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THE ACTIVITY COEFFICIENTS, IONIC CONCENTRATIONS AND KINETIC SALT EFFECTS OF FORMIC ACID IN NEUTRAL SALT SOLUTIONS

BY HERBERT S. HARNED

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In very dilute solutions we may express the variation of the activity coefficient of an electrolyte as a function of the total ionic concentration by an expression derivable from the Debye and Hückel theory,[1] namely,

$$\log \gamma = -0.495\, z_1 z_2 \sqrt{\mu} \qquad (1)$$

where z_1 and z_2 are the valences of the ions of the electrolyte, γ is its activity coefficient, μ the ionic strength of the solution, and where the solvent is water. Since the expression on the right of this equation is always negative, γ must decrease upon increasing the total concentration of the solution. In the case of a weak electrolyte, for example a uni-univalent organic acid, the validity of the equilibrium relation

$$k_a = \frac{a_H a_A}{a_{HA}} = \frac{\gamma_H \gamma_A}{\gamma_{HA}} \frac{c_H c_A}{c_{HA}} \qquad (2)$$

is thermodynamically necessary, where a_H, a_A and a_{HA} are the activities of the hydrogen ion, the acid ion and the undissociated molecule, γ_H, etc., c_H, etc., are the activity coefficients and concentrations of the species denoted by subscripts. Since for small changes in μ in dilute solutions, γ_{HA} is not to be expected to change appreciably, and since, according to Equation 1, $\gamma_H \gamma_A$ will decrease rapidly upon increasing the ionic strength, $c_H c_A / c_{HA}$ will exhibit a very rapid increase when a hetero-ionic salt is added to the acid.

Very recently,[2] an electromotive-force method has been devised for

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[1] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[2] Harned, *ibid.*, **47**, 930 (1925).

the determination of the ionic activity-coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, and accordingly the activity coefficient, $\sqrt{\gamma_H\gamma_{OH}}$, in salt solutions, relative to a given concentration such as 0.01 *M*. The values of this quantity in the 0.01 *M* salt solutions were calculated according to Debye and Hückel's theory, and the dissociation of water, or $\sqrt{c_Hc_{OH}}$, was calculated from the activity-coefficient product by an equation similar to Equation 2. So far $\gamma_H\gamma_{OH}/a_{H_2O}$ and $\sqrt{\gamma_H\gamma_{OH}}$ have been obtained in lithium, sodium and potassium chloride and sulfate solutions, and sodium and potassium bromide solutions.[3]

This change in concentration of a weak electrolyte upon the addition of a salt may be employed to explain the increase in reaction velocity of reactions involving the hydrogen- or hydroxyl-ion catalysis of a substance when the catalyst is a weak acid or hydroxide. Brönsted has thus been able to verify satisfactorily the conclusion already reached by Arrhenius[4] that these reaction-velocity constants were proportional to the concentrations of the catalyzing ion in dilute salt systems. This is true of certain reactions when the catalyzing ion is at very low concentration.

In the following, an attempt has been made to evaluate approximately the activity coefficient of a weak electrolyte, formic acid, from reaction-velocity measurements and to compare these results with the ionic activity-coefficient products of water computed from electromotive-force measurements.

1. Calculation of the Activity-Coefficient Product of Formic Acid from the Data of the Neutral Salt Catalysis of Ethyl Formate

The velocity of the reaction $HCOOC_2H_5 + H_2O = HCOOH + C_2H_5OH$ in pure aqueous and in aqueous salt solutions has been studied by Manning.[5] This reaction is autocatalytic and, therefore, upon the assumption that the velocity is proportional to the concentration of the hydrogen ion, the equation for the velocity becomes

$$dx/dt = k(a_0 - x)c_H \tag{3}$$

where c_H is the hydrogen-ion concentration, a_0 the initial concentration of ester and the other symbols have their usual significance. Now

$$x = c_H + c_{HF} \tag{4}$$

where c_{HF} is the concentration of the undissociated formic acid. Further, the equilibrium constant of formic acid, K_a, is given by

$$K_a = \frac{a_Ha_F}{a_{HF}} = \frac{\gamma_H\gamma_F}{\gamma_{HF}}\frac{c_Hc_F}{c_{HF}} = \frac{\gamma_H\gamma_F}{\gamma_{HF}}K_c \tag{5}$$

where the *a*'s, γ's and *c*'s are the activities, activity coefficients and con-

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[3] Harned and Swindells, This Journal, **48,** 126 (1926). Åkerlöf, *ibid.*, **48,** 1160 (1926). Harned and James, *J. Phys. Chem.*, **30,** 1060 (1926).

