[Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada]

The State of the Proton in Aqueous Sulfuric Acid[1]

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Use is made of literature data on the Hammett acidity function, the activity of water, and Raman spectral results for sulfuric acid solutions to construct a hydration model which will account quantitatively for the observed acidity in the 0–99% acid range. No activity coefficient corrections are applied. Calculations are not extended to higher concentrations because of complications due to the self-ionization of sulfuric acid. The results indicate that above 50 mole % sulfuric acid, the species H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ can account for the observed acidity, whereas at lower concentrations of acid more highly hydrated proton hydrates coexist in the same solution. The largest hydrate postulated to exist is $H_{21}O_{10}^+$. The average apparent hydration number of the proton as a function of acid concentration is predicted to pass through a maximum at about 2 M sulfuric acid. This is interpreted to result from a shift in the balance between the tendency of ions to hydrate and the tendency of water molecules to form clusters. No water clusters are believed to exist above 2 ± 1 M sulfuric acid.

1. Introduction

In the elucidation of the problem of the nature of the interaction between strong electrolytes and water, a study of strong acid solutions appears to be of special interest, because these solutions have one important unique property, namely their acidity. The acidity can in principle be measured quantitatively in terms of the Hammett acidity function[3-7] which is defined as

$$h_0 = a_{H^+}(f_B/f_{BH^+}) = [H^+]f_{H^+}(f_B/f_{BH^-}) \quad (1)$$

where $[H^+]$ is the concentration of the proton, f_{H^+} is the activity coefficient of the proton, and f_B/f_{BH^+} is the ratio of activity coefficients of an indicator and its conjugate acid. However, evidence has long existed for the hydroxonium ion, H_3O^+,[8] and it has been suggested that thermodynamicists could replace H^+ by H_3O^+ with at least equal logic.[9-11] Equation 1 would then become

$$h_0 = [H_3O^+]f_{H_3O^+}f_B/f_{BH} \cdot a_{H_2O} \quad (2)$$

where H_3O^+ is the concentration of the oxonium ion and a_{H_2O} is the thermodynamic activity of water, p/p^0, where p is the vapor pressure of water over the solution and p^0 is the vapor pressure of pure water. The well-known decrease in the activity of water with increasing acid concentration now becomes an obvious contributing factor to the acidity of the solution. If, however, the proton is in the form $H_9O_4^+$ in moderately concentrated acid,[12-14] then eq. 1 becomes

$$h_0 = [H_9O_4^+]f_{H_9O_4}f_B/f_{BH} \cdot a_{H_2O}^4 \quad (3)$$

The activity of water term, raised to the fourth power in the denominator, now becomes the major factor in explaining the acidity of moderately concentrated acid solutions.[15-18] A chemical explanation, such as the above, is much more satisfying than the attribution of the predominant part of the observed acidity in some unexplained fashion to the term $f_H \cdot f_B/f_{BH^+}$.

In very concentrated H_2SO_4 solutions, there is not enough water present to form $H_9O_4^+$, but attempts have been made here also to explain the observed acidity largely in chemical terms, the conclusion being that all available water hydrates the proton[19,20] and that the species $H_5O_2^+$ is also important in concentrated H_2SO_4.[21,22] An attempt to provide a chemical model to explain the acidity of the H_2SO_4–H_2O system at 25° over the entire concentration range has been made by Högfeldt,[23,24] and it is the purpose of the present paper to report a similar attempt for the 0.1–1000 m H_2SO_4 range (m = molal). Similarities to and differences from Högfeldt's treatment will be discussed later. Experimental results used include the activity of water data of Giauque, et al.,[25] the Raman spectral results of Young and co-workers,[11,26,27] and the recent redetermination of h_0 scale for concentrated H_2SO_4 by Jorgensen and Hartter.[28]

2. Description of the Model

As in previous models, it is assumed that the h_0 data provide a true measure of the acidity of the solutions. It is also assumed that up to four proton hydrate species can coexist in the same solution. Furthermore, when several species are present, they are assumed to contribute in an additive fashion to the total acidity. For example,

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(2) Holder of a Canadian Industries Ltd. Fellowship, an N.R.C. Studentship, and a Government of Alberta Fellowship.

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$$h_0 = \frac{[H_3O^+]f_{H_3O^+}f_B}{a_{H_2O}f_{BH^+}} + \frac{[H_5O_2^+]f_{H_5O_2^+}f_B}{a_{H_2O}^2 f_{BH^+}} +$$

$$\frac{[H_7O_3^+]f_{H_7O_3^+}f_B}{a_{H_2O}^3 f_{BH^+}} + \frac{[H_9O_4^+]f_{H_9O_4^+}f_B}{a_{H_2O}^4 f_{BH^+}} \quad (4)$$

Equation 4 and similar equations would be drastically simplified if it could be assumed that $f_{H^+(H_2O)_n}f_B/f_{BH^+} = 1$. Equation 4 would then become

$$h_0 = \frac{[H_3O^+]}{a_{H_2O}} + \frac{[H_5O_2^+]}{a_{H_2O}^2} + \frac{[H_7O_3^+]}{a_{H_2O}^3} + \frac{[H_9O_4^+]}{a_{H_2O}^4} \quad (5)$$

An experimental restriction is that

$$[H_5SO_5^+] + [H_3O^+] + [H_5O_2^+] + [H_7O_3^+] +$$
$$[H_9O_4^+] = [\text{total } H^+] \quad (6)$$

The total concentration of H^+ is readily calculated from the Raman measurements of the concentrations of H_2SO_4, HSO_4^-, SO_4^{-2}, and $H_5SO_5^+$ present. Below 50 m H_2SO_4, the concentrations of undissociated acid, HSO_4^-, and SO_4^{-2} are obtained by graphical interpolation of the numerical data of Young, Maranville, and Smith.[11] Above 40 m H_2SO_4, the concentrations of H_2SO_4, HSO_4^-, and $H_5SO_5^+$ are estimated from the graph of Young and Walrafen.[27] Finally, the restriction

$$[H_5SO_5^+] + [H_3O^+] + 2[H_5O_2^+] + 3[H_7O_3^+] +$$
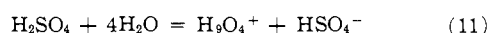$$4[H_9O_4^+] = [\text{total } H_2O \text{ of proton hydration}] \quad (7)$$
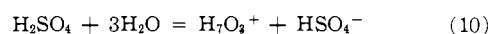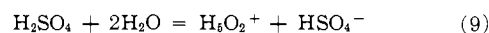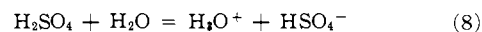
must be met. Equations 5–7 provide three simultaneous equations, so that unique values for the concentrations of three different proton hydrates can be obtained for any given concentration of acid, provided a satisfactory choice has been made for the total water which is involved in proton hydration. It was found, however, that use of a three-species program often led to the appearance of discontinuities in the concentrations of proton hydrates as a function of acid concentration. To eliminate these discontinuities, the program was changed where necessary to allow four proton hydrate species to coexist. This, of course, leads to ranges of concentrations, rather than unique concentrations. In practice, the three-species programs were used to obtain the acceptable ranges of total water of proton hydration, from which best-fit values were chosen. The chosen values of total water of proton hydration were then used in the four-species programs. For the four-species programs, arbitrary choices for the concentration of the least hydrated proton species were made, and originally those choices which led to positive concentrations of four proton hydrates were accepted. Later, a somewhat more severe restriction was imposed, namely that the equilibrium constant for a more highly hydrated species must be larger than that for a less hydrated species, a choice which reflects the driving force of the proton to become hydrated.

