# Electrolytic Nature of Aqueous Sulfuric Acid. 2. Acidity

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ABSTRACT: In part 1 of this study, I reported that the Debye–Hückel limiting law and the smaller-ion shell (SiS) model of strong electrolyte solutions fit nicely with the experimental *mean ionic activity coefficient* ($\gamma_\pm$) of aqueous sulfuric acid as a function of concentration and of temperature when the acid is assumed to be *a strong 1−3 electrolyte*. Here, I report that the SiS-derived activity coefficient of H⁺, γ_{H^+}, of the 1−3 acid is comparable to that of aqueous HCl. This agrees with titration curves showing, as well-known, that sulfuric acid in water is parallel in strength to aqueous HCl. The calculated pH is in good accord with the Hammett acidity function, H_0, of aqueous sulfuric acid at low concentration, and differences between the two functions at high concentration are discussed and explained. This pH−H_0 relation is consistent with the literature showing that the H_0 of sulfuric acid (in the 1−9 M range) is similar to those of HCl and the other strong mineral monoprotic acids. The titration of aqueous sulfuric acid with NaOH does not agree with the known second dissociation constant of 0.010 23; rather, the constant is found to be ~0.32 and the acid behaves upon neutralization as a strong diprotic acid practically dissociating in one step. A plausible reaction pathway is offered to explain how the acid may transform, upon base neutralization, from a dissociated H_4SO_5 (as 3H⁺ and HSO_5^{3-}) to a dissociated H_2SO_4 even though the equilibrium constant of the reaction H⁺ + HSO_5^{3-} ↔ SO_4^{2-} + H_2O, at 25 °C, is 10^{-37} (part 1).
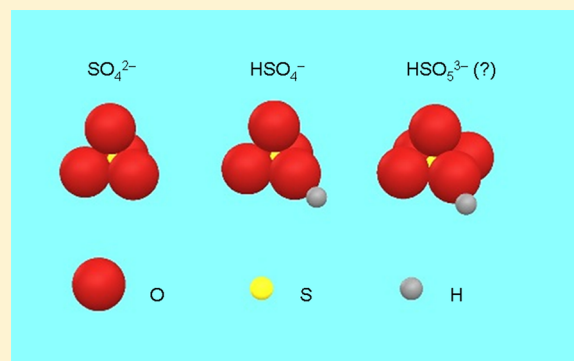
1. INTRODUCTION

The importance of sulfuric acid in nature and in science and technology,[1] and the great impact of the acid on our everyday life, makes it necessary for us to strive to understand the structural, physical, and chemical properties of the acid beyond the current knowledge, especially in its dissolved state, and in particular in water. In part 1 of this work, I have drawn attention to the fact that aqueous sulfuric acid, up to a concentration of ~5 M, behaves thermodynamically as a 1−3 electrolyte. Such a behavior can be explained by assuming that the "real" acid in water is H_4SO_5 that dissociates to 3H⁺ ($3H_3O^+$) ions and the trivalent anion HSO_5^{3-}. Here I investigate the nature of the acidity of aqueous H_2SO_4 in terms of its hydrogen activity—thus, pH—and its acidity functions, as well as the pattern of titration of the acid and its structural implications.

In my previous publications on the smaller-ion shell (SiS) treatment of strong electrolytes, I have emphasized[2] the usefulness of the method in explaining and clarifying the thermodynamic behavior of monoprotic mineral acids in water at 25 °C, and the behavior of HCl in polar solvents of varying permittivity.[3] The theoretical SiS treatment is an improved Debye–Hückel (DH) type electrostatic ionic theory in which the size dissimilarity of ions in a binary system, which is neglected in the classical DH theory, is taken into account.[4] The SiS treatment provides simple, easy-to-use analytic mathematical expressions for the single-ion activity coefficients of the cation (γ_+) and anion (γ_-) from which the *mean ionic activity coefficient* of the combined electrolyte system ($\gamma_\pm$) can

be computed based on the standard definition of this function. Among other things, the analysis has shown that the size of the proton in aqueous solution at 25 °C is 1.16 Å.[2] The computed $\gamma_\pm$ of HCl fits effectively with experimental $\gamma_\pm$ in solvents with permittivity, ε, of as low as 10, indicating that the acid is fully dissociated even under the harsh medium conditions of very low ε.[3] Sakaida and Kakiuchi have lately reported[5] *experimental* measurement of the activity coefficients of H⁺ (γ_{H^+}) and Cl⁻ (γ_{Cl^-}) in aqueous HCl solution; the calculated $\gamma_\pm$ based on these single-ion values agree well with the experimental $\gamma_\pm$ values as known in the literature. Sakaida and Kakiuchi further demonstrated the agreement of their γ_{H^+} and γ_{Cl^-} values, over a decent range of concentration, with theoretical γ_{H^+} and γ_{Cl^-} values as computed from the relevant SiS expresions.[2] Moreover, I have more recently demonstrated[6] that single-ion activity coefficients (γ_i) of a number of electrolytes of various families, as computed by the SiS expressions (i.e., as γ_+ and γ_-), are in good accord with values reported in the literature as estimation based on careful electrochemical potential measurements and data analysis.

The above-mentioned reports are highly relevant to the current article: first, we now have a solid value for the effective size of the proton in aqueous mineral acids, based on which reliable γ_{H^+} can be computed; from the theoretical γ_{H^+}, pH can be calculated as a function of ionic concentration up to a few

molal units. Second, there is enough overlap between the range of concentration at which the calculated pH is of excellent-to-good quality (e.g., up to ~4 m for HCl) and the range of concentration at which acidity function data are available; this allows a comparison between the two types of acid strength criteria; for example, pH and Hammett acidity function, H_0.[2] Third, the conclusion that ion association is not a necessary assumption in HCl solutions in solvents of even low permittivity[3] casts doubt on the necessity of similar assumptions when dealing with other strong mineral acids, e.g., aqueous sulfuric acid. Fourth, the ability of the SiS expressions to predict single-ion activities as obtained in experiment[5,6] establishes the credibility of the SiS treatment as a reliable theoretical tool for analyzing electrolyte solutions in general, and strong acid solutions in particular. In part 1 of the current study,[1] I attempted to extend the analysis as mentioned above to aqueous sulfuric acid. I have thus examined the acid in water in terms of the change of its $\gamma_\pm$ with concentration and temperature. A comparison was provided with other aqueous acids and other sulfur oxide electrolyte systems, especially in regard to the anion size. In the present article, (1) the pH of the aqueous acid is computed up to moderate acid concentration and is compared with H_0, (2) titration curves are discussed by comparing experiment with theoretical calculations, and (3) the conversion of the 1−3 acid (proposed in part 1) upon reaction with a base, to the conventional fully dissociated 1−2 acid, is rationalized.

