[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY]

The Calculation of the Ionization Constants of Inorganic Oxygen Acids from their Structures

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Introduction

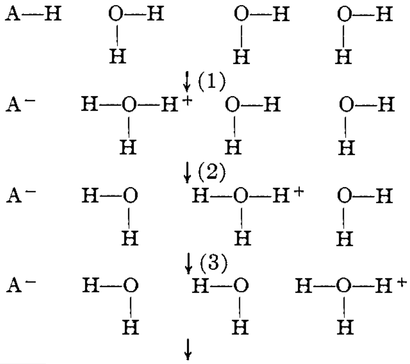
In a given solvent, the free energy of ionization of an acid is directly related to its atomic configuration. The object of this paper is the formulation of a theoretical approach to the evaluation of this relationship. Due to the importance which is generally attached to theoretical calculations correlating physical properties with the structures of molecular systems, it is hoped that the treatment presented here will prove of general interest.

The complicated nature of most acid molecules and of highly polar solvents renders a rigorous calculation of the free energy of ionization impracticable, if not entirely impossible. However, if the treatment is limited to non-resonating oxygen acids a number of reasonable assumptions may be made which facilitate a direct calculation of this quantity. The method of evaluation given here depends on the resolution of the free energy of ionization into one part which is essentially constant for all acids in a given solvent, and another part which depends strongly on the structure of the acid. The constant part constitutes a parameter in the equation; the variable part can be explicitly calculated from structural data. Having determined the parameter from the experimental ionization constant of a single acid, the constants of other acids are uniquely determined. The procedure is simple and direct, enabling a calculation of the ionization constant of an inorganic oxygen acid to be made in a short time with an average accuracy of ±0.8 in log K.

Previous Work.—The wide variation found in the ionization constants of acids has aroused the interest of many investigators. The majority of these have contented themselves with making purely qualitative observations. G. Oddo[2] noted that the ratio of oxygen to hydrogen atoms in an oxygen acid was related to its strength. Hantzsch and Langbein[3] observed that the strength of an acid increased with the number of oxygen atoms per replaceable hydrogen and with the negativity of the central atom. Similar qualitative correlations have been made by a number of other authors.[4]

The problem has been treated quantitatively by Smallwood[5] and by van Arkel and Carriere.[6] Smallwood calculated the relative strengths of some organic acids on the basis of dipole interaction. Since carboxylic acids are resonating systems, it is impracticable to check Smallwood's calculations by the method of this paper. Van Arkel and Carriere attempted to calculate the strengths of acids from the assumption that the charge distribution in the acid molecule is determined by the ions formed by the separate atoms. This assumption is not in agreement with the known structures for most of these molecules, and it is consequently not surprising that the treatment does not lead to results in agreement with experiment. It may be noted that neither Smallwood nor van Arkel and Carriere have considered the properties of the solvent.

Mechanism of Ionization.—There is good evidence that the ionization of an acid takes place through the transfer of the proton from the anion to a water molecule followed by the subsequent exchange of protons between water molecules.[7] The absence of free protons in solution, together with the abnormally large mobility of hydronium ion, provide ample justification for this picture. As will appear later, the mechanism involving proton exchanges is extremely valuable in simplifying the calculation of acid strength. The process may be symbolized thus



$$\begin{array}{llll}
A{-}H & \underset{H}{\underset{|}{O}}{-}H & \underset{H}{\underset{|}{O}}{-}H & \underset{H}{\underset{|}{O}}{-}H \\
 & \downarrow (1) & & \\
A^- & H{-}\underset{H}{\underset{|}{O}}{-}H^+ & \underset{H}{\underset{|}{O}}{-}H & \underset{H}{\underset{|}{O}}{-}H \\
 & \downarrow (2) & & \\
A^- & H{-}\underset{H}{\underset{|}{O}} & H{-}\underset{H}{\underset{|}{O}}{-}H^+ & \underset{H}{\underset{|}{O}}{-}H \\
 & \downarrow (3) & & \\
A^- & H{-}\underset{H}{\underset{|}{O}} & H{-}\underset{H}{\underset{|}{O}} & H{-}\underset{H}{\underset{|}{O}}{-}H^+ \\
 & \downarrow & &
\end{array}$$

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[1] American Can Co. Fellow, Johns Hopkins University.

[2] G. Oddo, *Gazz. chim. ital.*, **52**, 1, 56 (1922).

[3] A. Hantzsch and W. Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932).

[4] R. Oda, S. Namamoto, *J. Soc. Chem. Ind., Japan.*, **35**, Suppl. 543 (1932); H. S. Simms, THIS JOURNAL, **58**, 1239 (1936); T. M. Lowry, *Chemistry & Industry*, **42**, 1048 (1926).

[5] H. M. Smallwood, THIS JOURNAL, **54**, 3049 (1932).

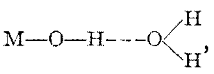
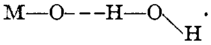
[6] A. E. van Arkel and Carriere, *Chem. Weekblad*, **33**, 182 (1936).

