

Acidity of Sulfuric Acid-Sodium Sulfate Solutions by Kinetic Measurements

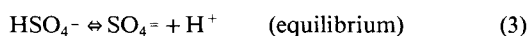
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Because of the industrial importance of sulfuric acid, acidic properties of sulfuric acid solutions have been studied at all levels of concentration. Aqueous solutions containing both sulfuric acid and sodium sulfate also have industrial importance, but have been studied to a lesser extent. The purpose of this work was to develop a scale that characterizes the acidity of solutions containing sulfuric acid and sodium sulfate and to determine the effect of a third ingredient, sodium chlorate, on the acidity function. The three component solutions are particularly important in the manufacture of chlorine dioxide, a chemical bleach used in the pulp and paper industry. The rate that chlorine dioxide is generated in a commercial operation depends highly on acidity. For processes with high acid dependence, it is important to have a quantitative measure of acidity of process solutions.

Background

Sulfuric acid and sodium sulfate solutions have been studied extensively to determine dissociation properties (Pitzer et al., 1977; Baes, 1957; Lindstrom and Wirth, 1969). These species dissociate in aqueous solution as follows:



The concentration equilibrium coefficient of Eq. 3,

$$Q = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-], \quad (4)$$

varies with solution composition. Values of Q have been measured over a wide range of conditions (Dickson et al., 1990). At 298 K and for sulfuric acid solutions at infinite dilution, Q equals the activity equilibrium constant, 0.0105. At acid concentrations in the range 0.5 to 3.5 M, Q increases from about 0.15 to 1.1. Q values are generally lower for sulfuric

acid-sodium sulfate solutions than for sulfuric acid solutions, when the solutions are compared at the same total (stoichiometric) sulfate concentration. Figure 1 shows proton concentration as a function of total sulfate based on Q values reported in several references. (The term "proton" here includes all hydrated as well as the unhydrated hydrogen ions). Proton concentration is nearly linear with total, stoichiometric sulfate except for very dilute solutions. Figure 1 shows that proton concentration is reduced when sodium sulfate is added to sulfuric acid, as one might expect based on the equilibrium, Eq. 3.

These dissociation properties relate directly to acidity only at solution concentrations below about 0.1 M. At higher concentrations, which are of more industrial importance, the pH scale breaks down, and empirical acidity scales are often used to characterize acidity. Acidity functions for sulfuric acid solutions can be found in many references, tabulated as functions

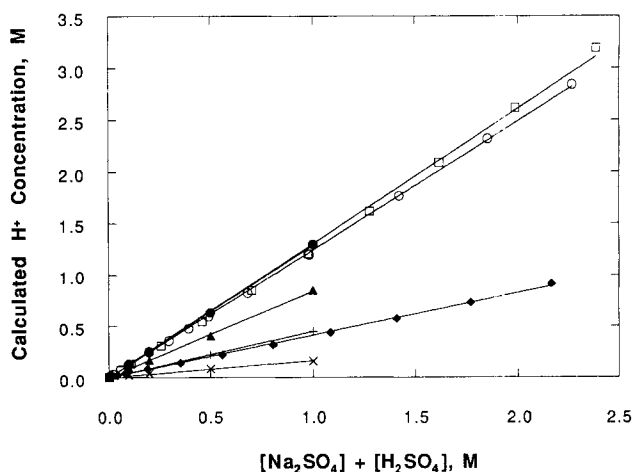


Figure 1. Hydrogen ion concentration calculated from published concentration equilibrium coefficients for Eq. 3.

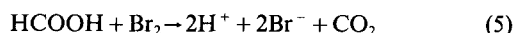
Key = symbol, parameter a , slope, reference: \circ , 1.00, 1.24, Pitzer et al. (1977); \square , 1.00, 1.30, Lindstrom and Wirth (1969); \blacklozenge , 0.50, 0.41, *ibid.*; \times , 0.25, 0.16, Baes (1957); $+$, 0.50, 0.45, *ibid.*; \blacktriangle , 0.75, 0.84, *ibid.*; \bullet , 1.00, 1.29, *ibid.*

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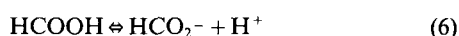
of stoichiometric sulfuric acid concentration (see, for example, Boyd, 1969; Rochester, 1970). Acidity functions of sulfuric acid-sodium sulfate solutions have not been previously reported.