3. Calculations

All data used in our calculations are summarized in Table I. The calculations which were carried out can be divided conveniently into two parts: those for concentrated acid, where the equilibria involve undissociated H_2SO_4, HSO_4^-, and $H_5SO_5^+$; and those for more dilute acid, where the equilibria involve SO_4^{-2}

and HSO_4^-. The two regions overlap in the 35–70 m H_2SO_4 range. All of the calculations are performed using molal concentrations, an arbitrary choice, based partly on the fact that the most precise data used are the activity of water data, reported for molal concentrations of acid; and also on the fact that resultant average proton hydration numbers are slightly lower than those obtained from molar concentrations. Because the molal scale gives undue emphasis to concentrated solutions, we report all concentrations on a molar basis (M = molar).

Calculations for Concentrated Sulfuric Acid.—The equilibria considered of importance here are

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^- \quad (8)$$

$$H_2SO_4 + 2H_2O = H_5O_2^+ + HSO_4^- \quad (9)$$

$$H_2SO_4 + 3H_2O = H_7O_3^+ + HSO_4^- \quad (10)$$

$$H_2SO_4 + 4H_2O = H_9O_4^+ + HSO_4^- \quad (11)$$
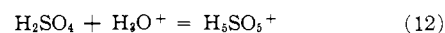
$$H_2SO_4 + H_3O^+ = H_5SO_5^+ \quad (12)$$

$$K_8 = \frac{[H_3O^+][HSO_4^-]}{a_{H_2O}[H_2SO_4]} \qquad K_9 = \frac{[H_5O_2^+][HSO_4^-]}{a_{H_2O}^2[H_2SO_4]}$$

$$K_{10} = \frac{[H_7O_3^+][HSO_4^-]}{a_{H_2O}^3[H_2SO_4]} \qquad K_{11} = \frac{[H_9O_4^+][HSO_4^-]}{a_{H_2O}^4[H_2SO_4]}$$

$$K_{12} = \frac{[H_5SO_5^+]}{[H_2SO_4][H_3O^+]}$$

These are obviously not true thermodynamic equilibrium constants, in that, with the exception of a_{H_2O}, concentrations rather than activities are used. The rate of drift of these constants with changing acid concentration should be an indication of the magnitude of the activity coefficient terms.

The data from Table I were fed into an IBM 1620 computer.[29] The ranges of the unknown concentrations were obtained from an iterative procedure on which the restriction that $K_{11} > K_{10} > K_9 > K_8$ was imposed. No calculations were performed above 99% H_2SO_4 because of complications owing to the self-ionization of H_2SO_4.[30,31]

Calculations for More Dilute Sulfuric Acid.—The equilibria initially considered for the more dilute region were

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{-2} \quad (13)$$

$$HSO_4^- + 2H_2O \rightleftharpoons H_5O_2^+ + SO_4^{-2} \quad (14)$$

$$HSO_4^- + 3H_2O \rightleftharpoons H_7O_3^+ + SO_4^{-2} \quad |(15)$$

$$HSO_4^- + 4H_2O \rightleftharpoons H_9O_4^+ + SO_4^{-2} \quad (16)$$
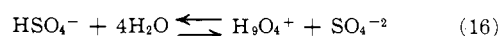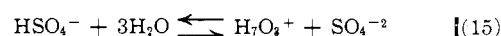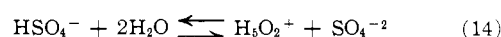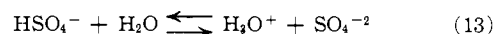
$$K_{13} = \frac{[H_3O^+][SO_4^{-2}]}{a_{H_2O}[HSO_4^-]} \qquad K_{14} = \frac{[H_5O_2^+][SO_4^{-2}]}{a_{H_2O}^2[HSO_4^-]}$$

$$K_{15} = \frac{[H_7O_3^+][SO_4^{-2}]}{a_{H_2O}^3[HSO_4^-]} \qquad K_{16} = \frac{[H_9O_4^+][SO_4^{-2}]}{a_{H_2O}^4[HSO_4^-]}$$

Calculations were performed in a manner analogous to that used for concentrated acid. Arbitrary choices for the concentration of H_3O^+ were made, and those choices which lead to $K_{16} > K_{15} > K_{14} > K_{13}$ were

(29) Assistance from the Department of Computing Science, University of Alberta, is gratefully acknowledged.

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TABLE I

DATA FOR SULFURIC ACID

Concn. of H₂SO₄[b]		a_{H_2O}[c]	h_0[a]	Total M H⁺	Total M H₂O of H⁺ hydration	SO₄⁻²	HSO₄⁻	M[d]	
m	M							H₂SO₄	H₅SO₅⁺
0.1	0.0994	0.9964	0.136	0.132	0.579	0.033	0.066		
0.2	0.1981	0.9928	0.275	0.260	1.38	0.062	0.136		
0.3	0.2961	0.9892	0.418	0.383	2.24	0.087	0.210		
0.4	0.3933	0.9857	0.572	0.508	3.26	0.114	0.279		
0.5	0.4899	0.9821	0.735	0.631	4.40	0.141	0.349		
0.6	0.5858	0.9784	0.907	0.754	5.68	0.168	0.418		
0.7	0.6809	0.9746	1.09	0.874	7.03	0.193	0.488		
0.8	0.7754	0.9706	1.28	0.992	8.46	0.217	0.558		
0.9	0.8691	0.9664	1.51	1.11	9.92	0.24	0.62		
1.0	0.9623	0.9621	1.77	1.24	11.49	0.28	0.68		
1.5	1.417	0.9402	3.43	1.82	18.12	0.40	1.01		
2.0	1.855	0.9130	6.28	2.46	24.24	0.60	1.25		
2.5	2.277	0.8833	10.6	3.01	28.78	0.73	1.55		
3.0	2.683	0.8514	17.5	3.58	33.02	0.90	1.78		
3.5	3.073	0.8169	27.1	4.08	35.76	1.01	2.06		
4.0	3.448	0.7800	40.6	4.59	37.37	1.14	2.31		
4.5	3.809	0.7421	59.8	5.06	38.88	1.25	2.56		
5	4.156	0.7035	87.0	5.52	39.40	1.36	2.79		
6	4.811	0.6257	152	6.35	40.09	1.54	3.27		
7	5.418	0.5503	301	7.10	40.18	1.69	3.73		
8	5.981	0.4806	565	7.76	39.57	1.78	4.20		
9	6.508	0.4175	1.08×10^3	8.34	38.70	1.84	4.67		
10	6.999	0.3611	2.08×10^3	8.86	37.74	1.86	5.14		
11	7.460	0.3113	3.71×10^3	9.31	36.77	1.85	5.61		
12	7.892	0.2678	6.38×10^3	9.71	35.80	1.82	6.08		
13	8.298	0.2303	1.04×10^4	10.06	34.84	1.77	6.53		
14	8.679	0.1980	1.64×10^4	10.38	33.91	1.70	6.98		
15	9.038	0.1701	2.54×10^4	10.66	33.02	1.62	7.41		
16	9.376	1.462×10^{-1}	3.84×10^4	10.91	32.16	1.54	7.84		
17	9.696	1.255×10^{-1}	5.81×10^4	11.14	31.34	1.45	8.25		
18	9.998	1.077×10^{-1}	8.49×10^4	11.35	30.55	1.36	8.64		
19	10.28	9.233×10^{-2}	1.21×10^5	11.55	29.79	1.27	9.02		
20	10.55	7.929×10^{-2}	1.73×10^5	11.73	29.06	1.18	9.38		
22	11.06	5.906×10^{-2}	3.52×10^5	12.08	27.70	1.03	10.03		
25	11.72	3.799×10^{-2}	8.77×10^5	12.55	25.87	0.84	10.88		
30	12.63	1.937×10^{-2}	3.13×10^6	13.24	23.27	0.61	12.02	0.00	
35	13.37	1.042×10^{-2}	8.59×10^6	13.58	21.12	0.41	12.77	0.19	0.00
40	13.96	5.09×10^{-3}	1.94×10^7	13.64	19.32	0.27	13.10	0.59	0.006
45	14.45	3.53×10^{-3}	3.87×10^7	13.24	17.78	0.16	12.93	1.36	0.01
50	14.86	2.23×10^{-3}	6.79×10^7	12.73	16.47	0.08	12.57	2.19	0.02
60	15.49	1.05×10^{-3}	1.62×10^8	11.63	14.32	0.02	11.59	3.82	0.05
70	15.95	5.80×10^{-4}	3.16×10^8	10.75	12.64	0.005	10.74	5.10	0.10
80	16.29	3.61×10^{-4}	5.27×10^8	10.05	11.30	0.00	10.05	6.08	0.16
90	16.56	2.47×10^{-4}	7.87×10^8	9.40	10.21		9.40	6.94	0.22
100	16.77	1.79×10^{-4}	1.14×10^9	8.79	9.31		8.79	7.69	0.29
150	17.42	6.27×10^{-5}	3.94×10^9	6.34	6.45		6.34	10.45	0.63
200	17.74	3.20×10^{-5}	7.53×10^9	4.89	4.92		4.89	11.91	0.94
300	18.05	1.38×10^{-5}	1.47×10^{10}	3.34	3.34		3.34	13.37	1.34
400	18.21	7.87×10^{-6}	2.06×10^{10}	2.52	2.53		2.52	14.04	1.64
500	18.30	5.20×10^{-6}	2.57×10^{10}	2.03	2.03		2.03	14.42	1.85
1000	18.46	1.50×10^{-6}	4.90×10^{10}	1.02	1.02		1.02	16.44	1.00

