[CONTRIBUTION FROM THE LABORATORIES OF THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

# The Thermodynamic Ionization Constants of Sulfurous Acid at 25°[1]

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The ionization constants of sulfurous acid have been reported from a number of researches. Though the constants reported have agreed in order of magnitude, considerable discrepancy was found in their actual numerical values. Johnstone and Leppla[1a] have calculated the value of the first ionization constant according to modern theories from the conductivity data of Maass[2] making the assumption, however, that the activity coefficient of sulfurous acid is the same as that of hydrochloric acid in solutions of the same ionic strength. The second thermodynamic constant has not been determined by a modern method. Inasmuch as sulfur dioxide solutions and the salts of sulfurous acid are of importance industrially, accurate values of these constants may be of considerable use. Procedures for their determination have been developed, starting with the work of Harned and his associates[3] and Hamer[4] on the determination of the dissociation constants of acids by electromotive force measurements, and the use by several investigators[5] of the glass electrode for this purpose with solutions in which the hydrogen electrode is inapplicable.

**The First Dissociation Constant of Sulfurous Acid.**—The primary dissociation of sulfurous acid follows the reaction

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

and has the dissociation constant

$$K_1 = \frac{a_{H^+}a_{HSO_3^-}}{a_{SO_2}} = \frac{[H^+][HSO_3^-]\,\gamma_{H^+}\gamma_{HSO_3^-}}{[SO_2]\,\gamma_{SO_2}} \qquad (1)$$

in which brackets represent molal concentrations and the $\gamma$ values are activity coefficients.

The determination of the constant $K_1$ required the measurement of the electromotive forces of cells of the type

$$\text{Ag, AgCl, NaCl}(m_1),\ \text{NaHSO}_3(m_2),\ \text{SO}_2(\text{dissolved})(m_2),\ \text{glass, buffer, AgCl, Ag} \qquad (A)$$

The e. m. f. of this cell is given by the expression

$$E_A = E_g + E_0 + (RT/F)\ln a_{H^+}a_{Cl^-} \qquad (2)$$

where $E_g$ is the e. m. f. of the cell

$$\text{Ag, AgCl, buffer, glass, ``solution x,'' H}_2\text{, Pt} \qquad (B)$$

Substituting from equation (1) into equation (2) we obtain

$$E_A = E_g + E_0 + \frac{RT}{F}\ln\frac{[Cl^-][SO_2]K_1}{[HSO_3]} + \frac{RT}{F}\ln\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{SO_2}}{\gamma_{H^+}\gamma_{HSO_3^-}} \qquad (3)$$

and on rearranging and expressing the negative logarithm of $K_1$ as $pK_1$, the quantity $pK_1'$ can be defined, as follows

$$pK' = pK_1 - \log\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{SO_2}}{\gamma_{H^+}\gamma_{HSO_3^-}} = \frac{E}{2.303(RT/F)} + \log\frac{[Cl^-][SO_2]}{[HSO_3^-]} \qquad (4)$$

in which $E = E_g - E_A + E_0$. For as strong an acid as sulfurous, it is necessary to correct the stoichiometric molalities of bisulfite ion and sulfurous acid for the portion of the acid that is ionized and equation (4) takes the form

$$pK_1' = pK_1 - \log\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{SO_2}}{\gamma_{H^+}\gamma_{HSO_3^-}} = \frac{E}{2.303(RT/F)} + \log\frac{[Cl^-][SO_2 - H^+]}{[HSO_3^- + H^+]} \qquad (5)$$

The value of $pK_1'$ approaches $pK_1$ as the activity coefficients approach unity at infinite dilution.

Measurements were made of the e. m. f. of cells of type A with a series of ionic strengths. From these data $K_1$ was determined by extrapolation.

**Apparatus and Methods Used in Measuring the First Ionization Constant.**—The form of the electrode vessel used is shown as G, Fig. 1; it has three openings. The glass electrodes $g_1$ and $g_2$ were similar to those described by MacInnes and Belcher[5] and were prepared with membranes of Corning 015 glass. The reference electrodes within the glass electrodes were the silver–silver chloride type in a buffer solution which was approximately 0.03 $M$ with respect to sodium chloride, sodium acetate and acetic acid. Two silver–silver chloride electrodes carried in a two-hole rubber stopper are shown in the third opening.

The readings were made using a Leeds and Northrup Type K potentiometer and a Compton quadrant electrometer with connections similar to those described by MacInnes and Belcher.[6] The potentiometer, storage

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(1) Original manuscript received November 27, 1939.

(1a) Johnstone and Leppla, THIS JOURNAL, **56**, 2233 (1934).

(2) O. M. Maass and O. Maass, *Can. J. Research*, **2**, 42 (1928); *ibid.*, **5**, 162 (1931).

(3) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

(4) Hamer, *ibid.*, **56**, 860 (1934).

(5) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); *ibid.*, **57**, 1683 (1935); Neuss and Rieman, *ibid.*, **56**, 2238 (1934); Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933); Britton and Dodd, *Trans. Faraday Soc.*, **29**, 537 (1933).

(6) MacInnes and Belcher, THIS JOURNAL, **53**, 3315 (1931).

battery and standard cell were enclosed in electrically grounded, brass-screened boxes. The electrometer was mounted on heavy steel plates electrically grounded, and a box shielded with brass screen covered the instrument and the electrometer batteries. The cell was installed in an electrically grounded copper box I, Fig. 1, and the cel leads carried to the potentiometer through sulfur blocks in brass pipes, 4.5 cm. diam., which were welded to the copper box. A mercury well switch mounted on sulfur blocks and carefully shielded was interposed between the electrometer and the glass electrode leads. The switch was tipped by a glass rod handle approximately one meter in length to connect the "floating" quadrants of the electrometer with either the glass electrode or to ground. The electrometer was used with a sensitivity of approximately one centimeter deflection per millivolt on a ground glass scale placed at one meter distance. The sensitivity remained very constant throughout the course of the experiments. The zero position shifted to some extent depending upon time of day and room temperature. The electrometer needle was kept continuously charged and once properly adjusted the electrometer rarely needed further adjustment. The electrometer was used as a "null point" instrument and the readings generally could be made to ±0.05 millivolt. The potentiometer was adjusted against a Weston (unsaturated) standard cell which was periodically checked against cells standardized by the United States Bureau of Standards.

