The above value for the negative ions is lower than these, as would be expected from the lower value of the coördination number occurring in this structure.

Conclusions

The treatment of mixed solutions of aluminum fluoride and sulfate with ammonia produces hydroxyfluorides falling within the range of composition $AlF(OH)_2$ to $AlF_2(OH)$. These compounds are cubic with space group O_h^7 —Fd3m. The lattice constant decreases with increasing fluorine content from 9.85 to 9.77 Å. The unit cell contains sixteen formula-groups plus six water molecules.

The hydroxyfluoride structure is stable up to 500°, the gradual loss of water being reflected by a corresponding contraction of the lattice. The remarkable stability of the lattice is demonstrated by the retention of the structure despite the destruction of more than half the hydroxyl groups at high temperatures. At 600°, the hydroxyfluoride structure is no longer evident. No oxyfluorides are formed, the hydroxyfluorides decomposing directly to aluminum oxide and fluoride.

MELBOURNE, AUSTRALIA RECEIVED MARCH 24, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Aqueous Ionization Constants of Inorganic Oxygen Acids

BY JOHN E. RICCI

It is presumably possible to determine independently the formulas, structures and aqueous ionization constants of inorganic acids. The data so obtained may then be correlated either empirically or on the basis of theories of molecular structure and of the process of ionization in solution, in which case the results of the comparison may serve as a test of the theories. A remarkably successful correlation has been obtained by Kossiakoff and Harker, in a paper on "The Calculation of Ionization Constants of Inorganic Oxygen Acids from their Structures,"[1] and the results have been interpreted as supporting the mechanism proposed as the basis of the calculation.[2] The purpose of this paper is to examine critically the treatment and results of Kossiakoff and Harker, and to determine which of their assumptions are supported by their calculations.

Kossiakoff and Harker assume (1) that the ionization constant of an oxygen acid is defined by the free energy of transfer of a proton from a hydroxyl group to the surrounding water structure, and (2) that this energy, in electrostatic terms, depends on (a) the formal charge of the central atom of the acid, (b) the number of non-hydroxyl oxygen atoms in the acid ion available for attachment of a proton, (c) the number of equivalent hydrogens available for "dissociation," and (d) the structure of the acid as determined by crystallographic data on its salts.[3]

We shall see that the first and main assumption is not effectively tested by the treatment of Kossiakoff and Harker, and that the test of 2(c) and 2(d) is entirely inconclusive, but that the assumptions 2(a) and 2(b) are effective and lead to very enlightening empirical correlations.

I. Calculations of Kossiakoff and Harker

The general expression used by Kossiakoff and Harker for the free energy change fixing a particular ionization constant is

$$\Delta F = \sum W_i - C + RT \ln n_O/n_H \qquad (1)$$

Here C is a solvent constant, n_O is the number of equivalent non-hydroxyl oxygens in the ion being formed, n_H is the number of equivalent (transferable) hydrogens in the acid, and W_i is the electrostatic energy of a single transfer. Furthermore

$$W_i = \sum_j \frac{m_j e}{\epsilon} \left(\frac{1}{r_j} - \frac{1}{r_j'}\right) \qquad (2)$$

in which $r_j' - r_j$ is the displacement of the proton relative to the j'th atom of the solute particle, whose formal charge is m_j; e is the charge of the electron and ϵ the dielectric constant of the medium. The formal charge of an atom is its group number in the periodic table minus the number of electrons in its valence shell, a shared pair being counted as one.

