[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE, COLUMBIA UNIVERSITY]

The Ionization Constant of Sulfamic Acid from Electromotive Force Measurements

BY EDWARD J. KING AND GRACE W. KING

The electromotive forces of hydrogen–silver, silver chloride cells containing sulfamic acid–sodium sulfamate–sodium chloride buffers have been measured at 5° intervals from 10 to 50°. From these data the thermodynamic ionization constant of sulfamic acid at each temperature has been calculated. Large uncertainties are introduced in this calculation not only by unavoidable errors in the electromotive force and stoichiometric molalities but also by difficulty in estimating the activity coefficient of hydrochloric acid in the buffer solutions. It is possible to set reasonable limits on this activity coefficient and thereby place the ionization constant between 0.11 and 0.08 at 25°; recent conductance measurements lead to values between 0.101 and 0.104. The most probable value of the ionization constant at 25° is 0.103. Equations are given for computing $-\log K$ as a function of the temperature. From them have been calculated the derived thermodynamic quantities ΔF^0, ΔH^0, $\Delta C_p{}^0$ and ΔS^0 associated with the ionization.

The ionization of amino acids containing other acid groups than the carboxyl has not been investigated by the electromotive force method developed by Harned, Owen and their collaborators.[1] This method has been used in the present investigation to determine the ionization constant of sulfamic acid from 10 to 50°. The cells were of the type

$$H_2 \mid NH_2SO_3H\ (m_1),\ NH_2SO_3Na\ (m_2),\ NaCl\ (m_3) \mid AgCl\text{-}Ag$$

where m_1, m_2 and m_3 are stoichiometric molalities. Since the ionization constant of sulfamic acid is about 0.1, this study will illustrate the difficulties attending the application of the electromotive force method to a moderately strong acid. Not only do large errors in the ionization constant result from small uncertainties in electromotive force and the stoichiometric molalities, but also the value of the constant is very sensitive to the choice of an expression for the activity coefficient of hydrochloric acid in the buffer solutions. These difficulties have also been encountered by Bates[2] in his investigation of the first ionization constant of phosphoric acid.

Sulfamic acid is interesting as the simplest amino sulfonic acid. Although the acid occurs in its crystals as a dipolar ion, $^+NH_3SO_3^-$,[3] the un-ionized acid in aqueous solution is largely in the form of the neutral molecule, NH_2SO_3H.[4] The *p*H titration curve of sulfamic acid with sodium hydroxide (Fig. 1) is typical of a moderately strong acid; at the equivalence point there is a sharp inflection and the *p*H is close to 7. By contrast, the titration curve for taurine, $^+NH_3CH_2CH_2SO_3^-$, resembles that of glycine and is affected in the same way by formaldehyde.[5] The existence of very small amounts of the dipolar form of sulfamic acid in equilibrium with the neutral molecule is not altogether ruled out. Maron and Berens[6] have postulated that the dipolar ion is an intermediate in the hydrolysis of sulfamic acid at temperatures somewhat above those used in this study. The basic ionization of sulfamic acid is believed to be very weak[4] and is neglected in this investigation.

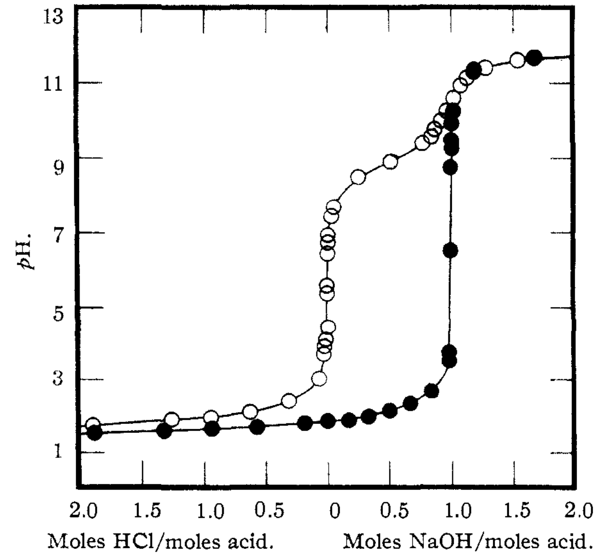

Fig. 1.—Titration of sulfamic acid (●) and taurine (○) with sodium hydroxide and hydrochloric acid.

Experimental

Apparatus.—The apparatus has been described previously.[7] A third Eppley standard cell was added. This and the Rubicon potentiometer were calibrated by the National Bureau of Standards in August, 1950. The maximum correction to the potentiometer readings recorded in this contribution is 0.02 mv.