[7] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

and so forth. This process removes the proton from the anion and reorients the water molecules in the immediate vicinity of that oxygen on the anion from which the proton has been removed. Thus, there is no extensive displacement of water, but there is a certain amount of reorientation. It will be seen from the subsequent discussion that a calculation of the free energy change involved in this process is a good approximation to the total free energy of ionization of an acid.

By confining our attention to non-resonating oxygen acids of the non-metallic elements, we are enabled to make approximations which permit the calculation of their free energies of ionization. Oxygen acids—those in which the removable proton is attached to an oxygen atom—comprise a large majority of the inorganic acids, and consequently the limitation of the treatment to this class causes no great loss in scope. The lack of knowledge concerning the energetics of resonating systems requires the elimination of the acids of boron, carbon, and nitrogen from the present treatment. A careful consideration of the ionization process for the non-resonating oxygen acids makes the following assumptions reasonable:

1. The forces between a proton and an acid ion are due to an electron-pair bond with the nearest oxygen atom and to the electrostatic field of the ion.
2. The hydroxyl electron-pair bond is the same for all acids. Variations in strength from one acid to another are due solely to changes in the electrostatic field and symmetry of the ion.
3. Acid and anion molecules form hydrogen bridges to adjacent water molecules, and orient the more distant water molecules by their electrostatic fields. These effects constitute the hydration of the molecules.

The first assumption is based on the fact that exchange forces diminish rapidly with distance and, therefore, will be extremely small between non-bonded atoms. The second assumption is reasonable due to the similarity of the binding of the central atom to the oxygens in the various acids. The third assumption is an expression of the geometry of hydration of anions and acid molecules. Hydroxyl groups rigidly orient the water molecules surrounding them thus:  $\mathrm{M{-}O{-}H{-}{-}{-}O}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix}$, non-hydroxyl oxygen thus:  $\mathrm{M{-}O{-}{-}{-}H{-}O}\diagdown_{\mathrm{H}}$.

Analysis of the Free Energy of Ionization.—Consider an elementary ionization process, in which a particular proton is transferred from a given acid molecule to a particular water molecule. The reversible work done on the system is the sum of the work done in each of the following processes.

1. Rupture of the O–H bond in the acid molecule.
2. Formation of the O–H bond in hydronium ion, H_3O^+.
3. Removal of the proton from the electrostatic field of the anion.
4. Reorientation of the water molecules.
5. Compression of the water molecules.
6. Change in volume of the system against atmospheric pressure.

Let A_1 to A_6 represent the reversible work done on the system in the processes 1 to 6, respectively. The work done on the system, ΔA, is given by the expression

$$\Delta A = \Delta F - \Delta(PV)$$

At constant pressure $\Delta(PV) = -A_6$, the work done against atmospheric pressure. Therefore, the free energy change, $\Delta F'$, for the elementary ionization process, defined above, may be written

$$\Delta F' = A_1 + A_2 + A_3 + A_4 + A_5 \qquad (1)$$

Assumption 2 implies that A_1 is constant for all the acids considered, and A_2 does not depend upon the acid involved.

A_5 is the change in the compression work during ionization. T. J. Webb,[8] in his calculation of the free energy of hydration of ions, has evaluated the compression work, W_c, in terms of the radii and charges of monatomic ions. For a univalent ion of radius 1.5 Å., W_c is calculated to be 1 kcal. It increases as the square of the charge for a monatomic ion. However, for a polyatomic ion containing widely separated centers of charge, W_c will increase approximately with the first power of the total charge. The polyatomic anions of the oxygen acids are cases intermediate between these two extremes. The increase of W_c with the charge of the acid anion will be, therefore, considerably less than second power. The deviations from constancy in A_5 for the large complex anions under consideration should not exceed 0.5 kcal. The error involved in assuming A_5 to be constant is, consequently, small enough to obviate the necessity of its calculation for each acid.

Since A_1, A_2, and A_5 are essentially constant for

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[8] T. J. Webb, THIS JOURNAL, **48**, 2589 (1926).

the acids under consideration, we make the approximation that

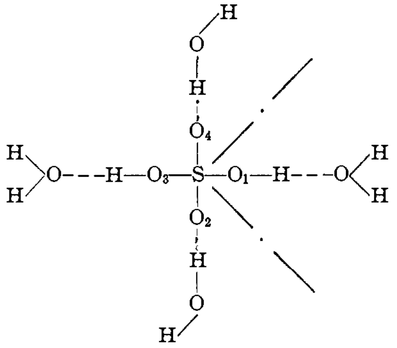
$$A_1 + A_2 + A_5 = C \qquad (2)$$

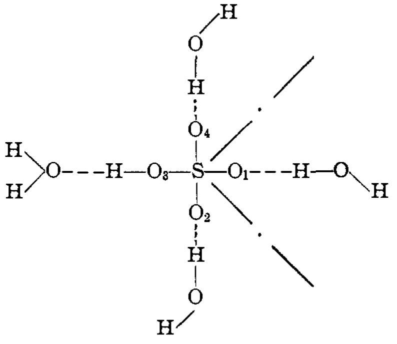
where C depends only on the temperature. Consequently

$$\Delta F' = A_3 + A_4 + C \qquad (3)$$

The Calculation of $A_3 + A_4$.—It is now necessary to show that $A_3 + A_4$ may be calculated by computing the work done in removing a proton from the anion by successive transfers between water molecules. It has been noted that this process reorients the water molecules in the immediate vicinity of that oxygen in the anion from which the proton has been removed. It remains to be shown that this work constitutes practically the entire work of reorientation resulting from the ionization process and, therefore, that A_4 is indeed included in the calculation.