This article is organized as follows. The present section (section 1) is a general background explaining the motivation for the reported study. In section 2, the main methods used in the current study are briefly mentioned and discussed; reference is given to the earlier work relevant to the present one; the physical quantities and special notations used are specified and/or defined. In section 3, the calculation of γ_{H^+} of aqueous 1−3 sulfuric acid and its comparison with γ_{H^+} of HCl is first presented (in subsection 3.1) followed by a comparison between pH and H_0 (in subsection 3.2); I then (in subsection 3.3) deal with the titration of the acid with a strong base and its analysis based on the literature view of the acid and on the current proposal; finally (in subsection 3.4), I make an attempt, through simplified modeling, to reconcile the observation that the acid behaves as a 1−3 electrolyte with the fact that it is neutralized as a strong diprotic acid. Section 4 summarizes this work in light of the conclusions of both parts 1 and 2.

2. METHODS

In part 1,[1] the SiS expression[2−4]

$$\log \gamma_\pm = -|z_s z_l| \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a}$$
$$\left\{ 1 - \frac{\nu_l}{\nu} \frac{2\exp[\kappa(a - b_s)] - \kappa(a - b_s) - 2}{1 + \kappa b_s} \right.$$
$$\left. + \frac{\nu_s}{\nu} \frac{2\exp[\kappa(b_l - a)] - 2\kappa(b_l - a) - 2}{1 + \kappa b_l} \right\} \quad (1)$$

was used to analyze aqueous sulfuric acid. In eq 1, $\gamma_\pm$ is on the weight-molal (m_w, or simply m) scale, κ (= $\mathcal{B}I^{1/2}$; I, ionic strength) is the reciprocal screening length; z's are ionic charges and ν's the ionic multiplicities (number of ions in the electrolyte molecular formula); subscript s denotes the smaller ion and subscript l, the larger ion; a, b_s and b_l are the ion size parameters (ISPs) relating, respectively, to the contact

distances of counterions, small co-ions and large co-ions, and one assumes $b_s \leq a \leq b_l$ and defines a nonadditivity factor $d/2$ as $[a - (b_s + b_l)/2]$. In the case of aqueous sulfuric acid, the smaller ion is the proton and thus $b_s = b_+ = b_{H^+}$, and the larger ion is a trivalent ion believed to be HSO_5^{3-} for which $b_l = b_- = b_{A^-}$, the symbol A^- representing the anion. $\mathcal{A}$ and $\mathcal{B}$ are the well-known parameters in the DH extended equation (EE, or eq 1 without the last two terms in the braces).

The molal activity coefficient of the proton, γ_{H^+}, has been calculated from the equation[2,3]

$$\log \gamma_{H^+} = -\frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a}$$
$$\left\{ 1 - \frac{2\exp[\kappa(a - b_{H^+})] - \kappa(a - b_{H^+}) - 2}{1 + \kappa b_{H^+}} \right\} \quad (2)$$

with optimized ISPs, based on fitting calculated $\gamma_\pm$, using eq 1, with experimental values.

The conversion of the activity coefficient from $\gamma_\pm$ (molal) to $y_\pm$ (molar), for calculating molar pH [pH(M)] at 25 °C, has been done following a procedure used previously for other acids.[2] The conversion of the concentration scale from m (moles of solute per kilogram of solvent) to M (moles of solute per liter of solution) was done following the conventional literature method. Density data of aqueous sulfuric acid at 20 °C, as given in ref 7 (pp 8-81−8-82), were employed without correction to 25 °C because the difference in the relevant solution density between these two temperatures is only 0.2−0.3%. The molar activity coefficient of the proton, y_{H^+}, has been calculated from the analogue of eq 2 for the molar case, i.e., by using (in κ) volume-based ionic strength, I_v instead of the weight-based I_w, and replacing $\mathcal{A}$ and $\mathcal{B}$ of the molal case by their molar analogues, $\mathcal{A}_C$ and $\mathcal{B}_C$ [at 25 °C, $\mathcal{B}_C$ = 0.328 97 Å^{-1}(L/mol solute)$^{1/2}$ and $\mathcal{A}_C/\mathcal{B}_C$ = 1.552 64 Å]. Optimized ISPs on the molar scale (ideally, identical with those on the molal scale) were obtained from fitting calculated $y_\pm$ (using the analogue of eq 1 for molarity) with $y_\pm$ values generated by converting experimental $\gamma_\pm$ from the m to C (M) scale.[2] a in eq 2 (molal scale) is the closest distance between the proton and the anion, and b_{H^+} is, of course, the diameter of the proton (H_3O^+).

3. RESULTS AND DISCUSSION

3.1. Proton Activity. In Figure 1, I compare theoretical single-ion activity coefficients of the proton as a function of ionic strength in aqueous solutions of HCl and of 1−3 sulfuric acid. The calculation was done with eq 2. Overall, there is good agreement between the γ_{H^+} values of the two acids, implying that the intrinsic strength of the proton in aqueous HCl and H_2SO_4 is similar at the same ionic strength; more specifically, at low I values, γ_{H^+} data of the two acids are almost identical (Figure 1, inset), but past I = ~0.05, sulfuric acid gives somewhat lower γ_{H^+} values, and thus is a weaker acid than HCl at the same ionic strength. The larger $b_l - b_s$ difference in sulfuric acid should increase γ_{H^+} when all other factors stay the same; however, a small negative $d/2$ (Table 2 in part 1), as opposed to a large positive $d/2$ (1.22 Å) in the case of HCl,[2] causes γ_{H^+} of sulfuric acid solutions to be smaller than γ_{H^+} of parallel solutions of HCl. Therefore, the relative intrinsic weakness of sulfuric acid, as acid, compared with HCl and other 1−1 acids, is apparently attributable to a relatively closer ionic collision distance (center-to-center) between H$^+$ and the sulfur
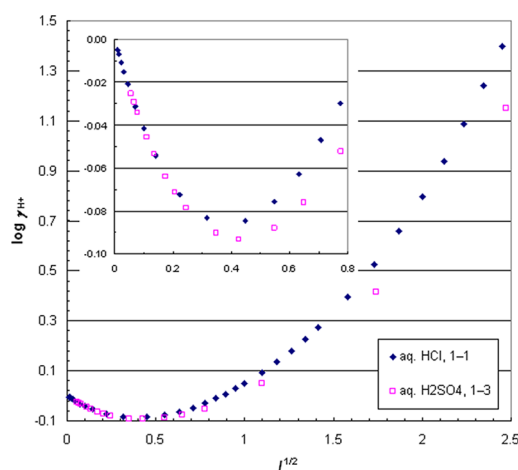
Figure 1. Logarithm of the proton activity coefficient as a function of the square root of ionic strength at 25 °C: HCl vs 1−3 sulfuric acid. The symbols are calculated values based on the $\gamma_\pm$ vs $I^{1/2}$ fit of theory with experiment.
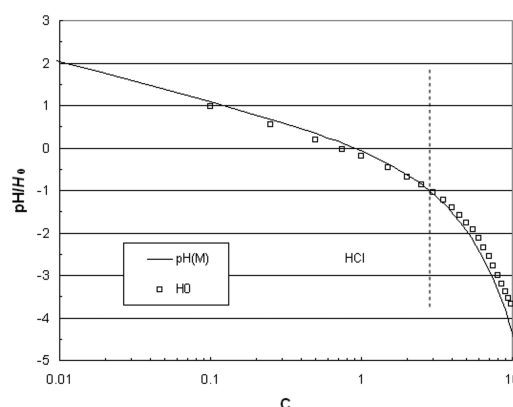