Materials.—The buffer solutions were prepared from weighed amounts of carbonate-free sodium hydroxide, sodium chloride, sulfamic acid and redistilled water. The estimated error in the stoichiometric molalities is less than 0.1%. Duplicate cells were filled with each solution in such a way as to exclude oxygen. The sample of sodium chloride has been described before.[7] The sodium hydroxide solution was standardized against potassium acid phthalate from the National Bureau of Standards with a precision of 0.03% and an estimated accuracy of 0.05%. Eastman Kodak Co. sulfamic acid was recrystallized according to the directions of Butler, Smith and Audrieth.[8] Two samples were prepared. By titration with standard carbonate-free sodium hydroxide they were found to be 99.97 and 99.90% pure. Some of the semi-quantitative tests given by Stoddard and Dunn[9] for amino acids were made on these samples. Neither was found to contain more than 0.004% ammonia, iron, phosphate or heavy metals. One sample contained less than 0.004% chloride, the other very slightly more. It is important to test also for sulfate since this might conceivably be introduced as a result of hydrolysis during recrystallization. By the method of Ricci and Selikson[10] the two samples were found to contain less than 0.005% sulfate.

---

[1] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 497–498.

[2] R. G. Bates, *J. Research Natl. Bur. Standards*, **47**, 127 (1951).

[3] F. A. Kanda and A. J. King, THIS JOURNAL, **73**, 2315 (1951).

[4] P. Baumgarten, *Ber.*, **62B**, 820 (1929).

[5] L. J. Harris and T. W. Birch, *Biochem. J.*, **24**, 1086 (1930).

[6] S. H. Maron and A. R. Berens, THIS JOURNAL, **72**, 3571 (1950).

[7] E. J. King, *ibid.*, **73**, 155 (1951).

[8] M. J. Butler, G. F. Smith and L. F. Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938).

[9] M. P. Stoddard and M. S. Dunn, *J. Biol. Chem.*, **142**, 329 (1942).

[10] J. E. Ricci and B. Selikson, THIS JOURNAL, **69**, 995 (1947).

The titration curves in Fig. 1 were obtained with a Beckman model G *p*H meter. Solutions between 0.01 and 0.02 *M* in sulfamic acid or taurine were titrated with 0.1 *N* solutions of sodium hydroxide and hydrochloric acid.

Procedure.—The electromotive force measurements were first made at 25°, then at 5° intervals from 10 to 25°. After the cells had been closed off overnight, measurements were repeated at 25° and then made at 5° intervals to 50° and, finally, for the fourth time, again at 25°. Measurements at 10° were omitted for three buffer solutions. Agreement between the measurements at 25° was used as a criterion of the performance of the cells. The readings for one cell which behaved erratically were discarded. The average agreement between successive readings at 25° was 0.030 mv.; the average agreement between initial and final readings at 25°, taken about 30 hours apart, was 0.048 mv.

The electromotive forces of cells containing solutions of indicated molalities corrected to a hydrogen pressure of one atmosphere can be represented as a function of temperature by the equation

$$E_t = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

The parameters of this equation for electromotive forces in absolute volts are given in Table I. The average deviation, without regard to sign, of the calculated values from those observed is 0.02 mv. Only one deviation is larger than 0.10 mv. and only six are greater than 0.05 mv.

TABLE I

PARAMETERS OF EQUATION (1)

m_1	m_2/m_1	m_3/m_1	E_{25}	$a \times 10^5$	$b \times 10^6$
0.004948	1.0364	1.0159	0.50301	30.5	−2.50
.005405	1.0022	1.0017	.49910	29.1	−2.68
.006903	0.9990	1.0002	.48765	25.4	−2.50
.007698	1.0020	1.0004	.48263	23.7	−2.52
.009339	0.9990	1.0002	.47372	20.7	−2.64
.010028	1.0364	1.0159	.47023	19.5	−2.70
.012241	1.0022	1.0017	.46131	16.5	−2.58
.012428	0.9990	1.0002	.46068	16.3	−2.52
.014894	1.0364	1.0159	.45231	13.5	−2.46
.015831	0.4911	1.1245	.44519	11.2	−2.36
.017300	1.0020	1.0004	.44592	11.2	−2.50
.02006	1.0022	1.0017	.43923	8.9	−2.42
.02242	0.4911	1.1245	.42948	6.1	−2.54
.02378	.9974	0.9988	.43193	6.2	−2.22
.03042	1.0022	1.0004	.42120	2.5	−2.10
.03094	0.4911	1.1245	.41521	1.3	−2.38
.04181	.9974	0.9988	.40770	−2.2	−2.14
.05356	.9974	.9988	.39734	−5.9	−1.98

