

method has been thoroughly tested with known compounds. On account of the geographical location of Notre Dame, station WGN of Chicago was selected for the work. For work above 25° a bath of Polarine lubricating oil was used as a heating medium instead of water. Temperature control was maintained to within  $\pm 0.01^\circ$  with a mercury filled regulator.

### Summary

1. The symmetrical dialkyl acetylenes have been shown to have zero moment.

2. The atomic polarization of these compounds has been determined and is seen to be somewhat higher than that of the more saturated hydrocarbons of the same molecular weight.

NOTRE DAME, INDIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Ionization Constant and Heat of Ionization of the Bisulfate Ion from Electromotive Force Measurements<sup>1</sup>

BY WALTER J. HAMER

Sulfuric acid is known to be a partially weak electrolyte. Several investigators by widely different methods have determined the extent to which the bisulfate ion dissociates, and the values of the dissociation constant obtained at 25° vary from 0.03 to 0.01. Part of this divergence depends upon whether or not corrections are made for interionic attraction. In 1926 Sherrill and Noyes<sup>2</sup> obtained 0.0115 at 25° from combined conductance and transference data of Noyes and Stewart<sup>3</sup> by taking into account the mobility and activity corrections which are given by the theory of interionic attraction developed by Milner and Debye and Hückel.<sup>4</sup> Since then, a method employing galvanic cells without liquid junctions has been developed for the determination of the ionization constants of weak electrolytes, and was applied to acetic acid solutions with a high degree of accuracy by Harned and Ehlers.<sup>5</sup> Their method with a slight modification for a uni-bivalent electrolyte has been employed in this research. This procedure possesses the advantage over previous methods in that it gives a determination of the constant from a single series of measurements. To extend the knowledge of this subject and to determine the heat of ionization of the bisulfate ion with accuracy, measurements were made at five-degree temperature intervals from 0 to 60°.

(1) This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator. This work was made possible by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with permission of the Secretary of the Navy.

(2) Sherrill and Noyes, *THIS JOURNAL*, **48**, 1861 (1926).

(3) Noyes and Stewart, *ibid.*, **32**, 1133 (1910).

(4) Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913); Debye and Hückel, *Physik. Z.*, **24**, 185, 305, 334 (1923).

(5) Harned and Ehlers, *THIS JOURNAL*, **54**, 1350 (1932).

### Discussion of the Method

The cell employed for the determination was  $\text{H}_2 | \text{NaHSO}_4(m_1), \text{Na}_2\text{SO}_4(m_2), \text{NaCl}(m_3) | \text{AgCl} | \text{Ag}^+$

which is seen to contain a sodium acid sulfate-sodium sulfate buffer mixture. The molalities were made nearly equal in order to give a one-one buffer mixture which is ideal experimentally and facilitates later calculations of hydrogen ion concentration. In this cell the hydrogen electrode is reversible to the hydrogen ion which is produced by the ionization of the bisulfate ion, and the silver-silver chloride electrode is reversible to the chloride ion.

The electromotive force of the cell in question is given by the well-known equation

$$E = E_0 - (RT/F) \ln m_{\text{H}} m_{\text{Cl}} \gamma_{\text{H}} \gamma_{\text{Cl}} \quad (1)$$

The thermodynamic equation for the second dissociation of sulfuric acid is

$$K_2 = \frac{m_{\text{H}} m_{\text{SO}_4} \gamma_{\text{H}} \gamma_{\text{SO}_4}}{m_{\text{HSO}_4} \gamma_{\text{HSO}_4}} \quad (2)$$

$K_2$  is the second dissociation constant, "m's" and "γ's" represent the molalities and activity coefficients, respectively, of the ionic species denoted by subscripts, and  $E_0$  is the normal electrode potential of the silver-silver chloride electrode. We shall proceed upon the assumption that the dissociation of sulfuric acid into hydrogen and bisulfate ions is complete. Upon elimination of  $m_{\text{H}}$  in equations (1) and (2) and using the limiting law of Debye and Hückel with an additional linear term for the individual ionic activity coefficients

$$\frac{(E - E_0)F}{2.3026RT} + \log m_{\text{Cl}} + \log m_{\text{HSO}_4} - \log m_{\text{SO}_4} + 2A\sqrt{\mu} = -\log K_2 + 2\beta'\mu \quad (3)$$