[a] See ref. 3 and 28; also K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).   [b] Density data for the conversion of molalities to molarities from "International Critical Tables," Vol. 3, McGraw–Hill Book Co., Inc., New York, N. Y., 1928, p. 56.   [c] From data of Giauque, *et al.*[25]; for calculations below 1 m, from data of H. Harned and W. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).   [d] See ref. 6, 7, and 11.

accepted. For a few concentrations of acid, the less-restrictive criterion that the concentrations of four proton hydrates must be positive was retained. The computer program was also modified, where necessary, to eliminate the less hydrated proton species and to take into account more highly hydrated species, with the restriction retained that not more than four species were considered at one time. Thus, the constants K_{17} to K_{22} refer to equilibria involving $H_{11}O_5^+$ to $H_{21}O_{10}^+$, respectively. No calculations were performed for acid concentrations less than 0.1 m, because

more than eight significant figures were required on the input data.

4. Results

Best-fit values of average apparent hydration numbers, n, which are obtained from programs involving not more than three proton hydrate species for any given concentration of acid are shown in Fig. 1 by the dot–dash line. The acceptable range of values of n is very restricted for both dilute and concentrated acid solutions. The corresponding values of total water of
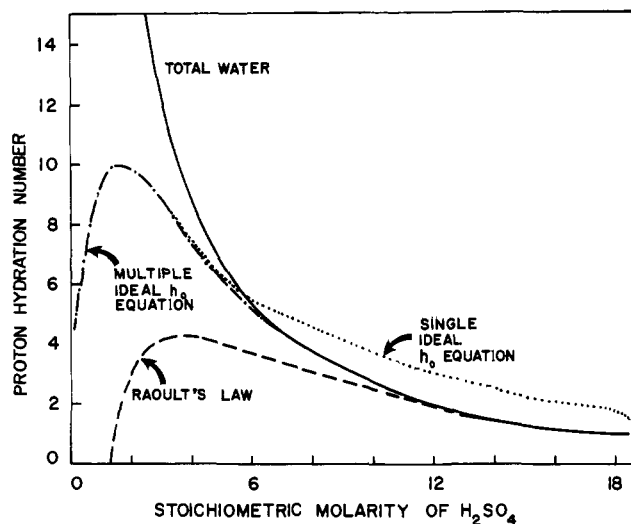
Fig. 1.—Plot of the average hydration number of the proton vs. concentration of sulfuric acid, predicted by the total water in the system, by Raoult's law, and by the ideal h_0 equations for both single and multiple proton hydrates.
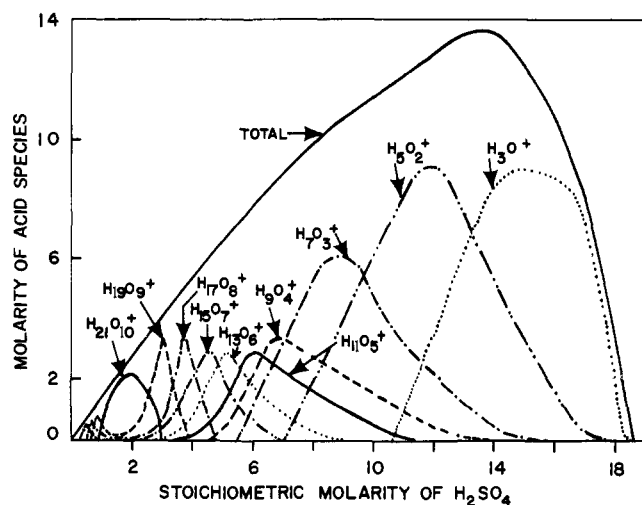

Fig. 2.—Plot of the molar concentrations of proton hydrate species vs. the concentration of sulfuric acid.

proton hydration (column six of Table I) were used to obtain all values for the molar concentrations of proton hydrates summarized in Table II. The ranges of proton hydrate concentrations reported in Table II are for regions where four proton hydrates are considered. Proton hydrate concentration curves, based on data of Table II, are shown in Fig. 2. Limits obtained on the corresponding constants, K_8 to K_{12}, and K_{13} to K_{22}, are summarized in Tables III and IV and in Fig. 3 and 4, respectively. The values in parentheses for 9–14 m H$_2$SO$_4$ in Tables II and IV were obtained by requiring only that four proton hydrates have positive concentrations.