Calculations and Discussion

The electromotive force (E) of the cells is related to the ionization constant

$$K = \frac{a_{\mathrm{H^+}}a_{\mathrm{NH_2SO_3^-}}}{a_{\mathrm{NH_2SO_3H}}} = \frac{m_{\mathrm{H^+}}m_{\mathrm{NH_2SO_3^-}}}{m_{\mathrm{NH_2SO_3H}}} \times \frac{\gamma_{\mathrm{H^+}}\gamma_{\mathrm{NH_2SO_3^-}}}{\gamma_{\mathrm{NH_2SO_3H}}} \qquad (2)$$

by the exact thermodynamic relation[1]

$$(E - E^0)(\mathfrak{F}/2.3026RT) + \log\,[m_3(m_1 - m_{\mathrm{H}})/(m_2 + m_{\mathrm{H}})] = -\log K - \log\,[\gamma_{\mathrm{Cl^-}}\gamma_{\mathrm{NH_2SO_3H}}/\gamma_{\mathrm{NH_2SO_3^-}}] \qquad (3)$$

When the hydrogen ion molality, m_{H}, is not very small in comparison with m_1 and m_2 it is convenient to estimate it by means of the relation

$$-\log m_{\mathrm{H}} = (E - E^0)(\mathfrak{F}/2.3026RT) + \log m_3 + \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} \qquad (4)$$

But the activity coefficient of hydrochloric acid in the buffer solutions is not known. Hence, log $\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ must be approximated either by means of the Debye–Hückel theory or by known values of this function in related systems. Equation (4) then leads to an approximate hydrogen ion molality, m'_{H}, and this is used to find an apparent $-\log K' \equiv pK'$ defined by

$$pK' = (E - E^0)(\mathfrak{F}/2.3026RT) + \log\,[m_3(m_1 - m'_{\mathrm{H}})/(m_2 + m'_{\mathrm{H}})] \qquad (5)$$

The apparent hydrogen ion molality should approach the true hydrogen ion molality as the concentrations decrease. The activity coefficient term on the right side of Equation (3) should vary linearly with the ionic strength in dilute solutions. On this basis, values of pK' are plotted against the apparent ionic strength, $\mu' = m_2 + m_3 + m_{\mathrm{H}}'$, and extrapolated linearly to infinite dilution to obtain $-\log K$.

When applied to sulfamic acid this method of calculation has serious limitations. In the first place, the difference, $m_1 - m'_{\mathrm{H}}$, is relatively small; analytical errors in m_1 will therefore be magnified to large errors in pK' and unavoidable errors in E and m_3 will influence m'_{H} and pK' to a large degree. Secondly, the errors involved in estimating log $\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ are large and are not removed by the extrapolation to infinite dilution.

For dilute solutions the Debye–Hückel theory leads to the following relation[11]

$$\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} = \frac{-2\mathcal{S}\sqrt{\mu d_0}}{1 + A\mathring{a}\sqrt{\mu d_0}} + 2\log\,(1 + 0.036\mu) \qquad (6)$$

where $\mathcal{S}$ and A are well-known constants[11] and $\mathring{a}$ is a semi-empirical parameter usually referred to as the mean distance of approach of the ions. The density of pure water, d_0, and the second term on the right side are introduced because of the use of activity coefficients on the molality scale. This second term is linear in the ionic strength in the concentration range we have used and can be absorbed in the choice of $\mathring{a}$

$$\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} = \frac{-2\mathcal{S}\sqrt{\mu d_0}}{1 + A\mathring{a}\sqrt{\mu d_0}} \qquad (6')$$

A third term, linear in the ionic strength, can be added to the right side of Equation (6), but this is not obligatory for the low concentrations used in this investigation.