Temperature control was maintained at 25 ± 0.02° in an oil thermostat. The air within the copper box was desiccated with a dish of concentrated sulfuric acid and could be stirred by a small fan driven by a belt from an externally-placed, shielded electric motor. The copper box was partitioned at the level of the oil with a wooden floor through which the cell leads were carried by means of sulfur plugs and the box itself covered with a tight fitting copper lid. Room temperature rarely varied from 23 ± 1.0°.

**Preparation of Electrodes and Materials.**—The silver-silver chloride electrodes were prepared according to the directions of Brown[7]; however, in this Laboratory the white electrodes were obtained.[8]

The hydrogen electrodes consisted of heavy platinum foil 1 cm.$^2$ and platinized as directed by Popoff, Kunz and Snow.[9] Two such electrodes carried by a two-hole rubber stopper could be mounted in one of the openings in the electrode vessel G, Fig. 1.

Tank hydrogen was purified by passing first through reduced copper oxide electrically heated in a quartz tube to 675°, and then through a series of washing tubes D, Fig. 1, filled with distilled water.

Nitrogen of a high grade of purity was passed through alkaline pyrogallol solution and washed with water.

A good grade of tank sulfur dioxide free of sulfur trioxide was used directly.

Sodium chloride "c. p. analyzed" was twice precipitated with hydrogen chloride, washed with water on a sintered glass filter and dried at 120°.

Hydrochloric acid was prepared by distilling six molar acid in an all-glass still liberally discarding the first and last fractions.

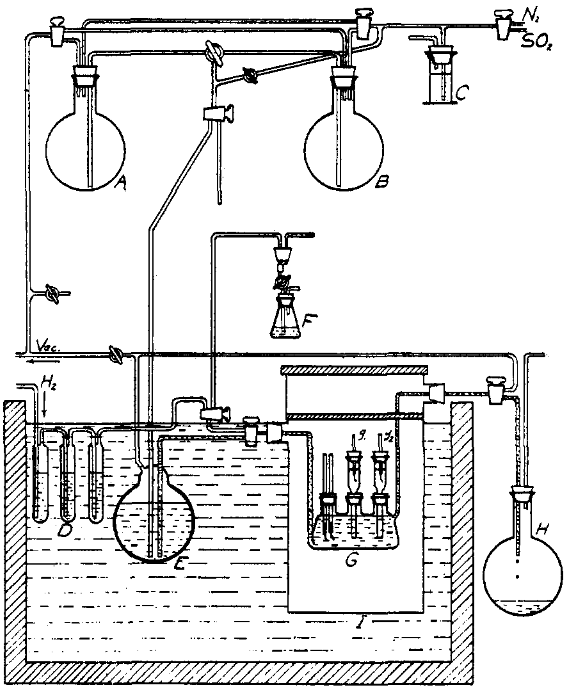

Fig. 1.

Carbonate-free sodium hydroxide solution was made using sodium amalgam.

A stock solution of approximately 0.10 *M* sodium chloride and 0.10 *M* sodium hydroxide was prepared with carbon dioxide-free water and stored in a paraffined bottle protected by a soda-lime guard tube. The water used in making all solutions and dilutions was of conductivity quality, specific conductance near (1) $10^{-6}$ mho. This solution was carefully analyzed and the ratio of the molality of sodium hydroxide to the molality of sodium chloride was obtained.

The gravimetric analysis of chloride or bromide in the presence of sulfite was performed by acidifying with nitric acid and precipitating the halide with silver nitrate and oxidizing the sulfite to sulfate with halide-free hydrogen peroxide.

The "total $SO_2$" was determined by titration with standard iodine solution. The titration of the sulfite was made according to the directions of Maass[10] with the modification that a starch end-point was used.

Concentrations are given in moles per thousand grams of water weighed *in vacuo*. The molality of sulfurous acid is expressed in moles of anhydrous sulfur dioxide per thousand grams of water.

The sodium acetate buffer solution was prepared by using sodium chloride, c. p. sodium acetate and distilled hydrochloric acid diluted with water, saturated with silver chloride, thoroughly boiled and stored in a glass-stoppered bottle.

The glass electrodes were kept filled with and immersed

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[7] Brown, This Journal, **56**, 646 (1934).

[8] Carmody, *ibid.*, **51**, 2901 (1929).

[9] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

[10] C. E. Maass and O. Maass, This Journal, **50**, 1352 (1928).

in distilled water. Occasionally the glass electrodes were allowed to stand overnight filled with cleaning solution.

The asymmetry potential correction for the glass electrode has been described by MacInnes and Belcher.[5] In this work it was measured in an auxiliary cell of the same design as G of Fig. 1, which could easily be removed from the copper box. A period of six to eight hours was found necessary before the asymmetry potentials assumed constant values.

The correction e. m. f., $E_g$, for the glass electrode, previously mentioned, was a constant for a given buffer solution. In the determination of $E_g$, "solution x" was a diluted solution of the buffer. The concentration showed no effect on the value of $E_g$ indicating no appreciable "sodium ion effect." Constant values were reached about one hour after the hydrogen gas flow was started and successive determinations agreed to ±0.05 millivolt after the customary corrections for the barometric, hydrostatic and vapor pressures.