For the evaluation of C, Kossiakoff and Harker chose K_1 of orthophosphoric acid H_3PO_4(pK_1 = 2.1, ΔF = 2.9) as reference; from structural data they calculated ΣW_i = 46.1. For this calculation, the first term of ΣW_i, or the term for the first transfer, from hydroxyl to adjacent water molecule, was taken as

$$W_1 = \frac{e^2}{\epsilon}\left[\left(\frac{1}{R} - \frac{1}{R'}\right) - \left(\frac{1}{\rho} - \frac{1}{\rho'}\right) + \left(\frac{1}{d} - \frac{1}{d'}\right)\right] \qquad (3)$$

in which $R' - R$ is the absolute displacement of the proton (R being the original O—H distance), ρ'-ρ its displacement relative to the central atom, phosphorus (with m = +1), and d'-d its displace-

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[1] A. Kossiakoff and D. Harker, THIS JOURNAL, **60**, 2047 (1938).

[2] For a discussion of their method and results, see O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 429–438.

[3] "Structure" refers not to the formula but to the physical quantities of bond angles and interatomic distances. A formula such as $Ge(OH)_4$, graphical or otherwise, is the result of chemical and analytical reasoning, independent of the physical determination of the structure of the substance.

ment relative to each (here only 1) non-hydroxyl oxygen (with $m = -1$) of the acid.

The distances R and R' are assumed to be constant for all oxygen acids in water, in all subsequent calculations. It will therefore be useful at this point to re-write equation (3) in the form

$$W_1 = W_0 + mf(\rho) + nf(\mathrm{d}) \qquad (4)$$

in which m is the formal charge of the central atom and n the number of non-hydroxyl oxygens of the acid. In the case of orthophosphoric acid, the values of these terms were

$$W_1 = 52.4 - 12.4 + 4.9 = 44.9 \text{ kcal.} \qquad (5)$$

The remaining terms of ΣW_i amounted to only 1.2, giving $\Sigma W_i = 46.1$. Now with $RT \ln n_O/n_H = -0.2$, $C = 46.1 - 2.9 - 0.2 = 43.0$ kcal. This value of C was then used in equation (1) to calculate the twenty-six other ionization constants, for acids with "non-resonating" structures (this excludes those of the first row elements: B,C,N). For the purpose of the calculation, the authors furthermore pointed out that since the difference, $\Sigma W_i - W_1$, ($\cong 1.2$ for orthophosphoric acid) is expected to be equally small and nearly constant for all the other acids to be considered, this quantity may be combined with the constant C, so that C_1 (to be used with W_1 alone) $= C - 1.2 = 41.9$. In other words, instead of equation (1) we may write, with negligible error

$$\Delta F = W_1 - C_1 + RT \ln n_O/n_H \qquad (6)$$

The over-all average deviation between observed and calculated log K, for these twenty-six calculations, was 0.89.[4] According to Kossiakoff and Harker, "The quantities calculated represent differences between large numbers (presumably meaning ΣW_i and C, or W_1 and C_1), making the resulting agreement all the more encouraging." The agreement is then taken as supporting the assumptions involved in calculating ΣW_i and through it C, and specifically the electrostatic theory of the work of separating a proton from the hydroxyl group to the first water molecule through the immediate distance R'-R.[5]

II. Criticism and Discussion

Since R and R' are assumed to be the same for all oxygen acids in water, and since C_1 is a solvent constant, then writing k for $W_0 - C_1$, and combining (4) and (6), we have

$$\Delta F = k + mf(\rho) + nf(\mathrm{d}) + RT \ln n_O/n_H \qquad (7)$$

With orthophosphoric acid as reference (*i.e.*, using its K_1), k has the value 10.5. The calculation of the other twenty-six ionization constants then involves this reference constant k, or the constant difference $W_0 - C_1$, but never the supposed actual values of W_0 and C_1 separately. For the purpose of the calculation of the other twenty-six constants it was in fact not necessary at all to derive or state separate values of the quantities $W_0 - C$. The actual "solvent constant" is the difference $W_0 - C$, and at no point do the subsequent calculations and comparisons test the separate values of W_0 and C. The whole set of calculations is then practically, if not completely, independent of the assumptions concerning the distances R and R', once it is assumed that W_0 and C are constants for all oxygen acids in water. Perhaps it should be pointed out, too, that even if the comparisons had succeeded in verifying the separate values of W_0 and C, the result would probably be equally explainable either as a transfer of proton from solute to solvent (according to the modern or Brönsted picture) or as a transfer of hydroxyl from solvent to solute, (as suggested some time ago by Werner[6]), giving rise in either case to a negative solute ion.