Theory

We have made use of an H_- acidity scale in a recent study of the kinetics and mechanism of the chlorine-formic acid reaction in sulfuric acid (Hoq et al., 1991). The scale was developed by Cox and McTigue (1964) for strong mineral acids and is derived from the rate of the bromine-formic acid reaction:



The mechanism of Eq. 5 involves equilibrium ionization of formic acid:



followed by a rate determining step,



The theoretical rate law,

$$-d[\text{Br}_2]/dt = k_{\text{obs}}[\text{HCOOH}][\text{Br}_2]/[\text{H}^+] \quad (8)$$

is easily derived from the mechanism. Experimentally, one finds that the rate does not have the simple negative first-order dependence on $[\text{H}^+]$ as the model implies. The reason for this discrepancy is that the observed rate coefficient, k_{obs} , contains activity coefficients, γ_i , which depend on acidity:

$$k_{\text{obs}} = k' K_a \{ \gamma_{\text{HCOOH}} / (\gamma_{\text{HCO}_2^-} \cdot \gamma_{\text{H}^+}) \} \quad (9)$$

In this equation, k' and K_a are the true rate constant of Eq. 7 and the ionization constant of formic acid, respectively.

In establishing an acidity scale, Cox and McTigue (1964) defined an acidity function,

$$h_- = [\text{H}^+] \gamma_{\text{H}^+} \cdot \gamma_{\text{HCO}_2^-} / \gamma_{\text{HCOOH}} \quad (10)$$

which, inserted into Eq. 8, yields,

$$-d[\text{Br}_2]/dt = k' K_a [\text{HCOOH}][\text{Br}_2]/h_- \quad (11)$$

In this expression, the rate coefficient, $k' K_a$, is a constant and is not a function of acidity. Cox and McTigue (1964) studied this reaction in nitric, perchloric and sulfuric acid solutions over the concentration range, 0.5 to 4 M. They calculated values of h_- from experimental rates for each acid concentration examined. These values are reported in logarithmic form,

$$H_- = -\log(h_-) \quad \text{or} \quad -H_- = \log(h_-) \quad (12)$$

For sulfuric acid concentrations of 0.5, 1, 2, 3 and 4 M, they reported the $-H_-$ values, -0.42 , -0.12 , 0.42 , 0.97 , and 1.51 ,

respectively. The h_- values corresponding to these $-H_-$ values are 0.38, 0.76, 2.63, 9.33 and 32.36, respectively. This scale, for example, shows that a 4 M H_2SO_4 solution is $32.36/0.38 = 85$ times more acidic than 0.5 M H_2SO_4 .

Experimental Studies

We experimentally determined values of $-H_-$ at 298 K for solutions of sulfuric acid and sodium sulfate, using the method developed by Cox and McTigue (1964). The equipment consisted of a 250-cm³ stirred reaction flask, partially submerged in a constant temperature bath. Total liquid volume in each experiment was 200 cm³. The experiments were begun by combining bromine, formic acid, sulfuric acid, and sodium sulfate. Bromine was the limiting reagent. The other reagents were added in large excess so their concentrations changed insignificantly during the experiment. The decrease in concentration of bromine was monitored as a function of time at 398 nm using a Milton Roy Spectronic 1201 UV spectrophotometer equipped with a 0.4-cm³ flow cell of 1-cm path length. Other details of the experimental apparatus and procedures have been previously described (Hoq et al., 1991). We extended the study by measuring the acidity of sulfuric acid-sodium sulfate-sodium nitrate solutions. Sodium nitrate was used as a model compound to represent sodium chlorate, since chlorate ions would react with bromide that forms in applying the Cox-McTigue method.

Results and Discussion

Sulfuric acid-sodium sulfate

Baes (1957) used two variables to conveniently describe absolute and relative stoichiometric amounts of sulfuric acid and sodium sulfate in solutions: a , the fraction of sulfuric acid in the solution, $[\text{H}_2\text{SO}_4]/([\text{H}_2\text{SO}_4] + [\text{Na}_2\text{SO}_4])$; and b , the total stoichiometric sulfate concentration, $([\text{H}_2\text{SO}_4] + [\text{Na}_2\text{SO}_4])$. We measured rates of reaction in solutions over a wide range of a and b parameters values. A value of h_- was calculated for each experimental rate using a rearranged form of Eq. 11:

$$h_- = -k' K_a [\text{HCOOH}] / \{ (d\ln[\text{Br}_2])/dt \} \quad (13)$$

We used the values reported by Cox and McTigue (1964), $k' = 20.1 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $K_a = 1.7 \times 10^{-4}$ in these calculations.