**The Course of the Determination of the First Constant.**—The sodium hydroxide–sodium chloride stock solution was placed in the liter flask A, Fig. 1, and nitrogen passed through the solution slowly for about one-half hour. Flask B was then filled with sufficient water, saturated with silver chloride, to give the desired degree of dilution. This water was boiled under vacuum with a slow stream of nitrogen passing through the water for ten or fifteen minutes in order to remove dissolved oxygen and carbon dioxide. Sulfur dioxide was then measured from a mercury gas buret into the solution in sufficient amounts to convert the sodium hydroxide to sodium bisulfite and supply the desired excess of dissolved sulfur dioxide. The solution was then forced by means of nitrogen into flask E in the thermostat where it was allowed to stand overnight.

The glass electrodes and silver chloride electrodes were then inserted into the electrode vessel, nitrogen passed through for several minutes and the solution then forced under nitrogen from flask E into the electrode vessel. The vessel was emptied by forcing the solution under nitrogen into a small Erlenmeyer flask connected in place of the sampling bottle F, Fig. 1. The cell was rinsed by filling and emptying in this manner three times and then a sample taken for chloride analysis. The cell was then filled with solution and the e. m. f. measured. The four electrodes permitted four separate readings. When the e. m. f.'s had been taken, the solution in the electrode vessel was forced out under nitrogen, which had passed through flask E. After a small portion of the solution had rinsed the outlet tube, the small weighed sampling flask F was connected by a rubber joint. Flask F contained sodium hydroxide solution with a small amount of sugar to inhibit oxidation of the alkaline sulfite and the sulfur dioxide–bisulfite solution was introduced under the sodium hydroxide. The flask was then disconnected, the connection wiped dry and the sample weighed, and titrated with standard iodine. This method of sampling and titrating was found to give very reproducible results. Sulfur dioxide gas was now measured into flask E and the sulfur dioxide content of the solution increased. Nitrogen gas was passed through flask E for several minutes to rid the gas line of sulfur dioxide and to mix the solution. The electrode vessel was then filled and a new set of readings taken. In this manner the original solution in flask E was made successively richer in sulfur dioxide. Generally four or five such solutions were used in a period of about fifteen hours.

The sodium chloride and sodium bisulfite molalities remained constant and were calculated from the results of the chloride analysis and the sodium hydroxide–sodium chloride ratio. The increasing molalities of sulfurous acid were obtained as the difference in molalities of "total $SO_2$" and molality of sodium hydroxide. In this manner e. m. f.'s were taken and analyses made for a series of solutions in which the molality of sulfurous acid was consecutively increased. The process described was repeated for each of a number of dilutions of the original sodium chloride–sodium hydroxide stock solution.

In general, the potentials of the electrodes were attained rapidly and were steady over a period of several hours, and agreed to ±0.1 millivolt after corrections for asymmetry potentials. In the more dilute solutions, especially when the dissolved sulfur dioxide content was low, the potentials tended to drift at a rate of from one to two-tenths millivolt per hour in the direction of lower acidity. Though such a potential was followed over a period of sixteen hours, with a drop of 2.6 mv., little change in the general rate and direction of drift was observed. For such a solution on long standing, the asymmetry potential corrections failed to bring agreement between the two glass electrodes. On emptying the electrode vessel and refilling with more of the same solution the initial potentials were restored and the two glass electrodes would again agree. With solutions containing the highest concentrations of sulfurous acid, the silver chloride electrodes would, in some cases, tend to differ by as much as two to three-tenths millivolt. This effect of sulfur dioxide on the silver chloride electrode did not produce a permanent injury. The potentials were taken before any appreciable drift commenced, in general for the first two hours after the electrode vessel had been filled and the values read to ±0.05 millivolt were averaged after asymmetry corrections. In all cases, the asymmetry potentials for the glass electrodes were determined before and after using a series of solutions, retaining the same silver chloride electrodes.

**Data for the Computation of the First Ionization Constant.**—Table I contains the measurements from six series of cells at 25°. For extrapolation of results to zero ionic strength it was found convenient to use values of $E$ corresponding to fixed ratios of the molality of sulfur dioxide to sodium bisulfite; this was accomplished by interpolations and some extrapolations of the e. m. f. data. It was also found that the ratio of the activity coefficients of hydrochloric acid and sulfurous acid is sufficiently constant in a solution of constant sodium ion and chloride ion concentration to make the variation of $E$ linear with respect to the logarithm of the ratio of the molalities of the un-ionized acid and the bisulfite ion, $m(\mathrm{SO_2}) - m(\mathrm{H^+})/m(\mathrm{HSO_3^-}) + m(\mathrm{H^+})$, (the logarithm of this ratio is later designated as $\log (a - \mathrm{H})/(b + \mathrm{H})$. This can be seen to follow directly from equation (4). To obtain the hydrogen ion concentration a procedure similar to that used by Hamer[11] for determining the second ionization constant of sulfuric acid was employed. The estimation of the hydrogen ion concentration is based upon equation (1) which in terms of logarithms and the Debye and Hückel limiting law for ionic activity coefficients is

$$\log K_1 = \log \frac{[\mathrm{H^+}][\mathrm{HSO_3^-} + \mathrm{H^+}]}{[\mathrm{SO_2} - \mathrm{H^+}]} - 2 A \mu^{1/2} \quad (6)$$

in which $A$ has the value 0.506. From an assumed value of $pK_1$, 1.77, the hydrogen ion concentration consistent with the ionic strength can be calculated by a few successive approximations. The values of $\log (a - \mathrm{H})/(b + \mathrm{H})$ and of $E$ calculated from the linear expression

$$E = E_{\mathrm{g}} - E_{\mathrm{A}} + E_0 = C \log \left(\frac{a - H}{b + H}\right) + D \quad (7)$$

are included in Table I. The linearity of equation (7) is quite insensitive to the value of $pK_1$ assumed in the calculation of $\log (a - \mathrm{H}/b + \mathrm{H})$.