To calculate pK' it is necessary to assume a reasonable value of $\mathring{a}$. Linearity of extrapolation cannot be used as a criterion, for a family of practically parallel extrapolations, all linear up to an ionic strength of about 0.1, can be obtained with values of $\mathring{a}$ between 3 and 6 Å. Values of $\mathring{a}$ generally range between 3.5 and 6 Å.[12] Values below 3.5 are not common[13] and may be indicative of ionic association.[14] Accordingly, we have calculated pK' and $-\log K$ using various values of $\mathring{a}$. The extrapolations at 25° are shown in Figs. 2 and 3. Values of $-\log K$ and K so obtained are collected in Table II. We have also calculated values of pK' based on the activity coefficient of hydrochloric acid at infinite dilution in a sodium chloride solution of ionic strength μ' under the assumption that this is a reasonable approximation to the activity coefficient of hydrochloric acid in a sulfamic acid–sodium sulfamate–sodium chloride

---

(11) Reference 1, Chapters 3 and 5 and Table B-1-2, p. 587.

(12) R. G. Bates, *Chem. Revs.*, **42**, 1 (1948).

(13) Reference 1, pp. 380–382; reference 12, p. 35.

(14) N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

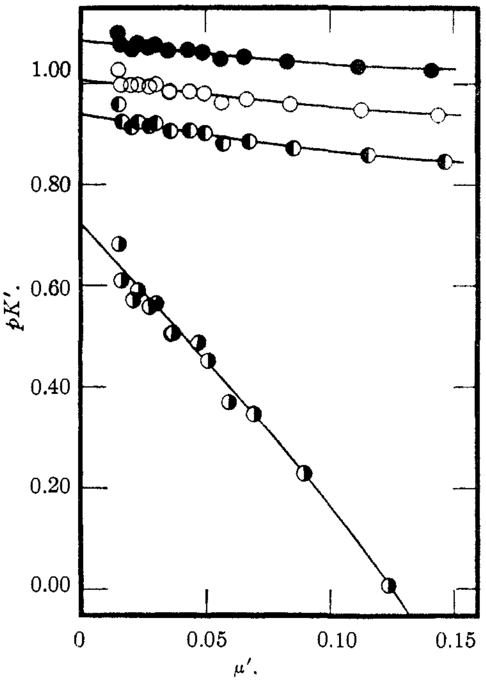

Fig. 2.—Effect of the ion size parameter on the determination of − log K of sulfamic acid: ◑, $\mathring{a}$ = 0; ◐, $\mathring{a}$ = 3.04; ○, $\mathring{a}$ = 4.30; ●, $\mathring{a}$ = 6.00 Å.

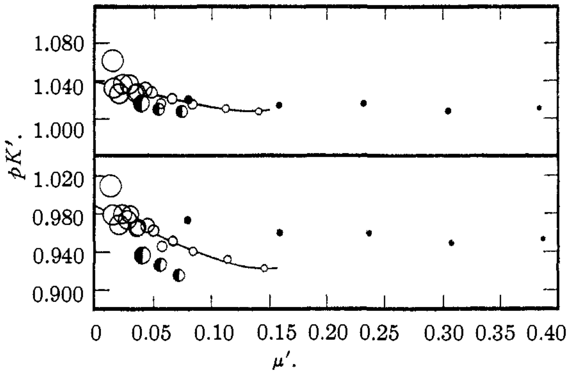

Fig. 3.—Effect of buffer ratio on the determination of −log K of sulfamic acid: ◐, m_1/m_2 = 2; ○, m_1/m_2 = 1; ●, m_1/m_2 = 0.2 (data of Bates). Upper curve based on Equation (7), lower curve on Equation (6′) with $\mathring{a}$ = 3.85 Å. Diameters of circles indicate errors in pK' caused by a combined uncertainty of 0.1% in the stoichiometric molalities and 0.10 mv. in the electromotive force.

buffer. In the concentration range used in this investigation the data at 25° given by Owen and King[15] for hydrochloric acid at infinite dilution in sodium chloride solutions are represented by the equation

$$\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} = \frac{-1.0130\sqrt{\mu}}{1 + 1.35\sqrt{\mu}} + 0.179\mu \qquad (7)$$

Values at other temperatures can be calculated from Equation (7) and data given in Table I of reference 15. Extrapolations of pK' values based on Equation (7) have smaller slopes than those based on Equations (6) and (6′), a probable consequence of the inclusion of a linear term in Equation (7).

TABLE II

VALUES OF K AND −LOG K BASED ON VARIOUS ESTIMATES OF LOG $\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$

$\mathring{a}$	Equation	−log $K_{10°}$	$K_{10°}$	−log $K_{25°}$	$K_{25°}$	−log $K_{50°}$	$K_{50°}$
0.00	(6′)	0.777	0.167	0.720	0.191	0.800	0.158
3.04	(6)	...	...	0.940	.115	...	...
3.85	(6′)	1.031	.093	0.988	.103	1.036	.092
4.30	(6)	1.048	.090	1.006	.099	1.055	.088
4.10	(7)	1.065	.086	1.038	.092	1.080	.083
6.00	(6′)	...	...	1.084	.082	...	...

