b] Calculated using $\alpha = -0.407$ and $\beta = 0.4705$. [c] Calculated using $\beta = 0.418$.

Displacement Rates on Oxygen.—Reactions of hydrogen peroxide with electron donors have rate laws which indicate that the mechanism involves displacement on oxygen.[16] In Table IVB, the correlations for two groups of rate constants of H_2O_2 reactions are presented. The agreement of calculated and observed values is satisfactory for the average deviation is 0.26 and the maximum deviation is 0.46. It is apparent, moreover, that these rates would be poorly correlated by either the E_n scale or the *H* scale alone.

TABLE IVB

OXIDATIONS BY HYDROGEN PEROXIDE[a]

	Rate law I		Rate law 11	
Base	Obsd.	Calcd.[b]	Obsd.	Calcd.[c]
Cl^- [d]	−6.96	−7.33	−4.30	−4.54
Br^- [d]	−4.64	−4.43	−1.85	−2.31
I^- [e]	−0.16	0.22	1.02	1.40
$S_2O_3^{=}$ [f]	−1.61	−1.84	0.22	0.27
CN^- [g]	−3.00	−3.01	....	....

[a] For details concerning the mechanisms, etc., see ref. 16. [b] Calculated using $\alpha = 6.31$, $\beta = -0.394$ and log $K_0 = -16.33$. [c] Calculated using $\alpha = 5.20$, $\beta = -0.279$ and log $K_0 = -11.83$. [d] A. Mohammed and H. A. Liebhafsky, THIS JOURNAL, **56**, 1680 (1934). [e] H. A. Liebhafsky and A. Mohammed, *ibid.*, **55**, 3977 (1933). [f] E. Abel, *Monatsh.*, **28**, 1239 (1907). [g] O. Masson, *J. Chem. Soc.*, 91, 1449 (1907).

Since the data available for the reactions of H_2O_2 with donors do not include the water rate, it is necessary to employ equation 1 in the long form

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(13) J. N. Brönsted, *Chem. Revs.*, **5**, 231 (1928).

(14) (a) H. M. Dawson and E. Spivey, *J. Chem. Soc.*, 2180 (1930); (b) C. G. Swain, THIS JOURNAL, **72**, 4578 (1950); (c) R. P. Bell and P. Jones, *J. Chem. Soc.*, 88 (1953).

(15) H. L. Pfluger, THIS JOURNAL, **60**, 1513 (1932).

(16) J. O. Edwards, *J. Phys. Chem.*, **56**, 279 (1952).

and to solve this equation using K_0 as an additional parameter.

There is another test which can be used to check the validity of these correlations. This test concerns the reaction of H_2O_2 with either H_2O or OH^- to give oxygen atom exchange. Using the correlation for rate law I, it is calculated that the second-order rate constant for the reaction

$$HOOH + \overset{*}{O}H^- \rightleftharpoons HO\overset{*}{O}H + OH^-$$

should be about 2×10^{-13} liter/mole/sec. Using the correlation for rate law II, it is calculated that the first-order rate constant for the reaction

$$HOOH + H\overset{*}{O}H \rightleftharpoons HO\overset{*}{O}H + HOH$$

is about 1×10^{-10} per sec. in normal acid. These calculations predict that the rate of oxygen isotope exchange of H_2O_2 with H_2O is extremely slow in aqueous solution at room temperature. It is reassuring to find that the exchange of labeled oxygen atoms between H_2O_2 and H_2O has never been observed.[17]

Although the lack of observed isotope exchange is not a quantitative test for the validity of log K_0 (the "calculated water rate") the predictions based on the calculated rate constants are certainly borne out qualitatively.

Ross[18] found that H_2O_2 oxidized $(HOC_2H_4)_2S$ to the corresponding sulfoxide with the same type of rate behavior as had been found for the oxidations of $S_2O_3^=$ and the halide ions.[16] Unfortunately, neither E_n nor H is known for this compound but it certainly should be strongly nucleophilic while being a weak base to protons. The nature of the product also indicates that displacement on oxygen in H_2O_2 has transpired.

Displacement Rates on Chalcogens.—Although there are few quantitative data available, it seems probable that the rates of displacements on the chalcogens can be correlated using equation 1.

It was found[2] that the rates of displacement of Cl^- from benzenesulfonyl chloride in 50% water–50% acetone at 0.5° decrease in the order

$$OH^- > C_6H_5NH_2 > H_2O$$

Using equation 1 and the observed rates, the values calculated for α and β are 2.56 and 0.094, respectively.