The molecules of oxygen acids are, in general, complex structures, the peripheries of which consist of strongly orienting groups. The assumption has been made that these groups (oxygen and hydroxyl groups) rigidly orient the water molecules surrounding them in a definite way. The consequence is that upon ionization, which changes one hydroxyl group in the molecule into a free oxygen, only the water molecules surrounding this hydroxyl are reoriented. As an example consider H_2SO_4, which changes upon ionization into HSO_4^-. The molecules in the immediate neighborhood will be arranged thus





The main reorientation takes place in the solid angle including O_1, the waters surrounding O_2, O_3, and O_4 maintaining their original orientations. Obviously, the first two proton transfers produce the total change in orientation of the nearest neighboring waters. While subsequent transfers will not reorient all the more distant water molecules, the energy of reorientation of those water molecules which are neglected in the process is small, due to the much greater dielectric constant at large distances and to thermal agitation. Since a rigorous calculation of the total orientation effect would result in only a small correction, and would be extremely involved, the approximation is justified that the proton transfer mechanism calculation includes practically all of the reorientation energy which depends on the structure of the acid.

We write, therefore, the work required to remove the proton from the electrostatic field of the anion, A_3, plus that required to reorient the water molecules, A_4, to a sufficient approximation, as the sum

$$A_3 + A_4 = W_1 + W_2 + W_3 + W_4 + \ldots = \Sigma W_i \qquad (4)$$

where W_i is the change in potential energy accompanying the ith proton transfer. Webb[8] has shown that a calculation of the electrical work involved in a process of this type leads to a term in the free energy change (ΔF) rather than to a term in the internal energy change (ΔE).

The calculation will consist in the evaluation of the W_i's using the familiar formula for the change in mutual potential energy of two particles with charges q_1 and q_2 as the distance between them changes from r_1 to r_2

$$\Delta V = \int_{r_1}^{r_2} \frac{q_1 q_2}{\epsilon r^2}\, dr \qquad (5)$$

where ϵ is the dielectric constant.

In order to apply the formula, we must investigate the charge distribution in the anion and the dielectric properties of the medium.

Distribution of Charge.—There is considerable evidence that in an electron-pair bond between non-metallic atoms the two electrons are shared approximately equally.[9] Since the molecules of the acids under consideration are held together by single electron-pair bonds, we assign to each atom all its non-bonding and half its bonding electrons for the purpose of calculating its effective charge.[10]

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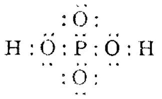
(9) L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

(10) L. Pauling, *ibid.*, **53**, 1367 (1931).

The numerical value of this charge will be equal to the atomic number of the atom minus the number of electrons assigned to it. This number has been called the "formal charge."

Let us take $H_2PO_4^-$ as an example. The Lewis structure of this ion is



$$\begin{array}{c} :\ddot{O}: \\ H:\ddot{O}:\ddot{P}:\ddot{O}:H \\ :\ddot{O}: \end{array}$$

The phosphorus atom has a formal charge of $15 - 14 = +1$, the two "free" oxygens each have a charge of $8 - 9 = -1$, all other atoms have zero formal charge.

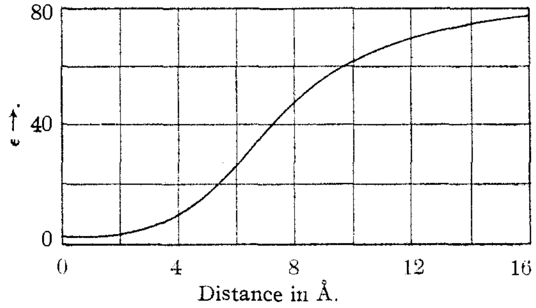


Fig. 1.

In general, the actual charge distribution in a molecule is only approximately represented by the formal charges assigned to its atoms. In addition to the single ionic structure $M^+—O^-$, the doubly covalent structures $M=O$ and completely ionic structures $M^{++}O^=$ must be taken into account in any exact calculation of the energy of the M–O bond. The effects of these two additional bond types on the charge distribution will be in opposite directions, and, therefore, will partially cancel. Moreover, since we shall make calculations only for oxygen acids of the elements in the last three columns of the periodic table (not including the first row), we feel that due to the similarity in the central atoms the small differences between the actual charge distributions and those given by the formal charge method should all be approximately equal. Since there is already a parameter C in the calculated free energy, this uniform difference can be appropriately included in the parameter.