[4] Brönsted, *J. Chem. Soc.*, **119,** 574 (1921). Arrhenius, *Z. physik. Chem.*, **31,** 197 (1899).

[5] Manning, *J. Chem. Soc.*, **119,** 2079 (1921).

centrations of the species denoted by subscripts, and $K_c = c_Hc_F/c_{HF}$. Further,

$$K_c = \frac{c_H^2}{c_{HF}} \tag{6}$$

if the ions of the added salt do not react to form complex ions with either the formate or the hydrogen ions. Therefore, $c_H = (K_c/2)\ (\sqrt{1 + 4x/K_c} - 1)$ by Equations 4 and 6. Substituting this value of c_H in Equation 3, we obtain

$$\frac{dx}{dt} = \frac{k}{2} K_c\,(a_0 - x) \left\{ \sqrt{1 + \frac{4x}{K_c}} - 1 \right\} \tag{7}$$

If during the course of the reaction $\gamma_H\gamma_F/\gamma_{HF}$ and, consequently, K_c do not vary perceptibly, this equation may be integrated and employed in the form

$$2a_0k(t_1 - t_0) = {}^{x_1}_{x_0}[2 \log (A - 1) + (B - 1) \log (B + A) - (B + 1) \log (B - A)] \tag{8}$$

where

$$A = \sqrt{1 + (4x/K_c)};\quad B = \sqrt{1 + (4a_0/K_c)} \tag{8a}$$

By employing these equations and 2.14 × 10^{-4} for K_c,[6] Manning obtained values for k which, during the course of an experiment, did not vary over ± 1% from the mean in all cases except those for the solutions containing potassium sulfate. Assuming a constant value for K_c, Manning found that k was increased very rapidly by the first addition of neutral salt, that it reached a maximum and then decreased slowly upon further addition.

Since we have mentioned that K_c or c_Hc_A/c_{HA} for a weak acid changes with salt addition, Manning's assumption regarding its constancy is illegitimate. We have, therefore, made the following assumptions: (1) that K_c equals 2.14 × 10^{-4} at 25° in pure aqueous solution so that k equals 4.84, the value obtained by Manning; (2) that K_c varies upon the addition of salt; thus, from the assumed constant value of 4.84 for k, we have computed K_c by Equations 8 and 8a; (3) that the assumption that K_c is constant during the course of the reaction in a medium of practically constant ionic strength is verified by the constancy of the velocity constants in a given experiment.

The method of calculating K_c needs some further comment. Since complete data for a determination were given by Manning in only a few of his experiments, it was not possible to calculate K_c directly from all of his results. Therefore, this quantity was computed by a method of arithmetical approximation for all cases where complete data were available. The values of K_c obtained in this manner were then plotted against the corresponding values of k computed by Manning upon his assumption that K_c was constant. From this plot, K_c could be read off for any value

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[6] Landolt-Börnstein, "Tabellen," Julius Springer, Berlin, **1912**, p. 1135.

of k given in Manning's tables. From the values of K_c thus obtained, we may compute $\gamma_H\gamma_F/\gamma_{HF}$, for by rearranging Equation 5, we obtain

$$\gamma_H\gamma_F/\gamma_{HF} = K_a/K_c \qquad (5)$$

If we let $K_a = K_c = 2.14 \times 10^{-4}$ at zero salt concentration, $\gamma_H\gamma_F/\gamma_{HF}$ may readily be calculated at any salt concentration. The results are compiled in Table I.