TABLE I

MEASURED E. M. F.'S AND MOLALITIES OF SULFUR DIOXIDE FOR SIX DILUTIONS AND E. M. F.'S CALCULATED BY EQUATION 6

| $m(\mathrm{SO_2})$ | $m(\mathrm{H^+})$ | $-\log \left(\frac{a - H}{b + \mathrm{H}}\right)$ | $E_{\mathrm{obsd.}}$ | $E_{\mathrm{calcd.}}$ |
|---|---|---|---|---|
| $m(\mathrm{NaCl}) = 0.05123$, $m(\mathrm{NaHSO_3}) = 0.05516$ | | | | |
| 0.001866 | 0.000737 | 1.6947 | +0.2800$_7$ | +0.28026 |
| .01042 | .003999 | 0.9642 | .2380$_5$ | .23772 |
| .02586 | .009495 | .5966 | .2163$_9$ | .21632 |
| .04434 | .01588 | .3909 | .2043$_2$ | .20434 |
| .06484 | .02184 | .2530 | .1963$_0$ | .19631 |
| .08100 | .02649 | .1755 | .1916$_2$ | .19180 |
| $m(\mathrm{NaCl}) = 0.03359$, $m(\mathrm{NaHSO_3}) = 0.03535$ | | | | |
| .004457 | .002042 | 1.1898 | + .2589$_9$ | + .26194 |
| .01325 | .005808 | 0.7428 | .2358$_4$ | .23601 |
| .02454 | .01025 | .5041 | .2223$_4$ | .22217 |
| .03689 | .01474 | .3544 | .2138$_4$ | .21349 |
| .04978 | .01910 | .2492 | .2070$_4$ | .20739 |
| $m(\mathrm{NaCl}) = 0.02495$, $m(\mathrm{NaHSO_3}) = 0.02686$ | | | | |
| .002457 | .001249 | 1.3668 | + .2794$_6$ | + .27938 |
| .008374 | .004094 | 0.8593 | .2498$_9$ | .25009 |
| .01715 | .007944 | .5774 | .2339$_8$ | .23381 |
| .02618 | .01159 | .4208 | .2247$_9$ | .22477 |
| .03700 | .01564 | .2987 | .2176$_9$ | .21772 |
| $m(\mathrm{NaCl}) = 0.01643$, $m(\mathrm{NaHSO_3}) = 0.01769$ | | | | |
| .01347 | .007054 | .5867 | + .2452$_2$ | + .24511 |
| .02163 | .01071 | .4147 | .2347$_6$ | .23485 |
| .03033 | .01426 | .2984 | .2277$_8$ | .22791 |
| .03876 | .01747 | .2177 | .2231$_6$ | .22309 |
| .04705 | .02043 | .1561 | .2194$_4$ | .21942 |
| .05500 | .02314 | .1078 | .2165$_7$ | .21653 |
| $m(\mathrm{NaCl}) = 0.009049$, $m(\mathrm{NaHSO_3}) = 0.009744$ | | | | |
| .006016 | .003848 | .7972 | + .2726$_0$ | + .27235 |
| .009990 | .006074 | .6063 | .2608$_0$ | .26124 |
| .01459 | .008437 | .4708 | .2534$_1$ | .25336 |
| .01861 | .01037 | .3872 | .2485$_8$ | .24850 |
| .02253 | .01215 | .3237 | .2447$_5$ | .24481 |
| .02771 | .01437 | .2569 | .2410$_4$ | .24092 |
| $m(\mathrm{NaCl}) = 0.008680$, $m(\mathrm{NaHSO_3}) = 0.009358$ | | | | |
| .005607 | .003635 | .8188 | + .2748$_7$ | + .27470 |
| .008271 | .005176 | .6717 | .2659$_0$ | .26622 |
| .01190 | .007126 | .5378 | .2585$_9$ | .25850 |
| .01577 | .009069 | .4393 | .2527$_6$ | .25280 |
| .02028 | .01119 | .3542 | .2479$_9$ | .24790 |
| .02552 | .01350 | .2793 | .2435$_5$ | .24358 |

The excellent agreement of equation (7) with the experimental data is potent evidence that the

TABLE II

CONSTANTS FOR EQUATION 7

| $m(\mathrm{NaCl})$ | $m(\mathrm{NaHSO_3})$ | $-C$ | $D$ |
|---|---|---|---|
| 0.05123 | 0.05516 | 0.05823 | 0.18158 |
| .03359 | .03535 | .05799 | .19294 |
| .02495 | .02686 | .05773 | .20048 |
| .01643 | .01769 | .05965 | .21011 |
| .009049 | .009744 | .05816 | .22598 |
| .008680 | .009358 | .05770 | .22746 |

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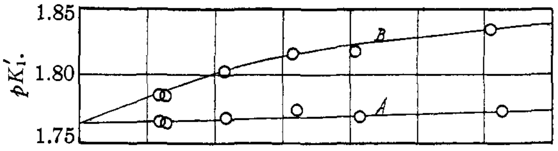
[11] Hamer, THIS JOURNAL, **56**, 860 (1934).