Figure 2 shows plots of absorbance data at 398 nm vs. time for one reaction experiment (lower set of data). The upper set of data shows that some bromine is lost during a blank experiment in the absence of formic acid. The trend of the data of the blank is linear. We suspect that this loss is due to evaporation of bromine. To correct the reaction data for the loss of bromine by evaporation, we subtracted the slope of the line through the blank data from the absorbances observed in the reaction experiments.

$$A_{398\text{corr}} = A_{398\text{obs}} + \text{slope}_{\text{blank}} \times t \quad (14)$$

The results of this calculation are illustrated as the middle set of points in Figure 2.

We used the corrected absorbances to develop semilogarithmic plots of normalized bromine concentration vs. reaction time. Figure 3 is such a plot corresponding to the data in Figure

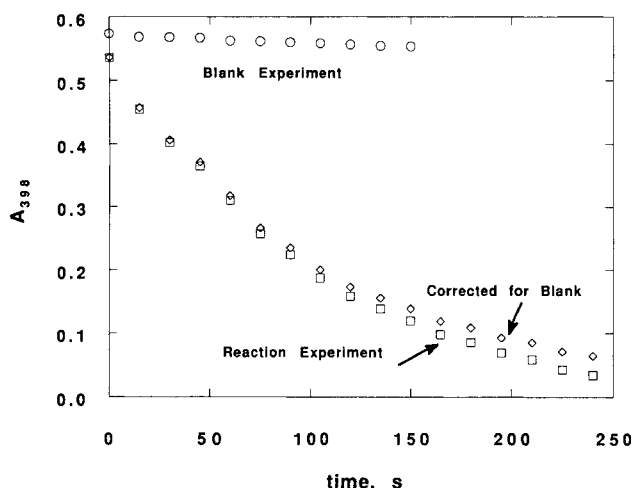


Figure 2. Data gathered in a bromine-formic acid reaction experiment at $[\text{Br}_2]_0 = 0.0036 \text{ M}$, $[\text{HCOOH}] = 0.3 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.75 \text{ M}$, $[\text{Na}_2\text{SO}_4] = 2.25 \text{ M}$, $T = 298 \text{ K}$.

2. The ratio, $[\text{Br}_2]/[\text{Br}_2]_0$ equals the ratio of absorbance measurements, $A_{398_{\text{corr}}}/(A_{398_{\text{corr}}})_0$. The plot is a good straight line showing the first-order dependence of the rate on bromine concentration.

Table 1 and Figure 4 show the results of this work. Table 1 lists all of the values of $-\text{H}_\text{L}$ which were determined in experiments. Figure 4 shows the trend of the data as a function of the a and b parameters. The range of parameter values in Table 1 and Figure 4 is the broadest range that we could measure with confidence using this experimental procedure. At lower acidities, the rate becomes too fast to measure with accuracy. At higher acidities the blank correction becomes significant. At some conditions, we were unable to dissolve the required amount of sodium sulfate.

The precision in our measurement of h_L was about constant at $\pm 10\%$. Thus, the uncertainty in $-\text{H}_\text{L}$ values in Table 1 is about $\pm \log(1.1)$ or 0.04. We have found that the following empirical equation predicts the values of $-\text{H}_\text{L}$ with reasonable accuracy:

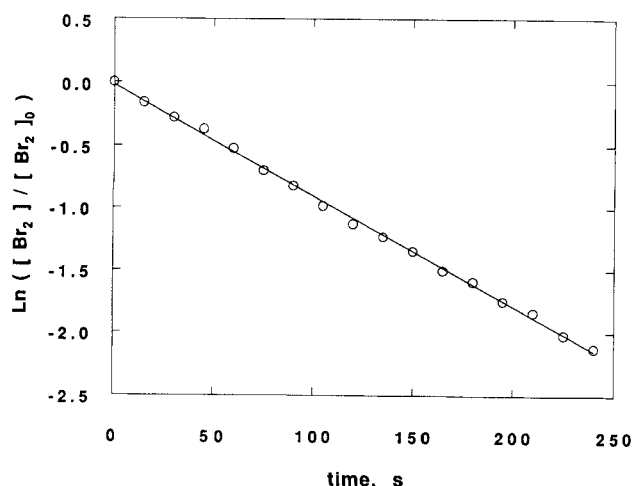


Figure 3. First-order plot of Figure 2 data (corrected for blank).

