Using these data the absolute entropy of $MgCd_3$ at 270° is found to be 16.12 e.u./g. atom. The present measurements together with published C_p data[18] for temperatures above 320°K. permit the calculation of $S_{270°} - S_{0°K}$ for $MgCd_3$. The above room temperature data extend to only 430°K. and must be extrapolated for about 110°. Ordinarily such an extrapolation would be rather questionable. In this case C_p is almost constant for the upper 70° on the measured curve so the extrapolation is probably fairly reliable. $S_{270°} - S_{0°K.} =$ 15.91 e.u./g. atom, of which approximately 1.2 e.u./g. atom is from the extrapolation above 430°K. Comparing the entropy gain between 0°K. and 270° with the absolute entropy at 270°, one sees that $S_{0°K.} = 0.21$ e.u./g. atom. Similar calculations for Mg_3Cd were made, but existing heat capacity data above 50° are so divergent that no significance could be attached to the results obtained.

The residual entropy in $MgCd_3$ can be accounted for if the number of Schottky defects observed[16] at 25° continue to exist at the absolute zero and are randomly distributed over the lattice sites. The number of Schottky defects at 25° is 1.7%. The entropy associated with these defects when randomly distributed is simply the ideal entropy of mixing. This calculates to be 0.17 e.u./g. atom. Experimentally, $S_{0°K.} = 0.21$ e.u./g. atom with a probable error of 0.07 e.u./g. atom, neglecting error in ΔS for the extrapolated region between 430° and 543°K. Thus, the observed residual entropies agree within the limit of error with the value calculated as mentioned. This agreement, while interesting, must be viewed with caution until direct experimental verification is forthcoming that: (1) the number of Schottky defects observed at 25° remain at reduced temperatures and (2) the composition of the superlattice is exactly 75 atomic per cent. cadmium, an assumption involved in arriving at the number of lattice imperfections.

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[18] K. G. Khomyakov, V. A. Kholler and V. A. Troshkina, *Vestnik Moskov Univ.*, *No.* **6**, *Ser. Fiz-Math. i Estest. Nauk No.* **4**, **5**, 43 (1950).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Concentrated Sulfuric Acid–Water

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RECEIVED MAY 18, 1953

The H_0 function of Hammett can be precisely evaluated from 83–99.8% (wt.) sulfuric acid and the activity of water can be estimated to a reasonable agreement with experiment from 83 to at least 95% acid. The method assumes that the reaction $H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$ is of primary importance in determining the properties of these solutions and a mole fraction equilibrium constant of 50 is shown to be applicable for this reaction over the entire range 83 to 99.8% sulfuric acid. These results are interpreted on the basis that the activity coefficients involved approach constancy in 83–99.8% sulfuric acid solutions. This ideal behavior is attributed to the high dielectric constant and similarity of the medium to that of fused salts. Several applications to reaction rates studied in the H_2SO_4–H_2O system are made. The rate data support the validity of the conclusions reached.

Calculation of H_0.—Brand[1] has shown that the Hammett acidity function,[2] H_0, in the region 90–99.8% sulfuric acid can be calculated by eq. 1

$$H_0 \text{ (calcd.)} = -8.36 + \log X_{HSO_4^-}/X_{H_2SO_4} \quad (1)$$

The ratio of the mole fractions $X_{HSO_4^-}/X_{H_2SO_4}$, are obtained from the stoichiometric amounts of water and sulfuric acid assuming that reaction 2 is complete. This assumption is in close agreement with the Raman spectra work of Young,[3] who found that

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad (2)$$

in this region, the addition of each mole of water gave one mole of bisulfate ion.

Since equimolar water–sulfuric acid corresponds to 84.5% acid, it seemed surprising to us that eq. 1 would fail from 85–90% acid unless reaction 2 was substantially incomplete.

We have found that the calculation of the H_0 function by eq. 1 can be extended with excellent precision to the region 89–83% sulfuric acid if a mole fraction equilibrium constant, K_2, of 50 is assumed to be valid for reaction 2 over this region. In Table I the observed values of H_0 are compared with values calculated from eq. 1 assuming reaction 2 to be complete (Brand's method[1]) and values calculated from eq. 1 using $K_2 = 50$.