Figure 2. Calculated pH(M) (line) and the experimental H_0 of HCl (symbols) vs concentration (in M), in water at 25 °C.[2] pH values are believed to be of especially good quality up to ∼2.5 M (vertical dashed line), but still effective even at ∼8 M.

oxide conjugate base since the smaller the acid's a, the weaker the acidity (see Figure 2 in ref 2 and related discussion therein on acid strength). This may be interpreted based on the apparent ability of the proton as a very small ion—the smallest univalent cation in water at 25 °C—to strongly polarize the counteranion. Halide ions are quite easily polarizable, but it appears that oxo anions, such as those of oxy/hydroxysulfur, cannot be polarized to a great extent. In hydrogen halide acids the $a - b_s$ factor in eq 1—the primary cause of electrostatic repulsion hence increased proton activity—is a combination of the size of the larger anion and its polarizability, but the latter factor is apparently contributing less in the case of oxo anions. Furthermore, at some orientation of the proton approach to the oxo anion, the closest distance between the counterions may be shorter than the formal sum of the proton's half-size and half the overall effective size of the anion. It should also be noted again that there is a very high extent of ISP additivity (i.e., $d/2 \approx 0$) in aqueous sulfuric acid (Table 2 in part 1), implying that $a - b_s \approx {}^1/_2(b_1 - b_s)$, as would ideally be expected; this prevails over the entire temperature range of 0−60 °C.

3.2. pH and Acidity Functions. The SiS treatment is unique among theories of electrolytes in easily allowing a believable[6] calculation of single-ion activities; moreover, this calculation is quite accurate at relatively high concentration. In the case of H⁺, this enables a reasonable estimate of the pH up to high molality (or molarity), exceeding unity. Recently, estimated γ_{H^+} and γ_{Cl^-} values of aqueous HCl were obtained from electrochemical experiments, as reported by Sakaida and Kakiuchi,[9] and they were shown to agree fairly well with parallel γ_{H^+} and γ_{Cl^-} values as predicted theoretically by the SiS treatment. As demonstrated for HCl in Figure 2 (imported from ref 2), the concentration range of the pH calculation overlaps with the concentration range at which acidity functions, such as Hammett's H_0,[8−11] are available. H_0, of course, approaches pH at low acid concentration in aqueous solutions because of the relation

$$H_0 = pH - \log \frac{y_B}{y_{HB^+}} \qquad (3)$$

where B is a weak base (Hammett indicator) and HB⁺ is its conjugate acid; for $C \to 0$, $y_B/y_{HB^+} \to 1$. Here, y_B is the molar

activity coefficient of the free base (indicator), and y_{HB^+} is the molar activity coefficient of its conjugate acid. [Note that literature H_0 data are usually on molar scale (M); hence, the activity coefficients in the H_0 expression are molar (y) and not molal (γ); therefore, in comparing pH with H_0, pH has to be computed on the molar scale.[2] Even though at low−to−moderate concentrations, pH(m) is very close to pH(M), the conversion of the concentration scale has been applied here for consistency reasons and for improved clarity and credibility of the analysis, especially at higher concentration.]

The results of Figure 2, as also discussed in ref 2, are not surprising, and they demonstrate that H_0 can closely follow the pH scale even at high concentration and negative pH values, up to about −2; a similar behavior is observed for HBr.[2] As seen in Figure 2, the line representing the pH of HCl is somewhat above the H_0 data at low concentration, and below those data at high concentration, >2.5 M. As concentration increases beyond 2.5 M, the pH decreases more steeply than H_0; and even though only the pH calculation up to the vertical broken line is at the highest accuracy range of computed y_{H^+}, the pH is still reasonably accurate beyond that line. It is obvious that, at high concentration, H_0 should differ from pH, as indeed shown in Figure 2, and the difference could gradually broaden when concentration is further increased; this is because H_0 does not represent the *activity* of the proton but rather the tendency of an acid to donate a proton to an uncharged weak base. The y_B/y_{HB^+} ratio of the base (eq 3) cannot be expected to remain about unity at high acid concentrations since y_{HB^+} should change with concentration differently than y_B (see below).[2] In comparing acids on an acidity function scale, it is usually assumed that the conjugate base of the acid (its anion) is not influencing y_{HB^+} or y_B. For the simple 1−1 acids, this assumption seems justified only up to moderate concentrations.

In contrast with HCl and HBr,[2] the calculated pH of sulfuric acid, as 1−3 electrolyte, departs from H_0 at a rather low concentration, as shown in Figure 3. The agreement between pH and H_0 is excellent at low concentration (with the H_0 data of Bascombe and Bell[11a]) up to ∼0.05 M, but is lost at and above ∼0.1 M. This concentration limit is much lower than the concentration limit (vertical line, Figure 3a) above which the fit of theory (SiS) with experiment becomes unsatisfactory; in this case, above 5 M. The H_0 values reflect much weaker acidity than the pH values. Figure 3 also depicts the H'_R acidity function of sulfuric acid.[9] It is well-known that acidity functions
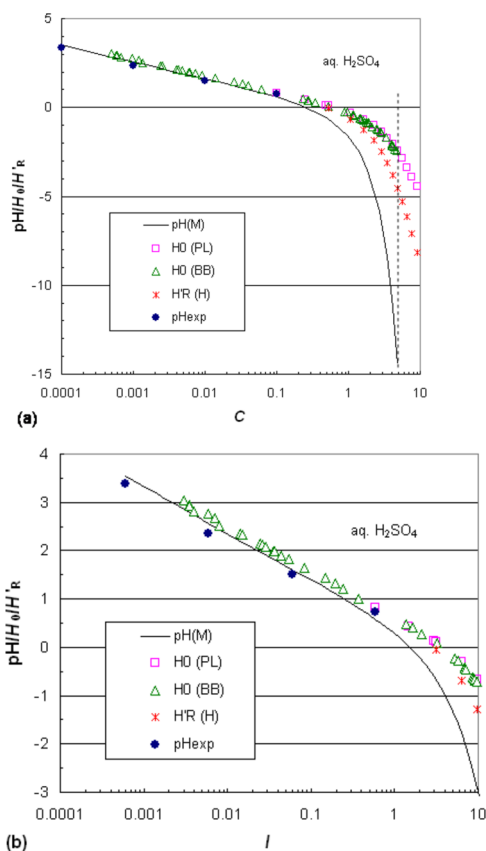
Figure 3. Calculated pH(M) (line), experimental pH (pHexp), and acidity functions[9] H_0 and H'_R of sulfuric acid as functions of concentration, in water at 25 °C. Source of data: Paul and Long, ref 10; Bascombe and Bell, ref 11a; Hammett, ref 9. (a) Molar scale; pH values are believed to be of good quality up to ∼5 M (vertical dashed line); (b) ionic strength scale, up to $I = 10$.

are subject to the reference indicator group used to generate them. The H'_R values are somewhat lower than the corresponding H_0 values and closer to the pH values. It is not impossible that on another acidity scale, results may be even closer to the calculated pH. Furthermore, Figure 3 also shows pH values obtained experimentally, using a pH meter (Oakton's pH 5 Acorn Series). These experimental values are in good agreement with the theoretical values derived from the SiS treatment (i.e., from calculated γ_{H^+} values).