Table 1. Experimental Acidity Functions ($-\text{H}_\text{L}$) of Sulfuric Acid-Sodium Sulfate Solutions as a Function of Sulfuric Acid Fraction (a) and Total Sulfate (b)

b	$a = 0.25$	$a = 0.50$	$a = 0.75$	$a = 1.00$
0.5	-1.62	-1.06	-0.79	-0.53
1.0	-1.45	-0.83	-0.44	-0.21
1.5	-1.24	-0.60	-0.16	0.17
2.0	-1.08	-0.40	0.08	0.38
2.5	-1.05	-0.31	0.22	0.70
3.0	-0.94	-0.17	0.49	1.04
3.5	-0.80	0.00	0.65	1.28
4.0	-0.65	0.25	0.87	**
5.0	*	0.53	**	**
6.0	*	0.78	**	**

*Approaches or exceeds the solubility of sodium sulfate.

**Rate of reaction is slow and becomes comparable to the evaporation rate of bromine.

$$-\text{H}_\text{L} = -2.32 + 2.64a + 0.219b$$

$$-1.16a^2 - 0.016b^2 + 0.44ab \quad (15)$$

This equation can be used to interpolate the data in Table 1. For example, consider a solution consisting of 1-M H_2SO_4 and 1.7-M Na_2SO_4 . Parameter values that characterize the solution are $a = 0.37$ and $b = 2.7$. Equation 15 yields an $-\text{H}_\text{L}$ value of -0.59 .

The H scale for sulfuric acid solutions can be extended to the study of reactions whose rates depend on the Hammett scale, H_0 . Boyd (1961; 1963) stated that a slight modification is needed to convert the H_L scale to the Hammett acidity scale, H_0 . He concluded that the error introduced by substitution of H_0 for H_L is probably not serious in view of the similarity between the two scales. Boyd determined the H_L scale by a more conventional method involving protonation of weakly basic indicators. Figure 5 shows there is deviation between Boyd's H_L scale and the H_L scale measured by the Cox and McTigue method. Boyd's scale agrees more closely with the Hammett scale; however, the scale determined by the Cox and McTigue method parallels the Hammett scale more closely.

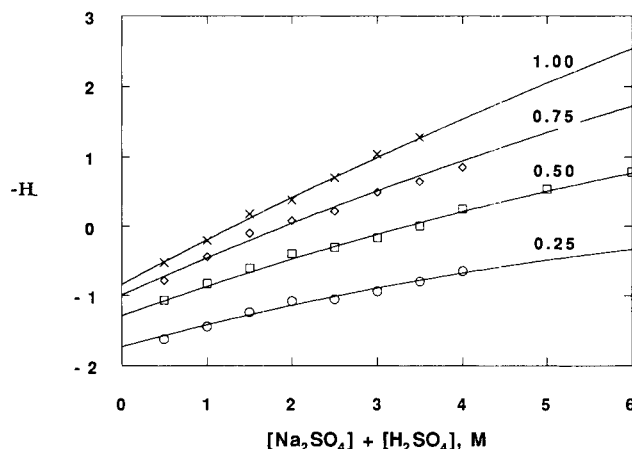


Figure 4. Acidity scale for sulfuric acid-sodium sulfate solutions.

Solid lines calculated from curve fit Eq. 15. Numbers refer to parameter b .

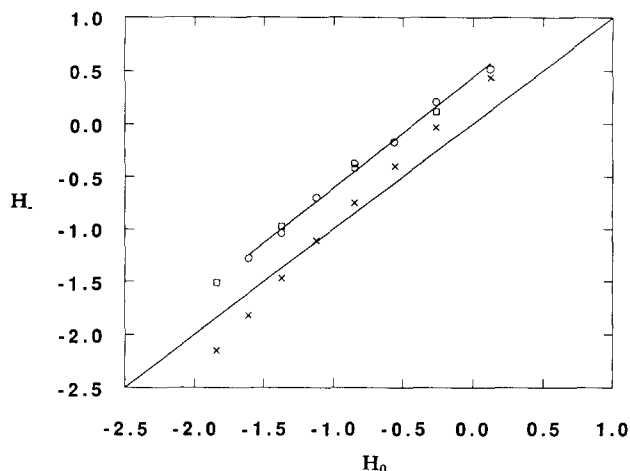


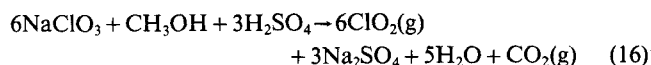
Figure 5. H_- acidity scales vs. Hammett, H_0 , scale for sulfuric acid solutions.