On the basis that observed H_0 values are accurate to 0.05 unit, the value 50 for K_2 is precise to ±10, since the H_0 values calculated by eq. 1 do not fit experimental values within this limit when larger or smaller values of K_2 are used to calculate the $X_{H_2SO_4}/X_{HSO_4^-}$ ratio. For example, a value of $K_2 =$ 40 leads to a deviation of 0.08 between calculated and observed H_0 values for 84.5% acid, the acid concentration for which calculated values are most sensitive to the value of K_2 used.

The following alternate equation can be used for the computation of H_0

$$H_0 = -6.66 + \log X_{H_2O}/X_{H_3O^+} \quad (3)$$

Equations 1 and 3 are equivalent by virtue of the mole fraction equilibrium constant for reaction 2 which can be written in the form

$$\log \frac{X_{HSO_4^-}}{X_{H_2SO_4}} - \log \frac{X_{H_2O}}{X_{H_3O^+}} = \log K_2 = 1.70 \quad (4)$$

In a later section $\log f_{H_2O}$ is evaluated, where f is the activity coefficient. Reference to Table III

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[1] J. C. D. Brand, *J. Chem. Soc.*, 1002 (1950).

[2] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

[3] T. F. Young, *Rec. Chem. Progress*, spring issue (1951).

TABLE I

COMPARISON OF CALCULATED AND OBSERVED VALUES OF H_0

	$-H_0$			
H_2SO_4, %	Obsd.[a]	Brand's method	Calcd. Eq. 1 or 3 with $K_2 = 50$	Eq. 5
99.8	10.27	10.32	Same as column 3	Same as column 4
99.5	9.91	9.91		
99.2	9.76	9.70		
99.0	9.61	9.60		
98	9.26	9.27		
97	8.97	9.05		
96	8.89	8.90		
95	8.75	8.76		
94	8.64	8.64		
93	8.54	8.52		
92	8.41	8.41		
91	8.31	8.29		
90	8.19	8.18		
89	8.08	8.05	8.07	
88	7.94	7.90	7.97	
87	7.84	7.72	7.85	
86	7.69	7.46	7.71	
85	7.60	6.97	7.58	
84	7.48		7.45	
83	7.32		7.32	7.32
82	7.17		7.21	7.18
81	7.01		7.12	7.02
80	6.85		7.03	6.85
79	6.71		6.96	6.69
78	6.56		6.93	6.61
77	6.43		6.86	6.49
76	6.29		6.80	6.38
75	6.16		6.75	6.28
74	6.03		6.70	6.18
71.53	5.67		6.59	5.95

[a] *Cf.* ref. 2.

will show the striking fact that the region in which $\log f_{H_2O}$ is constant (83–99% acid) is the same region that eq. 3 is valid.

If eq. 3 is corrected for the rapidly changing value of $\log f_{H_2O}$ below 83% acid, eq. 5 is obtained

$$H_0 = -6.66 + \log \frac{X_{H_2O}}{X_{H_3O^+}} + 1.67 + \log f_{H_2O} \quad (5)$$

In Table I the last column shows that this equation accurately evaluates H_0 from 79–99.8% sulfuric acid. In addition it is not in error by more than 0.1 H_0 unit down to 75% acid.

Calculation of the Activity of Water.—In Table II it is demonstrated that from 83–95% sulfuric acid, $\log a_{H_2O}$ can be calculated from the relation

$$\log a_{H_2O} = \log X_{H_3O^+} + H_0 + 5.00 \quad (6)$$

The constant, 5.00, is an empirical constant whose value was chosen to give a best fit between observed values of $\log a_{H_2O}$ and values calculated by eq. 6. This equation is essentially a rearranged form of eq. 5. In using eq. 6, $X_{H_3O^+}$ can be estimated simply from stoichiometric amounts of water and sulfuric acid for the region above 90%. Below 90%, this and $K_2 = 50$ are used.

The experimental values for $\log a_{H_2O}$ in Table II were obtained by two methods. In method I, applicable from 74–98% acid, the vapor pressure data of aqueous sulfuric acids measured at temperatures in the region 150–280°[4,5] were extrapolated to 25° using the Clausius–Clapeyron equation. To make this lengthy extrapolation as objective as possible, the original data were fitted to linear functions by the method of least squares.