Foss[7c] has found that catalysis of the decomposition of monotelluropentathionate ion by bases decreases in the order

$$OH^- > S_2O_3^= > I^- > H_2O$$

and that CH_3COO^- probably is a catalyst while Cl^- does not appear to be one. In the decompositions of $S_5O_6^=$ and $SeS_4O_6^=$, OH^- is a better catalyst than $S_2O_3^=$. Evidence that the decomposition is initiated by a displacement reaction is discussed by Foss[7c]; the fact[19] that the reaction of $S_5O_6^=$ and OH^- follows bimolecular kinetics is in agreement with a displacement mechanism in the rate-determining step. In order to correlate these data, both αE_n and βH terms probably are necessary.

Bases which react with polythionates and related compounds but do not appear to cause decomposition are CN^-, $SO_3^=$, $S^=$, $C_5H_{10}NH$, mercaptide ions, xanthate ions and dithiocarbamate ions; the products of these reactions indicate that displacements on sulfur have occurred.[6,7] The reactions of $S_4O_6^=$ and $S_5O_6^=$ with CN^- and $SO_3^=$ have been subjected to kinetic study[20–22]; all four reactions are bimolecular, all are rapid and in each case $S_5O_6^=$ reacts faster than $S_4O_6^=$. In the case of the $SO_3^=$ reactions, tracer studies[23] have proved that these reactions are indeed displacements. The recent tracer studies of the reaction of $S^=$ with $S_4O_6^=$ [24] are also in agreement with a displacement mechanism.

One can conclude from the data available for displacements on chalcogens that the donors which are most active usually are both strongly nucleophilic and strongly basic to protons. Alternatively, any correlations of chalcogen reactions will probably require positive values for both α and β.

Complex Ion Equilibria.—Using equation 1 and the values of E_n and H from Table I, the correlation of equilibrium, as well as rate, data has been attempted. The results of fourteen correlations of complex ion formation constants are presented in Table V; in Table VI, the values of α and β (obtained by least squares analysis of the observed constants) used to calculate the formation constants are given. As both of the standard states employed in this study are systems which involve covalent bonding to a fair degree, only those complex ions for which there is quite a bit of covalent character can be correlated by equation I.

Since these formation constants are really relative constants to water (the cations are undoubtedly hydrated), the value of log K_0 for equation 1 used for these correlations was 1.74 times the coördinated number of the cation for the particular series being investigated. For example, in the correlation of Hg^{+2} complexes, the values 1.74, 3.48 and 6.96 were used for HgN^{+2}, HgN_2^{+2} and HgN_4^{+2}, respectively. It is assumed that each entering donor replaces a water molecule; this is very likely a valid assumption.

The observed values in Table V for AgN_2^+, HgN_2^{+2}, CdN_4^{+2}, ZnN_4^{+2}, CuN_2^+ and CuN_4^{+2} come, with a few exceptions, from the review by Bjerrum.[5] A larger number of other values have been taken from this review[5] and from the book by Latimer.[9] Listings of Hg^{+2} complexes with the halides are given by Sillen,[25] of $SO_4^=$ complexes by Whiteker and Davidson,[26] of Fe^{+3} complexes by

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[17] (a) E. R. S. Winter and H. V. A. Briscoe, THIS JOURNAL, **73**, 496 (1951); (b) P. Baertschi, *Experientia*, **7**, 215 (1951); (c) J. Halperin and H. Taube, THIS JOURNAL, **74**, 380 (1952); (d) M. Dole, G. Muchow, DeF. P. Rudd and C. Comte, *J. Chem. Phys.*, **20**, 961 (1952).

[18] S. D. Ross, THIS JOURNAL, **68**, 1484 (1946).

[19] J. A. Christiansen, W. Drost-Hansen and A. E. Nielsen, *Acta Chem. Scand.*, **6**, 333 (1952).

[20] F. Ishikawa, *Z. physik. Chem.*, **130**, 73 (1930).

[21] F. Foerster and K. Centner, *Z. anorg. Chem.*, **157**, 45 (1926).

[22] B. Foresti, *Z. anorg. allgem. Chem.*, **217**, 33 (1934).

[23] J. A. Christiansen and W. Drost-Hansen, *Nature*, **164**, 759 (1949).