○, this work; □, Cox and McTigue (1964); ×, Boyd (1961); upper line, fit through ○; lower line is a 45 degree line.

The relationship between the two scales based on our experimental values is $H_0 = 0.95H_- - 0.42$. The fact that the two scales are parallel indicates that the H_- scale determined by the Cox and McTigue method could be used instead of the Hammett scale in a kinetic study of an acid-dependent reaction. A plot of $\log(\text{rate})$ vs. either H_- or H_0 will yield the same reaction order. We suspect that the two scales may also be parallel for sulfuric acid-sodium sulfate solutions; however, we were unable to find a published Hammett scale for these solutions. Although the present work was limited to 298 K, both scales should be applicable at other temperatures in that the H_0 scale is relatively independent of temperature (Rochester, 1970).

Application to the chlorine dioxide process

Chlorine dioxide is produced by reducing sodium chlorate in sulfuric acid solution (Masschelein 1979; Ernst et al., 1988; Tenney et al., 1990). The most widely used version of this process utilizes methanol as the reducing agent,



During the start-up of a chlorine dioxide process, the solution in the reactor initially consists of sulfuric acid, sodium chlorate and methanol. As the reaction progresses sodium sulfate forms and gradually increases in concentration. This change in species distribution changes the acidity of the solution and the rate of reaction.

Kinetic data have not been reported for this reaction in the open literature. According to an industrial source (Norell, 1987), the generation rate of chlorine dioxide is highly acid-dependent. The initial rate has about a 10th-order dependence upon stoichiometric sulfuric acid concentration.

In our approach to characterizing the acidity of such solutions, we modified the acidity function in Table 1 and Eq. 15 to take into account the presence of sodium chlorate. (Methanol concentration is relatively small at process conditions

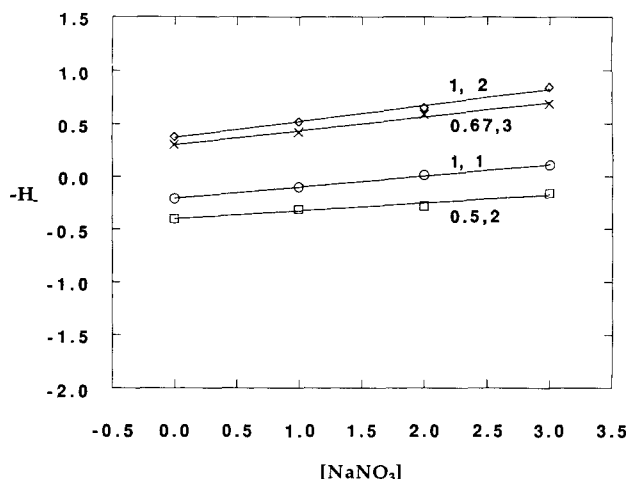


Figure 6. Effect of sodium nitrate on acidity scale for sulfuric acid-sodium sulfate solutions.

Numbers refer to parameters a and b , respectively.

compared to other species and is expected to have negligible influence on acidity.)

From previous studies of Harbottle (1951), Challis and Ridd (1962), Lee and Stewart (1964), Day and Wyatt (1966) and Hong et al. (1967), we concluded that the sodium ions contributed by the sodium chlorate in the solution would increase the solution acidity, whereas chlorate ions would have little or no effect on acidity.

Unfortunately, chlorate reacts with bromide under the experimental conditions of the Cox-McTigue method, precluding us from making kinetic measurements directly on this system. Nitrate ions, however, do not interfere with the Cox-McTigue method, and have a negligible effect on acidity of sulfuric acid solutions (Hong et al., 1967). These findings opened up the possibility of substituting sodium nitrate for sodium chlorate in this study.