5. Discussion

It was assumed that h_0 is a simple sum of contributions from the various H$^+$(H$_2$O)$_n$ species (eq. 4). This is probably not quite true, but it is difficult to assign relative acidities. H$_9$O$_4^+$ has six protons available as opposed to three in H$_3$O$^+$ and therefore on a statistical basis would be expected to be twice as strong an acid, but its "conjugate base" has three sites as opposed to one in H$_2$O. Also, it would appear plausible that there would be resonance stabilization in the
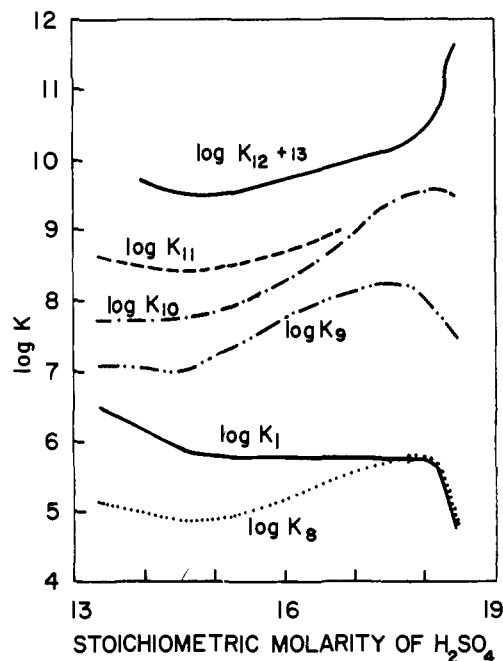
Fig. 3.—Plot of the logarithm of the molal equilibrium constants for H$_2$SO$_4$–HSO$_4^-$ equilibria as a function of sulfuric acid concentration. $K_1 = [\text{H}^+(\text{H}_2\text{O})_n][\text{HSO}_4^-]/a_{\text{H}_2\text{O}}{}^n[\text{H}_2\text{SO}_4]$; otherwise notation as described in text.
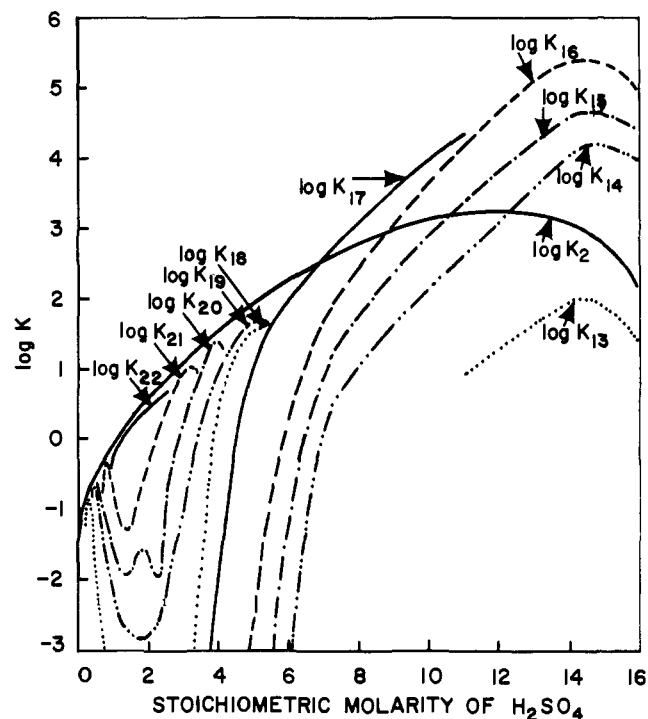
Fig. 4.—Plot of the logarithm of the molal equilibrium constants for HSO$_4^-$–SO$_4^{-2}$ equilibria vs. the concentration of sulfuric acid. $K_2 = [\text{H}^+(\text{H}_2\text{O})_n][\text{SO}_4^{-2}]/a_{\text{H}_2\text{O}}{}^n[\text{HSO}_4^-]$; otherwise notation as described in text.

larger aggregate. In more concentrated acid, at least, the overwhelming contribution to the acidity is the activity of water factor raised to the appropriate power, located in the denominator of eq. 4.

For all of the acid concentrations considered, at least one of the acid species HSO$_4^-$, H$_2$SO$_4$, and H$_5$SO$_5^+$, is present. By use of Wyatt's value of 2550 for $K_{\text{H}_2\text{SO}_4}$,[21,22] it is possible to show that the contribution of H$_2$SO$_4$ to h_0 is negligibly small. It was assumed that H$_5$SO$_5^+$ makes the same contribution to the total

Table II

SUMMARY OF MOLAR CONCENTRATIONS OF PROTON HYDRATE SPECIES

H_2SO_4, m	H_3O^+	$H_5O_2^+$	$H_7O_3^+$	$H_9O_4^+$	$H_{11}O_5^+$	$H_{13}O_6^+$	$H_{15}O_7^+$	$H_{17}O_8^+$	$H_{19}O_9^+$	$H_{21}O_{10}^+$
0.1		0.000	0.006	0.040	0.067					
		0.006	0.021	0.055	0.071					
0.2			0.000	0.012	0.081	0.120				
			0.012	0.047	0.116	0.132				
0.3			0.000	0.002	0.034	0.338				
			0.002	0.009	0.040	0.340				
0.4				0.000	0.016	0.168	0.258			
				0.016	0.066	0.217	0.275			
0.5				0.000	0.001	0.010	0.618			
				0.001	0.003	0.012	0.618			
0.6					0.000	0.016	0.228	0.448		
					0.016	0.062	0.274	0.464		
0.7						0.000	0.250	0.290	0.304	
						0.008	0.273	0.312	0.312	
0.8						0.000	0.020	0.310	0.584	
						0.020	0.079	0.368	0.604	
0.9						0.000	0.004	0.069	1.025	
						0.004	0.017	0.081	1.029	
1.0							0.000	0.068	0.401	0.507
							0.068	0.270	0.600	0.573
1.5							0.000	0.005	0.054	1.743
							0.005	0.020	0.069	1.747
2.0							0.000	0.024	0.137	2.204
							0.024	0.094	0.204	2.226
2.5							0.000	0.002	1.256	1.739
							0.002	0.009	1.262	1.741
3.0							0.000	0.243	0.956	1.488
							0.243	0.935	1.612	1.694
3.5						0.000	0.043	0.640	3.240	
						0.043	0.166	0.754	3.276	
4.0						0.000	0.926	2.043	1.603	
						0.004	0.939	2.054	1.606	
4.5					0.000	0.143	0.546	3.875		
					0.143	0.534	0.901	3.981		
5.0					0.000	0.665	2.131	1.906		
					0.240	1.315	2.709	2.075		
6.0				0.000	0.229	2.682	2.690			
				0.229	0.832	3.198	2.834			
7.0				0.000	3.605	2.145	1.228			
				0.042	3.711	2.232	1.251			
8.0			1.107	1.140	1.219	1.510	0.770			
			1.138	2.360	3.140	1.601	0.792			
9.0			(1.6)	(0.1)	(0.1)	(0.1)	(0.5)			
			(2.9)	(5.8)	(2.4)	(3.4)	(0.9)			
10.0			(3.1)	(0.1)	(0.0)	(2.2)				
			(4.3)	(3.0)	(2.2)	(2.7)				
11.0		0.818	1.306	2.436	3.467					
		1.306	2.433	3.227	3.619					
12.0			(5.5)	(0.1)	(0.1)	(0.9)				
			(6.8)	(2.9)	(2.0)	(1.2)				
13.0		(3.6)	(0.1)	(0.1)	(0.1)	(0.1)				
		(4.6)	(8.0)	(2.2)	(4.1)	(0.8)				
14.0		(3.0)	(0.0)	(0.0)	(0.0)	(0.4)				
		(5.0)	(9.1)	(2.8)	(2.9)	(0.5)				
15.0		4.266	2.184	1.770	1.718					
		4.573	2.852	2.183	1.770					
16.0		4.232	2.356	1.220	1.091					
		5.110	4.240	2.355	1.220					
17		4.611	2.326	0.841	0.691					
		5.803	4.846	2.324	0.840					
18		5.185	2.202	0.558	0.413					
		6.537	5.050	2.201	0.558					
19		5.976	2.007	0.441	0.230					
		7.296	4.770	2.005	0.352					
20		6.925	1.778	0.336	0.135					
		8.109	4.240	1.708	0.229					
22	2.500	3.261	1.314	0.170	0.060					
	3.618	9.691	3.260	2.010	0.104					