Method II employed directly the data of Shankman and Gordon[6] for activities of water at 25° in sulfuric acids up to 68.94%. From 69–86% acid $\log a_{H_2O}$ was obtained by an extrapolation using an empirical formula given by the above authors.

TABLE II

COMPARISON OF CALCULATED AND OBSERVED VALUES OF LOG a_{H_2O}

			Log a_{H_2O}		
			Calcd.	Measured	
H_2SO_4, %	Log $X_{H_3O^+}$	H_0		Method I	Method II
98.06	−1.012	−9.30	−5.31	−5.50[a]	
95.94	− .727	−8.88	−4.61	−4.85[b]	
95.06	− .657	−8.76	−4.42	−4.48[a]	
91.26	− .465	−8.33	−3.80	−3.80[a]	
91.01	− .456	−8.30	−3.76	−3.68[b]	
88.40	− .401	−8.00	−3.40	−3.23[b]	
86.61	− .371	−7.78	−3.15	−3.12[b]	−3.19
85.14	− .360	−7.62	−2.98	−2.81[b]	−2.95
83.00	− .364	−7.34	−2.70		−2.64
81.15	− .380[c]	−7.03	−2.41[c]	−2.56[b]	−2.40
78.50	− .396[c]	−6.60	−2.00[c]	−2.04[b]	−2.09
77.26	− .415[c]	−6.42	−1.91[c]	−1.99[b]	−1.96
74.36	− .460[c]	−6.08	−1.58[c]	−1.78[b]	−1.69
71.53	− .500[c]	−5.67	−1.21[c]		−1.46
68.94	− .538[c]	−5.40	−0.98[c]		−1.27
66.95	− .567[c]	−5.14	−0.75[c]		−1.14

[a] Vapor pressure data of Thomas and Barker (ref. 4). [b] Vapor pressure data of Burt (ref. 5). [c] The calculation of these values by the method indicated is not strictly valid since K_2 appears to increase below 83% acid. However, the errors introduced are quite small since below 83% acid the calculation of $X_{H_3O^+}$ becomes increasingly less sensitive to the value of K_2 used.

The average deviation between calculated and measured values of $\log a_{H_2O}$ is 0.05 using the values by method II whenever possible. If one point at 88.4% acid is neglected, the average deviation becomes 0.03. However, the average deviation between the two experimental methods for $\log a_{H_2O}$ is 0.09 in the region in which they overlap. It is thus evident that eq. 6 cannot be given a precise test at present. The deviations between observed and calculated values of $\log a_{H_2O}$ are somewhat greater at 96 and 98% sulfuric acid. However, this may not be significant because the experimental values are in greatest error in this region.

A second independent method of determining K_2 can now be made from the constants 8.36 of eq. 1, 5.00 of eq. 6, and $\log f_{H_2O}$. The relationship between $\log K_2$ and the above constants is obtained by combining eq. 1 and 6, so that

$$-8.36 + \log \frac{X_{HSO_4^-}}{X_{H_2SO_4}} = \log a_{H_2O} - \log X_{H_3O^+} - 5.00 \quad (7)$$

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(4) J. S. Thomas and W. F. Barker, *J. Chem. Soc.*, **127**, 2820 (1925).

(5) B. C. Burt, *ibid.*, **85**, 1339 (1904).

(6) S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939).

and thus

$$\log K_2 = \frac{X_{H_3O^+}X_{HSO_4^-}}{X_{H_2O}X_{H_2SO_4}} = 8.36 - 5.00 + \log f_{H_2O}$$

The constants 8.36 and 5.00 can be evaluated solely from data above 90% sulfuric acid and are therefore not dependent on the value of log K_2 obtained originally.

To obtain a value of log f_{H_2O} which is independent of the previously selected value of log K_2, the following procedure was used. Reaction 2 was provisionally assumed to be complete in 83% sulfuric acid; this permits one to obtain a first approximation for log X_{H_2O} simply from the stoichiometry. Together with the log a_{H_2O} value from Table III a first approximation of 1.43 can be obtained for log f_{H_2O}. This value can be substituted in the above equation to obtain a first approximation for log K_2. A series of two successive approximations leads to limiting values of 1.66 for log f_{H_2O} and 1.69 for log K_2. The latter is in excellent agreement with the value 1.70, which was obtained originally from the best fit of observed H_0 values and those calculated by eq. 1 or 3 in the region 83–89% sulfuric acid.