results.<sup>6</sup> This equation is suitable for the determination of  $K_2$  since all quantities on the left side may be obtained. The first two members are found experimentally;  $E$  is the measured electromotive force,  $E_0$  the normal electrode potential of the silver-silver chloride electrode, and  $m_{\text{Cl}}$  is equal to  $m_3$  the stoichiometrical molality of the sodium chloride. However, the third and fourth terms cannot be obtained directly, since  $m_{\text{HSO}_4}$  and  $m_{\text{SO}_4}$  are not equal to  $m_1$  and  $m_2$ , the respective stoichiometrical molalities of sodium bisulfate and sodium sulfate but are equal to  $(m_1 - m_{\text{H}})$  and  $(m_2 + m_{\text{H}})$ , respectively, due to the ionization of the bisulfate ion, and the ionic strength,  $\mu$ , is not simply  $(m_1 + 3m_2 + m_3)$  which would be the case if the  $\text{HSO}_4^-$  ion remained as an undissociated ion, but is  $(m_1 + 3m_2 + m_3 + 2m_{\text{H}})$ . To obtain this hydrogen-ion concentration and the corresponding ionic strength, a value of  $K_2$  is assumed in equation (2) and the activity coefficient ratio is evaluated from the limiting law of Debye and Hückel. This is done for each concentration. The values of  $m_{\text{H}}$  and  $\mu$  obtained in this manner are used to correct  $m_{\text{HSO}_4}$  and  $m_{\text{SO}_4}$ . All the values are then substituted in equation (3) and the left side is plotted against  $\mu$ , and extrapolated to zero ionic strength. This extrapolated value which is  $(-\log K_2)$  is then used in the re-estimation of  $m_{\text{H}}$  and  $\mu$  in equation (2) and the process repeated until the extrapolated value equals the one assumed. This procedure is similar to that employed by Harned and Ehlers,<sup>5</sup> and is well adapted for the treatment of weak univalent electrolytes such as acetic acid. However, in this work, the above procedure is tedious as well as cumbersome, since the values of  $K_2$  extrapolated by equation (3) without corrections varies from 0.0006 or 0.003 depending upon the temperature and very gradually rises to a value of the order of  $10^{-2}$  as the arithmetical approximation described above proceeds. Consequently, a second method which was not so tedious was devised in order to obtain a close approximation of a value of  $K_2$ .

It is evident that two quantities are unknown in equation (1), namely,  $m_{\text{H}}$  and  $\gamma_{\text{H}}\gamma_{\text{Cl}}$ . The

(6) The activity coefficient ratio after substitution is equal to  $\gamma_{\text{H}}\gamma_{\text{Cl}}\gamma_{\text{HSO}_4}/\gamma_{\text{H}}\gamma_{\text{HSO}_4}$ . Each individual ionic activity coefficient is given in dilute solutions by  $\log \gamma = -Az^2\mu^{1/2} + \beta\mu$  from the theory of interionic attraction of Debye and Hückel.  $A$  is the universal constant of the Debye and Hückel theory and is given by  $1.41412 \times 2.954 \times 10^6/D^3/zT^3/2$ ,  $\beta$  is an empirical constant proportional to the ionic diameter, and  $z$  is the valence of the ion. This procedure for individual ions was justified by Brönsted and La Mer, *This Journal*, **46**, 555 (1924), and by La Mer and Mason, *Ibid.*, **49**, 363 (1927).

latter one is given in dilute solutions by the limiting law of Debye and Hückel. With aid of this law, an "apparent hydrogen ion" concentration may be obtained from a rearranged form of equation (1)

$$\frac{(E - E_0)F}{2.3026RT} + \log m_{\text{Cl}} - 2A\sqrt{\mu} = -\log m_{\text{H}} \quad (4)$$

The linear term has been neglected in this equation but such a procedure is justified in dilute solutions as will be evident from later considerations. In this case successive approximations at each concentration must again be made to obtain  $m_{\text{H}}$  since the ionic strength is a function of the hydrogen-ion concentration. On an average, three approximations are required. The  $m_{\text{H}}$  and  $\mu$  values obtained from this equation are substituted in the logarithmic expression of  $K_2$

$$\log K_2 - 2\beta\mu = \log m_{\text{H}} + \log m_{\text{SO}_4} - \log m_{\text{HSO}_4} - \frac{4A\sqrt{\mu}}{4A\sqrt{\mu}} \quad (5)$$