While the lack of agreement between H_0 and pH in the case of sulfuric acid at high concentration is not entirely understood currently, two plausible explanations may be offered. (1) It is, of course, quite possible that the analysis provided in this article is inaccurate, leading to false pH values as a result of erroneous calculation of the activity coefficient of the proton. (2) Alternatively, one may suggest[2] that in eq 3, the ratio y_B/y_{HB^+} compensates considerably for y_{H^+} (in the pH) keeping H_0 high and decreasing weakly with concentration. This mostly relates to y_{HB^+} "following" y_{H^+} because HB^+ "joins" H^+ in the electrolyte, making the binary acid system a pseudoternary system ($H_3O^+ - HB^+ - A^{3-}$). I shall proceed here with this second explanation and elaborate on it, following a similar discussion given in ref 2.

Both B and HB^+ are at very low concentration compared to the acid (here, "H_3A"); but while B, like HB^+ and H^+, participates in the equilibrium reaction of weak-base protonation ($H^+ + B \leftrightarrow HB^+$), not being an ion, it is not involved in

the electrostatic interaction in the electrolyte solution. In contrast, HB^+, like H^+, interacts electrostatically with all the other ions (negative and positive) in solution, and this strongly affects its activity. In the electrolyte, HB^+ is not entirely distinguishable from H^+; its activity coefficient may be somewhat smaller due to its being effectively a somewhat larger cation than H^+ (i.e., H^+ solvated by the base B has an effective size that is a bit greater than that of H^+ "solvated" by H_2O) and due to a difference in a (see above), that is, a difference between the $HB^+ - A^{3-}$ and the $H_3O^+ - A^{3-}$ contact distances. At very small concentration of B, $y_B \approx 1$, and this should not change substantially with the acid concentration. Thus, we may safely assume that in aqueous acid solutions up to moderate concentration (say, <10 M), the y_B value is about unity. If at ∼5 M log $y_{H^+} \approx 14$ and log (y_B/y_{HB^+}) is about −12 (meaning that log y_{HB^+} is ∼12) then an H_0 value of −2.3, as obtained by the acidity measurement, is not unexpected. Therefore, $H_0(M) \approx pH(M) + \log y_{HB^+}$. At low concentration, $y_{HB^+} \approx y_{H^+}$ and $H_0(M) \approx -\log C_{H^+} \approx pH(M)$.

It is easy to explain why, in view of the above, an acid can have a very high proton activity (very low pH) and still exhibit relatively low tendency to transfer a proton to a weak base (neutral indicator): the high proton activity converts much of the B into HB^+, but HB^+ should have a very high activity due to its own small effective cationic size and due to the large size of the A^{3-} counteranion; this indeed should diminish the Hammett acidity by counteracting the pH term in eq 3. Such an effect is expected to be considerably weaker in the case of the smaller, univalent anions Cl^- and Br^-, as indeed found;[2] in the respective halo acids, both H^+ (H_3O^+) and HB^+ have much lower activity coefficient even at $C = 10$ M (calculated/ estimated). For better clarity, the 1−3 sulfuric acid behavior is depicted in Figure 3b on the ionic strength scale; such a presentation provides easier visual comparison with the concentration dependence of 1−1 acids[2] because for the latter acids, $C = I$. Indeed, Figure 3b compares better with Figure 2, and even more so with the parallel presentation for HI.[2]

I have made an attempt to estimate y_{HB^+}/y_B (as before[2]) by subtracting pH(M) from H_0, according to eq 3. For this, both pH(M) and H_0 had to be expressed as functions of molarity (see Methods). This turned out ineffective when applied to the entire concentration range of interest, and therefore, I divided the molarity range into two portions: one below and the other above 0.1 M. For the low concentration range, simple logarithmic functions were found suitable in both cases (as, of course, expected) whereas for $C > 0.1$, the adequate functions are seven-term polynomials. Figure 4 shows the results of this analysis. The SiS fit with experiment in the molar scale (using the analogue of eq 1 for molarity) yielded the following ISPs: $a = 3.40$, $b_s = 1.13$, $b_l = 5.77$ Å. The slight differences[2] from the ISPs of the molal case (Table 2 of part 1, at 25 °C) seem insignificant and may have resulted from small inaccuracies in converting m to M and/or $\gamma_\pm$ to $y_\pm$.

Figure 4a demonstrates that H_0 approaches pH at very low concentration, as required. However, in reality, the approach should be asymptotic. Due to choosing a logarithmic expression for fitting the H_0 data, the asymptotic approach, of course, cannot be shown by extrapolation. It is nevertheless evident that, at a certain high dilution, H_0 becomes indistinguishable from pH when $y_{HB^+}/y_B \approx 1$. The current analysis indicates that this occurs at about 10^{-6} M, at pH 5.4, but the extrapolation accuracy is not sufficient to prove this. Figure 4b shows that y_{HB^+}/y_B increases monotonously, but weakly, with the logarithm
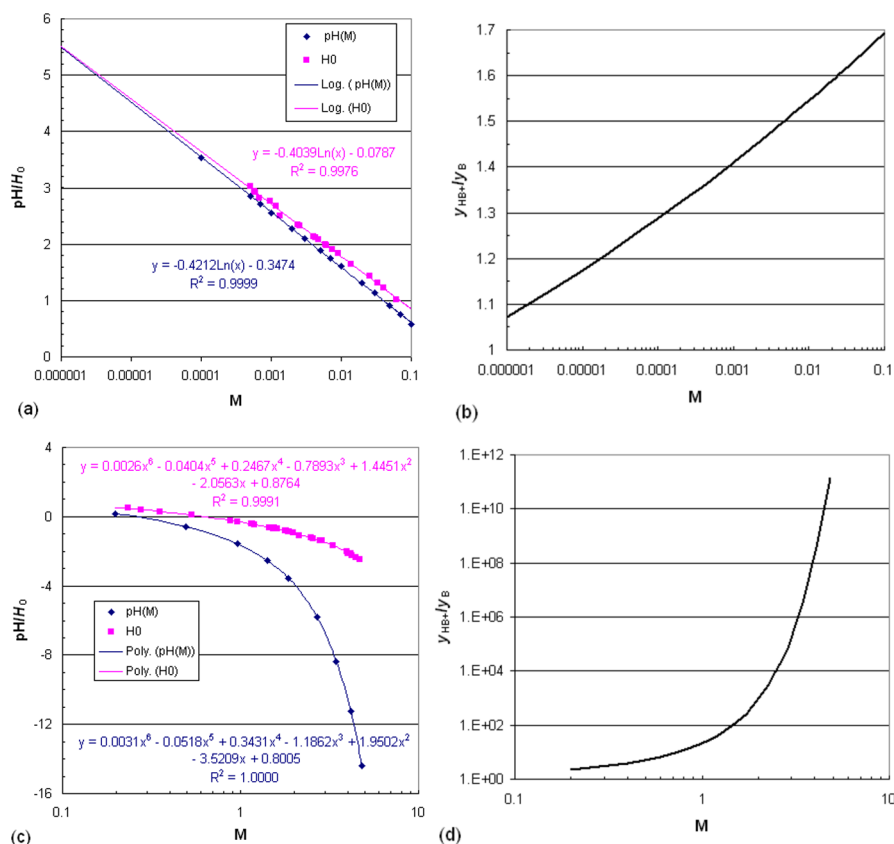
Figure 4. y_{HB^+}/y_B based on subtracting pH(M) from H_0 (eq 3): (a,b) at $C < 0.1$; (c,d) at $C > 0.1$.