Furthermore, W_0 is by far the largest term in equations (4) and (5). When it is realized that the difference between the two largest quantities of equation (6), namely, $W_0 - C_1$, is a constant in all the calculations, the final agreement between calculated and observed ionization constants is perhaps no longer very impressive. The over-all agreement is nevertheless sufficient to suggest that at least the difference, $W_0 - C_1$, has been verified, as a fundamental constant for oxygen acids in water. But even this conclusion may be questioned. As a purely mathematical problem, it would seem that the best determination of the solvent constant, k (or $W_0 - C_1$), from equation (7), would be through the known first ionization constant (and hence ΔF) of what may be called a "true ortho-acid," for which both m and $n = 0$.[7] For an acid of this class, with the formula H_aMO_a, in other words, we have

$$k = (W_0 - C_1) = \Delta F + RT \ln a \qquad (8)$$

presumably requiring no information about structure, but only knowledge of its formula. In the list of acids considered by Kossiakoff and Harker, hypochlorous acid is the only acid believed beforehand to be a true ortho-acid; it gives $k = 10.0$,[8] in close agreement with the value 10.5 from ortho phosphoric acid. Three other acids, of doubtful formula beforehand, are classified as true ortho-acids on the basis of the calculated constants; these are H_3AsO_3, H_4GeO_4 and H_6TeO_6. But these give $k = 13.3$, 12.7 and 11.0, respectively.

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[4] Based on observed values as listed in ref. 2 itself; relative to values listed below (Table I), the deviation is hardly changed, being 0.91.

[5] In ref. 2, O. K. Rice states that the calculations give a "remarkable check" and discusses the "reasonableness" of the value of C (and hence by implication, of W_0 and of the distances R and R') given by the method.

[6] Alfred Werner's ideas on this subject, in "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," and *Z. anorg. Chem.*, **3**, 267 (1893), and **15**, 1 (1897), are rarely mentioned. They are presented (but with disapproval) in P. Walden's book, "Salts, Acids and Bases," McGraw-Hill Book Company, New York, N. Y., 1929, p. 118-120.

[7] A true ortho-acid has the formula $M(OH)_a$, or H_aMO_a; as a result the formal charge on the central atom is always zero, and n, the number of non-hydroxyl oxygens, is also zero.

[8] Ionization constants used in the present discussion are listed below, in Table I, where sources are also stated.

Hypobromous and hypoiodous acids, not mentioned by Kossiakoff and Harker, give $k = 12.0$ and 15.2, respectively. Altogether this is a rather large range for what is presumably a fundamental constant not involving the functions $f(\rho)$ and $f(d)$ of equation (7) at all for its determination; this is so even if we disregard hypoiodous acid, here and later, because of the uncertainty about its ionization constant.[9]

It must be noted clearly that in the case of true ortho-acids, the calculation of Kossiakoff and Harker does not involve their structures at all. Despite the title of their paper, the calculations for HClO, H_3AsO_3, H_4GeO_4 and H_6TeO_6, as ortho-acids, involved nothing more than their written formulas.[10] If the fundamental assumptions for the application of equation (7) are correct, and $W_0 - C_1$ is a constant, then according to equation (8) all these ortho-acids should have values of K_1 identical except for the small differences due to the term $-RT \ln a$. The actual great variation, even in so close a series as the hypohalous acids, which should on this basis have identical ionization constants, suggests that the equation is overlooking some fundamental difference in the properties (perhaps in what may be called the property of "acidity," or the electronegativity) of the central atom. The nature of the central atom, M, presumably affects the calculation through the effect on the M–O distances (and the angles between the oxygens) in the structure of the acid, and hence through the second and third terms of equation (7). But even this effect is assumed to disappear entirely in the ortho-acids, since there is no formal charge on either the M or the oxygens of the acid. While the calculated K_1 for H_4GeO_4, in other words, agrees with the observed value, the identical value would be calculated for any other acid of the general formula H_4MO_4 or H_aMO_a, which is probably not to be expected in reality.