[24] (a) H. B. v. d. Heijde and A. H. W. Aten, Jr., THIS JOURNAL, **74**, 3706 (1952); (b) H. B. v. d. Heijde, *Rec. trav. chim.*, **72**, 510 (1953).

[25] L. G. Sillen, *Acta Chem. Scand.*, **3**, 539 (1949).

[26] R. A. Whiteker and N. Davidson, THIS JOURNAL, **75**, 3081 (1953).

TABLE V

COMPLEX ION FORMATION CONSTANTS (LOG K_f)

N	AgN^+		AgN_2^+		HgN_2^{+2}		CdN_4^{+2}		ZnN_4^{+2}		HgN_4^{+2}		HgN^{+2}	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
NO_3^-	..	...	(−3.9)	−1.5	0.0	*	(−5.4)	−4.8	.....	.....	..	..	...	..
$SO_4^=$	0.2	−0.2	0.2	−0.1	2.3	3.8	(2.2)	−1.9	(2.2)	−1.1	..	..	...	..
$ClCH_2COO^-$	.6[a]	.1	.5[a]	*	....	..	.....	...	.....	.....	..	..	...	..
CH_3COO^-	.7[a]	.7	.6[a]	1.8	....	..	1.8	1.3	(−0.2)	2.8	..	..	...	..
C_5H_5N	2.0	1.4	4.2	3.5	10.3	11.3	1.8	3.2	1.9[d]	4.7	11.1	11.9	5.1	5.2
Cl^-	3.1[b]	2.3	5.1[b]	6.0	13.2	12.9	2.2	0.9	−1.0	−1.6	15.0	14.4	6.7	6.8
Br^-	..	...	(9.0)	8.7	17.3	16.6	2.7[c]	2.0	−2.6	−1.9	21.0	19.6	9.0	9.0
OH^-	2.3	2.0	3.6	4.3	22.7	16.1	9.8	9.0	15.4	14.2	..	..	(7.9)	6.6
$C_6H_5NH_2$	1.4	3.2	3.2	7.8	....	..	....	...	.....	.....	..	..	...	..
SCN^-	..	...	7.6	9.4	(16.9)	20.0	2.6	6.0	(−4.2)	4.5	19.2	23.6	...	..
NH_3	3.4	3.1	7.2	7.1	17.5	19.2	7.4	8.7	9.4	11.2	19.3	21.9	8.8	8.7
I^-	..	...	(14.0)	13.3	23.8	24.0	5.6[c]	5.1	(−5.4)	−0.6	29.8	29.4	12.8	13.0
$S_2O_3^=$	..	...	13.0	13.7	...	..	7.4	11.5	(−0.2)	10.3	..	..	...	..
$SO_3^=$	..	...	8.5	12.8	....	..	.....	...	.....	.....	..	..	...	..
CN^-	..	...	18.7	14.0	(34.9)	31.5	18.6	15.3	19.0	16.7	41.6	38.0	...	..

N	CdN^{+2}		CuN_4^{+2}		CuN_2^+		PbN^{+2}		FeN^{+3}		AuN_4^{+3}		InN^{+3}	
NO_3^-	..	...	.....	...	....	..	0.4[f]	−0.8	0.0	−0.8	..	..	...	..
$SO_4^=$	0.8	−0.2	(2.2)	−0.6	....	..	.....	...	2.0	1.8	..	..	...	..
CH_3COO^-	..	...	3.4	3.6	...	..	2.1[g]	2.7	.....	.....	..	..	...	..
C_5H_5N	..	...	5.8	5.4	....	..	.....	...	.....	.....	..	..	...	..
Cl^-	1.2[c]	0.8	−4.6	−4.1	5.5	5.0	1.1	1.0	0.6	−0.3	(25.3)	24.4	2.4[h]	1.7
Br^-	1.5[c]	1.1	(−6.6)	−5.7	5.9	6.2	1.1	0.9	−0.3	−1.3	(32.2)	30.5	2.2[h]	1.7
OH^-	..	...	16.2	17.5	...	..	7.8	7.6	11.3	12.2	(40.9)	41.1	10.2[h]	10.2
SCN^-	1.4[e]	2.3	.....	...	....	..	.....	...	3.0	3.4	(42.6)	40.9	...	..
NH_3	2.7	3.1	13.0	12.4	10.9	13.6	.....	...	.....	.....	..	..	...	..
I^-	2.0[c]	2.1	.....	...	8.9	9.5	1.5	1.7	.....	.....	..	..	2.0[h]	2.6
CN^-	5.5	5.1	.....	...	(22.9)	20.7	.....	...	.....	.....	..	..	...	..