of C, when C changes by 5 orders of magnitude, going from 10^{-6} to 0.1 M; y_{HB^+}/y_B starts with a value of about 1 and reaches 1.7. The picture at $C > 0.1$ is very different (Figure 4c), and, as depicted in Figure 4d, over a change in C of less than 2 orders of magnitude, between 0.1 and 5 M, y_{HB^+}/y_B increases by 12 orders of magnitude! Note also that, in accord with the example given above, at 5 M log y_{HB^+} is indeed 12 if log $y_B \approx 0$ (Figure 4d). In comparison, log y_{H^+} is, as expected, somewhat larger: 13.845. HB^+ cannot be at concentration higher than the initial concentration of B, and is thus at very high dilution. HB^+ is, therefore, at orders of magnitude smaller concentration than H^+ (i.e., "$H(H_2O)^+$"). Since we may assume that in practice $y_{HB^+}/y_B \approx y_{HB^+}$, the change in the activity coefficient of HB^+ with concentration of the acid is very reminiscent of the parallel change in y_{H^+}. Since H^+ and HB^+ are on opposite sides of the equation of the reaction with Hammett indicators, $H^+ + B \leftrightarrow HB^+$, they compensate for each other, causing H_0, or "the intrinsic tendency of the acid to protonate a base", to be less than a true reflection of the *activity* of the proton, especially at high acid concentrations. A similar behavior was found with HCl, HBr and HI.[2] It is thus appropriate, for completing this analysis, to show the change of y_{HB^+} (y_{HB^+}/y_B) as a function of y_{H^+}, as done in Figure 5. A pseudolinear relation between log(y_{HB^+}/y_B) and log y_{H^+}, as found, allows a good estimation of H_0 using the empirical equation

$$H_0 = -\log C_{H^+} - 0.1722 \log y_{H^+} + 0.3184 \qquad (4)$$

The coefficient of log y_{H^+} reflects the extent of the deviation of H_0 from pH: the smaller this coefficient is (below 1.0000), the larger is the difference between H_0 and pH; thus, the lesser is the acidity strength as reflected by H_0. The coefficient of log y_{H^+}
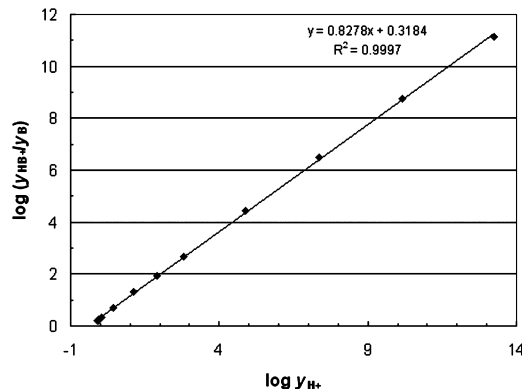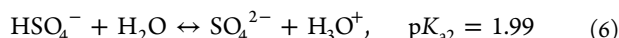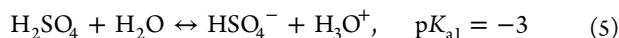

Figure 5. Correlation between log (y_{HB^+}/y_B) and log y_{H^+} in 1–3 sulfuric acid.

in eq 4 is numerically between that of HBr and that of HI.[2] The 0.3184 factor quantifies the extent of the merging of H_0 with pH at high acid dilution. Ideally, for complete merging at infinite dilution (i.e., when $y_{H^+} = 1$), this factor should be zero. In reality, the departure from complete merging may be the result of experimental inaccuracies of H_0, and/or errors in the calculation of the pH and/or the lack of complete suitability of the logarithmic functions for representing H_0 and pH at low concentration (Figure 4a).

In concluding this subsection, it may be stated that, while the proton activity coefficient is similar between HCl and "1–3 sulfuric acid" on ionic strength scale, the agreement of the calculated pH(SiS) with H_0 up to $C \approx 2$ in the case of HCl (and other 1–1 acids[2]) is not demonstrated for aqueous sulfuric acid; however, this lack of "fit" above $C \approx 0.1$ may

mostly be attributed to the change of the acid from a 1−1 to a 1−3 strong electrolyte; thus, it does not appear to discount the validity of the calculated pH of sulfuric acid based on the current analysis.

3.3. Neutralization of Aqueous Sulfuric Acid by Titration with a Strong Base. Aqueous sulfuric acid is claimed in the literature to be a partially weak (or partially strong) acid.[1] Its stepwise dissociation is given by the expressions[12]

$$H_2SO_4 + H_2O \leftrightarrow HSO_4^- + H_3O^+, \quad pK_{a1} = -3 \quad (5)$$

$$HSO_4^- + H_2O \leftrightarrow SO_4^{2-} + H_3O^+, \quad pK_{a2} = 1.99 \quad (6)$$

This conflicts with the present postulate that the acid in water is a fully ionized triprotic H_4SO_5. It should be noted a priori that I make no attempt here to convince the reader that aqueous sulfuric acid requires 3 equiv of a strong base to become fully neutralized, nor am I trying to deny that neutralization produces the well-known tetrahedral anions HSO_4^- and SO_4^{2-}. However, it is in order to revisit the titration curve of sulfuric acid and examine its agreement with the above dissociation reactions and constants; this is especially important in view of literature claims that the titration curve of sulfuric acid is very similar to that of hydrochloric acid (except for the need of two base equivalents instead of one);[12] the latter acid is undeniably a very strong acid. Furthermore, H_0 of HCl, HBr, HClO$_4$, and H_2SO_4 in water between 1 and 10 m is about the same,[10,11b,13] meaning that the extent of dissociation of H_2SO_4 at high concentration is similar to that of the other strong acids, in contradiction with the literature argument[14,15] that sulfuric acid is only partly dissociating (according to eq 5) at high concentration. It is also imperative to try to quantify the inherent notion[1] that the postulated pentacoordinate structure of HSO_5^{3-} is stable only under strongly acidic conditions, and it collapses to the tetrahedral SO_4^{2-} structure upon neutralization.