containing the Debye and Hückel expression for the activity coefficient ratio and the right side is plotted against  $\mu$  and extrapolated to zero  $\mu$ . The extrapolated value is equal to  $(+\log K_2)$  and no further approximations are required. This method is more direct than Method I, but is very sensitive to the ratio of  $m_{\text{SO}_4}$  to  $m_{\text{HSO}_4}$  and to accidental experimental errors due to the nature of the function. A scattering of points was obtained in dilute solutions, but with the aid of higher points an extrapolation was possible and gave a good location of  $K_2$  in most cases, particularly for intermediate temperatures, where the values checked excellently the values obtained by Method I. This check justifies the omission of the linear term in equation (4). This second method has another disadvantage of yielding imaginary values of " $m_{\text{H}}$ " at 0.05 and 0.07 chloride concentration below  $15^\circ$  due to the failure of the limiting law of Debye and Hückel at this concentration range. Because of this fact and the scattering in dilute solutions, this method was not employed as a final evaluation of  $K_2$ , but as an evaluation of an approximate  $K_2$  which was used as the starting point for Method I. This procedure reduced the number of successive approximations in Method I from about fifteen to from three to four. In short, Method II was used to locate an approximate value of  $K_2$  and Method I was employed for a final evaluation because it was less sensitive to concentration ratios and experimental errors and gave a more rigorous extrapolation. It is to be noticed that the two methods

are comparable if the value of  $m_H$  given by equation (4) is substituted in equation (5) and that the two methods differ primarily in the method of calculating the hydrogen-ion concentration. By Method I,  $m_H = f(m_1, m_2, m_3, \gamma_{SO_4}, K_2)$  and by Method II,  $m_H = f(E, E_0, m_1, m_2, m_3, \gamma_H \gamma_{Cl})$  which points out the sensitive nature of the latter method.

It must be emphasized that the hydrogen ion concentration and ionic strength calculated by these methods are "apparent," but become more nearly the true concentrations as the solution becomes more dilute, leading to a correct thermodynamic constant. That this is true is clearly shown by the extrapolations by equations (3) and (5), which gave identical values although different apparent hydrogen-ion concentrations and ionic strengths were used.

The methods outlined above presuppose complete ionization of the first hydrogen of sulfuric acid. This assumption was justified by Sherrill and Noyes (Ref. 2, p. 1873). They obtained the same dissociation constant for the  $HSO_4^-$  ion in solutions of pure sulfuric acid and in solutions of pure sodium hydrosulfate. Since un-ionized  $H_2SO_4$ , if it exists in solution, would be in larger proportions in sulfuric acid, their assumption as regards complete dissociation of the first hydrogen is substantially correct. If the first step is not complete, it should be so much greater than the second which is of the order of  $10^{-2}$  as not to affect seriously this determination.

### Experimental Procedure

**Solutions.**—The solutions were made by adding the calculated amount of hydrochloric acid (0.1 *M*) to a solution of sodium sulfate (0.1 *M*) so that the resulting solution contained equal molalities of the three constituents. A little excess of sodium sulfate was added. This stock solution was then diluted to desired strengths. The solutions were boiled *in vacuo* and kept under hydrogen until delivered into the cells.

**Hydrochloric Acid.**—Twice distilled hydrochloric acid was diluted to approximately 0.1 *M* and analyzed gravimetrically. The concentration of the solution was known with an accuracy of  $\pm 0.03\%$ .

**Sodium Sulfate.**—An analyzed chemical of high grade was twice recrystallized and dried in an oven at  $110^\circ$ . A solution (0.1 *M*) was prepared and analyzed by evaporation to dryness in a muffle furnace. Analysis was known with an accuracy of  $\pm 0.06\%$ .

**Hydrogen.**—Tank hydrogen purified by passing over copper heated to  $700^\circ$  was employed.

**Hydrogen Electrodes.**—Platinum foil electrodes were used. These were plated in a chloroplatinic acid solution for three to four minutes at a current density of 400

milliamperes. At temperatures above  $45^\circ$  they were plated for two minutes longer. This prevented a slight fluctuation in electromotive force which occurred at higher temperatures when too thinly coated electrodes were employed.

**Silver-Silver Chloride Electrodes.**—The electrodes were of the type (2) described by Harned.<sup>7</sup> Freshly prepared hydrogen and silver-silver chloride electrodes were employed in each cell. They were washed with cell solution before use.