Also indicated in Fig. 3 are some values of pK' based on unpublished results at 25° kindly sent us by Dr. Bates of the National Bureau of Standards.[16] He used the same type of cell as ours but with potassium chloride in place of sodium chloride. His measurements extended to much higher ionic strengths and the stoichiometric molality ratios were $m_1 : m_2 : m_3 = 1:5:2$.

It is apparent from Table II and Figs. 2 and 3 that the values of −log K and K are very sensitive to the choice of $\mathring{a}$. If it is assumed that $\mathring{a}$ should lie between 3.5 and 6 Å., the ionization constant should fall between the limits 0.11 and 0.08 at 25°.

The dependence of pK' on $\mathring{a}$ can be shown to be an inescapable consequence of the method of calculation. By differentiation of Equations (4), (5) and (6′) we obtain for $\Delta pK'$, the error in pK' produced by an uncertainty $\Delta\mathring{a}$

$$\Delta pK' = \frac{(m_1 + m_2)m'_{\mathrm{H}}}{(m_1 - m'_{\mathrm{H}})(m_2 + m'_{\mathrm{H}})} \times \frac{2f\mathcal{S}A\mu}{(1 + A\mathring{a}\sqrt{\mu})^2} \times \Delta\mathring{a} \equiv XY\Delta\mathring{a} \qquad (8)$$

where f is $[1 - 2.3\, m'_{\mathrm{H}}\, \mathcal{S}/\sqrt{\mu}(1 + A\mathring{a}\sqrt{\mu})^2]^{-1}$ and is approximately equal to unity in the experimental concentration range. For acids as strong as sulfamic acid m'_{H} is not small in comparison with m_1 and factor X is relatively large; as a result, variations in $\mathring{a}$ have a sizable effect on pK'. Extrapolation of pK' does not remove this dependence, for as the ionic strength decreases the decrease in factor Y is more than compensated for by an increase in factor X. It may be mentioned also that for cation acids, like glycine in hydrochloric acid solutions, it can be shown that $\Delta pK'_1 = (1 + X)Y\Delta\mathring{a}$. From this it can be predicted that for the first ionization of glycine and alanine the choice of $\mathring{a}$ will appreciably affect pK' but that this effect will disappear in the extrapolation of pK'_1 to obtain $-\log K_1$.

Conductance measurements have recently been used by Taylor, Desch and Catotti[17] to determine the ionization constant of sulfamic acid at 25°. Using a method of calculation developed by Shedlovsky[18] they found K to be 0.100_9 or $-\log K = 0.996_3$.[19] The Shedlovsky method involves the use of the square of the mean molar activity coefficient of sulfamic acid, y^2. We have investigated the effect of variation of $\mathring{a}$ on the conductance

---

(15) B. B. Owen and E. J. King, THIS JOURNAL, **65**, 1612 (1943).

(16) R. G. Bates, private communication. His data are: m_1 0.05185; E 0.39709 abs. v.; 0.04095, 0.40547; 0.03083, 0.41624; 0.02080, 0.43127; 0.010206, 0.46024.

(17) E. G. Taylor, R. P. Desch and A. J. Catotti, THIS JOURNAL, **73**, 74 (1951).

(18) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

(19) For purposes of comparison their value of K has been divided by the density of water to convert it to the molality scale.

value of the ionization constant. Taking $\log y^2 = -2\mathcal{S}\sqrt{\alpha C}/(1 + A\mathring{a}\sqrt{\alpha C})$ with $\mathring{a} = 4$, we obtain $K = 0.103_2$ or $-\log K = 0.986_4$ as compared with the values given above which correspond to $\mathring{a} = 0$. Thus, an increase in $\mathring{a}$ of 4 Å. causes a *decrease* of 0.010 $-$in $\log K$ as compared with an *increase* of 0.203 in the electromotive force method. Since the effects are opposite in sign and since $\mathring{a}$ is very probably greater than 3.5 Å. for both methods, it is possible to state that the ionization constant at 25° should lie between 0.103 and 0.108. The same value of K, namely, 0.103, is obtained from both electromotive force and conductance data if the same value, 3.85 Å., is used for $\mathring{a}$.[20] We have therefore adopted 0.103 as the most probable value of K at 25°.