The excellent agreement between the experimental and the calculated free energies of ionization leads us to believe that the actual charge distribution for the acids considered can deviate only slightly from that given by the "formal charge" method.

Dielectric Constant.—The dielectric constant of a solvent in the immediate neighborhood of a charged particle, such as an ion, has an abnormally low value due to the electrical saturation effect produced by the orientation of the solvent dipoles by the field. By the application of the Langevin theory to this problem, Debye[11] has calculated the effective dielectric constant of water as a function of the distance from a univalent ion. The result is shown in the graph, Fig. 1.

It is significant that the dielectric constant remains at a value of 3.0 up to a distance of about 2 Å. from the charged particle. Since the first proton transfer occurs within a distance of 1.8 Å. from the nearest free oxygen atom (which determines the value of ϵ in this region), the change in potential energy, W_1, of the proton during this transfer should be calculated using a constant value of 3.0 for ϵ. For W_1, equation (5) now reduces to the simple form

$$W_1 = \Sigma_j \frac{q_j e}{3.0}\left(\frac{1}{r_{j1}} - \frac{1}{r_{j2}}\right) \qquad (6)$$

where j refers to the jth atom in the anion.

Since the subsequent proton transfers occur at larger distances from the ion, where ϵ is much greater, their contribution to ΣW_i is small compared to W_1. Consequently, deviations of the dielectric constant at distances of over 2 Å. from the ion from the values predicted by Debye will not seriously affect the result.

The Calculation of the Free Energy of Ionization, ΔF, from $\Delta F'$.—It is now necessary to consider the relation between the free energy change $\Delta F'$ and ΔF which is defined in terms of the measured ionization constant

$$\Delta F = -RT \ln K$$

where, for an acid HA

$$K = \frac{(A^-)(H_3O^+)}{(HA)}$$

It will be shown that the difference between $\Delta F'$ and ΔF consists of two terms: one independent of the nature of the acid, the other depending only upon the symmetry of the acid and anion molecules.

In the process to which $\Delta F'$ refers, it is implied that a particular proton is transferred from an acid molecule to a particular position on a certain water molecule; in the reverse process it is im-

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[11] M. P. Langevin, *Ann. chim. phys.*, [8] **5**, 70 (1905); P. Debye, "Marx' Handbuch der Radiologie," Akademische Verlagsgesellschaft, Leipzig, 1925, Vol. VI, pp. 618-680; "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929.

plied that a particular proton is transferred from a hydronium ion to a certain free oxygen on an anion. ΔF, however, refers to a process in which this differentiation between equivalent positions is not made.

That term in the difference between the two quantities which arises from the equivalence of positions on water molecules, and of protons in hydronium ions, is dependent on the concentration of the solution, but not on the nature of the acid. Inasmuch as ionization constants are generally extrapolated to infinite dilution, this term is constant and can be absorbed in the parameter.

The term in the difference between $\Delta F'$ and ΔF which varies with the nature of the acid can be calculated as follows: Let n_{H} be the number of equivalent hydrogens on the acid molecule and n_{O} the number of equivalent oxygens in the anion. Accordingly, in K'—calculated from the relation, $\Delta F' = -RT \ln K'$—the acid concentration to be used is $n_{\mathrm{H}}(\mathrm{HA})$ and the anion concentration is $n_{\mathrm{O}}(\mathrm{A}^-)$. Therefore, disregarding factors independent of the nature of the acid

$$K' = \frac{n_{\mathrm{O}}(\mathrm{A}^-)(\mathrm{H_3O}^+)}{n_{\mathrm{H}}(\mathrm{HA})} = \frac{n_{\mathrm{O}}}{n_{\mathrm{H}}} K$$

Consequently

$$\begin{aligned} \Delta F &= -RT \ln K' + RT \ln \frac{n_{\mathrm{O}}}{n_{\mathrm{H}}} \\ &= \Delta F' + RT \ln \frac{n_{\mathrm{O}}}{n_{\mathrm{H}}} \\ &= \Sigma W_i + RT \ln \frac{n_{\mathrm{O}}}{n_{\mathrm{H}}} + C \qquad (7) \end{aligned}$$

The Numerical Computation of ΔF.—The first step in the calculation of the work involved in the various proton transfers is the construction (on paper) of a scale model of the hydrated acid molecule. The correct distances between atoms and the bond angles are obtained from published results of X-ray and electron diffraction investigations.[12] The electrostatic energy of the proton in the acid molecule is calculated, and from this is subtracted its energy in a position adjacent to the oxygen in the nearest water molecule. This is the work W_1. The work involved in the subsequent proton transfers is calculated in an analogous manner.

We have taken the O–H–O hydrogen bridge distance to be 2.70 Å. and the O–H bond distance to be 0.95 Å. Each proton transfer, therefore, moves the proton a distance 0.80 Å. along the hydrogen bridge.

To evaluate C we take the experimentally determined free energy of ionization of a single acid for which both the structure and the ionization constant are well known. We have chosen $\mathrm{H_3PO_4}$ for this purpose. From this one experimental free energy we are enabled to calculate uniquely the ionization constant of any non-resonating oxygen acid for which the structure is known. Conversely, if a number of structures can be written for a given acid, the experimental value of the ionization constant allows us to choose the true one.