TABLE I

VALUES OF $\gamma_H\gamma_F/\gamma_{HF}$ AT 25°

Concn. of salt (Normal)	KCl	NaCl	KNO_3	$NaNO_3$	$CaCl_2$	$BaCl_2$
0	1.00	1.00	1.00	1.00	1.00	1.00
0.1	0.68	0.67	0.70	0.67	0.58	0.60
.25	.59	..	.63	.59	..	.45
.5	.51	.46	.60	..	.29	.33
1.0	.42	.37	.60	.51	.21	.23
2.0	.43	.32	.76	.54	..	..

The values of $\gamma_H\gamma_F/\gamma_{HF}$ in Table I calculated upon the basis of the concentration hypothesis are quite reasonable. Thus, at 0.1 N potassium chloride, upon the approximate assumption that γ_{HF} equals unity, γ or $\sqrt{\gamma_H\gamma_F}$ equals 0.826. This agrees as well as could be expected with the activity coefficient of other uni-univalent acids. Thus, γ of 0.1 N hydrochloric acid is 0.81. This agreement has led to the adoption of the concentration law of velocity and not the activity-rate theory. Had we adopted the latter, the fundamental equation would have been

$$dx/dt = k(a - x)\ \gamma_H c_H a_{H_2O} \qquad (9)$$

and the left-hand member of the integrated equation would have been $2a(k\gamma_H)\ (t_1 - t_0)$, while the right-hand member would have been the same as the right of Equation 8. The variation of the activity or concentration of water has been omitted. This effect is small in the dilute solutions, and not sufficiently different for the different salts to affect the relative distribution of the results in the cases of the different salts. If at 0.1 M potassium chloride, we take γ_H equal to 0.8, $k\gamma_H$ would equal 4.84×0.8, K_c would equal 1.98×10^{-4}, $\gamma_H\gamma_F/\gamma_{HF}$ would equal 1.08, and upon the assumption that γ_{HF} equals unity, γ would equal 1.04. From this, it is obvious that the concentration hypothesis yields more reasonable results than the activity rate theory.

According to Brönsted's theory and neglecting the activity of water,[7] the velocity of the reaction would be given by

$$dx/dt = k(a - x)\ \gamma_H\gamma_e/\gamma_c\, c_H \qquad (10)$$

where γ_e is the activity coefficient of the ester and γ_c that of the intermediate complex. As the total concentration of the solution decreases $\gamma_H\gamma_e/\gamma_c$ approaches unity and this theory approaches the concentration

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[7] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

hypothesis. When we come to deal with the concentrated solutions, it is impossible to apply Brönsted's theory since we cannot evaluate γ_c and consequently $\gamma_H\gamma_e/\gamma_c$. For the present, therefore, our expedient has been to apply the simple concentration hypothesis, see whether such an assumption is reasonable and the results are comparable to similar values derived from electromotive-force measurements.

2. Discussion of Results

In Fig. 1 the values of $\gamma_H\gamma_F/\gamma_{HF}$ in the uni-univalent salt solutions taken from Table I are plotted against the square root of the ionic strength.

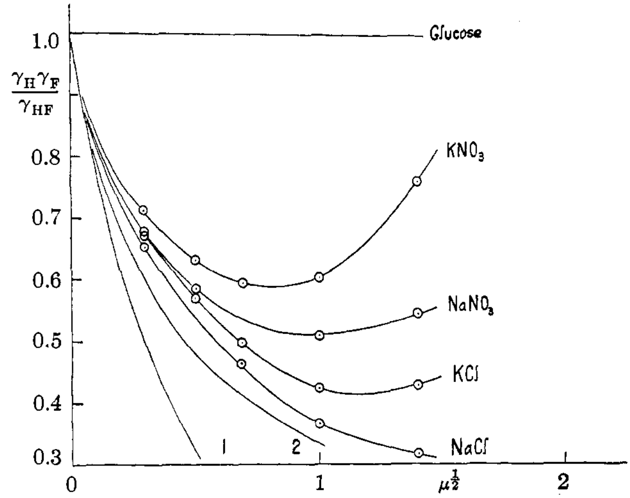

Fig. 1.—Activity coefficient product of formic acid in uni-univalent salt solutions.