Added weight is given to this choice when the influence of the buffer ratio, m_1/m_2, on the electromotive force results is examined. Bates found in his study[2] of the first ionization constant of phosphoric acid that at constant $\mathring{a}$ the slope of the extrapolations used to obtain $-\log K_1$ decreases with decreasing ratio of acid to salt. In the present study, if we assume that the value of $\mathring{a}$ is independent of the buffer ratio, then by proper choice of $\mathring{a}$ the results at different buffer ratios can be extrapolated to the same value of $-\log K$. We have used ratios of 2 and 1, but the pK' values for the higher ratios are only three in number and are too sensitive to analytical errors to be useful. The results of Bates,[16] who used a ratio of 0.2, are in good agreement with ours when calculations are based on an $\mathring{a}$ value of 3.85 Å. As can be seen from Fig. 3, extrapolation of pK' values based on Equation (7) with $\mathring{a} = 4.3$ leads to a lower value of $-\log K$ from Bates' data than that obtained from our measurements. While variations in buffer ratio are not sufficiently sensitive to be used alone as criteria for the proper value of $\mathring{a}$, they do lend support to the use of 3.85 Å. as opposed to higher values.

Bates[21] has recently developed a method of determining the ionization constant of a weak acid from the electromotive forces of cells containing the sodium or potassium salt of this acid together with a second weak acid. By a suitable choice of the second acid, m_H can be kept small in comparison with m_1. The ionization constant of the second acid must be accurately known and should not be more than a hundred-fold smaller than that of the first acid. For sulfamic acid it would be most desirable to have a second weak acid with an ionization constant of about 0.001. Such data of the requisite accuracy are not yet available. We have, on that account, not pursued this method of attack further.

The Variation in Ionization Constant with Temperature and Related Thermodynamic Properties.—The Harned and Robinson[22] equation is frequently used to represent $-\log K$ as a function of temperature. For calculations based on the value 3.85 Å. for $\mathring{a}$ this equation is

$$-\log K = (3792.8/T) - 24.122 + 0.041544T \quad (9)$$

The experimental values of $-\log K$ are: 10°: 1.031 (−5); 15°: 1.020 (+9); 20°: 0.994 (0); 25°: 0.988 (+3); 30°: 0.978 (−5); 0.984 (−4); 40°: 1.000 (+1); 45°: 1.025 (+8); 50°: 1.036 (−4). The numbers in parentheses following the values of $-\log K$ are the differences in the third decimal place between the experimental value and that calculated from Equation (9). The average difference is 0.004_3.

From Equation (9) can be derived by conventional thermodynamic methods the changes in free energy (ΔF^0), enthalpy (ΔH^0), heat capacity ($\Delta C_p{}^0$) and entropy (ΔS^0) associated with the ionization reaction in the standard state. At 25° these functions are, respectively, 1350 cal. mole^{-1}, 460 cal. mole^{-1}, -110 cal. deg.$^{-1}$ mole^{-1} and -3.0 cal. deg.$^{-1}$ mole^{-1}. The maximum value of the ionization constant is 0.104 at 29°. The large negative value for the change in heat capacity is noteworthy, but the experimental error in this quantity is probably large. For comparison, the values of $-\log K$ based upon Equation (7) have been fitted to the Harned and Robinson equation: $-\log K = (2823.5/T) - 17.708 + 0.031094T$. The corresponding values of the thermodynamic functions at 25° are: ΔF^0, 1410; ΔH^0, 270; $\Delta C_p{}^0$, -85; ΔS^0, -3.8. The method of calculation very obviously has a large effect on the values of these functions.

Acknowledgments—The authors wish to acknowledge the assistance of Misses Janet Bloch and Sandra Dobin in making the sulfate test and of Miss Pauline Gostinsky in the preparation of one sample of sulfamic acid. They also wish to thank Dr. B. B. Owen for a stimulating discussion and Dr. R. G. Bates for the use of his unpublished data and for sending us his paper on phosphoric acid before its publication.

NEW YORK, N. Y. RECEIVED AUGUST 27, 1951

---

[20] The agreement between the two $\mathring{a}$ parameters may be fortuitous since they refer to different systems. In the conductance method $\mathring{a}$ is the mean distance of approach of the ions in pure sulfamic acid solutions whereas in the electromotive force method it refers to sulfamic acid-sodium sulfamate-sodium chloride buffers.

[21] R. G. Bates, THIS JOURNAL, **73**, 2259 (1951).

[22] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).