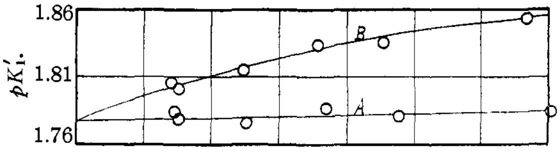
TABLE III

DATA FOR COMPUTING THE FIRST IONIZATION CONSTANT

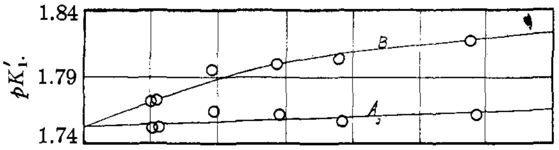
| $m$(NaCl) | $m$(NaHSO$_3$) | $E$ | Method A | | Method B | |
|---|---|---|---|---|---|---|
| | | | $\mu$ | $pK_1'$ | $\mu$ | $pK_1'$ |
| | | $m(SO_2) = 2m(NaHSO_3)$ | | | | |
| 0.05123 | 0.05516 | 0.18580 | 0.1405 | 1.7824 | 0.1338 | 1.8534 |
| .03359 | .03535 | .20059 | .09436 | 1.7801 | .09103 | 1.8353 |
| .02495 | .02686 | .21051 | .07300 | 1.7870 | .07089 | 1.8338 |
| .01643 | .01769 | .22487 | .05018 | 1.7750 | .04914 | 1.8114 |
| .009049 | .009744 | .24760 | .02950 | 1.7765 | .02913 | 1.8017 |
| .008680 | .009358 | .24947 | .02843 | 1.7824 | .02810 | 1.8081 |
| | | $m(SO_2) = m(NaHSO_3)$ | | | | |
| .05123 | .05516 | .19968 | .1255 | 1.7723 | .1220 | 1.8332 |
| .03359 | .03535 | .21438 | .08324 | 1.7682 | .08155 | 1.8169 |
| .02495 | .02686 | .22424 | .06374 | 1.7738 | .06270 | 1.8152 |
| .01643 | .01769 | .23913 | .04315 | 1.7686 | .04266 | 1.8009 |
| .009049 | .009744 | .26177 | .02476 | 1.7631 | .02461 | 1.7853 |
| .008680 | .009358 | .26346 | .02383 | 1.7650 | .02367 | 1.7850 |
| | | $2m(SO_2) = m(NaHSO_3)$ | | | | |
| .05123 | .05516 | .21487 | .1167 | 1.7633 | .1159 | 1.8184 |
| .03359 | .03535 | .22945 | .07670 | 1.7577 | .07584 | 1.8024 |
| .02495 | .02686 | .23925 | .05829 | 1.7617 | .05777 | 1.7998 |
| .01643 | .01769 | .25468 | .03901 | 1.7642 | .03877 | 1.7941 |
| .009049 | .009744 | .27712 | .02200 | 1.7510 | .02193 | 1.7712 |
| .008680 | .009358 | .27881 | .02114 | 1.7509 | .02107 | 1.7709 |



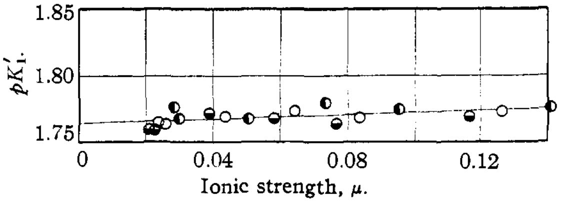
(1) $m$(NaHSO$_3$) = $m$(H$_2$SO$_3$), $pK_1$ = 1.764.



(2) $m$(NaHSO$_3$) = $^1/_2m$(H$_2$SO$_3$), $pK_1$ = 1.778.



(3) $m$(NaHSO$_3$) = $2m$(H$_2$SO$_3$), $pK_1$ = 1.753.



(4) ○, $m$(NaHSO$_3$) = $m$(H$_2$SO$_3$); ◐, $m$(NaHSO$_3$) = $^1/_2m$(H$_2$SO$_3$); ⊖, $m$(NaHSO$_3$) = $2m$(H$_2$SO$_3$); $pK_1$ = 1.764.

Fig. 2.—Values of $pK_1'$ as functions of the ionic strength. Curves A, method A; curves B, method B.

glass electrodes are reversible with respect to hydrogen ion throughout the *p*H range of these measurements. The constants in equation (7) were calculated from the experimental data by the method of least squares and the values for six series of dilutions given in Table II were used in obtaining the first ionization constant. The value of $E_0$ was taken as $-0.22239$.[12]

**The Computation of the First Ionization Constant.**—The hydrogen ion concentrations computed according to equation (7) were used in equation (5) with the requirement that the values of $\mu$ and $pK_1'$ finally obtained, yielded on extrapolation the value of $pK_1$ used. This was done for the three series of solutions with ratios of molality of sulfur dioxide to the molality of sodium bisulfite, 2:1, 1:1, and 1:2. The data are presented in Table III, the values of $\mu$ and $pK_1$ being under Method A.

In Fig. 2, curves 1A, 2A and 3A give the final extrapolations of $pK_1'$ as a function of the ionic strength yielding $pK_1$ values 1.764, 1.778 and 1.753, respectively. In the last two cases, some of the e. m. f.'s $E$ were extrapolated from the experimental data. In the first (curve 1A), the e. m. f.'s all lie within the experimental range and hence $pK_1$ 1.764 ($K_1$, $1.72 \times 10^{-2}$) is chosen as the best value.

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[12] Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

Figures 2, 4, presents the values of $pK_1'$ for all three molality ratios plotted against ionic strength, the value $pK_1$, 1.764, being assumed in the calculations; the small slope of the curve justifies plotting together the data from the three series. The extrapolation yields the assumed value of $pK_1$, 1.764. A comparison of curves 2A and 3A with 4 reveals the sensitivity of the values of $pK_1'$ upon the assumed values of $pK_1$.

As a check on the operation of the Debye and Hückel limiting law for individual activity coefficients, equation (6) was rewritten in the form

$$pK_1 = \log \frac{[H^+][HSO_3^- + H^+]}{[SO_2 - H^+]} + \log \gamma_{H^+}\gamma_{Cl^-} \quad (8)$$

The use of this expression also serves to correlate the results presented above with those of Johnstone and Leppla,[1a] who assumed that the activity coefficient of sulfurous acid equals that of hydrochloric acid in solutions of the same ionic strength. The use of equation (8) is based upon the fact that the equality of the activity coefficients of the two acids holds when the ionic strength approaches zero. The activity coefficients for hydrochloric acid were those given by Harned and Ehlers.[12] The values of $\mu$ and $pK_1'$ calculated in this way are reported in Table III under Method B and plots of $pK_1'$ against ionic strength are given in Fig. 2, curves 1B, 2B, 3B. Although the curvature makes the extrapolations uncertain, the method confirms the straight line extrapolations by Method A.