Curve 1 is a plot of the values of γ^2 for a uni-univalent electrolyte calculated by the limiting equation of the theory of Debye and Hückel, namely

$$\log \gamma = -0.354\sqrt{2\mu} \qquad (11)$$

and Curve 2 is a plot of similar values obtained from their equation which contains the "mean apparent ionic diameter," A, and which is

$$\log \gamma = -\frac{0.354\sqrt{2\mu}}{1 + A\sqrt{2\mu}} \qquad (12)$$

A probable value of 0.8 was used for A. In the first place, these curves all approach in a reasonable manner the values given by the limiting function. Further, in the more concentrated solutions three of the four plots exhibit minima, a behavior characteristic of many other electrolytes at high concentrations. The most important feature of these values lies in the fact that $\gamma_H\gamma_F/\gamma_{HF}$ is greater in the solutions of the salt which possesses the lower activity coefficient. Thus, it is known that the activity coefficients of these salts at a given concentration are less in the order sodium, potassium chlorides, sodium, potassium nitrates.

We are thus led to the conclusion that formic acid and most likely other weak electrolytes are dissociated to the greatest extent in the solution of the salt which has the highest activity coefficient. That this salt action is essentially electrical is borne out by the fact that a non-electrolyte, glucose, was shown by Manning to produce very little effect, if any, on the velocity of hydrolysis of ethyl formate and according to the present interpretation little or no effect on the activity coefficient of formic acid.

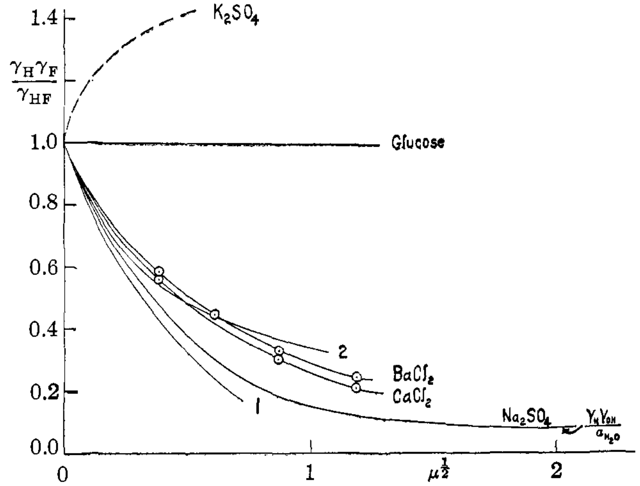

Fig. 2.—Activity coefficient product of formic acid in bi-univalent salt solutions.

In Fig. 2, the data in Table I on $\gamma_H\gamma_F/\gamma_{HF}$ in calcium and barium chloride solutions are plotted against $\mu^{1/2}$. For purposes of comparison, Curves 1 and 2 of the Debye and Hückel theory as well as the values $\gamma_H\gamma_{OH}/a_{H_2O}$ in sodium sulfate solutions taken from Fig. 3 are added. Further, $\gamma_H\gamma_F/\gamma_{HF}$ in potassium sulfate solutions calculated in the same manner from Manning's results are plotted, as well as the curve which shows the effect of glucose. In the first place, the values of $\gamma_H\gamma_F/\gamma_{HF}$ in the bi-univalent chlorides are of the same order of magnitude as the values of $\gamma_H\gamma_{OH}/a_{H_2O}$ in the sulfate solutions. Second, $\gamma_H\gamma_F/\gamma_{HF}$ is less in the calcium than in the barium chloride solutions, which again agrees with the rule that this quantity is less at a given concentration in the solution which contains the salt that in aqueous solution possesses the higher activity coefficient. That calcium chloride has a greater activity coefficient than barium chloride has been shown by Lucasse.[8] An explanation of the apparently anomalous behavior in the case of the

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[8] Lucasse, This Journal, **47**, 743 (1925).

neutral sulfates is not difficult if we assume that the acid sulfate ion is a weak acid. In this case, our method for evaluating $\gamma_H\gamma_F/\gamma_{HF}$ by calculating c_Hc_F/c_{HF} from velocity measurements is illegitimate since the sulfate ion will remove hydrogen ions to form the acid sulfate ion and c_Hc_F/c_{HF} will have a value which is too low and $\gamma_H\gamma_F/\gamma_{HF}$ a value which is too high.