Freezing Point of Water–Sulfuric Acid.—Kunzler and Giauque[7] have made accurate measurements of the freezing point of water–sulfuric acid solutions particularly in the equimolar region. In this system the solvent may be considered to be hydronium bisulfate (H_3O^+—HSO_4^-) and the foreign solute to be water and sulfuric acid. If we use the value of K_2 (50) to evaluate the mole fraction of foreign particles, the freezing point may be estimated. Using the following simple formula with values of 86.1 for k and 10.65 for T_0, the data of Kunzler and Giauque from 83.4 to 86.9% acid may be fitted with an average deviation of 0.01° for the m.p. ranges 8.00 to 8.489° and 8.489 to 5.80°.

$$T_0 + \theta = k(X_{H_2O} + X_{H_2SO_4}) \qquad (8)$$

T_0 is the difference between the observed freezing point of equimolar water–sulfuric acid and the hypothetical freezing point that would obtain if no self-dissociation occurred. θ is the observed freezing point depression.

We have chosen the values of k_1 and T_0 in eq. 8 which gave the best fit for the data. Data below 83% acid were not considered because the activity coefficient for water is no longer constant (Table III). Above 86.9% acid eq. 8 does not fit with this precision. The problem is complicated by the fact that the solvent is not a single chemical species but a mobile equilibrium. Under these circumstances the heat of fusion is variable.[8] It changes with addition of water or sulfuric acid and with change in temperature.

In spite of these objections and the additional fact that the calculation of θ by eq. 8 with adjustable parameters k and T_0 is rather insensitive to the value of K_2 used to calculate mole fractions, we feel the present correlation of the freezing point data is at least consistent in order of magnitude with our K_2 value and the conclusions drawn in the next section.

Activity Coefficients.—By virtue of the relationships[9]

$$\log K_1 = \log \frac{a'_{H^+}a_{HSO_4^-}}{a_{H_2SO_4}} \text{ and } a = fX \qquad (8a)$$

and the definition of H_0

$$H_0 = -\log a_{H^+} - \log \frac{f_B}{f_{BH^+}} = -\log K_{BH^+} + \log \frac{X_B}{X_{BH^+}} \qquad (9)$$

the condition of eq. 1 that H_0 quantitatively parellels log $X_{HSO_4^-}/X_{H_2SO_4}$ from 90–99.8% sulfuric acid requires that

$$\frac{f_{HSO_4^-}f_{BH^+}}{f_{H_2SO_4}f_B} = \text{constant} \qquad (10)$$

Further, the fact that the use of log K_2 = 1.70 for the range 83–89% acid permits an estimation of the $X_{HSO_4^-}/X_{H_2SO_4}$ ratio which extends the validity of eq. 1 throughout this range, requires by virtue of the equilibrium expression for reaction 2 the condition

$$\frac{f_{H_3O^+}f_{HSO_4^-}}{f_{H_2O}f_{H_2SO_4}} = \text{constant} \qquad (11)$$

Since both eq. 10 and 11 are markedly invalid in more dilute sulfuric–water solutions (where individual f's are known to vary with acid concentration), and since these equations would necessitate a cancellation of activity coefficient ratios involving species of different charge types, the validity of these equations seems reasonable to us only on the basis that individual f's are also constant in the region 83–99.8% sulfuric acid. Since the species involved in Eqs. (10) and (11) are not unique, one might conclude that activity coefficients for any species in the region 83–100% sulfuric acid approach constancy. This conclusion is certainly not true for such non-electrolytes as hydrogen chloride, air, sulfur dioxide, methyl chloride, and isobutane as shown by their variable distribution ratios between the vapor state and 85–100% sulfuric acid. On the other hand several investigators have concluded that activity coefficients are constant based on (1) cryoscopic work in 99–100% sulfuric acid,[10] (2) computation of H_0 in 90–100% acid and (3) the solubility of barium sulfate in 94–100% acid.[10] We are therefore faced with a considerable uncertainty as to the type of species which have constant activity coefficients in the region 83–99.8% sulfuric acid, but it appears most likely for ions, questionable for polar non-electrolytes, and definitely not true of non-polar non-electrolytes.