One may of course attribute the variation among these ortho-acids to incorrect assignment of their formulas in some cases, although this is hardly likely for hypobromous acid (and hypoiodous acid). Moreover, the agreement for the four ortho-acids in Kossiakoff and Harker's list already involves a choice of formula for all but hypochlorous acid, to give the agreement.

This insensitivity to the nature of the central atom in the case of true ortho-acids suggests that an equation like (7) is essentially only a semi-empirical equation concerned with the relative effects of the formal charge on the central atom (m) and of the number of oxygens, in a given series of acids. Most of the examples in Kossiakoff and Harker's list are acids with $m = 1$. For higher values of m the strengths become so high that reliable data are not in general available. At any rate there are hardly two acids in the list with $m > 1$, having formulas and structures similar enough for a clear check on the effect of the secondary variables (n and $f(d)$). Of the twenty-seven acids: four are ortho ($m = 0$); seventeen are the molecules and ions of seven acids with $m = +1$ and n varying from 1 to 3 depending on the charge on the acid; four are the molecule and ions of $H_4P_2O_7$, a special case with two central atoms each having $m = 1$; and the remaining two are HIO_3 ($m = 2$, $n = 2$) and the bisulfate ion ($m = 2$, $n = 3$).

Now the remarkable thing, despite "the wide variation found in the ionization constants of acids" noted by Kossiakoff and Harker, is the striking simplicity and repetition of the values for the inorganic oxygen acids in water; this simplicity or grouping becomes apparent when the acids are classified according to their values of m and n. The actual pK's are then seen to be grouped in such a way as to suggest a (rough) linear dependence upon m and n without detailed dependence upon the structure (angles, M–O distances, etc.) of the acid. Nor is there, in fact, any systematic correlation between the deviations found by Kossiakoff and Harker (between observed and calculated constants) and relative changes of structure, to suggest, within the precision of the comparison, any dependence upon this structure (see Table II, below). This may be entirely the fault of the inaccuracy and uncertainty of the observed values. But the fact remains that we may assume the functions, $f(\rho)$ and $f(d)$, of equation (7) to be constants for all the acids, and still obtain as good an over-all average agreement between calculated and observed constants, as was obtained by the laborious calculations of Kossiakoff and Harker. The precision of their comparison is so low, for example, (and with no trend) that the average error is greater than the average value of the term, $RT \ln n_O/n_H$, so that even the sign of this particular effect is not being tested.

Assuming then that (whatever the length and angles of the M–O bonds) the effect of the formal charge, m, of the central atom is uniform and constant, and similarly that the effect of each non-hydroxyl oxygen is also constant, and incorporating in the constant k the term $RT \ln n_O/n_H$, we may test the following empirical expression

$$pK = 8.0 - m(9.0) + n(4.0) \tag{9}$$

Here K is the acid ionization constant of the species H_aMO_b, whatever its net or total charge; m is the formal charge of M; $n = b - a$. The equation has been used to calculate not only the ionization constants of the twenty-seven species listed by Kossiakoff and Harker, but nine more in addition: $HGeO_3^-$ (or $H_3GeO_4^-$), $H_4IO_6^-$, H_3PO_2, $HSeO_4^-$, HBrO, $H_2S_2O_4$, $HS_2O_4^-$, $H_2P_2O_6^{=}$, $HP_2O_6^{\equiv}$. In applying equation (9) the acids

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(9) See W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 57.