We explored the effect of sodium nitrate on the acidity function of sulfuric acid-sodium sulfate solutions. Figure 6 shows that sodium nitrate has a much smaller effect on $-H_-$ than parameters a and b . Within experimental error, there is a linear dependence of $-H_-$ on sodium nitrate concentration in sulfuric acid at all levels of sodium sulfate concentration. The lines are nearly parallel with an average slope of 0.12 ± 0.03 . For practical purposes, one can estimate the acidity function for a solution of sulfuric acid, sodium sulfate, and sodium nitrate (or sodium chlorate) by selecting a value of $-H_-$ from Table 1 at the approximate a and b values, and adding $0.12[\text{NaNO}_3]$ (or $0.12[\text{NaClO}_3]$).

Acknowledgment

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Literature Cited

- Baes, C. F., Jr., "The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid-Sodium Sulfate Solutions," *J. Amer. Chem. Soc.*, **79**, 5611 (1957).
- Boyd, R. H., "Cyanocarbon Chemistry: XXIII. the Ionization Behaviour of Cyanocarbon Acids," *J. Phys. Chem.*, **76**, 737 (1963).

- Boyd, R. H., "The Strengths of Cyanocarbon Acids and an H_0 Acidity Scale for Concentrated Acid Solutions," *J. Amer. Chem. Soc.*, **83**, 4288 (1961).
- Boyd, R. H., "Acidity Functions," *Solute-Solvent Interactions*, p. 97, J. F. Coetzee and C. D. Ritchie, eds., Marcel Dekker (1969).
- Challis, B. C., and J. H. Ridd, "Nitrosation, Diazotisation, Deamination: XI. the Acid-Catalyzed Diazotisation of the Anilinium and Related Ions in Aqueous Perchloric Acid (up to 3.0 M)," *J. Chem. Soc.*, 5208 (1962).
- Cox, B. G., and P. T. McTigue, "Kinetics of Oxidation of Formate Ions with Bromine," *J. Chem. Soc.*, 3893 (1964).
- Day, J. S., and P. A. H. Wyatt, " H_0 Measurements in Some Salt-Acid Mixtures of Fixed Total Anion Concentration," *J. Chem. Soc. B*, 343 (1966).
- Dickson, A. G., D. J. Wesolowski, D. A. Palmer, and R. E. Mesmer, "Dissociation Constant of Bisulfate Ion in Aqueous Sodium Chloride Solutions to 250 C," *J. Phys. Chem.*, **94**, 7978 (1990).
- Ernst, W. R., M. Shoaie, and L. Forney, "Selectivity Behavior of the Chloride-Chlorate Reaction System in Various Reactor Types," *AIChE J.*, **34**, 1927 (1988).
- Harbottle, G., "The Hammett Acidity Function in 6 Formal Perchloric Acid-Sodium Perchlorate Mixtures," *J. Amer. Chem. Soc.*, **73**, 4024 (1951).
- Hong, C. C., F. Lenzi, and W. H. Rapson, "The Kinetics and Mechanism of the Chloride-Chlorate Reaction," *Canad. J. Chem. Eng.*, **45**, 349 (1967).
- Hoq, M. F., B. Indu, W. R. Ernst, and H. M. Neumann, "Kinetics of the Reaction of Chlorine with Formic Acid in Aqueous Sulfuric Acid," *J. Phys. Chem.*, **95**, 681 (1991).
- Lee, D. G., and R. Stewart, " H_0 Acidity Functions for Nitric Acid and Phosphoric Acid Solutions Containing Added Sodium Perchlorate," *Canad. J. Chem.*, **42**, 486 (1964).
- Lindstrom, R. E., and H. E. Wirth, "Estimation of the Bisulfate Ion Dissociation in Solutions of Sulfuric Acid and Sodium Bisulfate," *J. Phys. Chem.*, **73**(1), 218 (1969).
- Masschelein, W. J., *Chlorine Dioxide*, Ann Arbor Science, Ann Arbor (1979).
- Norell, M., private communication, Eka Nobel AB, Sundsvall, Sweden (1987).
- Pitzer, K. S., R. N. Roy, and L. F. Silvester, "Thermodynamics of Electrolytes: 7. Sulfuric Acid," *J. Amer. Chem. Soc.*, **99**, 4930 (1977).
- Rochester, C. H., *Acidity Functions*, Academic Press, New York (1970).
- Tenney, J., M. Shoaie, T. Objeski, W. R. Ernst, R. Lindstroem, B. Sundblad, and J. Wanngard, "An Experimental Investigation of the Chloride-Chlorate Reaction System," *Ind. Eng. Chem. Res.*, **29**, 916 (1990).

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