The crystal structures of $\mathrm{BPO_4}$ and $\mathrm{KH_2PO_4}$ have shown the system $\mathrm{PO_4}$ to be tetrahedral. The average P–O distance from these and other measurements is 1.53 Å. Taking the P–O–H angle as 110° we can construct a scale model for the molecule $\mathrm{H_3PO_4}$.

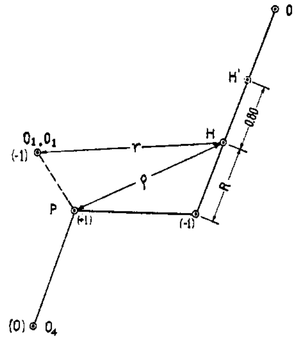

Fig. 2.—$\mathrm{O_2}$ and $\mathrm{O_3}$ out of plane of fig. Formal charges given in parentheses. $\mathrm{O_3}$ and $\mathrm{O_4}$ are hydroxyl oxygens.

By the use of equation (6) we find for the first proton transfer

$$W_1 = \frac{1.44 \times 10^{13} e^2}{3.0} \left[\left(\frac{1}{R_1} - \frac{1}{R_2} \right) - \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) + \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \right]$$

$$= 52.4 - 12.4 + 4.9 = 44.9 \text{ kcal.}$$

Subsequent proton transfers contribute 1.2 kcal. more (calculated by the use of equation (5)), so that $\Sigma W_i = 46.1$ kcal. Since there are three equivalent protons in $\mathrm{H_3PO_4}$ and two equivalent free oxygens on $\mathrm{H_2PO_4}^-$, $RT \ln \frac{n_{\mathrm{O}}}{n_{\mathrm{H}}} = RT \ln \frac{2}{3} = -0.2$ kcal. Experimentally $-RT \log K$ for $\mathrm{H_3PO_4}$ in water at 298.1°K. is 2.9 kcal. From these data we can evaluate the parameter C in equation (7).

$$2.9 = 46.1 - 0.2 + C \qquad C = -43.0 \text{ kcal.}$$

Since W_1, which is very easy to compute, turns

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(12) *Zeitschrift für Kristallographie*, Ergänzungsband (Strukturbericht) I, II, III, Akademische Verlagsgesellschaft, Leipzig.

TABLE I

Acid	d^a	W_1	W_i	$RT \ln \frac{n_O}{n_H}$	$\Delta F'$	ΔF	$-\log K_1$	$-\log K$	$-\log K_{\text{obsd.}}$ Tables[14]	
H_4GeO_4	1.59	52.4	53.7	−0.8	9.8	9.9	7.2	7.3	8.6	
H_3PO_4	1.53	44.9	46.1	− .2	2.9	2.9	2.1	2.1	2.1[b]	
$H_2PO_4^-$	1.53	49.8	51.7	+ .2	8.2	8.9	6.0	6.5	7.2	
$HPO_4^=$	1.53	55.6	58.0	+ .6	14.3	15.6	10.5	11.4	11.9	
H_3PO_3	1.53	44.9	46.1	.0	3.1	3.1	2.3	2.3	1.6	
$H_2PO_3^-$	1.53	49.8	51.6	+ .6	8.6	9.2	6.3	6.7	6.7	
$H_4P_2O_7$	1.53[c]	44.4	45.6	− .6	2.0	2.0	1.5	1.5	0.9	
$H_3P_2O_7^-$	1.53	46.3	47.6	+ .6	5.1	5.2	3.7	3.8	2.0	
$H_2P_2O_7^=$	1.53	52.0	53.8	− .4	9.8	10.4	7.2	7.6	6.7	
$HP_2O_7^{\equiv}$	1.53	53.9	55.9	+1.1	13.2	14.0	9.7	10.3	9.4	
H_3AsO_4	1.66	45.4	46.6	−0.2	3.4	3.4	2.5	2.5	2.3	
$H_2AsO_4^-$	1.66	49.4	51.3	+ .2	7.8	8.5	5.7	6.2	7.0	
$HAsO_4^=$	1.66	54.6	56.8	+ .6	13.4	14.4	9.8	10.5	9.2	
H_3AsO_3	1.66	52.4	53.7	− .6	10.0	10.1	7.3	7.4	9.2	
HSO_4^-	1.50	43.3	44.9	+ .8	2.3	2.7	1.7	2.0	1.7	1.9[15]
H_2SO_3	1.50	44.8	46.1	.0	3.0	3.1	2.2	2.3	1.9	
HSO_3^-	1.50	50.0	52.0	+ .6	8.8	9.6	6.4	7.0	5.3	7.0[16]
H_2SeO_3	1.73	45.6	46.9	.0	3.8	3.9	2.8	2.9	2.3	
$HSeO_3^-$	1.73	49.2	51.0	+ .6	8.0	8.6	5.9	6.3	8.1	
H_2TeO_3	1.84[d]	46.0	47.3	0	4.2	4.3	3.1	3.1	2.5	
$HTeO_3^-$	1.84	49.2	51.0	+ .6	8.0	8.6	5.9	6.3	7.7	
H_6TeO_6	1.97[d]	52.4	53.7	−1.1	9.5	9.6	7.0	7.0	6.2	7.7[16]
$H_5TeO_6^-$	1.97	55.0	56.5	−0.4	12.8	13.1	9.4	9.6	10.4	11.2[16]
HOCl	1.54	52.4	53.7	.0	10.6	10.7	7.8	7.8	6.2	7.4[17]
$HClO_2$	1.54	45.0	46.2	+ .4	3.6	3.6	2.6	2.6	..	2.0[18]
HIO_3	1.80	39.3	41.0	+ .6	−1.9	−1.4	−1.4	−1.0	0.7	
H_5IO_6	1.93	46.2	47.3	− .4	4.0	3.9	2.9	2.9	1.6	