[a] F. H. MacDougall and L. E. Topol, *J. Phys. Chem.*, **56**, 1090 (1952). [b] E. Berne and I. Leden, *Svensk Kem. Tidskrift*, **65**, 88 (1953). [c] P. M. Strocchi and D. N. Hume, A.C.S. Meeting at Los Angeles, Cal., March, 1953. [d] C. J. Nyman, THIS JOURNAL, **75**, 3575 (1953). [e] I. Leden, *Z. physik. Chem.*, [A] **188**, 160 (1941). [f] H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953). [g] S. M. Edmonds and N. Birnbaum, *ibid.*, 62, 2367 (1940). [h] L. G. Hepler and Z. Z. Hugus, Jr., *ibid.*, **74**, 6115 (1952).

TABLE VI

COMPLEX ION SUBSTRATE CONSTANTS

Complex[a]	M[b]	α	β	I_p[e]	Ionic radius[f]
CuN_2^+	5	7.55	0.284	7.736	0.96
CuN_4^{+2}	7	4.69	.958	20.287	0.80
AgN^+	8	3.08	− .078	7.575	1.13
AgN_2^+	15[c]	7.14	− .226	7.575	1.13
AuN_4^{+3}	4	26.02	.294	....	..
ZnN_4^{+2}	11	5.94	.650	17.960	0.83
CdN^{+2}	7	2.18	.071	16.9052	1.03
CdN_4^{+2}	12	6.98	.255	16.9052	1.03
HgN^{+2}	6	6.57	− .137	18.752	1.12
HgN_2^{+2}	10[c,d]	12.92	− .099	18.752	1.12
HgN_4^{+2}	7	16.84	− .187	18.752	1.12
InN^{+3}	4	3.61	.342	28.04	0.92
PbN^{+2}	6	2.83	.270	15.03	1.32
FeN^{+3}	6	2.52	.557	43.43	0.67

[a] Data for TlN_4^{+3}, PbN_4^{+2}, AuN_2^+, SnN_4^{+2} and FeN_6^{+3} are given by Bjerrum[5] but they are not deemed sufficiently accurate to justify correlation. [b] Number of donors correlated, not including H_2O. [c] One value used for a secondary standardization. [d] OH^- value not used to calculate α and β. [e] Ionization potential, ref. 9, pp. 15–16. [f] Ref. 5.

Rabinowitch and Stockmayer,[27] and of various complexes by C. L. van Panthaleon van Eck.[28] Equilibrium constants obtained from other sources are referenced in Table V. Those observed values which are estimates are placed in parentheses. All formation constants are given as log values with only one figure after the decimal point.

There are 108 pieces of data given in Table V; of these two were used for secondary standardizations and 20 are estimates of complexity constants from indirect measurements. Of the 86 other data, 59 or over two-thirds of the observed and the calculated values agree within an order of magnitude, and only for 13 are the deviations greater than two orders of magnitude. Since the observed log values range from −4.6 for $CuCl_4^{-2}$ to +41.6 for $Hg(CN)_4^{-2}$, the agreement certainly is encouraging.

It should be mentioned at this point that errors in complexity constants are liable to be much greater than in rate constants. An excellent discussion of certain of the difficulties which arise in the evaluation of complexity constants has been given by Young and Jones.[29] For this reason, and since the values of α are exceptionally large (it would require an error of only 0.06 in E_n to cause an order of magnitude error in K_f for a HgN_4^{+2} complex), large discrepancies between calculated and observed values are to be expected in complex ion correlations.

The values of α probably should correlate with the ionization potentials of the metals.[28,30] It would be expected that the value of α would increase as the ionization potential of the metal increased. For related metals in Table V, this is generally true; the exceptions noted are similar to those observed by van Panthaleon van Eck.[28] The values of β should correlate with ionic radii and with charge. As the radius gets larger in a particular family of the Periodic Chart, it is expected that β should get smaller since the electrostatic attraction of metal ion to ligand should decrease.

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(27) E. Rabinowitch and W. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(28) van Panthaleon van Eck, *Rec. trav. chim.*, **72**, 50, 529 (1953).

(29) T. F. Young and A. C. Jones, Section on "Solutions of Electrolytes" in *Ann. Rev. Phys. Chem.*, **3**, 275 (1952).

(30) A summary and a list of references which deal with correlation of complex stabilities and ionization potentials may be found in ref. 28.