(10) The calculated values of ΔF for HClO, H_3AsO_3, H_4GeO_4, H_6TeO_6, were 10.7, 10.1, 9.9, 9.6; corrected for the statistical factors of 0, −0.6, −0.8, −1.1, respectively, these are all 10.7. The M–O distances listed in Kossiakoff and Harker's paper for these acids (1.59, 1.66, 1.97 and 1.54 Å., respectively) do not enter the calculation at all.

$H_4P_2O_7$, $H_2S_2O_4$ and $H_4P_2O_6$, with $m = +1$ for each of the two central atoms, are treated as though the central complex were a single atom with $m = +2$. Phosphorous acid (dibasic) and hypophosphoric acid (monobasic) are treated as $H_2(PH)O_3$ and $H(PH_2)O_2$, respectively, the central complex having in each case the formal charge of +1. These assignments of total formal charge will be found to be in accord with the definition of formal charge already given. For the twenty-seven constants of Kossiakoff and Harker's list, the average deviation between observed and calculated values of log K (according to equation 9), is 0.93, while for the entire thirty-six constants the average deviation is 0.91.[11] Since this is as good as the result of the application of equation (1), using the structure of the acids, the implication is that either the data (ionization constants and structural information) or the assumptions required in the application of equation (1) are not fine enough for a significant test of the assumptions themselves.

It has already been pointed out that the first term of this equation, here the empirical constant 8.0, corresponding to $W_0 - C_1$, was likewise essentially an empirical constant in Kossiakoff and Harker's treatment. Their treatment, however, does apparently succeed in calculating the coefficients of the m and n terms of this expression, as determined, presumably, by the structural data. But since the resulting agreement was not better than that obtained through equation (9), it may be concluded that the theory can predict the rough value of these coefficients but not their detailed dependence upon structure, and that the most that may be deduced is a roughly constant dependence merely on the values of the parameters m and n.

III. Similarity of Ionization Constants for Inorganic Oxygen Acids

Equation (9), although tested indiscriminately on all the thirty-six available (and presumably dependable) ionization constants, is of course not to be suggested as an actual formula for the ionization constant of any oxygen acid in water. It is useful primarily because it suggests certain regularities in the values of the ionization constants. According to such a formula the values of the ionization constants of oxygen acids should fall into groups represented by the various possible combinations of m and n. These classes are listed in Table I, which shows the individual acids and their ionization constants, falling in various classifications.

TABLE I

CLASSIFICATION OF THE CONSTANTS[a]

Class	Example	pK_1	pK_2	pK_3	pK_4
$m = 0$		$(n = 0)$	$(n = 1)$		
	H_4GeO_4	8.6	12.7		
	H_3AsO_3	9.2			
	H_6TeO_6	(6.2; 8.8)[b]	10.4[c]		
	$HClO$	7.2			
	$HBrO$	8.7			
	(HIO)	(11.0)			
$m = 1$		$(n = 1)$	$(n = 2)$	$(n = 3)$	
	H_3PO_4	2.1	7.2	12.0	
	H_3PO_3	1.8	6.2		
	H_3PO_2	2.0			
	H_3AsO_4	2.3	7.0	13.0	
	H_2SO_3	1.9	7.0		
	H_2SeO_3	2.6[d]	8.3[d]		
	H_2TeO_3	2.7	8.0		
	$HClO_2$	2.0			
	H_5IO_6	1.6	6.0		
$m = 2$		$(n = 2)$	$(n = 3)$	$(n = 4)$	$(n = 5)$
	H_2SO_4		1.9		
	H_2SeO_4		2.0		
	HIO_3	0.8[e]			
	$H_4P_2O_7$[f]	.9	2.0	6.7	9.4
	$H_4P_2O_6$[g]	(2.2)[g]	(2.8)	7.3	10.0
	$H_2S_2O_4$	0.3	2.5		