For the purposes of comparison, similar plots for the activity-coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, in halide and sulfate solutions are given in Fig. 3 along with the theoretical plots of the Debye and Hückel theory. As in the case of formic acid, the value of the activity coefficient of water is greater in the solution of an electrolyte of a given type which has the lower activity coefficient, a fact which signifies a similarity in behavior between the hydroxyl and formate ions.

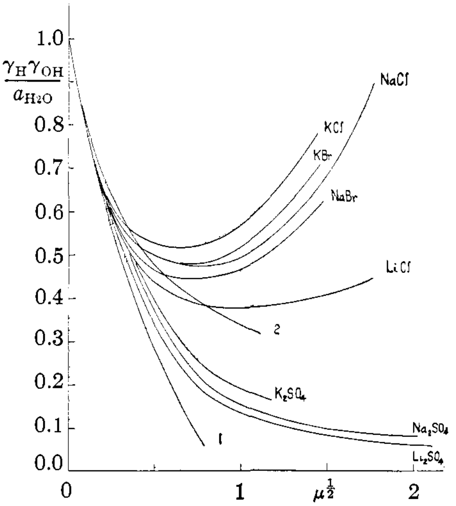

Fig. 3.—Ionic activity coefficient product of water in chloride and sulfate solutions.

3. Theoretical Considerations

We shall consider as typical the data for $\gamma_H\gamma_{OH}/a_{H_2O}$ shown in Fig. 3. At ionic strength below 0.1 μ, all the results begin to approach the same limiting values. Therefore, if Debye and Hückel's limiting function is the correct one, then this and the thermodynamic law of water equilibrium, namely, $K_w = (\gamma_H\gamma_{OH}/a_{H_2O})c_Hc_{OH}$, are the necessary and sufficient conditions for a theory of the increasing dissociation of water in very dilute solutions upon salt addition.

At higher concentrations, specific effects of varying magnitudes due to the different salts are noticeable, and the character of the distribution of the curves is of considerable importance since the activity-coefficient product is always less in a solution of an electrolyte of a given valence type which has the higher activity coefficient. Now, according to Hückel's theory[9] of concentrated solutions, the increase in activity coefficient of an electrolyte above the value given by Equation 12 is due to a decrease in the dielectric constant of the medium according to the law $D = D_0 - \Sigma\delta_ic_i$ where D is the dielectric constant of the salt solution, D_0 that of the pure solvent, c_i is the concentration of an ion, and δ_i a constant char-

[9] Hückel, *Physik. Z.*, **26**, 93 (1925).

acteristic of the effect of an ion on the dielectric constant of the solution. The introduction of this consideration leads to the term $(B2\mu)$ in the general equation of Hückel's extension of the Debye and Hückel theory. In the case of a single electrolyte, the higher the value of $\Sigma\delta_i c_i$, the higher $(B2\mu)$, and the higher the activity coefficient. Further, by this theory, the activity coefficient of an electrolyte in a solution of another electrolyte will be greater when the latter electrolyte possesses the higher $\Sigma\delta_i$ value. This has been shown experimentally by Harned[10a] and by Harned and Brumbaugh[10b] to be the case for hydrochloric acid in chloride solutions, and by Harned and Sturgis[10c] and by Åkerlöf[10d] for sulfuric acid in sulfate solutions. Thus, $\gamma_{\mathrm{HCl(LiCl)}} > \gamma_{\mathrm{HCl(NaCl)}} > \gamma_{\mathrm{HCl(KCl)}}$. But when we come to consider the activity coefficients of the alkali metal hydroxides in chloride and sulfate solutions, the reverse is true. Thus, $\gamma_{\mathrm{LiOH(LiCl)}} < \gamma_{\mathrm{NaOH(NaCl)}} < \gamma_{\mathrm{KOH(KCl)}}$. To explain this behavior, Harned and Åkerlöf[11] have suggested that the total electrical field in the different electrolytic solutions influences to different extents the electrostatic moment of the hydroxyl ion, and in this manner changes its free energy. As compared with the ions of the alkali metals and the halide ions, the hydroxyl ion has a highly unsymmetrical structure. For this reason it will be more easily distorted and will acquire a greater or less asymmetry depending on the ions in the solution with it. For example, the hydroxyl ion will be deformed to a greater extent in the order potassium chloride, bromide, sodium chloride, bromide, and lithium chloride solutions or, according to theory, in the solution of the electrolyte which at a given strength possesses the highest electrical field intensity.