The value of $K_1$, $1.72 \times 10^{-2}$, is considerably higher than $1.3 \times 10^{-2}$ obtained by Johnstone and Leppla.[1a] In the work presented herein any assumptions made regarding activity coefficients are corrected by extrapolation to zero ionic strength.

**The Second Dissociation Constant of Sulfurous Acid.**—The second dissociation constant of sulfurous acid

$$K_2 = \frac{(H^+)(SO_3^{--})}{(HSO_3^-)} = \frac{[H^+][SO_3^-]}{[HSO_3^-]}\,\frac{\gamma_{H^+}\gamma_{SO_3^{--}}}{\gamma_{HSO_3^-}} \quad (9)$$

was determined by measurements of cells of the type

Ag, AgX, NaX($m_1$), $Na_2SO_3$($m_2$), $NaHSO_3$($m_3$), glass,
buffer, AgX, Ag (C)

where NaX is either sodium chloride or sodium bromide. Silver chloride and silver bromide are appreciably soluble in sulfite solutions, the latter showing the lesser solubility; consequently the silver–silver bromide electrodes are better adapted for use in this cell. The solubility of the silver halide will be discussed below.

The theoretical development is similar to that for the first ionization constant and $pK_2'$ is defined by the equation

$$pK_2' = pK_2 - \log \frac{\gamma_H\gamma_X\gamma_{HSO_3^-}}{\gamma_H\gamma_{SO_3}} = \frac{E}{0.2303\frac{RT}{F}} + \log \frac{[HSO_3^-][X^-]}{[SO_3^{--}]} \quad (10)$$

in which $X^-$ represents a halogen ion constituent. E. m. f.'s of cells of the type C were measured using a series of ionic strengths and $pK_2$ determined by means of an extrapolation.

**Apparatus and Materials Used in the Determination of the Second Ionization Constant.**—The silver bromide electrodes were prepared thermally according to the directions of Keston.[13]

Hydrobromic acid was distilled from over a few strips of tin in an all-glass still.

Sodium sulfite solutions were prepared by four or five recrystallizations of sodium sulfite crystals of good quality from oxygen-free water between 0 and 40°, and under an atmosphere of nitrogen. On testing the solution with hydrochloric acid and barium chloride a trace of cloudiness due to sulfate was always present which further recrystallization failed to remove.

The sodium bromide, sodium sulfite, sodium bisulfite stock solution was prepared by running dilute oxygen-free hydrobromic acid from flask A, Fig. 1, under sodium sulfite solution in flask B to make the volume approximately one liter, and the resulting solution was then returned to flask A into which had been placed freshly precipitated silver bromide, which had been carefully washed free of acid. The apparatus and flasks were kept thoroughly flushed with nitrogen. The stock solution thus prepared was of equal molality in sodium bisulfite and sodium bromide and the molality of the sodium sulfite was obtained as the difference in molality of the "total sulfur dioxide" and the molality of the sodium bromide.

After standing overnight the stock solution was diluted by running a portion of the solution from flask A into the desired amount of oxygen-free water in flask B and this diluted solution then passed into flask E in the thermostat where it was allowed to stand from three to four hours. The electrodes were then installed in the manner previously described except that in one series of measurements silver bromide electrodes were used. The cell was rinsed and filled in the manner described in the case of the first constant. The solution was allowed to stand from fifteen to thirty minutes and then the electrode vessel emptied and the solution flowed from flask E slowly through the cell into flask H. The rate of flow was regulated to approximately one liter an hour and the potentials read repeatedly throughout the duration of the flow. The first portion of the solution was used to rinse flask H, and a sample then taken for sulfite determination in a sampling flask similar to F, Fig. 1. The remainder of the solution was collected

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[13] Keston, THIS JOURNAL, 57, 1671 (1935).

in the flask H and duplicate samples taken for bromide analysis. The sulfite determination was made by diluting the alkaline sulfite sample to which some sucrose had been added to retard oxidation in a volumetric flask and titrating into a measured volume of standard iodine solution. Successive dilutions of the original stock solution were made and flowed through the electrode vessel according to the above procedure; except that the sulfite determination was made only on the first most concentrated solution. The degree of dilution was calculated from the bromide determination.

Sodium chloride, sodium sulfite, sodium bisulfite stock solutions were prepared in a fashion similar to those discussed under the first constant except that less sulfur dioxide was used. These solutions were saturated with silver chloride and a series of successive measurements made in the same manner as above but using silver chloride electrodes. In the chloride stock solution a larger concentration of chloride was used than sulfite in order to reduce the solubility of silver chloride as much as possible.

**The Behavior of Glass Electrodes in Sulfite-Bisulfite Solutions.**—A large number of preliminary experiments demonstrated the necessity of flowing the solutions. On standing in static sulfite–bisulfite solution the potentials of the glass electrodes drifted steadily, generally in the direction of increasing acidity. Two glass electrodes would check each other, when asymmetry potential corrections were made, only immediately after the electrode vessel was filled; on standing for several hours they would, in some cases, differ as much as ten millivolts, even though asymmetry potentials showed no change. This drifting of potential was much more rapid with the more dilute solutions, often two to three millivolts an hour. Some of these potentials were followed for several days with little change occurring in the rate of direction of drift. With the more concentrated solutions the drift was much less, in some cases in the direction of decreasing acidity. Bubbling nitrogen through the cell had little effect, whereas bubbling air through gave a potential change much greater than could be accounted for readily by assuming oxidation to sulfate.

Solutions containing a small amount of sucrose were found to give somewhat steadier potential readings. It was further observed that if the electrode vessel and the glass electrodes were soaked overnight in sulfite solution containing 1–2% sugar, then, when thoroughly rinsed and filled with solution, the potentials would remain fairly constant over long periods of time. Similar experiments using methylene blue instead of sugar failed to have any appreciable effect on the electrode behavior. Both sucrose and methylene blue in small quantities inhibit the oxidation of sulfurous acid and sulfites.[14] Whether the disturbing reaction, which apparently occurs at the electrode surface, is oxidation the writers are unable to say.