Within this study, the titration of 50 mL H_2SO_4 0.1 M with NaOH 0.1 M has been conducted experimentally, using the standard literature method, and theoretical titration curves under the same and other conditions were computed. The pH meter used was the same as that mentioned before (subsection 3.2). In the computation, I have assumed that the first dissociation stage goes virtually to completion, so $[H_2SO_4]_{init} = [HSO_4^-]_{init} = [H_3O^+]_{init} = 0.1$ where subscript "init" denotes initial concentration, i.e., concentration not including the contribution of the second dissociation stage. At the equilibrium state of reaction 6, the ionic composition is $HSO_4^- = (5 - y)$ mmol, $SO_4^{2-} = y$ mmol, and $H_3O^+ = (5 + y)$ mmol. Upon titration, when we add x mL of NaOH ($0.1x$ mmol), the solution volume becomes $(50 + x)$ mL. The trivial algebraic workup results in a quadratic equation for y, whose solution is

$$y = -\frac{b}{2} \pm \sqrt{\frac{b^2}{4} - c} \quad (7)$$

with $b = 5 - 0.1x + (50 + x)K_{a2}$ and $c = -(250 - 5x)K_{a2}$, and we choose the positive root of the second right-hand term of the equation. Throughout the course of the titration, $[H_3O^+] = (5 + y - 0.1x)/(50 + x)$. A simple Microsoft Excel program was used to calculate pH (as pH(C), or "concentration-based pH"; see below) against x up to the neutralization (equivalence) point, ignoring the OH$^-$ contribution.[16] This simple exercise was done to validate the specific method used here for diprotic

H_2SO_4; indeed, the obtained theoretical titration curve, up to pH ∼ 7, is practically identical with a reported one under the very same conditions.[12] It should be noted that the pH versus mL-base-added function is for pH(C), i.e., $-\log[H^+]$ and K_{a2} is assumed to be $K_{a2}(C)$, i.e., the ratio of the product of the concentrations of the right-hand ionic species to the concentration of the left-hand ionic species in reaction 6. In a more accurate titration curve, we should compute pH(M), i.e., $-\log(y_{H^+}[H^+])$ but this also requires the K_{a2} value based on activities. The activities of the sulfate species in reaction 6 are, however, unknown; they cannot be derived from the dissociation of H_2SO_4 because the acid does not behave as a 1−1 or 1−2 electrolyte.

Plots of various theoretical titration curves of H_2SO_4 for different pK_{a2} values are depicted in Figure 6. The line
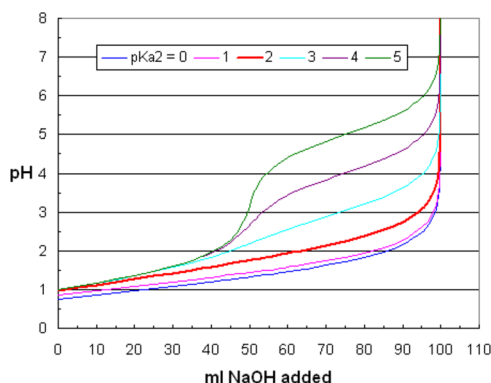

Figure 6. Theoretical titration curves up to the equivalence point (neglecting the OH$^-$ contribution, see text) for 50 mL of 0.1 M aqueous H_2SO_4 neutralized by 0.1 M aqueous NaOH, for different theoretical values of pK_{a2}.

corresponding to pK_{a2} = 2 is emphasized (drawn thicker). Indeed, up to this value, there is no second transition (hump or inflection) on the curve due to the second ionization; this lack of a secondary equivalence point (i.e., after addition of one equivalent of a base) is fully recognized in the literature.[12] Starting from $pK_{a2} \approx 3$, the first equivalence point, after adding 50 mL of base, becomes visually distinguished. It is thus clear that HSO_4^- is a stronger acid than an acid with pK_a value of 3 or higher. But is the pK_{a2} value of reaction 6 2 (more "precisely", 1.99), as claimed in various literature sources? Figure 7 presents the theoretical curve with pK_{a2} = 2 along with experimental values of three consecutive sets of measurement. The experimental points of the three sets are in fair agreement with one another but clearly at odds with the calculated curve; they fit instead with the curve of $pK_{a2} \approx 0.5$. This contrasts with the literature since different measurements of the second equilibrium constant of sulfuric acid, as reported in the literature, always generated the value $pK_{a2} \approx 2$, or $K_{a2} \approx 0.01$. The present work thus casts doubt on the mechanism of dissociation of aqueous sulfuric acid, as claimed, and on the identity of the dissociated sulfur species in water, as reported. Calculating back the amount of HSO_4^- at the first equivalence point based on the fitted curve, that is, with K_{a2} = 0.316, suggests that the acid is 80% dissociated at this stage. This justifies regarding H_2SO_4 in water—to a first approximation—as a strong diprotic acid, almost as strong as HCl (as indeed recognized; see above) and thus considering it as a diprotic acid dissociating essentially in a single step:
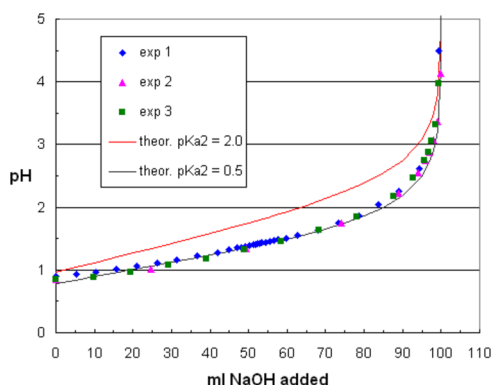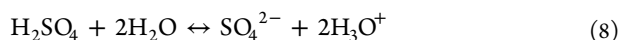
Figure 7. Theory−experiment comparison of H_2SO_4 titration under conditions as in Figure 6: the fit between theory and experiment is reached with pK_{a2} value of 0.5; the literature value of 2.0 (producing the red line) is in clear disagreement with experiment.

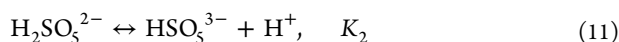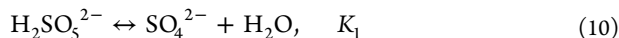$$H_2SO_4 + 2H_2O \leftrightarrow SO_4^{2-} + 2H_3O^+ \qquad (8)$$

Reaction 8 is, of course, the sum of the above reactions 5 and 6, and we may, again to a first approximation, disregard HSO_4^- throughout the entire titration process.