It is readily apparent from eq. 9 that our interpretations of relations 10 and 11 require that the H_0 function in 83–99.8% sulfuric acid is a quantitative measure of the change of proton (H^+ not H_3O^+) concentration with wt. % H_2SO_4. It also follows that K_2 is a thermodynamic equilibrium

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(7) J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 5271 (1952).

(8) P. A. H. Wyatt, *J. Chem. Soc.*, 1175 (1953).

(9) The log a'_{H^+} term in eq. 8a is not identical with the log a_{H^+} term in eq. 9, but differs from it by a constant. This non-identity has arisen as a result of the fact that we have used activities on a mole fraction basis whereas the identification of the H_0 scale with the *p*H scale in infinitely dilute aqueous acid solutions has resulted in the condition $a_{H^+} \rightarrow M_{H_3O^+}$, where M is molarity. The constant difference between log a'_{H^+} and log a_{H^+} therefore involves both log 55.5 and log K_{H^+}, where K_{H^+} is the thermodynamic constant for the reaction $H_2O + H^+ \rightleftarrows H_3O^+$.

(10) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

constant based upon 83–99% sulfuric acid as the standard state. To obtain the value based upon water as the standard state it would be necessary to know the value of the H_0 function at 83% acid which has not yet been measured.

The ideal behavior of these solutions is probably a result of the high dielectric constant for sulfuric acid[11] coupled with the similiarity of these systems to those of fused salts, which are known to closely approximate ideal behavior.[12] It is also reasonable to expect because of the similarity of oxygen atoms in sulfuric acid and in the hydrogen sulfate ion that replacement of one by the other does not markedly alter the environment created by the solvent. It seems quite likely that the ideal behavior exhibited by concentrated sulfuric acid solutions will also be shown by concentrated aqueous solutions of other strong acids and bases.

The failure of eq. 3 below 83% acid indicates that eq. 11 is invalid in this region and the K_2 increases with increasing acid dilution. In the region 83–79% acid the failure of eq. 11 and 3 is apparently caused only by the fact that activity coefficient for water changes (see next section and eq. 5 of the first section).

Since eq. 3 corresponds to the general definition of the H_0 function,[2] *cf.* eq. 9, it is important to consider why it fails below 83% sulfuric acid. The generality of the H_0 function depends on the term log f_B/f_{BH^+} being independent of the indicator used. This was demonstrated using a series of rather large organic molecules as indicators in the water–sulfuric acid system.[2,13] However, the determinations were all made spectroscopically so that the indicators were in very low concentration (around 10^{-4} *M*). In the H_2SO_4–H_2O system the concentrations of the base-conjugate acid pair, H_2O–H_3O^+, are large. Since the log f_B/f_{BH^+} has been shown recently to be independent of B even for small molecules such as isobutene[14] and β-propiolactone[15] at low concentrations, it seems likely that the large concentration of H_2O and H_3O^+ are responsible for the failure of eq. 3 below 83% acid, and not a specific property of the water molecule.

Activity Coefficient of Water.—The values of log X_{H_2O} calculated from the stoichiometric mole fractions of water and sulfuric acid using K_2 = 50, together with corresponding values of log a_{H_2O} from Table II lead to values for the logarithm of the activity coefficient, log f_{H_2O}

$$\log f_{H_2O} = \log a_{H_2O} - \log X_{H_2O}$$

Values so obtained are listed in Table III. The results confirm at least with respect to water, the conclusion of the previous section, that the activity coefficient is constant above 83% acid. Log f_{H_2O} approaches the limiting value, 1.67 ± 0.01, at 83% acid. Although the values of log f_{H_2O} below 83% acid are strictly only approximate (see footnote of Table III), the data indicate that most of the change in log f_{H_2O} from 1.67 to zero (log $f_{H_2O} \rightarrow 0$ as $X_{H_2O} \rightarrow 1$) occurs from 82–50% sulfuric acid.