**Cells and Bubble Tubes.**—The cells employed consisted of two compartments, one for each electrode, and were connected by an inverted U-tube device containing a three-way stopcock. This was done to prevent the hydrogen gas stream from coming into contact with the silver-silver chloride electrode. Four Pyrex glass cells of 150 cc. capacity were installed in three thermostats controlled to within  $\pm 0.05^\circ$ , in order that the same solution could be measured over the entire temperature range. The cells were drained at the side of the thermostat and no stopcocks were in the thermostat water. To each of the cells, a spiral hydrogen gas bubble tube was sealed which could be filled with cell solution and then drained after each run. The cells and bubblers were evacuated, washed twice with air-free solution and then filled over hydrogen. No air entered the train during a measurement.

**Behavior of Cells.**—The cells were steady above 0.001 molal chloride ion concentration for twelve hours. Below this concentration the electromotive forces fell slightly over a period of twelve hours, a behavior commonly found in such dilute solutions. The effect of air was tested. At low temperatures the electromotive forces fell slowly as air was introduced and at high temperatures they increased slightly. This phenomenon was similar to an increased hydrogen-ion concentration. No effect of sulfate ion on the silver-silver chloride electrode was noticed.

### Electromotive Forces of the Cell

Table I contains the measurements of the cells at  $25^\circ$ . Measurements at the twelve other temperatures for the sake of brevity are not included. Suffice it to say that these electromotive forces were reproducible to  $\pm 0.05$  mv. and increased with temperature, the increase being on an average of 200 mv., for every five degree increase in temperature.<sup>8</sup>

(7) Harned, *THIS JOURNAL*, **51**, 416 (1929).

(8) The complete data may be obtained from the author or from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut. A few electromotive forces at temperatures other than  $25^\circ$  will be given here for illustration. At 0.0009713 molal chloride ion concentration the electromotive forces obtained were: 0.56876, 0.57251, 0.57616, 0.57973, 0.58302, 0.58920, 0.59207, 0.59481, 0.59760, 0.60030, 0.60299 and 0.60557 at 0, 5, 10, 15, 20, 30, 35, 40, 45, 50, 55 and  $60^\circ$ . At 0.001947 they were 0.53858, 0.54237, 0.54503, 0.54816, 0.55116, 0.55628, 0.55928, 0.56125, 0.56374, 0.56624, 0.56845, 0.57100, at 0, 5, 10, 15, 20, 30, 35, 40, 45, 50, 55 and  $60^\circ$ . At 0.002926 they were 0.52142, 0.52464, 0.52731, 0.52991, 0.53311, 0.53816, 0.54033, 0.54249, 0.54445, 0.54670, 0.54911 and 0.55150 at 0, 10, 15, 20, 30, 35, 40, 45, 50, 55 and  $60^\circ$ . At 0.04975 they were 0.40644, 0.40848, 0.41050, 0.41247, 0.41397, 0.41811, 0.41974, 0.42194, 0.42419, 0.42654, 0.42821, 0.43012 at 0, 5, 10, 15, 20, 30, 35, 40, 45, 50, 55 and  $60^\circ$ .

TABLE I

ELECTROMOTIVE FORCES OF THE CELL, H<sub>2</sub> (1 ATM.) | NaHSO<sub>4</sub>(*m*<sub>1</sub>), Na<sub>2</sub>SO<sub>4</sub>(*m*<sub>2</sub>), NaCl(*m*<sub>3</sub>) | AgCl | Ag AND VALUES OF APPARENT DISSOCIATION CONSTANTS CALCULATED FROM EQUATIONS (3) AND (5)

<i>m</i> <sub>1</sub> = <i>m</i> <sub>3</sub>	<i>m</i> <sub>2</sub>	E. m. f. (25°)	<i>K</i> <sub>2</sub> ' (eq. 3)	<i>K</i> <sub>2</sub> ' (eq. 5)
0.0009713	0.0009798	0.58622	0.01205	0.01215
.0009780	.0009830	.58591	.01200	.01204
.0009788	.0009873	.58579	.01204	.01255
.0009700	.0009760	.58620	.01202	.01258
.001947	.001957	.55388	.01206	.01271
.001959	.001976	.55377	.01204	.01219
.001957	.001968	.55374	.01204	.01240
.002926	.002956	.53565	.01209	.01256
.002933	.002959	.53550	.01211	.01267
.002924	.002939	.53565	.01210	.01258
.004871	.004913	.51320	.01220	.01301
.004929	.004955	.51260	.01222	.01314
.004867	.004892	.51326	.01222	.01291
.006815	.006874	.49873	.01230	.01340
.006865	.006925	.49869	.01217	.01344
.009724	.009776	.48356	.01249	.01411
.009732	.009817	.48348	.01252	.01426
.01957	.01968	.45429	.01304	.01702
.01970	.01987	.45403	.01316	.01700
.02931	.02946	.43727	.01339	.02020
.02934	.02959	.43723	.01366	.02032
.04975	.05018	.41608	.01440	.02868
.05010	.05054	.41622	.01447	.02594
.06934	.06994	.40392	.01450	.03812
.06919	.06956	.40388	.01455	.03941