3.4. How the 1−3 Strong Acid Can Be Neutralized as a 1−2 Acid.

How can sulfuric acid be a strong diprotic acid according to reaction 8, yet also behave as a 1−3 electrolyte strong acid whose molecular formula is H_4SO_5? It is obvious that we need to assume that the proposed H_4SO_5 acid, in its dissociated state, is only stable in unneutralized acid solution. The following is an attempt to quantify this assumption through simple modeling involving some empirical factors.

Let us assume a simplified picture in which the reaction of H_2SO_4 with H_2O to give H_4SO_5 goes to completion and H_4SO_5 dissociates fully according to

$$H_4SO_5 \leftrightarrow H_2SO_5^{2-} + 2H^+, \quad pK \ll 0 \qquad (9)$$
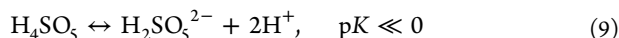
$H_2SO_5^{2-}$ can subsequently react further in two ways:

$$H_2SO_5^{2-} \leftrightarrow SO_4^{2-} + H_2O, \quad K_1 \qquad (10)$$

$$H_2SO_5^{2-} \leftrightarrow HSO_5^{3-} + H^+, \quad K_2 \qquad (11)$$

Let us again consider 50 mL of 0.1 M acid and titrate it with 0.1 M strong base (e.g., NaOH). Taking the number of mmol of SO_4^{2-} at equilibrium as y, as before, and denoting the amount of HSO_5^{3-} as w mmol, the mmol amount of $H_2SO_5^{2-}$ is $(5 - y - w)$, and that of H^+, $(10 + w - 0.1x)$, with x being the volume, in milliliters, of base added. A quite simple algebraic workup results in a quadratic equation (similar to eq 7) for w as a function of K_1, K_2, and x, with "b" $= 10 - 0.1x + K_2x - K_1K_2x/(1 + K_1) + 50K_2 - 50K_1K_2/(1 + K_1)$ and "c" $= 250K_1K_2/(1 + K_1) + 5xK_1K_2/(1 + K_1) - 250K_2 - 5xK_2$.

At this stage, it is necessary to choose proper values for K_1 and K_2. A good estimate for K_2 appears to be $K_2 = 10^5$. This is consistent with the H_4SO_5 acid, before titration, being practically fully ionized to $3H^+$ and HSO_5^{3-}, as proposed above. K_1 should be varying with the addition of the base and one can regard this as a "medium effect" influencing the Gibbs free energy of reaction 10. It is thus perhaps right to suggest that K_1 is a function of $\Delta[H^+]$, defined as $([H^+]_0 - [H^+]_x)$ where the subscripts denote the amount of base added. It is natural to choose for K_1 the general expression $K_1 = K_{1o} \exp(\theta\Delta[H^+])$, K_{1o} and θ being free, adjustable parameters

serving to afford a best fit with experimental results of $pH(C)$ versus x. I have again used a straightforward Excel program, except that here, because of the closed circle of the calculation ("circular reference"), the program was set to perform iterations until the $[H^+]$-dependent K_1 value, at each give x, has agreed with the $[H^+]$ value calculated from this K_1 value. Results for the set of parameters $\{K_{1o} = 10^{-32}; \theta = 10^3\}$, with 100-iteration limit, are presented in Figure 8 as the titration line. This
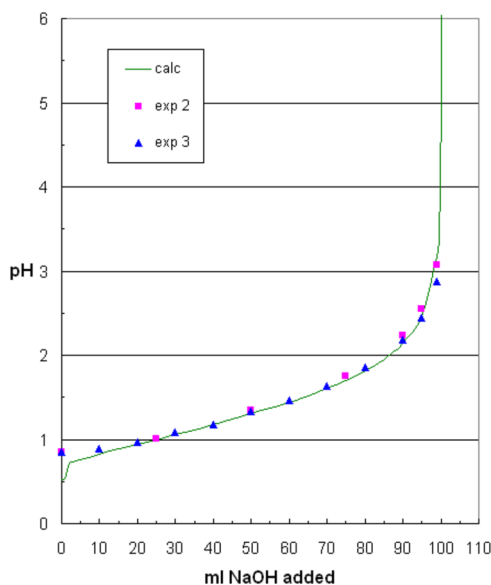

Figure 8. Theory−experiment fit for the titration of aqueous sulfuric acid, considered as H_4SO_5 fully dissociated to $3H^+$ and HSO_5^{3-}, with a strong base; see text for details of the calculation.

computed line is compared with the experimental titration results of experiments 2 and 3 (Figure 7). As seen, there is an excellent agreement between "theory" and experiment above $x \approx 10$; there is a small disagreement at the initial stage of the base addition, at very low pH (well below 1), which perhaps is attributable to experimental artifacts and to model imperfection and oversimplification, as well as to the inadequacy of $pH(C)$ as discussed above, and the pH concept in general at pH < 1.[17] The functional "foot" at low x represents the shift from reaction 11 to reaction 10.

It is important to note that the above modeling exercise is put forth to be in accord with the proposed modified electrochemical cell as presented in part 1.[1] There, the half-cell describing the conversion of HSO_5^{3-} to SO_4^{2-} (i.e., eq 6f in ref 1) has a reaction constant of 10^{-37}. The full cell (obtained by adding the hydrogen half-cell) is

$$HSO_5^{3-} + H^+ \leftrightarrow SO_4^{2-} + H_2O, \quad K = K_1/K_2 \qquad (12)$$
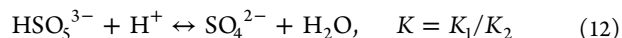
This is simply reaction 10 minus reaction 11. At $x = 0$, before titration has begun, K ($= K_1/K_2$) is indeed 10^{-37}, as required. Thus, the treatment provided in this section for modeling and computing the titration curve of aqueous sulfuric acid is inherently consistent with the electrochemical treatment provided in part 1 for the 1−3 acid H_4SO_5. Furthermore, according to the above analysis, one does not have to assume that the collapse of HSO_5^{3-} to SO_4^{2-} occurs through $H_2SO_5^{2-}$ (eq 10). The direct reaction (eq 12) works as well, giving a titration curve identical to that of the above case involving $H_2SO_5^{2-}$ as intermediate. In this second, shortened case, the

equilibrium amounts of SO_4^{2-}, HSO_5^{3-}, and H^+ are respectively y, $(5 - y)$, and $(15 - y - 0.1x)$ mmol, and in the quadratic equation for y, eq 7, "b" $= -[20 - 0.1x + (50 + x)/K]$ and "c" $= 75 - 0.5x$, and the equation is solved for the negative root. In this solution, $K = K_o \exp(\theta\Delta[H^+])$, with the set of free parameters for the best fit (Figure 8) being $\{K_o = 10^{-37}; \theta = 10^3\}$.