TABLE III

CALCULATION OF LOG f_{H_2O}

H_2SO_4, %	Log a_{H_2O}[a]	Log X_{H_2O}[b]	Difference ($-\log f_{H_2O}$)
95.06	−4.42	−2.762	1.66
91.26	−3.80	−2.128	1.67
88.40	−3.40	−1.710	1.69
86.61	−3.15	−1.503	1.65
85.14	−2.98	−1.300	1.68
83.00	−2.70	−1.026	1.67
81.15	−2.41	−0.850	1.56
78.50	−2.09	− .705	1.38
77.26	−1.96	− .636	1.32
74.36	−1.69	− .516	1.18
71.53	−1.46	− .434	1.03
68.94	−1.27	− .375	0.89
66.95	−1.14	− .339	.80
59.73	−0.778	− .242	.54
55.15	−0.619	− .202	.42
52.42	−0.524	− .178	.35
49.85	−0.451	− .160	.29

[a] For values at 81.15% acid and above, we have used our calculated values of log a_{H_2O} given in Table II. Values at acid strengths below 66.95% were taken directly from the data of Shankman and Gordon (ref. 6). Between 66.95 and 81.15% acid, log a_{H_2O} calculated by Method II was used. [b] The method used to estimate X_{H_2O} values below 83% acid is not strictly correct. Since K_2 appears to increase below 83% acid, the value 50 is not strictly applicable. Fortunately, however, the region below 83% acid is one in which water is stoichiometrically in excess of H_2SO_4, and therefore as acid dilution increases the values calculated for X_{H_2O} become increasingly less sensitive to the value of K_2 used. For example, the value of log f_{H_2O} calculated for 81% acid assuming $K_2 = \infty$ is 1.49 compared with the value 1.56 obtained using K_2 = 50; for 77% acid, corresponding values are 1.31 and 1.32. Since the actual value of K_2 cannot be greatly different between 77–83% acid, the value 50 therefore permits estimates of log X_2 of sufficient precision for present purposes. This is confirmed by the agreement between observed values of H^0 and those calculated by eq. 5—see Table I, 79–83% acid.

Application to Rate Problems

The H_0 Function.—The conclusions reached above have an important bearing on the relation of kinetics to the acidity function, H_0. For example, Hammett[16] has shown that in the rate of decomposition of oxalic and citric acids, a plot of log *k vs.* H_0 is linear with slope equal to −2. This was interpreted to mean that reaction proceeds through the reversible equilibrium $S + 2H^+ = SH_2^{++}$ with the decomposition of SH_2^{++} as the rate-controlling step.

However, for this interpretation to be valid, it can be shown from the definition of H_0 and the Brönsted rate equation[17] that it is also necessary that

$$f^2_{BH^+}f_s/f^2_Bf_{X^{++}} = \text{constant}$$

where X^{++} represents the reaction transition state). Since it is doubtful that the above equation is generally valid even in the water–sulfuric acid system, the success of Hammett's interpretation

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(11) J. C. D. Brand, J. C. James and A. Rutherford have reported a value of 110 (*J. Chem. Phys.*, **20**, 530 (1952)).

(12) R. P. Seward, THIS JOURNAL, **67**, 1189 (1945).

(13) That this may not be true for other solvent systems, particularly with low dielectric constants and/or low ionic strengths, has been demonstrated by Grunwald, *et al.*, THIS JOURNAL, **75**, 565 (1953).

(14) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952).

(15) F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 284.

(17) *Cf.* ref. 16, p. 127.

appears to be the result of the fact that the kinetics were measured in the region 83–100% sulfuric acid where these activity coefficients approach constancy.

It is also obvious that the Hammett theory for explaining the dependence of rates of acid-catalyzed reactions upon the acidity function, h_0 (antilog of H_0) or the hydronium ion concentration[14,15,18] cannot be applied in the region 83–100% sulfuric acid, for this interpretation depends upon the activity coefficients of the transition states, f_{SH^+} and $f_{SOH_3^+}$ being different functions of acid concentration (S represents the substrate in the acid catalyzed reaction).