TABLE VII

SOLUBILITY PRODUCT CORRELATIONS ($-$LOG K_{sp})[a]

	AgX		CuX		Hg_2X_2		TlX		PbX_2	
X^-[b]	Obsd.	Calcd.[c]	Obsd.	Calcd.[d]	Obsd.	Calcd.[e]	Obsd.	Calcd.[f]	Obsd.	Calcd.[g]
CH_3COO^-	2.6	3.9	..	..	9.4	12.3	Sol.	0.8	V.Sol.	7.4
Cl^-	9.6	9.2	6.5	7.6	16.9	16.6	3.7	3.6	4.8	5.4
Br^-	12.3	12.0	8.2	8.5	21.3	20.3	5.4	5.0	5.3	5.7
N_3^-	8.6	8.0	..	..	(12)	20.7	(4)	2.2	(12)	10.7
OH^-	[h]	..	[h]	..	[h]	..	0.1	-0.1	14.8	15.2
SCN^-	12.0	11.6	13.4	13.1	19.5	24.3	3.2	4.1	(8)	10.0
I^-	16.1	16.6	12.0	11.3	27.5	27.7	7.1	6.9	8.1	7.4
CN^-	13.8	14.3	Ins.	23.1	39.3	36.7	(1)	4.1	V.S. Sol.	18.7

[a] Sol. = soluble, V.Sol. = very soluble, V.S.Sol. = very slightly soluble, Ins. = insoluble. Values in parentheses are estimates; they plus the CH_3COO^- values have not been used to calculate values of α and β. [b] X^- is used to symbolize a monovalent anion. [c] Calculated using $\alpha = 6.52$ and $\beta = -0.354$. [d] Calculated using $\alpha = 6.97$ and $\beta = 0.335$. [e] Calculated using $\alpha = 13.28$ and $\beta = 0.040$. [f] Calculated using $\alpha = 2.36$ and $\beta = -0.231$. [g] Calculated using $\alpha = 5.24$ and $\beta = 0.373$. [h] No OH^- precipitate known.

Such is the case, as may be seen by comparing β values for ZnN_4^{+2}, CdN_4^{+2} and HgN_4^{+2}, etc. As the charge on the metal ion gets larger, the value of β probably should increase. Since the charge affects the radius and since β is a function of radius, it is difficult to say with certainty whether the charge is exerting any direct effect on β.

Solubility Product Equilibria.—Quantitative correlation of solubility product equilibria using equation 1 would, at first sight, seem very improbable. Correlative attempts are, however, worthy of further consideration since it has been found in recent studies[31] that the solubility of a salt is sometimes related to the stability of the corresponding complex.

In Table VII, five correlations of solubility product data are presented along with the values of α and β which were employed to obtain the calculated values. The estimated values (given in parentheses) and the values of $-\log K_{sp}$ for acetates were not used in the calculation of α and β. Also it was assumed that $\log K_0$ of equation I was zero.

The agreement between the observed values and the calculated values is surprisingly good when one considers that the forces acting in a crystal are in many ways different from those acting in homogeneous liquid solution. There is evidence, furthermore, that this correlation of solubility product data is not fortuitous; this evidence is found in the values of α and β. Comparing values for the precipitates AgX and CuX, the value of α for AgX is slightly lower than that of CuX; this is exactly the same trend as is found for the complexes AgN_2^+ and CuN_2^+ and as is noted for the ionization potentials. The values of β also are close to those found for AgN_2^+ and CuN_2^+. Similar qualitative agreement is found for PbX_2 precipitates and PbN^{+2} complexes.

As the other seven anions being considered are roughly symmetrical and can take part in bonding at both ends of an axis, it is not surprising that the acetate salts are more soluble than would be predicted by the values of α and β given in Table VII.

Most of the observed values of solubility products were obtained from the book by Latimer.[9] The mercurous halide values are those given by Sillen,[25] and the approximate values were estimated from solubility data as given by Seidell.[32]

Equilibria Involving Iodine.—In Table VIII some results for correlation of the reactions

$$I_2(aq.) + X^- \rightleftarrows I_2X^-(aq.)$$

are presented. Since iodine is known to be present in aqueous solution as a water complex, equation 1 was employed for the calibrations in the same way as for complex ions. Use of the value 1.74 for log K_0 gave the results to be found in the column marked log K_1 of the table. Although the worst deviation is only 0.44, this deviation is large in respect to the value of α and the calculated values differ from the observed values in a manner which does not seem to be random. Using the value of 3.48 for log K_0, the results presented in the last column of the table were obtained. The calculated values are in excellent agreement with the observed values, for the largest deviation is only 0.06.