Evaluation of Apparent and Real Dissociation Constants

The functions in equations (3) and (5) which are plotted against  $\mu$  will be designated  $K_2'$  or the apparent dissociation constants. The  $E_0$  and "A" values used in these computations are those given by Harned and Ehlers.<sup>9</sup> Any error introduced by using their  $E_0$  values should be negligible as the same type of electrode and procedure was employed as was used by them in their determination. The values of  $K_2'$  calculated by Method I are given in the fourth column of Table I. Those calculated by Method II are given in the fifth column of the same table. It will be noticed that the  $K_2'$  values calculated by Method II vary more rapidly with concentration than those obtained by Method I, and that the values calculated by the two methods approach each other as the concentration decreases. The divergence between the two methods decreases with temperature and becomes negligible at about 43°. At temperatures above 45° the values cal-

(9) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933). The  $E_0$  values employed are those given by their equation (7), p. 2183, and the "A" values are their " $\mu$ " values given in Table VII, column 2, on page 2188.

culated by Method II are lower than those obtained by Method I at high concentrations and approach each other as the concentration de-

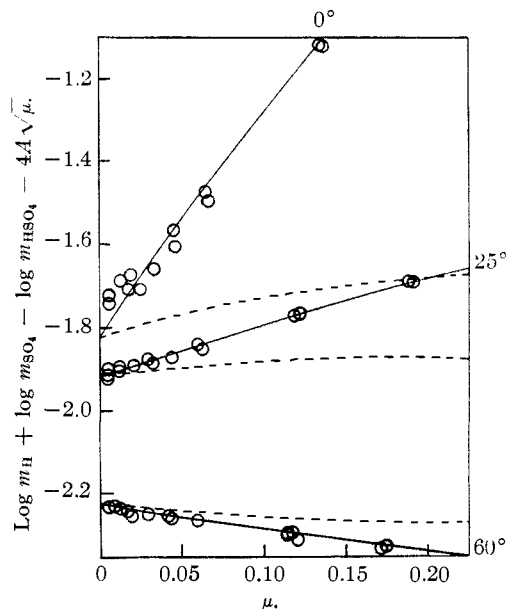


Fig. 1.—Plots of the right side of equation (5) used for the determination of an approximate dissociation constant of the bisulfate ion.

creases. In Fig. 1 the plots of the right side of equation (5) against  $\mu$  are given at 0, 25 and

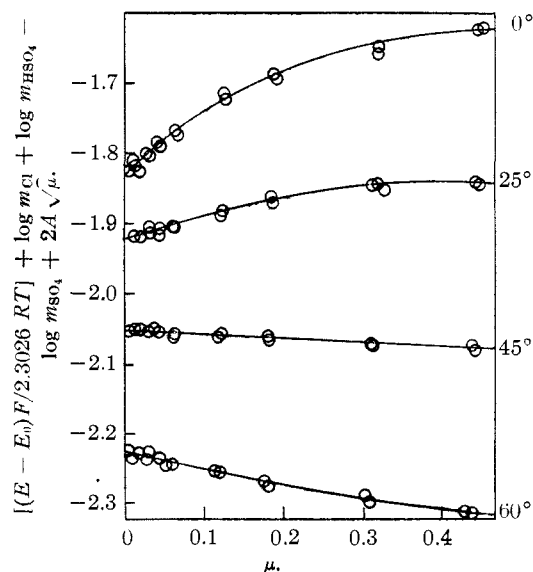


Fig. 2.—Plots of the left side of equation (3) used for the determination of the final value of the dissociation constant of the bisulfate ion.

60°. The slope of the curves changes with temperature and is sharp in the neighborhood of 0°. In Fig. 2 the plots of the left side of equation

(3) against  $\mu$  are given at 0, 25, 45 and 60°. These same plots are represented by the dotted lines in Fig. 1. These extrapolations are more rigorous than those given in Fig. 1. The slope changes with temperature but the change is not so marked nor is the slope so great.