The J_0 Function.[19]—The calculation of H_0 and $\log a_{H_2O}$ is in effect also a calculation of the J_0 function of Gold and Hawes.[19] These authors defined J_0 by eq. 12 and showed that the ionization of two triarylcarbinols followed this function in agreement with the theory that they ionized to carbonium ions. One of us has found that a number of other carbinols also follow this function in their ionization.

$$J_0 = H_0 + \log a_{H_2O} \qquad (12)$$

To our knowledge the only previously recognized example of acid-catalyzed kinetics giving a linear plot of unit slope for log *k vs.* J_0 is the rate of nitration of benzene studied by Westheimer and Kharasch (discussed in ref. 19). We have noted another example of a linear plot of essentially unit slope (0.99 ± 0.07; median deviation 0.03 log unit) for log *k vs.* J_0 in the rates of decarbonylation of triphenylacetic acid which were obtained by Dittmar.[20] The rate data at 22° and a demonstration of this correlation are summarized below

H_2O, %	4.00	5.00	6.00	7.00
log K	− 0.90	− 1.11	− 1.50	− 1.74
J_0 (calcd.)	−13.50	−13.17	−12.88	−12.62
$-(J_0 + \log k)$	14.40	14.28	14.38	14.36

This result is consistent with a mechanism in which protonation of triphenylacetic acid leads to a reversible equilibrium with the oxocarbonium ion, which then loses carbon monoxide in the rate-determining step

$$(C_6H_5)_3C—COOH + H^+ = H_2O + (C_6H_5)_3C—CO^+ \qquad \text{equilibria}$$

$$(C_6H_5)_3C—\overset{+}{C}O = (C_6H_5)_3C^+ + CO \qquad \text{rate determining}$$

This interpretation removes the necessity of attempting to interpret the non-integral slope in a plot of log *k vs.* H_0.[21] Triphenylacetic acid is thus exceptional among the acids studied[21] in its mechanism of decarbonylation, preferring to ionize to the oxocarbonium ion rather than to its conjugate acid, $RCOOH_2^+$. This behavior is related to the ionization of 2,6-dimethylbenzoic acids to oxocarbonium ions.[10] These acids characteristically ionize to oxocarbonium ions and thus change the coördination number of carbon from three to two which reduces the repulsive forces around the highly crowded carboxyl group.

The Molecular Sulfuric Acid Concentration.—Sommer, *et al.*,[22] found recently that in the reaction of β-trimethylsilylpropionic acid with sulfuric acid to form methane, a plot of first-order constants, k_1, *vs.* molarity of molecular H_2SO_4 was linear from 97–89% sulfuric acid. The molarity of molecular H_2SO_4 was calculated by assuming that reaction 2 is complete. Dr. Sommer has very kindly provided us with rate data for this reaction in 89–85% sulfuric acid. In this region, the above plot shows increasingly severe deviation from linearity.

However, when the values of k_1 are plotted against the molecular H_2SO_4 concentration calculated using K_2 = 50 for reaction 2, an excellent linear plot is obtained throughout the range 85–97% sulfuric acid. Even though the rate data were obtained at 20° and K_2 has been estimated from data at 25°, this result provides striking confirmation of our value of K_2 within the limits of precision indicated in an earlier section. Table IV contains a relevant summary of the data.

Table IV

Rates of Methyl Cleavage of β-Trimethylsilylpropionic Acid in Sulfuric Acid Solutions at 20°

H_2SO_4, %	$k_2 = k_1/M$ of H_2SO_4 Method A[a]	 Method B[b]
90–97	1.32[c]	1.32[c]
89	1.40	1.30
88	1.50	1.32
87	1.54	1.20
86	2.06	1.26
85	4.80	1.30

[a] The molarity of H_2SO_4 was calculated on the basis that reaction 2 is complete, *cf.* ref. 21. [b] The molarity of H_2SO_4 was calculated on the basis of K_2 = 50 for reaction 2. [c] This is an average value for the 10 points obtained in this region. The average deviation is 0.09.

Acknowledgment.—We would like to acknowledge the assistance of Dr. Leo Sommer, who drew our attention to the present problem and contributed in discussions. We are also pleased to acknowledge the helpful comments of Drs. L. P. Hammett, F. A. Long, M. Paul, R. Seward, A. W. Davidson and E. Grunwald in the preparation of this manuscript.

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