It was observed that the initial potentials taken were very nearly always the same for the same stock solution even after the stock solution was several days old; and, further, that on gently rocking the electrode vessel the two glass electrodes could be brought into agreement. It was due to these observations that the apparatus was designed for a flowing solution. The flowing solution gave very steady potentials which were the same as were obtained on initially filling the cell. For the more concentrated solutions the potentials would remain constant to ±0.02 millivolt during the period of flow. For the more dilute solutions a somewhat increased rate of flow was necessary and for the greatest dilutions a variation of one to two-tenths millivolts was found.

As has been mentioned, somewhat similar effects were observed in measurement in cell (A) for the first constant when the dilution was great and the sulfurous acid content low. However, the effect of flowing on solutions containing sulfur dioxide could not be satisfactorily investigated because of loss of sulfur dioxide in transferring and flowing the solutions.

TABLE IV

POTENTIALS AND $pK_2'$ VALUES FOR THE BROMIDE SOLUTIONS

| $m(NaBr)$ and $m(NaHSO_3)$ | $m(Na_2SO_3)$ | $\mu^{1/2}$ | $E_g - E_e + E^0$ | $pK_2'$ |
|---|---|---|---|---|
| 0.01449 | 0.01517 | 0.2729 | 0.52760 | 7.0614 |
| .01088 | .01139 | .2365 | .53619 | 7.0821 |
| .004438 | .004648 | .1511 | .56203 | 7.1298 |
| .02114 | .02110 | .3250 | .51541 | 7.0404 |
| .01306 | .01304 | .2554 | .53001 | 7.0784 |
| .007185 | .007171 | .1894 | .54731 | 7.1113 |
| .003100 | .003094 | .1244 | .57041 | 7.1367 |

TABLE V

POTENTIALS AND $pK_2'$ VALUES FOR THE CHLORIDE SOLUTIONS

| $m(NaCl)$ | $m$ $(Na_2SO_3)$ | $m$ $(NaHSO_3)$ | $\mu^{1/2}$ | $E_g - E_e + E^0$ | $pK_2'$ |
|---|---|---|---|---|---|
| 0.03313 | 0.006303 | 0.02196 | 0.2720 | 0.46999 | 7.0088 |
| .01892 | .003600 | .01254 | .2056 | .48679 | 7.0495 |
| .01372 | .002610 | .009092 | .1750 | .49624 | 7.0697 |
| .007777 | .001480 | .005155 | .1318 | .51159 | 7.0827 |
| .05417 | .01279 | .03094 | .3514 | .46389 | 6.9607 |
| .02329 | .005500 | .01330 | .2304 | .48989 | 7.0338 |
| .009763 | .002305 | .005576 | .1492 | .51529 | 7.0856 |
| .006699 | .001582 | .003826 | .1236 | .52549 | 7.0944 |

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[14] Bassett and Henry, *J. Chem. Soc.*, 914 (1935); additional references are given.

**Data for Computing the Second Ionization Constant.**—The data obtained from two series of dilutions of bromide stock solutions are compiled in Table IV and the data from two chloride solutions in Table V. The value for $E_0$ for the silver bromide electrode is taken as $-0.07103$.[15]

**The Sodium Silver Sulfite Complex.**—It is a well known fact that the silver ion forms a soluble complex with sodium sulfite; however, a search of the literature yielded little information as to the properties or formula of the complex. It is of importance in connection with the use of silver halide electrodes in the presence of sulfite to estimate with some degree of accuracy the equilibrium of the supposed reaction

$$Ag(SO_3)_2^{=} = Ag^+ + 2SO_3^{=}$$

This was investigated in the following manner. Silver sulfite was precipitated from silver nitrate solution with sodium sulfite and twice washed by decantation, filtered and washed with cold water in a sintered glass filter. The moist silver sulfite was then dissolved in sodium sulfite solution and sodium chloride added. The partially precipitated solutions were allowed to stand in completely filled, glass-stoppered bottles. Samples of the clear solution were taken for analysis and the dissolved silver precipitated as silver chloride on addition of nitric acid. The total sulfur dioxide content was determined by titration against standard iodine, total chloride by precipitation with silver nitrate. The sodium sulfite content was calculated as the molality of the total sulfite less twice the molality of the silver. The data from these analyses are presented in Table VI. The experiments were made at room temperature.

From the solubility product for silver chloride

$$[Ag^+][Cl^-] = K_{AgCl}$$

and from the dissociation constant for the silver sulfite complex

$$K_c = \frac{[Ag(SO_3)_2^{=}]}{[Ag^+][SO_3^{=}]^2}$$

we obtain

$$K_c' = K_c \times K_{AgCl} = \frac{[Ag(SO_3)_2^{=}][Cl^-]}{[SO_3^{=}]^2} \qquad (11)$$

the calculated values for $K_c'$ are shown in the fourth column of Table V. The agreement in $K_c'$ is sufficient to demonstrate the validity over this range of concentration for this formula, for the complex ion since $K_c'$ is very sensitive to the assumed power of the sulfite ion. Equation (11) shows that the chloride and bromide stock solutions will remain essentially saturated with silver ion on dilution, and the fact that as much as ten to twenty liters of solution could be flowed over the silver chloride electrodes without any observable injury to their potentials confirms this conclusion.

TABLE VI

SOLUBILITIES OF SILVER CHLORIDE IN SODIUM SULFITE SOLUTIONS

| $m(Cl^-)$ | $m(SO_3^{=})$ | $m(AgSO_3)_2$ | $K_c' \times 10^2$ |
|---|---|---|---|
| 0.2246 | 0.2400 | 0.01286 | 5.01 |
| .2174 | .1155 | .003363 | 5.48 |
| .1475 | .1353 | .005787 | 4.66 |
| .2294 | .2468 | .01374 | 5.18 |
|  |  |  | (5.08) |

**Computation of the Second Dissociation Constant.**—The values of $pK_2'$ have been computed from the data by means of equation (10) and are given in the last column of Tables IV and V. A correction for the hydrolysis of the sodium sulfite and ionization of bisulfite ion was not found necessary. The values of $pK_2'$ for the bromide solution are shown plotted in Fig. 3 against the square root of the ionic strength. The value of $pK_2$ was calculated by the method of least squares and yields a value of 7.205, or $K_2$, $6.237 \times 10^{-8}$. The values of $pK_2'$ for the chloride solutions are shown plotted in Fig. 3 and yield by least squares a value for $pK_2$, 7.175, or $K_2$, $6.685 \times 10^{-8}$.