The final extrapolated values are given in the second column of Table II. The value of 0.0120

TABLE II

THE SECOND IONIZATION CONSTANT AND HEAT OF IONIZATION OF BISULFATE ION OF SULFURIC ACID

$t$ , °C.	$K_2$	$K_2$ (eq. 7)	$\Delta H_i$	$\Delta C_p$
0	0.0148	0.0145	- 146	- 76.0
5	.0143	.0143	- 533	- 78.9
10	.0139	.0140	- 934	- 81.8
15	.0134	.0135	-1351	- 84.8
20	.0127	.0129	-1782	- 87.9
25	.0120	.0122	-2229	- 91.9
30	.0113	.0114	-2692	- 94.1
35	.0105	.0105	-3172	- 97.3
40	.00973	.00961	-3665	-100.6
45	.00888	.00871	-4176	-103.7
50	.00794	.00781	-4704	-107.2
55	.00698	.00697	-5249	-110.7
60	.00596	.00611	-5811	-114.1

obtained at 25° is in good agreement with 0.0115 obtained by Sherrill and Noyes<sup>2</sup> by an entirely different method of approach. Enklaar<sup>10</sup> obtained 0.013 from  $P_H$  measurements and Dawson, Pycock and Spivey<sup>11</sup> arrived at a value of 0.010 from catalysis of ethyl acetate with sulfuric acid. All these values are considerably below 0.03, 0.02 and 0.017 previously reported by the investigators,<sup>3,12</sup> who omitted corrections due to the interionic attraction theory of Debye and Hückel. The value given by this method is obtained more directly than by the above methods and should be more accurate. The check with the value obtained by Sherrill and Noyes by a very involved calculation of combined conductance and transference data is all that could be desired.

#### Heat of Ionization of the Bisulfate Ion

In order to obtain the heat of ionization of the bisulfate ion,  $\Delta H_i$  was assumed to vary according to the equation,  $\Delta H_i = a + bT + cT^2 + dT^3$ . A four-constant equation was employed because

(10) Enklaar, *Chem. Weekblad*, **9**, 28 (1912).

(11) Dawson, Pycock and Spivey, *J. Chem. Soc.*, 291 (1933).

(12) Drucker, *Z. physik. Chem.*, **96**, 381 (1920); Kolthoff, *Rec. trav. chim.*, **43**, 207 (1924); Livingston, *This Journal*, **48**, 52 (1926).

In  $K_2$  varies rapidly with temperature and when plotted against the temperature, a decided curve is obtained. This expression was substituted in the van't Hoff equation and integrated. The equation obtained is

$$\log K_2 = -\frac{a}{2.3026RT} + \frac{b}{R} \log T + \frac{c}{2.3026R} T + \frac{d}{4.6052R} T^2 + e \quad (6)$$

The equation with the numerical values is

$$\log K_2 = -1387.6/T + 1.15612 \log T - 0.0001355T - 0.000038182T^2 + 3.27632 \quad (7)$$

The values of  $K_2$  computed by this equation are given in the third column of Table II. The equation reproduces the experimental results with an accuracy of 1%.

The heat of ionization is given in calories by

$$\Delta H_i = 6353.2 + 2.29894T - 0.00006204T^2 - 0.00034965T^3 \quad (8)$$

and  $\Delta C_p$ , or the difference in specific heat of the ions and the undissociated bisulfate ion by

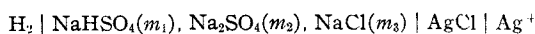
$$\Delta C_p = 2.29894 - 0.00012408T - 0.00104895T^2 \quad (9)$$

Values of  $\Delta H_i$  and  $\Delta C_p$  computed by these equations are given in the fourth and fifth columns of Table II. The accuracy of the heat data depends upon the least squared equation (7) and the assumption as regards the variation of  $\Delta H_i$  with temperature. The accuracy in the middle range of temperatures is estimated to be  $\pm 100$  cal.

The author wishes to express his appreciation to Professor Herbert S. Harned for help and suggestions during the course of this work.

#### Summary

1. From measurements of the cells



the dissociation constant of the bisulfate ion has been determined from 0 to 60° at 5° intervals.

2. The values of this constant at any temperature between 0 to 60° may be computed by equation (7) with an accuracy of 1%.

3. By means of equations (8) and (9) the heat of ionization of the bisulfate ion,  $\Delta H_i$ , and the differences in specific heats of the ions and undissociated bisulfate ion may be computed.

NEW HAVEN, CONN.

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