TABLE VIII

CORRELATION OF IODINE COMPLEXES

X^-	log K Obsd.	log K_1 Calcd.[d]	log K_2 Calcd.[e]
Cl^-	0.32[a]	0.76	0.29
Br^-	1.08[b]	1.36	1.11
SCN^-	2.04[c]	1.82	2.09
I^-	2.85[a]	2.50	2.79

[a] Ref. 35. [b] F.-H. Lee and K.-H. Lee, *J. Chinese Chem. Soc.*, **4**, 126 (1936). [c] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **31**, 868 (1935). [d] Calculated using $\alpha = 1.96$, $\beta = -0.023$ and $\log K_0 = -\log [H_2O]$. [e] Calculated using $\alpha = 3.044$ and $\log K_0 = -2 \log [H_2O]$.

It is surprising to find that these equilibria appear to involve a loss of two water molecules from the iodine molecule when it is being complexed by an anion. Using equation 1 without the βH term, a least squares analysis of the observed constants gave a value of 3.52 for log K_0, in excellent agreement with the value 3.48 which one would expect if two water molecules are freed. As the writer does not know of any data in the literature that can substantiate this rather surprising conclusion, quantitative significance should only be assigned with caution to this log K_0 value[33] at the present time.

In contrast to the above series of equilibrium

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(31) *Cf.* R. J. P. Williams, *J. Chem. Soc.*, 3770 (1952).

(32) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Ed., D. Van Nostrand Co., New York, N. Y., 1940.

(33) Since no similar difficulty arose in the assignment of log K_0 values for the complex ion correlations of Table V and since the calculated values based on the log K_0 value of 3.48 are in such good agreement with the observed values, it is doubtful if this anomaly can be blamed either on the use of 1.74 for log $[H_2O]$ or on experimental errors in evaluating the equilibrium constants.

constants, a definite need for the βH term is found for reactions of the type

$$I_2 + N \rightleftharpoons IN^+ + I^-$$

From the data of Bell and Gelles,[34] it is possible to calculate relative equilibrium constants. For N equals H_2O, I^- and OH^-, these are 2.2×10^{-13}, 1 and 30, respectively. The data, when substituted into equation 1, give the values $\alpha = 6.85$ and $\beta = 0.162$. From the work of Awtrey and Connick[35] one can estimate a lower limit for $N = S_2O_3^=$. This estimate, which is that the relative equilibrium constant (see above) is $\geq 10^6$, is in fair agreement with the calculated relative equilibrium constant of 2×10^5. Although the quantitative calculations on this reaction are not convincing, it is certain that correlation of the data requires a significantly large and positive value of β as well as a large value of α.

Equilibria Involving Sulfur Compounds.—Although the available data for equilibria involving displacement on sulfur are qualitative in nature, there is much information that is interesting and pertinent. Foss[6,7] places considerable emphasis on the importance of electrode potentials of the donors in sulfur reactions and on the displacement nature of these reactions. He has, however, found it necessary to divide up his donors into two classes, the "thio anions" such as $S_2O_3^=$ and SCN^- and the "anthio anions" such as $SO_3^=$ and CN^-.

The thio anions can be arranged in order of increasing displacement ability. From studies of displacement reactions of compounds containing formally positive sulfur atoms, Foss[6,7] has found that the order of increasing strength of thio anions is $Cl^- < SCN^- < (CH_3O)_2POS^- < C_2H_5SO_2S^- <$ p-$CH_3C_6H_4SO_2S^- < S_2O_3^= <$ thiocarbonyl anions and mercaptides.[36] For example: (a) from disulfur dithiocyanate $S_2(SCN)_2$, $CH_3C_6H_4SO_2S^-$ displaces SCN^- to give $S_2(SO_2SC_6H_4CH_3)_2$; and (b) ethyl xanthate (a thiocarbonyl anion) will displace a thiosulfate ion from tetrathionate ion in accordance with the equation

$$O_3S_2 \cdot S_2O_3^= + S_2COC_2H_5^- \rightleftharpoons O_3S_2 \cdot S_2COC_2H_5^- + S_2O_3^=$$

Comparison of this series of displacement strengths with the known electrode potentials shows good agreement.