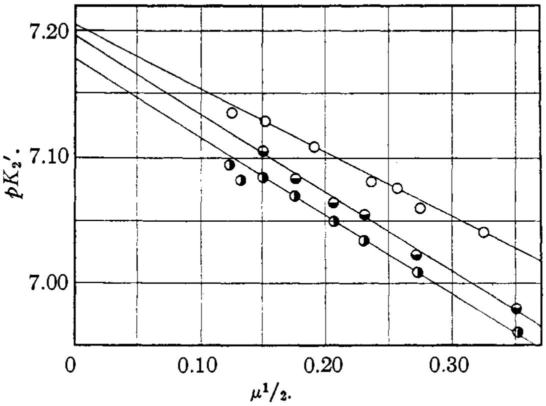

Fig. 3.—Values of $pK_2'$ as functions of the square root of the ionic strength: ○, NaBr solutions; ◑, NaCl solutions, ⊖, NaCl solutions corrected for Ag complex.

Using the value for $K_c'$ the concentrations in the chloride solutions were corrected. However, the effect of a probable hydrolysis of the complex silver sulfite ion is not known. In making these corrections it is necessary to correct the sodium

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[15] Harned, Keston and Donelson, THIS JOURNAL, 58, 989 (1936).

chloride–sodium hydroxide ratio for the amount of dissolved silver chloride. The extrapolation of these corrected values of $pK_2'$ is shown in Fig. 3. With these corrections the chloride solutions yield a value for $pK_2$, 7.192 or a value for $K_2$, $6.427 \times 10^{-8}$. Because of the uncertainties which prevailed with the use of the silver–silver chloride electrodes, in sulfite solutions, the authors have taken $K_2$, $6.24 \times 10^{-8}$, as the best value for this constant.

These values are in qualitative agreement with the previously reported $pK_2$ values. Britton and Robinson[16] report in measurements with glass electrodes by a titration method a value of $pK_2$, 6.99. Rumpf[17] reported a value of $pK_2$, 6.96, also measured by electrometric titration with glass electrodes; Britton and Robinson[18] 7.74 by titrations with the antimony-antimonous oxide electrode and 8.78 by titration experiments with tungsten electrodes.[19]

The correction for the solubility of silver bromide was found insignificant and therefore the value of the constant as determined by the bromide electrode is taken as the more reliable. The fact that the solubility correction for the chloride solutions is in the direction of the bromide value supports this view.

## Summary

Determinations of the first and second ionization constants of sulfurous acid at 25° have been described. The values obtained are $1.72 \times 10^{-2}$ for the first constant and $6.24 \times 10^{-8}$ for the second. The first of these values is in fair agreement with previous determinations made by conductivity measurements. The value for the second constant is only in qualitative agreement with other reported values made by much less accurate methods.

The general behavior of glass electrodes in sulfite solutions has been described.

An investigation of the solubility of silver chloride in sodium sulfite has been described in consequence of which the complex ion, $\mathrm{Ag(SO_3)_2^{=}}$, was detected.

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[16] Britton and Robinson, *Trans. Faraday Soc.*, **28**, 531 (1932).

[17] Rumpf, *Compt. rend.*, **197**, 686 (1933).

[18] Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

[19] Britton and Dodd, *ibid.*, 829 (1931).

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

# Some Reactions of the Acetyl Radical

BY H. W. ANDERSON AND G. K. ROLLEFSON

The presence of the acetyl radical as an intermediate in the photolysis of certain carbonyl compounds has been reported by several investigators,[1–6] and its instability at higher temperatures has been noted. If, in addition to its decomposition into a methyl radical and carbon monoxide, the acetyl radical disappears by some other reactions which do not liberate carbon monoxide, the yield of carbon monoxide should be a measure of the importance of the decomposition relative to other competing reactions. If the stability of the acetyl radical decreases with increasing temperature, the carbon monoxide yields in the photolyses of different compounds which can form an acetyl radical might be expected to show similarities in their variation with temperature. To test this point, the temperature dependence of the carbon monoxide yield in the photolysis of acetone, diacetyl, and acetyl bromide vapor has been investigated from 0 to 140°, and is reported in this paper.

## Experimental Details

**Apparatus.**—The vapors were decomposed in a cylindrical quartz reaction cell 5.0 cm. in diameter, 5.5 cm. in length, with plane faces. The cell was connected to a click gage, a reservoir closed by a greaseless glass valve, and a high vacuum system. The volume of the reaction system was 113.5 cc., of which 3.3% was dead space. The connection between the reaction system and pumps was closed by a stopcock lubricated with Airco Hy-Vac grease, which proved very resistant to the vapors of acetone and acetyl bromide. Sufficient experiments were run with acetone and acetyl bromide in which the stopcock was replaced by a greaseless glass valve to show that the presence of stopcock grease had no appreciable effect. Pressures were measured by a sulfuric acid manometer connected through the click gage to the reaction system. The gaseous products of the photolyses were transferred

[1] Barak and Style, *Nature*, **135**, 307 (1935).

[2] Spence and Wilde, *J. Chem. Soc.*, 352 (1937).

[3] Glazebrook and Pearson, *ibid.*, 567 (1937).

[4] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[5] Etzler and Rollefson, THIS JOURNAL, **61**, 800 (1939).

[6] Herr and Noyes, *ibid.*, **62**, 2052 (1940).