4. SUMMARY AND CONCLUSION

In this article, as in the preceding one (part 1[1]), I propose that, counterintuitively and against conventional wisdom, aqueous sulfuric acid up to ~6 m may be *not* a fully or partially dissociated H_2SO_4 but rather a fully dissociated H_4SO_5 (*para*sulfuric acid) as a 1−3 electrolyte. More specifically, the present work sheds light on the following.

1. Acid Strength. While on an ionic strength scale the "1−3 acid", or *para*sulfuric acid, is a somewhat weaker acid than HCl in terms of proton activity coefficient, it is by far stronger on a molar (or molal) scale. Thus, at 5 M, at 25 °C, the proton activity of aqueous H_4SO_5 is calculated to be $1.87 \times 10^{+14}$ whereas that of aqueous HCl is only 18. The very low pH of the 1−3 acid at high concentration, computed using the relevant SiS mathematical expression, departs strongly from the measured H_0; it thus resembles, on ionic strength scale, the behavior of HI.[2] The high values of H_0 at high concentration may imply that there is a "compensating effect" between the activity coefficient of the protonated base (Hammett indicator) and that of H^+ (as protonated H_2O, H_3O^+). The acid, as strong electrolyte, "identifies" HB^+ as a "proton in disguise"[2] mimicking H^+ (H_3O^+) but failing to achieve the very small size of the hydronium ion. Nonetheless, HB^+ is a sufficiently small cation to "drag" behind H^+ in terms of activity coefficient, which increases H_0 compared to pH, thus manifesting a weaker acid strength than that inferred from pH. Stated otherwise, as concentration increases beyond ~0.1 M, the tendency of the acid to deliver a proton to a weak base is becoming gradually lesser (and at higher concentration, considerably lesser) than what would be expected from the calculated chemical potential of the proton in solution. This phenomenon has also been encountered with HCl, HBr, and HI.[2]

2. Trivalent Ion Stability and Neutralization. If the major (or only) sulfur-containing species in aqueous solution (up to ~6 m) is indeed the trivalent ion HSO_5^{3-}, then two questions arise: (1) Why has the ion never been isolated? (2) How can one explain the known pattern of sulfuric acid neutralization, giving first the bisulfate ion, then, at higher pH, the sulfate ion? Question (1) may be answered by simply suggesting that the trivalent ion is thermodynamically stable only in strong acid solution; the pentacoordinate anion collapses upon acid neutralization, that is, at higher pH, thereby giving the more stable tetrahedral sulfur oxide structures, primarily SO_4^{2-}. The answer to question (2) requires somewhat more elaboration. As claimed in the literature, aqueous sulfuric acid is a quite peculiar acid. It is said to be a strong (fully dissociated) acid in its first ionization stage, $H_2SO_4 \rightarrow HSO_4^- + H^+$ ($pK_a = -3$) and a weak acid in the second ionization stage, $HSO_4^- \rightarrow SO_4^{2-} + H^+$ ($pK_a = 2$). Yet,

(A) Apart from being neutralized by two base equivalents rather than one, sulfuric acid is very similar to hydrochloric acid, hence behaving as strong acid, with

the inflection point on the titration curve, after full neutralization, occurring at pH ≈ 7.

(B) Sulfuric acid does not exhibit the first "hump" in its titration curve, as typical to diprotic acids (e.g., oxalic acid); that is, before and after the completion of the addition of the first base equivalent, the titration line continues with exactly the same trend (about linear positive slope, or, more precisely, a positive and monotonically increasing tangent); this is explained by claiming[12] that the second ionization is actually considerable and adding to the first one, so titration continues to the second stage as if the two stages are practically behaving as one stage, and that makes the aqueous acid a *strong diprotic acid*. The latter literature claim appears to contradict with the literature argument that the second deprotonation event is limited and HSO_4^- is a weak acid.

(C) Furthermore, the experimental titration, as reported in this article, suggests that HSO_4^- is perhaps 30 times stronger than what its literature acid constant reflects, and at the first equivalent point, it is 80% ionized to H^+ and SO_4^{2-}; this is at odds with the common view of aqueous sulfuric acid, and casts doubt on the validity of the literature reported K_a measurements of the HSO_4^- dissociation.

My claim that the actual acid in water may be H_4SO_5 as a completely dissociated 1−3 electrolyte seems to further complicate the acid neutralization picture: aqueous sulfuric acid has almost the same acid strength as that of the monoprotic HCl, but it is in fact a diprotic acid, and it contains three H^+ equivalents. To disentangle the above findings, one may assume that, to a first approximation, HSO_4^- can be ignored in aqueous sulfuric acid solutions and during their base titration; rather, what may be neutralized are two of the three protons in the system $\{HSO_5^{3-} + 3H^+\}$, the process proceeding (as one option) by $H_2SO_5^{2-}$, the immediate precursor of HSO_5^{3-}, collapsing through dehydration to SO_4^{2-}; this may occur at the beginning of the neutralization/titration of the acid. Isolation of the HSO_4^- salt at about the first equivalence point (at pH ~1.3) by precipitation/crystallization from the aqueous solution may then be visualized as occurring through the idealized reaction

$$SO_4^{2-} + H^+ + M^+ \rightarrow M^+HSO_4^-$$

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Notes
The authors declare no competing financial interest.

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(17) On the meaning, validity and applicability range of the pH concept, Rochester writes in ref 8, pp 5−6: "*It must be noted that the pH scale will only have any real theoretical significance for solutions of ionic strength less than 0.1 M. At higher ionic strengths the Bates−Guggenheim (1960) activity coefficient expression... will not be applicable, neither will the assumption made in the British interpretation of pH that the activity coefficients of different uni-univalent electrolytes show similar variations with increasing ionic strength. Thus although e.m.f. measurements can be made and pH deduced... for any solution, no matter how concentrated, the precise interpretation of the pH values is lost. The cancellation of liquid junction potentials... also becomes progressively more questionable for comparison of solutions of very high ionic strength with a conventional pH standard with ionic strength in the acceptable range. This limits the usefulness of pH as a measure of acidity in aqueous solution to the approximate range 1 < pH < 13.*" In the present article, I report on theoretical and experimental titration of 0.1 M sulfuric acid in water. If the acid is considered as a 1−2 electrolyte, then its ionic strength is 0.3; if it is a 1−3 electrolyte, its ionic strength is 0.6. The lack of excellent agreement between theory and experiment in titration (Figures 7 and 8) occurs only below pH 1. It is also important to mention here that both Bates−Guggenheim assumption (in Bates, R. G.; Guggenheim, E. A. *Pure Appl. Chem.* **1960**, *1*, 163−168) and the "British interpretation" are now proven wrong by the smaller-ion shell treatment, see refs 2−4 and 6. For example, for aqueous HCl at 25 °C and at ionic strength 0.1, γ_{H^+} is 0.8255 and γ_{Cl^-} is 0.7633, and even at 0.01 M, the activity coefficients of the proton and the chloride are still substantially different: 0.9083 and 0.9003, respectively.