[a] With the exceptions noted, these values are taken from Latimer, ref. 9. [b] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 351. The value 6.2, from Blanc, *J. chim. phys.*, 18, 28 (1920); the value 8.8, from Rosenhaim and Janders, *Kolloid Z.*, 22, 23 (1918). [c] From Blanc, referred to in [b]. [d] Yost and Russell, p. 331. [e] Ricci and Naidich, THIS JOURNAL, 61, 3268 (1939). [f] Yost and Russell, p. 228. [g] Yost and Russell, p. 206. The first and second constants of $H_4P_2O_6$, like that of HIO, were not included in testing equation 9. About hypophosphoric acid, Yost and Russell state (p. 207) that the data are unsatisfactory, and that "no definite statement about the ionization constants K_1 and K_2 can be safely made yet."

The group with $m = 1$ is the most complete and most uniform. The un-ionized forms of these acids are all assigned the formula $H_aMO_{(a+1)}$, and all have approximately the same values of the ionization constants, given by the expression, $pK = 2.1 + (n - 1)(4.9)$, with $n = 1, 2, 3$ for K_1, K_2, K_3, respectively. In other words, the experimental values of the pK's for this class, if they are significant, show a surprising independence from structural characteristics, despite a range, in fact, of M–O distance, from 1.50–1.54 for H_2SO_3, H_3PO_4, H_3PO_3, $HClO_2$, through 1.66 for H_3AsO_4, 1.73 for H_2SeO_3, 1.84 for H_2TeO_3 to 1.93 Å. for H_5IO_6.[12] The calculations of Kossiakoff and Harker, involving the structures, do not even reproduce the order of the slight differences between each acid and the reference acid, orthophosphoric acid; this is shown in Table II. (The acids listed

TABLE II

COMPARISON WITH H_3PO_4

	(pK_1 = 2.1)		(pK_2 = 7.2)	
Acid	Obs.	Calcd., K. and H.	Obs.	Calcd., K. and H.
H_3PO_3	−0.3	+0.2	−0.7	−0.5
H_3AsO_4	+ .2	+ .4	− .2	−1.0
H_2SO_3	− .2	+ .2	− .4	− .2
H_2SeO_3	+ .4	+ .8	+1.0	− .9
H_2TeO_3	+ .5	+1.0	+ .7	− .9
$HClO_2$	− .1	+0.5		
H_5IO_6	− .5	+ .8		

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(11) In terms of root mean square deviation, or $\sqrt{\Sigma\Delta^2/N}$, the deviation is 1.03 in the calculations of Kossiakoff and Harker's paper (relative to their own listed observed values, and 1.11 relative to the observed values listed here in Table I (26 constants). For the 36 constants tested through equation 9, the root mean square deviation is 1.16.

(12) Quoted from ref. 1.

with $m = 2$ are not so comparable among themselves; they furthermore involve much more uncertainty both as to structures and as to values of ionization constants.)

The similarities in Table I are both surprising and instructive. The acids here listed in the class $m = 1$, for example, are usually considered as unrelated, and if related, they are usually thought of as having widely different ionization constants, for the reason that they have never (to the writer's knowledge)[13] been grouped together in this fashion to bring out both the uniformity of their strengths and the similarity of constitution underlying this uniformity. The similarity is simply that the formal charge on the central atom is the same, and this seems to be the controlling factor for the aqueous ionization constant despite the variety of the elements represented, of their oxidation states and of the (analytical) formulas of the acids. The similarity of the first ionization constants of H_3PO_4, H_3PO_3 and H_3PO_2 has been noted by Yost and Russell (Table I, ref. [b], p. 193), who remark that these are "unlike other series of acids (H_2SO_3, H_2SO_4, for example)." But H_2SO_4 (with $m = 2$, $n = 2$) and H_2SO_3 (with $m = 1$, $n = 1$) would not be expected to have similar values of K_1 at all, while the three phosphorus acids would, from this point of view, which may therefore be a useful one for correlation and systematization in general.