That this effect must be a specific action of these electrolytes on the character of the hydroxyl ion is evidenced by a consideration of $\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}/a_{\mathrm{H_2O}}$ in the salt solutions, for in the same aqueous solution of a salt, both the activity coefficients of water and salt are known. From the unmodified Hückel theory, $\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}/a_{\mathrm{H_2O}}$ should be greater in the solution of the salt which possesses the higher $\Sigma\delta_i$ value. This prediction is just the opposite to what we observe and therefore, since the hydrogen and hydroxyl ions are present to an extent too small to change appreciably the nature of the medium as a whole, we are forced to a theory which makes the activity coefficient of the hydroxyl ion a function of its nature under a given set of conditions. That this effect depends upon some property of the medium, and is not specific for the cations is evidenced by the fact that the anions also produce a similar result.

From this point of view, it would appear that we may be dealing with the conditions which are the beginning of the formation of undissociated

[10] (a) Harned, This Journal, **48,** 326 (1926). (b) Harned and Brumbaugh, *ibid.*, **44,** 2729 (1922). (c) Harned and Sturgis, *ibid.*, **47,** 945 (1925). (d) Åkerlöf, *ibid.*, **48,** 1160 (1926).

[11] Harned and Åkerlöf, *Physik. Z.*, **27,** 411 (1926).

molecules in the solution, and a definite chemical equilibrium between the ions and undissociated molecules. In order for such combination to occur, in which, according to the conceptions of Knorr,[12] Pauling[13] and others, electronic orbits may surround both atomic nuclei, it is first necessary to have an effect similar to the Stark effect which deforms one or both of the ions. Thus, since the lithium ion lowers the dielectric constant of the medium and deforms the hydroxyl ion to a greater extent than the sodium ion, the formation of non-polar bonds would be more probable in the case of lithium than sodium hydroxide, and much more probable in the case of water. Very similar considerations would also apply to the activity coefficient of formic acid in the salt solutions, in which case a similar effect would have to be assumed in the case of the formate ion which we have premised in the case of the hydroxyl ion.

Summary

1. From the results of Manning and the assumption that the velocity of hydrolysis of ethyl formate in neutral salt solutions is proportional to the hydrogen-ion concentration, the activity-coefficient products of formic acid in salt solutions of various kinds and strengths have been calculated.

2. The values thus obtained parallel very satisfactorily the behavior of the ionic activity-coefficient product of water in salt solutions.

3. A theory of the thermodynamic behavior of hydroxyl and formate ions has been discussed.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE REACTION BETWEEN ELEMENTARY PHOSPHORUS AND POTASSIUM IODATE AND ITS UTILIZATION IN THE VOLUMETRIC DETERMINATION OF PHOSPHORUS[1,2]

BY THEO. F. BUEHRER AND O. E. SCHUPP, JR.

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When either white or red phosphorus is mixed with potassium iodate, and a few drops of water are added, the mixture reacts violently, sometimes even explosively, liberating iodine and evolving a considerable quantity of heat. When more water is initially taken, the rate of the reaction is greatly decreased. Since the reaction starts slowly and gradually speeds

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[12] Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923).

[13] Pauling, THIS JOURNAL, **48**, 1132 (1926).

[1] Presented by O. E. Schupp, Jr., before the Physical Sciences Section at the Spring Meeting of the Southwestern Division of the American Association for the Advancement of Science, February 15–18, 1926, Phoenix, Arizona.

[2] The initial work on this method was carried out by one of us at the University of California during the session 1919–1920 in conjunction with solubility studies under Professor J. H. Hildebrand.