[a] d = central atom-oxygen distance. [b] The parameter, C, is determined by this value. [c] The P–P distance in $H_4P_2O_7$ = 3.12 Å. [d] Since the Te covalent radius is 0.04 Å. greater than that for I,[13] this distance has been added to the experimentally determined I–O distances to obtain the Te–O distances in corresponding compounds.

out to be a good approximation to ΣW_i, we have thought it worth while to evaluate a parameter C_1 for the simpler calculation by means of the relation

$$\Delta F_1 = W_1 + RT \ln \frac{n_O}{n_H} + C_1 \qquad (8)$$

and to list values of $-\log K_1$ calculated from ΔF_1 to show the relatively good results obtainable in this way.

$$2.9 = 44.9 - 0.2 + C_1 \qquad C_1 = -41.9 \text{ kcal.}$$

Having fixed the parameter in our equation, it can be used for the prediction of the free energy of ionization of other acids. For instance, for the second ionization step of H_3PO_4 (the ionization of $H_2PO_4^-$) ΣW_i is found to be 51.7 kcal., and $RT \ln \frac{n_O}{n_H} = RT \ln \frac{3}{2} = +0.2$ kcal. Adding C, $\Delta F = 8.9$ leading to a value of $-\log K = 6.5$ as compared to be experimentally determined value of 7.2.

Numerous other acids have been treated in the same way as $H_2PO_4^-$ and the results are set forth in Table I. In Fig. 3 $-\log K$ (observed) is plotted against $-\log K$ (calculated). A line of unit slope appears in the plot on which all points would fall if the agreement were perfect. The horizontal distance from a point to the line is numerically equal to the deviation of the calculated from the experimental result.

The agreement of the calculated with the observed values is quite striking in view of the simplicity of the calculation. While the acids included are all oxygen acids of the elements in the last four columns of the periodic table, the elements considered range from chlorine, whose properties are typically non-metallic, to tellurium, which is a metalloid. Moreover, the ion acids, such as HSO_4^-, fit nicely into the scheme. The quantities calculated represent differences between large numbers, making the resulting agreement all the more encouraging.

The values of $-\log K$ (calculated) for the first

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(13) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(14) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Erganzungsband II. 1931.

(15) W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

(16) H. T. S. Britton and R. A. Robinson, *Trans. Faraday Soc.*, **28**, 531 (1932).

(17) J. W. Ingram and Morrison, *J. Chem. Soc.*, 1200 (1933).

(18) Barnett, Thesis, University of California, 1935.

ionization step, for which the assumptions should be most nearly valid, show a mean absolute deviation of about 0.8 from $-\log K$ (observed). This means an average agreement of the calculated with the experimental ionization constants within a factor of 6. When the ion acids are included, the total mean absolute deviation in $-\log K$ is 0.9, or an average agreement of the ionization constants within a factor of 8. There seems to be no trend in the deviations, notwithstanding the fact that there is only one parameter to be determined from experimental data.

Prediction of Structures.—In case several reasonable atomic configurations can be postulated for a given acid, the true one usually can be chosen by comparing the strength calculated for each of these structures with the experimental value, since the calculated strength is very sensitive to change in the structure of the acid. In general, the strength corresponding to one structure agrees closely with the observed value, while the strengths corresponding to the other structures differ from that observed by far more than the error of the method. Calculations of this type have been made for a number of such acids and the results appear in Table II.

It is seen that the structures $Ge(OH)_4$, $HPO(OH)_2$, $As(OH)_3$, $Te(OH)_6$, and $IO(OH)_5$ give calculated ionization constants in good agreement with those observed. The alternate structures, on the other hand, lead to completely unreasonable values. The correct structures of phosphorous, arsenious,[12] telluric,[19] and periodic[20] acids have been determined previously by other methods; this calculation merely confirms these results. We believe that our result provides the first evidence concerning the structure of germanic acid.

Strong Acids.—There are a number of oxygen acids which are completely ionized in aqueous solution. The calculated values of $-\log K$ for these acids are all negative, in general agreement with experiment (see Table III). The theory predicts that in any hydroxylated solvent, such as alcohol, the free energies of ionization of non-resonating oxygen acids will differ from those in aqueous solution only by a change in the parameter C. The relative strengths of the acids would be the same as in water, the change being an additive constant in the expression for $-\log K$.