At any rate there may be a significant suggestion in the simplicity and uniformity of the ionization constants as arranged in Table I, that whatever the process of ionization may be in water solution, it is much less dependent upon the structure and constitution of the acid—as these are currently pictured, at least—than one would have expected. One wonders to what extent our ideas of these "structures" may be at fault, being possibly preconceived upon the assumption that the structure of the acid is the same as that of its salt, an apparently necessary consequence of the customary but arbitrary definition that an "acid" is something which "dissociates" in water solution to "give off" a proton; that an oxygen acid, in other words, is of necessity a hydrogen compound to begin with, whether we use the Arrhenius or the thermodynamically equivalent Brönsted point of view.

It is possible that a concept of ionization through coördination, more or less as originally suggested by Werner,[6] amounting to capture of hydroxyl ion and capture of proton as the acid and base ionization processes, respectively, might be developed, in which the emphasis would be laid upon the coördination requirements of the actual solute itself (SO_3) and not upon the structure of its ion ($SO_4^{=}$ or HSO_4^-) in its salts, as the determining factor for the ionization constant.

Summary

Critical examination of theoretical calculations of the aqueous ionization constants of inorganic oxygen acids shows that the treatment does not constitute a test of the fundamental assumption of a proton transfer from solute to solvent. An empirical correlation and grouping of these ionization constants based on the formal charge of the central atom and the number of non-hydroxyl oxygens in the acid, is presented. This grouping, apparently independent of the supposed "structures" of the acids, may indicate the need of a different picture of the process of ionization.

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(13) The referee examining this paper kindly brought to the author's attention a book entitled "General Chemistry," by Linus Pauling (Edward Bros., Inc., Ann Arbor, Michigan, 1944), presenting a classification of ionization constants, based on coördination, which is in several respects similar to that in Table I.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NANKING]

The Influence of Dipolar Ions on the Solubility of Some Sparingly Soluble Salts

BY FANG-HSUIN LEE AND LI-KWON LUH

The interionic attraction theory applied to dipolar ions and real ions in solution has been formulated by Scatchard and Kirkwood.[1,2] This theory has been supported chiefly by experiments of Cohn.[3] Although much work has been done in finding the effect of varying the concentration of salts on the activity of amino acids, only few experiments have been done on influence of amino acids on the activity of salts. Solubility, f. p. and e. m. f. were the method chiefly used for the latter purpose. Among the amino acids glycine was the one most commonly used. The salts studied by previous workers are NaCl,[4,5] KCl,[6] TlCl,[4,7] $CaCl_2$,[4] $AgIO_3$,[8] $TlIO_3$,[9] $Ba(BrO_3)_2$,[8] $ZnCl_2$,[4] $Ca(IO_3)_2$[8] and $Pb(IO_3)_2$.[8]

According to Kirkwood, the solubility, S, of a sparingly soluble salt is related to the molality, m, of amino acid by the simplified experimental equation

$$\log S/S_0 = K(Z_+ \cdot Z_-/2)m \qquad (1)$$

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(1) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); *Chem. Rev.*, **19**, 275 (1936).

(2) G. Scatchard and J. G. Kirkwood, *Physik.*, 2, **33**, 297 (1932).

(3) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides." Reinhold Publishing Corp., New York, N. Y., 1943.

(4) N. R. Joseph, *J. Biol. Chem.*, **111**, 489 (1935).

(5) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486 and 2314 (1934).

(6) R. M. Roberts and Kirkwood, *ibid.*, **63**, 1373 (1941).

(7) C. F. Failey, *ibid.*, **54**, 576 (1932).

(8) R. M. Keefer, H. C. Reiber and C. S. Bisson, *ibid.*, **62**, 2951 (1940); **63**, 689 (1941).

(9) C. F. Failey, *ibid.*, **55**, 4374 (1933).