TABLE II (*Continued*)

H_2SO_4, m	H_3O^+	$H_5O_2^+$	$H_7O_3^+$	$H_9O_4^+$
25	1.668	3.732	0.812	0.709
	4.380	9.259	3.730	0.812
30	3.753	3.220	0.178	0.122
	6.681	9.133	3.220	0.178
35	6.196	3.802	0.076	0.019
	7.924	7.275	1.839	0.037
40	7.981	4.812	0.029	0.002
	8.381	5.614	0.433	0.004
45	8.730	4.008	0.018	0.001
	8.968	4.485	0.257	0.001
50	8.973	3.525	0.008	0.0002
	9.072	3.723	0.108	0.0003
60	8.858	2.632	0.004	0.00002
	8.904	2.724	0.050	0.00005
70	8.770	1.869	0.001	0.000002
	8.776	1.879	0.006	0.000007
80	8.639	1.244	0.0004	
	8.641	1.248	0.002	
90	8.359	0.812	0.0002	
	8.359	0.813	0.001	
100	7.990	0.514	0.0001	
	7.990	0.514	0.0003	
150	5.610	0.104	0.0001	
200	3.928	0.030	0.00002	
300	1.986	0.004	0.000002	
400	0.882	0.001		
500	0.180	0.0002		
1000	0.026	0.00004		

TABLE III

SUMMARY OF CONSTANTS FOR EQUILIBRIA INVOLVING H_2SO_4-HSO_4^-

H_2SO_4, m	log K_1	log K_{12}	log K_3	log K_9	log K_{10}	log K_{11}
35	6.47	....	5.03	6.80	7.08	8.46
		....	5.13	7.08	8.46	8.75
40	6.19	-3.31	5.00	7.07	7.14	8.32
		-3.28	5.02	7.14	8.32	8.60
45	5.89	-3.47	4.87	7.03	7.12	8.26
		-3.49	4.88	7.07	8.26	8.54
50	5.82	-3.51	4.89	7.14	7.17	8.27
		-3.50	4.89	7.16	8.27	8.56
60	5.80	-3.43	5.00	7.45	7.46	8.35
		-3.42	5.00	7.46	8.35	8.63
70	5.80	-3.29	5.15	7.71	7.73	8.49
		-3.29	5.15	7.71	8.48	8.75
80	5.78	-3.21	5.29	7.89	8.02	8.61
		-3.21	5.29	7.89	8.59	8.84
90	5.76	-3.15	5.40	7.99	8.25	8.71
		-3.15	5.40	7.99	8.65	8.90
100	5.74	-3.10	5.48	8.04	8.30	8.78
		-3.10	5.48	8.04	8.78	9.00
150	5.75	-2.90	5.67	8.14	9.35	
200	5.79	-2.75	5.75	8.14	9.47	
300	5.79	-2.52	5.78	7.99	9.55	
400	5.65	-2.22	5.65	7.88	9.56	
500	5.13	-1.58	5.13	7.49	9.55	
1000	4.78	-1.37	4.78	7.74	9.48	

acidity as H_3O^+. However, although the concentrations of the latter species are large in concentrated solutions, its contribution to the total acidity is always negligible compared to that of much smaller amounts of more highly hydrated species. If the thermodynamic $K_{HSO_4^-}$ = 0.012 is applied without activity coefficient correction for 1 M H_2SO_4, a contribution of 2% by HSO_4^- to the total acidity is predicted.

It is worthy of note that the conversion from a three- to a four-species program largely, but not entirely,

made it possible to eliminate discontinuities from the proton hydrate concentration curves. This might be taken as some evidence that in more dilute H_2SO_4 at least four proton hydrates coexist. When the less stringent requirement that three (or four) proton hydrate concentrations must be positive was replaced by the requirement that the negative standard free energy of proton hydration must be greater, the greater the extent of hydration, the only change in results that was noted was a narrowing of acceptable concentration ranges.

Högfeldt's treatment[16,23,24] of a hydration model is quite dissimilar to our own in formalized approach, but since both use the same kind of data—acidity function, activity of water, and dissociation data— the two models might be expected to yield similar results. This seems to be true as far as average hydration numbers are concerned. However, the attempts by Högfeldt and ourselves to construct specific models based on the coexistence of multiple hydrate species in the same solution show marked differences. Högfeldt has assumed that the best result is that involving the least number of proton hydrate species, and mainly for reasons of symmetry,[32] he has selected the species H_3O^+, $H_5O_2^+$, $H_9O_4^+$, and presumably as a best fit of the remainder, $H_{23}O_{11}^+$. In our own work, no special weight was given to any one species. Of the mass spectrometer work on proton hydrates,[33-35] the most recent reference shows that the heats of the reaction $H^+(H_2O)_n + H_2O \rightarrow H^+(H_2O)_{n+1}$ decrease in a regular fashion as n increases from 0 to 7, with no special preference being shown for the formation of $H_9O_4^+$. Högfeldt required that the equilibrium constants, which are composed of concentrations of hydrated species, but include no activities other than a_{H_2O}, be independent of concentration of acid. This he was able to accomplish by assigning hydration numbers to the anions in dilute solutions, a procedure which we have not attempted. All of the treatments of concentrated acid solutions[16,19-24] have shown that reasonable "constants" are obtained by assuming that proton hydration only occurs (compare Fig. 3 and 4).

Other Models for Proton Hydration.—Various other models might be considered for the prediction of the amount of water of proton hydration. For example, the acidity function can be written in the form

$$h_0 = [H^+(H_2O)_{n'}]/a_{H_2O}^{n'} \qquad (5a)$$

where n' is an apparent hydration number of the proton, if one can neglect the activity coefficient factor $f_{H^+(H_2O)_n}f_B/f_{BH^+}$. The result, which could be called a single species, ideal h_0 equation, provides a method for the calculation of n'. On the other hand, in the computer work, eq. 5 was used, in which a sum is taken of terms for various proton hydrates, none of which contain an activity coefficient factor. Therefore, eq. 5 could be termed a multiple species, ideal h_0 equation. What is the precise operational difference between eq. 5 and 5a? That there is a difference is shown clearly in Fig. 1, where values of n obtained

(32) R. Grahn, *Arkiv Fysik*, **21**, 1, 13 (1962).
(33) H. D. Beckey, *Z. Naturforsch.*, **14a**, 717 (1959); **15a**, 822 (1960).
(34) P. F. Knewstubb and A. W. Tickner, *J. Chem. Phys.*, **38**, 464 (1963).
(35) P. Kebarle and A. M. Hogg, to be published in "Advances in Mass Spectrometry," 1964.