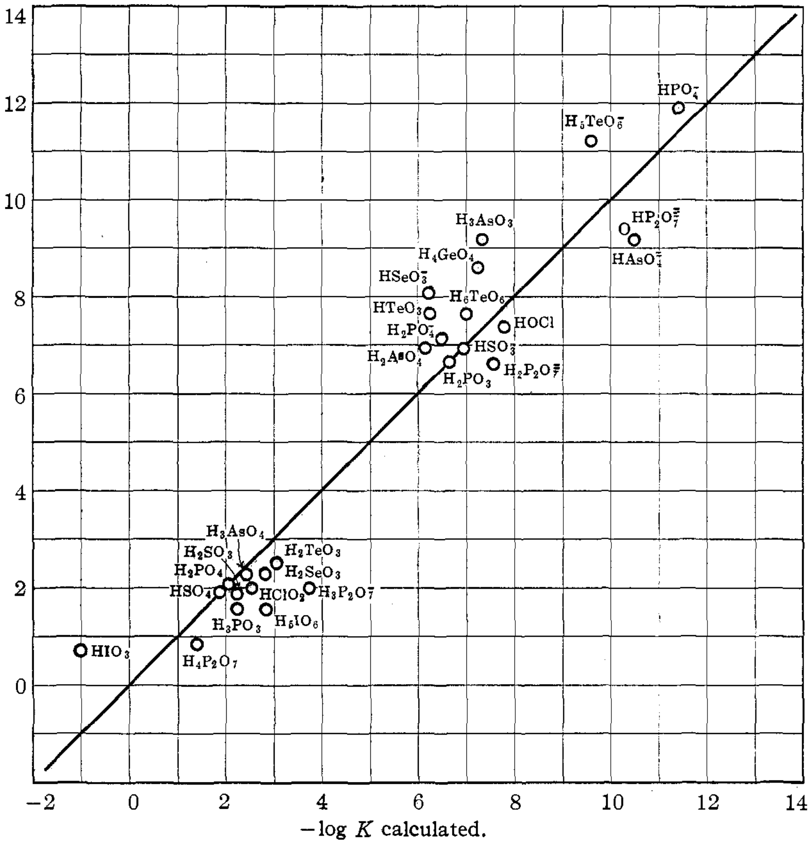

Fig. 3.—$HPO_4^{=}$, $HTeO_3^-$, $H_2AsO_4^-$, $H_2PO_3^-$, H_3PO_4, etc.

At present there are insufficient data on the strengths of these acids in non-aqueous solvents to permit a reliable evaluation of C. However, we have tabulated the results of the calculations for some of these acids so that, when the data become available, we may compare our results with experiment. The results of these calculations appear in Table III.

Oxygen Acids of First Row Elements.—Boric, carbonic, nitric, nitrous, and the carboxylic acids have atomic configurations which permit more than one electron structure to be written either

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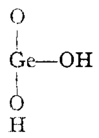
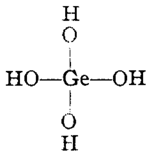
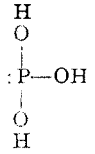
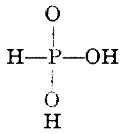
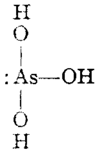
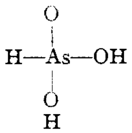
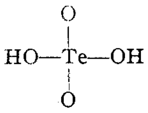
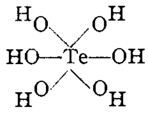
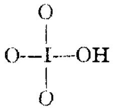
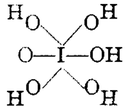
(19) L. M. Kirkpatrick and L. Pauling, *Z. Krist.*, **63**, 502 (1926).
(20) L. Helmholz, THIS JOURNAL, **59**, 2036 (1937).

TABLE II

Acid	Structure I	Structure II	−log $K_{\text{calcd.}}$ I	−log $K_{\text{calcd.}}$ II	−log $K_{\text{obsd.}}$	Difference I	Difference II
Germanic[a]			2.6	7.3	8.6	−5.0	−1.3
Phosphorous			7.4	2.3	1.6	+5.8	+0.7
(2nd)			11.9	6.7	6.7	+5.2	0.0
Arsenious			7.4	2.8	9.2	−1.8	−6.4
Telluric			−1.2	7.0	7.7	−7.4	−0.7
(2nd)			2.0	9.6	11.2	−8.4	−1.6
Periodic			−4.8	2.9	1.6	−6.4	+1.3

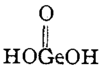
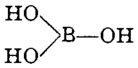
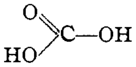
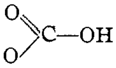
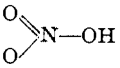
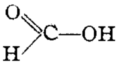
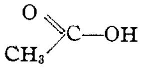
[a] The calculation does not exclude the possibility of a carbonic acid structure for germanic acid:  $\mathrm{HO\overset{\overset{O}{\|}}{Ge}OH}$. However, double bonds to elements in the second row of the periodic table are rare, and have never been found for third row elements. Together with crystal structure data for GeO_2, this fact makes the existence of the double bonded structure for germanic acid extremely improbable.