For the anthio anions, Foss[6,7] observed that the order of increasing strength was

$$CH_3C_6H_4SO_2^- < C_2H_5SO_2^- < SO_3^= < CN^- \sim (CH_3O)_2PO^-$$

Although this order is not conclusive by itself since the E_n values for three of these anions are unknown, it is interesting to find that $SO_3^=$ and CN^- are able to displace the stronger (more nucleophilic) thio anions such as mercaptide ions and xanthate ions in some cases. As these anthio anions are stronger bases to protons than are thio anions, it is probable that the difference between Foss' two classes lies in the need of a positive βH term as well as a large αE_n term in correlation of sulfur equilibria.

Other data such as: (a) the dissolution of sulfur in solutions containing amines, $S^=$, $SO_3^=$, CN^- and OH^-, but not in solutions containing SCN^-, $S_2O_3^=$ and the halide ions; and (b) the observation[6] that $CH_3C_6H_4SO_2S^-$ is a stronger thio anion than $C_2H_5SO_2S^-$ while, for the corresponding anthio anions, $C_2H_5SO_2^-$ is stronger than $CH_3C_6H_4SO_2^-$, also indicate that correlations of displacement equilibria of sulfur compounds require both αE_n and βH terms.

Miscellaneous Correlations.—In the previous sections, rate constants of displacement reactions and equilibrium constants for allied reactions have been discussed in terms of equation 1. In this section, data of various sorts which cannot be classified in either of the above groups will be correlated.

A.—Jette and West[37] found that the abilities of anions to quench the fluorescence of quinine bisulfate follow the order

$$I^- > SCN^- > Br^- > Cl^- > C_2O_4^= > CH_3COO^- > SO_4^= > NO_3^- > F^-$$

Ignoring $C_2O_4^=$ for which there is no E_n value available this order is identical to the order of E_n values.[38] The quenching of fluorescence of disodium fluorescein (Uranin), uranyl salts, and other compounds was found to follow the same general order.[37,39] Further it is reported[39] that $S_2O_3^=$ and $SO_3^=$ are quenching agents for the fluorescence of these compounds.

A study of the quenching of the fluorescence of uranin by various amines showed "that the basicity of the nitrogen atom (*i.e.*, the availability of the unshared pair of electrons for bond formation) is not important in the quenching reaction."[40] For example, with three amine donors of known E_n value, the order was found to be

$$C_6H_5NH_2 > C_5H_5N > NH_3$$

Although the above data on quenching of fluorescence indicate that the nucleophilic strength of the quencher is of primary importance, it should be mentioned that the fluorescence of certain other compounds is quenched by an entirely different group of anions which include IO_3^-, BrO_3^-, NO_3^-, $S_4O_6^=$ and $AsO_4^{\equiv}$.[39]

B.—In the course of their studies on the mechanism of displacement reactions in coördination compounds, Basolo, Pearson and co-workers[41] found that the rates of reaction of entering donors with *cis*-$[Co(en)_2NO_2H_2O]^{+2}$ follow the order

$$NO_2^- > N_3^- > SCN^- > H_2O$$

in aqueous solution at 35°. It seems probable that these data could be satisfactorily correlated using equation 1.

C.—In a recent study of the differential capacity of the electrical double layer at a mercury solution interface,[42] it was found that the anion present in

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(34) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

(35) A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1341 (1951).

(36) Foss[6,7] estimated that the E^0 values for the various thiocarbonyl anions and mercaptides are about +0.3, thus the E_n values should be about 2.9.

(37) E. Jette and W. West, *Proc. Roy. Soc.* (*London*), **A121**, 299 (1928).

(38) From the data of Latimer,[9] the E_n value for F^- is calculated to be −0.27.

(39) G. K. Rollefson and R. W. Stoughton, THIS JOURNAL, **63**, 1517 (1941).

(40) J. C. Rowell and V. K. LaMer, *ibid.*, **73**, 1630 (1951).

(41) (a) F. Basolo, *Chem. Revs.*, **52**, 459 (1953); (b) R. G. Pearson, personal communication.

(42) D. C. Grahame, M. A. Poth and L. J. Cummings, THIS JOURNAL, **74**, 4422 (1952).

solution exerted a marked effect. The order of increasing capacity was found to be

$$ClO_4^- < NO_3^- < F^- < SO_4^= < CH_3COO^- < HCO_3^- < Cl^- < CO_3^= < OH^- < CNS^- < Br^- < I^-$$

The investigators[42] pointed out that their capacities correlate well with the solubilities of Hg_2^{+2} salts (*cf.*, section on solubility products).