Table IV

Summary of Constants for Equilibria Involving HSO_4^{-}–SO_4^{-2}

H_2SO_4, m	Log K_2	Log K_{13}	Log K_{14}	Log K_{15}	Log K_{16}	Log K_{17}	Log K_{18}	Log K_{19}	Log K_{20}	Log K_{21}	Log K_{22}
0.1				−2.51	−1.69	−1.46					
	−1.17		<−2.54	−1.96	−1.55	−1.44					
0.2					−2.25	−1.41	−1.24				
	−0.91			<−2.26	−1.66	−1.26	−1.20				
0.3					−2.98	−1.83	−0.82				
	−0.77			<−3.01	−2.40	−1.75	−0.82				
0.4					−2.13	−1.12	−0.92				
	−0.63				<−2.14	−1.53	−1.00	−0.90			
0.5					−3.48	−2.35	−0.54				
	−0.53				<−3.50	−2.90	−2.26	−0.54			
0.6						−2.14	−0.96	−0.66			
	−0.44					<−2.15	−1.54	−0.88	−0.36		
0.7							−0.92	−0.84	−0.81		
	−0.36					<−2.43	−0.88	−0.81	−0.80		
0.8							−2.01	−0.80	−0.51		
	−0.29					<−2.02	−1.41	−0.73	−0.50		
0.9							−2.66	−1.44	−0.25		
	−0.21					<−2.67	−2.06	−1.36	−0.24		
1.0								−1.40	−0.61	−0.50	
	−0.12						<−1.42	−0.80	−0.44	−0.44	
1.5									−2.45	−1.40	0.13
	0.15							<−2.48	−1.86	−1.29	0.14
2.0									−1.59	−0.79	0.45
	0.49							<−1.63	−1.00	−0.62	0.46
2.5									−2.50	0.30	0.49
	0.71							<−2.55	−1.91	0.30	0.49
3.0									−0.30	0.36	0.62
	0.95							<−0.37	0.28	0.59	0.68
3.5								−1.00	0.25	1.05	
	1.12						<−1.09	−0.42	0.32	1.05	
4.0								0.48	0.93	0.93	
	1.30						<−1.95	0.48	0.93	0.93	
4.5							−0.30	0.41	1.39		
	1.46					<−0.43	0.27	0.62	1.40		
5.0							0.51	1.17	1.27		
	1.60					<−0.08	0.80	1.27	1.31		
6.0						0.15	1.42	1.62			
	1.86				<−0.06	0.70	1.49	1.64			
7.0						1.62	1.66	1.67			
	2.08				<−0.57	1.63	1.67	1.68			
8.0				0.75	1.08	1.43	1.84	1.87			
	2.26			0.76	1.40	1.84	2.29	1.88			
9.0				(1.07)	(0.32)	(0.40)	(0.88)	(2.10)			
	2.42			(1.33)	(2.02)	(2.02)	(2.55)	(2.35)			
10.0				(1.53)	(0.37)	(0.64)	(2.71)				
	2.54			(1.68)	(1.97)	(2.27)	(2.79)				
11.0			0.61	1.32	2.10	2.76					
	2.66		0.82	1.59	2.22	2.78					
12.0				(2.12)	(0.82)	(1.27)	(3.04)				
	2.75			(2.20)	(2.41)	(2.81)	(3.18)				
13.0			(1.46)	(0.60)	(0.97)	(1.66)	(3.19)				
	2.84		(1.56)	(2.44)	(2.52)	(3.43)	(3.34)				
14.0			(1.48)	(0.37)	(1.01)	(1.81)	(3.40)				
	2.91		(1.70)	(2.66)	(2.86)	(3.57)	(3.51)				
15.0			1.73	2.21	2.88	3.64					
	2.97		1.76	2.32	2.98	3.65					
16.0			1.82	2.40	2.95	3.74					
	3.02		1.90	2.66	3.24	3.78					
17			1.96	2.56	3.02	3.84					
	3.07		2.05	2.88	3.46	3.92					
18			2.10	2.70	3.07	3.90					
	3.11		2.20	3.06	3.66	4.04					
19			2.26	2.82	3.20	3.95					
	3.15		2.35	3.20	3.86	4.14					
20			2.42	2.93	3.31	4.01					
	3.17		2.49	3.30	4.01	4.24					
22		0.94	2.28	3.12	3.46	4.23					
	3.21	1.10	2.75	3.51	4.53	4.48					

TABLE IV (Continued)

H_2SO_4, m	Log K_2	Log K_{13}	Log K_{14}	Log K_{15}	Log K_{16}
25		0.86	2.63	3.38	4.74
	3.24	1.28	3.02	4.05	4.80
30		1.37	3.02	3.47	5.02
	3.21	1.62	3.47	4.73	5.18
35		1.69	3.46	3.75	5.13
	3.13	1.80	3.74	5.13	5.42
40		1.96	4.04	4.11	5.29
	3.15	1.98	4.10	5.28	5.57
45		1.97	4.09	4.23	5.38
	3.00	1.98	4.13	5.37	5.66
50		1.94	4.18	4.22	5.32
	2.87	1.94	4.21	5.32	5.60
60		1.77	4.22	4.26	5.13
	2.57	1.77	4.24	5.13	5.39
70		1.45	4.01	4.03	4.80
	2.10	1.45	4.02	4.78	5.05

from eq. 5 and of n' obtained from eq. 5a are both shown. It is clear that $n' \geq n$. We attempt to answer this question by means of the following example. Suppose that the value of n is 3 and that this, in fact, represents an equimolar mixture of $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$. When one considers that in the h_0 equation (5), $H_5O_2^+$ is divided by $a_{H_2O}^2$, whereas $H_9O_4^+$ is divided by $a_{H_2O}^4$, it is clear that if a_{H_2O} is appreciably less than unity, then $H_9O_4^+$ contributes much more to the observed acidity than if only $H_7O_3^+$ were present. Therefore, the corresponding value of n' in eq. 5a must be larger than 3 to predict the same value of h_0. Notice that the values of n and n' are virtually identical up to 2.5 M acid and are still very similar up to 5 M acid. The values of n and n' then begin to diverge considerably as a_{H_2O} becomes smaller, until in concentrated acid, n becomes identical with the average hydration number predicted by the total amount of water in the system, whereas the water of proton hydration predicted by n' exceeds the total amount of water in the system. Furthermore, the range of acceptable values of n is extremely narrow for both very dilute and very concentrated acid. A remarkable feature of the results is the apparent maximum in both n and n', observed for about 2 M acid. It should be noted that the value of 4 for the hydration number of the proton at infinite dilution is not obtained directly from the "raw" data, but is assumed, and the h_0 data is corrected to give a smooth curve. This involves an adjustment of less than 0.02 logarithm units, which is a reasonable estimate of the error in H_0 data. The importance of such an error in our treatment rapidly decreases with increasing acid concentration, and in no way affects the presence of the apparent maximum in n.