TABLE III

Acid	d	W_i	$RT \ln n_O/n_H$	ΔF	−log $K_{\text{calcd.}}$
H_2SO_4	1.50	38.7	+0.2	−4.1	−3.0
$H_2S_2O_6$	1.50[a]	38.7	−0.4	−4.7	−3.4
$HS_2O_6^-$	1.50[a]	41.6	+1.1	−0.3	−0.2
$HClO_4$	1.54	32.7	+0.8	−9.9	−7.3
$HClO_3$	1.54	38.7	+0.6	−3.7	−2.7

[a] The S–S distance in $H_2S_2O_6$ = 2.01 Å.

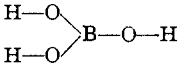
TABLE IV

Acid	Classical structure	−log $K_{\text{calcd.}}$	−log $K_{\text{obsd.}}$	Difference
Boric		7.4	9.2	−1.8
Carbonic		7.5	6.5	+1.0
(2nd)		12.2	10.4	+1.8
Nitric		−0.1	≪0	...
Nitrous	O=N—OH	7.8	3.3	+4.5
Formic		7.8	3.7	+4.1
Acetic		7.8	4.7	+3.1

for the acid molecule, or for the anion, or for both. This fact makes it impossible to assign a unique formal charge to each atom and, consequently, the calculation of the ionization constants of these acids cannot be made by the method of this paper. However, we can calculate the ionization constant corresponding to any one electron structure and compare it with the experimental result. If the true charge distribution is close to that used in the calculation, the calculated and observed ionization constants should be in good agreement.

The ionization constants of these acids, calculated on the basis of their classical structures, all turn out to be smaller than the observed values, except for the case of H_3BO_3. While the deviations may be considered to be within the error of the calculation for carbonic acid and bicarbonate ion, the deviations for nitric, nitrous, and the carboxylic acids are far outside the error of the calculation. Measurements of absorption spectra[21] and bond distances[12] for these latter substances indicate the absence of localized double bonds, and therefore the classical structures should not be expected to lead to true ionization constants.

The resonance phenomenon accounts not only for the absence of localized double bonds but also for the decrease in the work of ionization. Resonance in the acid molecule decreases the negative charge on the hydroxyl oxygen. The removal of the proton increases the resonance of the system, thereby producing a further decrease in the work of ionization. Thus, the presence of this effect may well account for the magnitude and direction of the differences between the calculated and observed ionization constants of these acids.

The case of boric acid deserves special mention in view of the interest attached to the type of bonding present in boron compounds. The structures of a large number of boron compounds have been determined recently.[22–26] It has been assumed generally that the boron halides (except perhaps BF_3) possess double bond resonance of the graphite type. On the other hand, boron trimethyl has been shown by Lévy and Brockway[25] to have a structure containing three coplanar single bonds (*sp*^{2}). Evidence as to the type of bonding present in boric acid can be obtained from its ionization constant. The ionization constant calculated from the planar, single bond structure,  $\mathrm{(H{-}O)_2{>}B{-}O{-}H}$ agrees with experiment within the error of the calculation, showing that the *sp*^{2} structure is a good approximation to the true one. The deviation between the calculated and observed values is in the opposite direction from the deviations observed for acids exhibiting double bond resonance and, therefore, indicates that such resonance is absent or very small in the structure of boric acid. The calculation points to the presence of ionic structures such as $(OH)_2B^+(OH)^-$, although the deviation is not great enough compared to the error of the experiment to justify an estimate of the importance of these structures.

Acknowledgment.—We are deeply indebted to Dr. Joseph E. Mayer, of this department, and to Dr. Linus Pauling and Mr. Henri Lévy, of the California Institute of Technology, for many constructive suggestions and criticisms which were extremely valuable in the preparation of this paper.

Summary

The calculation of the ionization constants of inorganic oxygen acids has been carried out on the basis of reasonable assumptions concerning the structures of the acid molecules and the mechanism of ionization. Most of the calculated ionization constants agree with the experimental ones to within a factor of 8.

1. The free energy of ionization has been shown to consist of a term depending only on the structure of the acid and a term depending only on the solvent and the temperature. The constant term has been evaluated from the ionization constant of a single acid of known structure.
2. The ionization constants of a large number of acids have been evaluated, and have been found to agree well with experimental values.
3. On the basis of the calculation the structures of a number of acids have been determined from their known strengths.
4. The effect of resonance on the strength of acids has been discussed.

BALTIMORE, MD.

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(21) A. Hantzsch, *Ber.*, **50**, 1422 (1917).

(22) L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

(23) S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

(24) S. H. Bauer, *ibid.*, **59**, 1906, 1804 (1937).

(25) H. A. Lévy and L. O. Brockway, *ibid.*, **59**, 2085 (1937).

(26) W. H. Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937).