Discussion

In this article, a new equation for the correlation of the reactions of electron donors has been presented, and a new nucleophilic scale, based on electrode potentials, has been defined. A large amount of quantitative and qualitative data has been given in support of the equation and scale. The results are generally good, but in several correlations (*e.g.*, ZnN_4^{+2} complexes in Table V) the agreement between calculated and observed values leaves much to be desired. It seems quite conclusive, however, that further efforts in the fields of correlation of reactions of electron donors (and acceptors, too) will require an equation of the general type of equation I and a set of constants akin to those of Table I.

The values of E_n and H for some of the donors probably will require revision as better data become available; it may even be necessary to assign separate E_n values for different types of correlations. For example, the E_n value for CN^- gives low calculated results with cation complexes; yet there are indications that high results will be obtained with displacements on carbon when this E_n value is employed.[43] Similar difficulties arise with NH_3; while the results for this donor are good with cation complexes and displacements on hydrogen, data on displacements in aromatic compounds[3a] and on quenching of fluorescence[40] indicate that the ammonia E_n value is too large for these cases. All of the results for $SO_4^=$ indicate that the present E_n value is low. Since the E_0 value assigned to the couple

$$2SO_4^= \rightleftharpoons S_2O_8^= + 2e^-$$

is not accurately known,[9] it is difficult to find the correct reason for these discrepancies with $SO_4^=$. In order to be as general and as fundamental as possible, no attempt was made to obtain the best possible correlation by trying different standard substrates. For this reason and so that the important discrepancies may be recognized as such, the calculated values are tabulated in their presently imperfect form.

Although the new equation and its nucleophilic scale are not final and despite the fact that cases which cannot be correlated will arise, there is much to be said for this treatment of rate and equilibrium constants. In order: (a) the new scale for the nucleophilic character of a donor is a thermodynamic scale and is related to electrode potentials which can be measured; (b) the worst discrepancies in the previous correlations of displacement on carbon[2] have been eradicated; (c) the data available indicate that this correlation equation can be extended to displacement rates on other atoms such as oxygen and the chalcogens; it is also possible that the deviations from Brönsted's equation may be explained, in part,[44] by equation 1; (d) contrary to previous feelings[2] that the word nucleophilic should be used only in discussion of rate and that the word basic refers to equilibrium conditions, it is obvious that almost any correlation made will require a greater or lesser contribution of both basic and nucleophilic character to the covalent bonds; (e) the equation can be applied to equilibrium constants for complex ions of certain types, solubility products (albeit poorly), iodine displacements and sulfur displacements. This writer does not know of any previous correlation of complex ion constants or solubility product constants in which the influence of the donors was studied.

One of the most important conclusions which has come out of this study is that Lewis acids can now be quantitatively correlated along with the proton. In Table IX, the substrate constants (α and β) for ten acids for which there are quantitative data on the reaction

$$\text{acid} + \text{donor} \rightleftharpoons \text{salt}$$

in aqueous solution at 25° are given. Because of its very small diameter, and its charge, the proton has a low value of α and a high value of β. The differences between the proton and the other cations probably are not of kind but, rather, of degree.

TABLE IX

SUBSTRATE CONSTANTS FOR VARIOUS ACIDS[a]

Acid	α	β	Acid	α	β
H^+	0.00	1.000	Hg^{+2}	6.57	−0.137
Ag^+	3.08	−0.078	Pb^{+2}	2.83	.270
Cu^{+2}	2.04	.275	In^{+3}	3.61	.342
Zn^{+2}	1.32	.206	Fe^{+3}	2.52	.557
Cd^{+2}	2.18	.071	I_2	3.04	.000

[a] The data for CuN^{+2} (5 donors) and ZnN^{+2} (6 donors) have not been presented in detail. All calculated values of the 11 constants agree with the observed values within an order of magnitude.

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[43] In the displacements of I^- from ICH_2COO^-, CN^- is less active than $S_2O_3^=$ or $SO_3^=$, and the calculated rate is too large by almost two orders of magnitude.

[44] Although the nucleophilic strength of the electron donor may be one of the prime reasons for deviations from the Brönsted equation, steric factors,[45] etc., can also cause significant deviations.

[45] R. G. Pearson and F. V. Williams, THIS JOURNAL, **75**, 3073 (1933).