It could also be assumed that all water in the system hydrates the proton, as shown in Fig. 1. However, such an assumption neglects anion hydration, which must be important in dilute solution. Alternatively, it could be assumed that the activity of water is a measure of the "free" water in solution; that is, the water not involved in ion hydration, and that the solution obeys Raoult's law. This means that the activity of water is equal to the mole fraction of "free" water, given by

$$a_{H_2O} = X_{\text{"free" } H_2O} =$$

$$M_{\text{"free" } H_2O} / (M_{\text{"free" } H_2O} + \Sigma M_{\text{ions}})$$

Therefore, the water of ion hydration would be given by

$$M_{H_2O \text{ of ion hydration}} = M_{\text{total } H_2O} - \frac{a_{H_2O}}{1 - a_{H_2O}} \Sigma M_{\text{ions}}$$

The resultant apparent hydration numbers, which are really an apparent average for all ions in solution, and not for the proton only, are also shown in Fig. 1. It can be seen that the predicted numbers are negative in dilute solution, but pass through a maximum at about 4 M sulfuric acid, and are reasonable at all acid concentrations ≥ 4 M.

The Maximum in Apparent Proton Hydration Number.—A maximum in the apparent proton hydration number is predicted by three of the models which have been discussed. In order to test its reality, three different approaches were used. First, apparent n' values were calculated from four other acidity functions expressed in ideal form completely analogous to eq. 5a used for the H_0 function. The other functions used were the G function of Michaelis and Granick,[36] the H_- function of Boyd,[37] the H_0''' function of Arnett and Mach,[38] and the H_R functions determined by Deno, et al.[39] All of these functions give maxima in apparent hydration numbers in the 2 $\pm$ 1 M acid region. It would appear to be a remarkable coincidence for primary anilines, thiazines, cyanocarbons, tertiary amines, and arylmethanols all to exhibit these apparent maxima in n' in the same concentration region. One might interpret this result as some evidence supporting the idea that the observed maximum in n' is a real property of the solution. Furthermore, the maximum value of n' predicted by the H_0, H_-, and G functions is 9.9 $\pm$ 0.1 (Fig. 5). The H_R and H_0''' data give maxima in n' of 29 and 18, respectively, which are not reasonable values. These results are discussed further below.

Next, the effect that hydration of the indicators and their conjugate acids would have upon our model was examined.[17] The equation

$$H^+(H_2O)_h + B(H_2O)_i \rightleftarrows BH^+(H_2O)_j + (h + i - j)H_2O$$
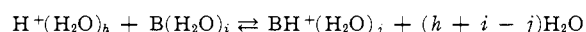
leads to an activity coefficient expression

$$\frac{f_{H^+(H_2O)_h} f_{B(H_2O)_i}}{a_M^{(h + i - j)} f_{BH^+(H_2O)_j}} \qquad (a)$$

This shows clearly that our preliminary treatment, disregarding all other assumptions, can only be correct if $i = j$. Taft,[40] in his comparison of the H_R and H_0 functions, arrived at a j value of 4 in the 52–62% H_2SO_4 interval by assuming that $i = 0$, that R^+ and ROH, the H_R indicators, are both unhydrated, and that the activity coefficients cancel. If $i = 0$ and $j = 4$, the a_{H_2O} factor in eq. a is raised to a very small power or in some cases, even a negative power,[38] which means that the most obvious contributing factor to the high acidity of the solution[15,18] essentially has been destroyed. The assumption that the neutral species are unhydrated, in particular, appears sus-

(36) L. Michaelis and S. Granick, J. Am. Chem. Soc., **64**, 1861 (1942).

(37) R. H. Boyd, ibid., **83**, 4288 (1961).

(38) E. M. Arnett and G. Mach, ibid., **86**, 2671 (1964). We are indebted to Dr. Arnett for access to his paper prior to publication and also for helpful discussions of the present work.

(39) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, ibid., **77**, 3044 (1955).
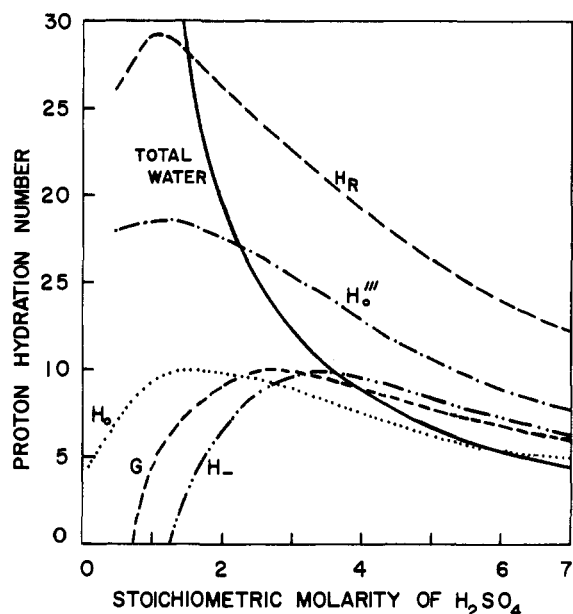
(40) R. W. Taft, Jr., ibid., **82**, 2965 (1960).

Fig. 5.—The average hydration number of the proton in sulfuric acid as calculated from the H_0, H_0''', H_R, H_-, and G single species "ideal" acidity functions.
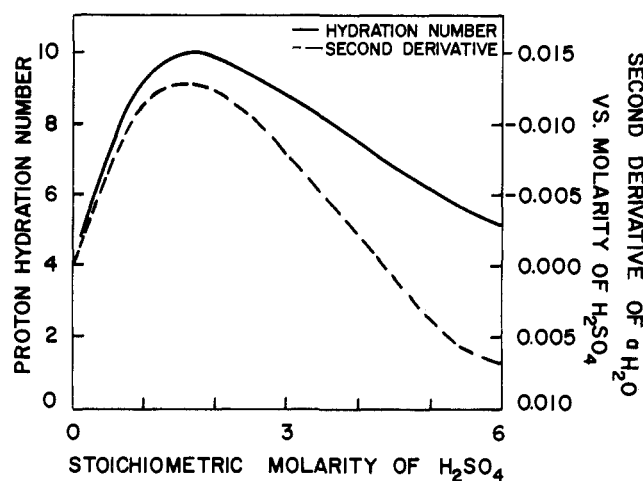

Fig. 6.—The second derivative of the activity of water in sulfuric acid with respect to the stoichiometric molality of acid, as compared to computed average proton hydration numbers.

pect.[18,41] It would appear reasonable, however, to assume that BH^+ does have a somewhat greater tendency to hydrate than B. If so, the apparent values of n' really represent $h + i - j$ values. Therefore, for the region in which the ideal h_0 equation appears to be most valid (0–5 M H_2SO_4), the true values of n' would be higher. This would shift the maximum in n' upward, but if the difference $i - j$ remains constant, there would be little other effect. It should be noted that resonance structures for primary anilines tend to minimize the difference in hydrophilic character between the anilines and their conjugate acids.

Boyd's data[42] indicate that f_{BH^+} increases considerably with increasing acid concentration compared to that of the tetraethylammonium ion, f_{TEA^-}, whereas the corresponding changes in f_B are quite small in the dilute region. In contrast, for a neutral H_R indicator, its activity coefficient f_{ROH} increases markedly, whereas the activity coefficient for the corresponding cation, f_{R^+}, changes little with respect to f_{TEA^+} as a function of acid concentration. According to the hydration interpretation, the increase in f_{BH^+} and f_{ROH} with increasing acid concentration would be attributed to decreasing hydration and hence decreasing solubility. For the ideal h_0 equation, the sign in front of the hydration number for BH^+ is negative in the exponent of the activity of water term; for the corresponding equation for the H_R function, the sign in front of the hydration number of ROH is positive, which on the basis of consideration of hydration only would indicate that the true picture for the hydration number of the proton might be between that predicted by ideal H_0 and H_R equations. However, when the same arguments are applied to Boyd's data for the H_- indicators, one concludes that the n' values obtained from H_0 are too large.

Finally, the maximum in n' was examined from the standpoint of perhaps most widely accepted model

for the structure of water, the "flickering cluster" model of Frank and co-workers,[43,44] which proposes that on a time average, water consists of large clusters and monomeric water only. We are suggesting that the critical concentration of electrolyte required to make the clusters vanish is reached near the point where the maximum in n' is observed. There is a slight but definite shoulder in a plot of a_{H_2O} vs. concentration of acid, which shows up clearly as a minimum when a second derivative of the curve is obtained. The negative of this second derivative, as well as values of n, as function of acid concentration, are shown in Fig. 6. The maximum in the two curves occurs at the same concentration within experimental error.[45] Frank and co-workers have shown that the formation of water cluster is a cooperative phenomenon, with formation of one hydrogen bond facilitating the formation of the next. Therefore, it is perhaps not surprising that clusters might disappear rather abruptly at a critical concentration of electrolyte. Whether the maximum in n is a real phenomenon, it does indicate a drastic change in the properties of the solution at 2 ± 1 M sulfuric acid. This is also supported by the observation that there is a sharp discontinuity in the second derivative of ion conductivity as a function of acid concentration at 1 M acid.[46] Partial molal heats of solution of organic bases pass through a minimum near 3 M H_2SO_4, independent of the strength of the bases.[47]

General Discussion.—Of the hydration models which have been proposed to date for more dilute acid, none has previously proposed that the proton hydration number may pass through a maximum. Bascombe and Bell[15] assumed a fixed proton hydration number of 4; largely because of this, their model fails above 8 m acid. It would appear that in some cases, the importance of $H_9O_4^+$ has been over-emphasized. Wicke, Eigen, and Ackermann,[12] who originally discussed $H_9O_4^+$, showed that additional hydration occurs involving on the average 3.7 to 1.5 water molecules

(41) P. T. McTigue, *Trans. Faraday Soc.*, **60**, 127 (1964).
(42) R. H. Boyd, *J. Am. Chem. Soc.*, **85**, 1555 (1963).

(43) H. S. Frank and W.·Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).
(44) H. S. Frank and A. S. Quist, *J. Chem. Phys.*, **34**, 604 (1961).
(45) The second derivative of the activity of water curve was estimated from second differences on data quoted for integer molalities.[26]
(46) S. U. Pickering, *J. Chem. Soc.*, **57**, 64 (1890).
(47) E. M. Arnett, unpublished results.

for the temperature range 0–100°. Bascombe and Bell also assumed that $f_{H_3O_4^+} = f_{BH^+}$ and that the value of f_B is given by a Setschenov salting-out equation, $\log f_B = 0.1\ M$. However, Boyd[42] has shown that f_B is decreasing above 2 M acid and is negative above 4 M acid. It therefore follows that our hydration model, which applies no correction for the $f_{H^+(H_2O)_n}$·f_B/f_{BH^-} factors, should be more satisfactory above 4 M acid. It is worthy of note that in our treatment, the use of h_0 data corrected for the activity coefficient of the uncharged base from Boyd's results still leads to a predicted maximum in n at the same acid concentration, although the value of n is reduced.

It may be possible at the present time to account for the observed differences in proton hydration numbers predicted by the various acidity functions in terms of differences in the hydration of the various indicators that are involved. However, there is some evidence which cautions us in this regard. The proton hydration numbers predicted from Raoult's law above 4 M sulfuric acid are most comparable, of the hydration numbers obtained from the models discussed above, with those obtained by treatments which do not rely upon acidity function data.[13,14,48] Below this concentration, precisely in the region where Raoult's law might be expected to be most nearly correct, negative hydration numbers are predicted. In dilute sulfuric acid, the apparent proton hydration numbers obtained from h_0 data appear more reasonable than those obtained from other acidity functions. However, a treatment of indicator hydration indicates that the apparent hydration numbers from h_0 are likely to be too small, whereas a correction based on Boyd's f_B data indicates that the numbers are too large. It may be possible shortly to apply reasonable corrections for single ion activity coefficients.[49,50] However, at present, somewhat arbitrary assumptions must be made,[42] which makes impossible interpretation of results in an unequivocal fashion.

Solvation by solvent cages which involve no specific points of water attachment is undoubtedly important in some cases.[51] For the H_R indicators, removal of OH^- leads to a change in configuration at the carbon atom to which it was attached. The resultant planar ion might be solvated entirely by a solvent cage. The H_R function is markedly dependent upon the anion which is present,[18,52] just as the Setschenov

(48) B. E. Conway and J. E. Desnoyers, *Phil. Trans. Roy. Soc. London,* in press.

(49) H. S. Frank, *J. Phys. Chem.,* **67,** 1554 (1963).

(50) R. M. Noyes, *J. Am. Chem. Soc.,* **86,** 971 (1964).

(51) H. S. Frank and M. W. Evans, *J. Chem. Phys.,* **13,** 507 (1945).

(52) E. Högfeldt, *Acta Chem. Scand.,* **16,** 1054 (1962).

factors for benzene are markedly dependent upon the nature of the electrolyte.[53] It is not possible at the present time to predict how solvent cages affect calculations of apparent hydration numbers.

Finally, the problem with all hydration models is that they emphasize the importance of hydration to the possible exclusion of other effects. Thus Wyatt has accounted quantitatively for the acidity of concentrated sulfuric acid solutions on the basis of H_3O^+ and $H_5O_2^+$. We are able to perform the same feat using H_3O^+, $H_5O_2^+$, and $H_7O_3^+$ on a revised h_0 scale. Similarly, "quantitative" models for dilute acid solutions are not unique. In all cases, other factors of importance might be neglected.

6. Conclusions

The model which we have outlined can explain the observed acidity of sulfuric acid solutions quantitatively over the 0.1–1000 m range. It is shown that a multispecies program is superior to a model which is based upon only one proton hydrate species being present in any given solution. However, the proton hydrate concentrations which are obtained are not unique. It would appear clearly established that specific hydration is a predominant factor in determining the behavior of electrolytic solutions, but the extent that nonspecific interactions with solvent is important, particularly for organic molecules, remains to be established. Of the acidity functions studied here, the h_0 function predicts the most reasonable proton hydration numbers in dilute solution. This does *not* mean that it deserves *a priori* attention for any other purpose, however. The recently determined acidity functions for tertiary amines[38] and amides[54] emphasize clearly that each class of compounds might be expected to have its own unique acidity function.

Whether the maximum predicted for the average hydration number of the proton at 2 ± 1 M sulfuric acid is a real effect, it indicates that drastic changes in the solution are occurring in this region, an observation supported by a wide variety of evidence. The maximum can be interpreted to indicate that, in the 0–2 M acid region, the balance between the structure-breaking effect of acid on the large clusters of water molecules, and the tendency of the ions to hydrate, favors an increasing hydration number of the proton with increasing acid concentration and that, beyond 2 ± 1 M sulfuric acid, clusters of water molecules are nonexistent.

(53) F. A. Long and W. F. McDevit, *Chem. Rev.,* **51,** 119 (1952).

(54) K. Yates, J. B. Stevens, and A. R. Katritzky, Abstracts, 47th Canadian Chemical Conference, Kingston, Ontario, 1964.