

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Activity of Each Component in Aqueous Solutions of Sulfuric Acid and Acetic Acid¹

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Introduction

The theory of Debye has become a highly useful guide in the study of the thermodynamic properties of solutions of electrolytes; it not only relates the activity of the electrolytes to the ionic strength of the solution but also makes predictions as to the activity of the non-electrolytes that are present. An aqueous solution of sulfuric acid and acetic acid contains one strong electrolyte; the other two components may be considered to exist almost entirely in un-ionized forms. The experimental work to be described in this paper led to a determination of the activity of each component of the system. It seemed worth while to test the applicability of the theory of Debye to this ternary system. The first part of the work consisted of electromotive force measurements which gave the activity of the sulfuric acid; the second part was devoted to vapor pressure measurements from which the activities of the water and the acetic acid could be calculated.

Experimental Work, Part I

Electromotive Force Measurements.—E. m. f. measurements were made on cells of the type



where HA stands for acetic acid. The various solutions used in these cells were made by dilution with redistilled water of standard solutions of sulfuric acid and of acetic acid. The standard sulfuric acid solutions were analyzed gravimetrically, the acetic acid solutions were analyzed by weight titration with barium hydroxide which had been standardized against a solution of hydrochloric acid. The strength of the hydrochloric acid solution was determined gravimetrically. The densities at 25° of all solutions used in making up the cells were determined by means of specific gravity bottles. The hydrogen used in these experiments came from tanks and was purified by being passed through concentrated silver nitrate, concentrated potassium permanganate in sulfuric acid, a solution of pyrogallol in concentrated potassium hydroxide and finally distilled water.

The hydrogen electrode apparatus was essentially the same as that described by Lewis, Brighton and Sebastian,² except that instead of one

(1) This paper gives the essential portions of the thesis presented by D. R. Blumer to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2249 (1917).

tube leading to the mercury electrode, there were three tubes, each with a stopcock, so that any one of three mercury electrodes could be put into the circuit with a given hydrogen electrode. The mercurous sulfate used in these experiments was prepared electrolytically.³ Two S-shaped sheets of platinum each about 2 cm. by 2.5 cm. were welded by means of a platinum weld to heavy platinum leads which were sealed into soft glass stoppers having ground-glass joints so that the two electrodes could be used interchangeably in the gas chamber of the apparatus. These electrodes were platinized according to the method recommended by Harned.⁴

After the system had apparently come to equilibrium, five to ten readings of the e. m. f. were made over a period of an hour with a given hydrogen electrode and a given mercury electrode and the average of these values was calculated. Then similar readings were made with each of the other mercury electrodes. Finally the second hydrogen electrode was in-

TABLE I

C_1, C_2 denote moles per liter of solution; E is the e. m. f. in volts

Soln.	C_1 (H_2SO_4)	C_2 (HA)	Density	E	Soln.	C_1 (H_2SO_4)	C_2 (HA)	Density	E
1	0.0502	0.0991	1.0022	0.7540	30	0.2738	1.369	1.0252	0.7061
2	.0480	.9454	1.0102	.7515	31	.5458	1.365	1.0418	.6873
3	.0457	1.801	1.0167	.7489	32	1.091	1.366	1.0747	.6653
4	.0417	3.299	1.0268	.7444	33	1.637	1.364	1.1069	.6492
5	.0383	4.538	1.0330	.7404	34	2.177	1.361	1.1385	.6353
6	.0504	0.0	1.0019	.7544	35	0.0546	2.184	1.0178	.7430
7	.1369	.0	1.0060	.7290	36	.1087	2.186	1.0213	.7260
8	.2741	.0	1.0147	.7115	37	.2731	2.184	1.0319	.7027
9	.5472	.0	1.0315	.6929	38	.5478	2.186	1.0483	.6838
10	1.093	.0	1.0648	.6712	39	1.093	2.186	1.0804	.6616
11	1.642	.0	1.0977	.6555	40	1.640	2.186	1.1126	.6449
12	2.184	.0	1.1296	.6418	41	2.184	2.187	1.1440	.6308
13	0.0545	.0991	1.0016	.7517	42	0.0543	3.280	1.0258	.7379
14	.1004	.0991	1.0042	.7367	43	.1089	3.284	1.0293	.7209
15	.1473	.0991	1.0075	.7268	44	.2732	3.279	1.0392	.6979
16	.2008	.0991	1.0105	.7193	45	.5471	3.278	1.0556	.6789
17	.4016	.0991	1.0230	.7012	46	1.091	3.276	1.0875	.6567
18	.8197	.0991	1.0489	.6802	47	1.639	3.278	1.1194	.6398
19	1.642	.0991	1.0983	.6550	48	2.181	3.270	1.1503	.6248
20	3.278	.0991	1.1927	.6153	49	0.0545	4.388	1.0333	.7325
21	0.0547	.5491	1.0052	.7496	50	.1086	4.368	1.0364	.7156
22	.1366	.5487	1.0100	.7269	51	.2729	4.364	1.0466	.6928
23	.2733	.5485	1.0190	.7095	52	.5482	4.382	1.0627	.6734
24	.5453	.5483	1.0356	.6908	53	1.093	4.383	1.0945	.6505
25	1.092	.5475	1.0688	.6690	54	1.643	4.386	1.1261	.6334
26	1.637	.5474	1.1013	.6531	55	2.185	4.369	1.1569	.6181
27	2.179	.5470	1.1331	.6392	56	0.0	1.087	1.0059	
28	0.0546	1.367	1.0116	.7463	57	.0	2.175	1.0145	
29	.1364	1.368	1.0169	.7237					

(3) Hulett, *Phys. Rev.*, **33**, 259-263 (1911).

(4) Harned, *THIS JOURNAL*, **48**, 327 (1926).

serted in place of the first one and the whole set of readings repeated. The final average only of these readings, corrected to a hydrogen pressure of one atmosphere, is given in the tables. As an illustration of the accuracy and reliability of the measurements, we may give here the results with 0.0506 molal sulfuric acid as the cell solution. The values run: 0.75429, 0.75440, 0.75440; 0.75449, 0.75447, 0.75450; 0.75445, 0.75443; the average is 0.75443. For the same cell, Randall and Cushman⁵ obtained 0.7544, 0.7545, 0.7543; average, 0.7544.

In Table I are given density, concentration and e. m. f. data for 55 different solutions. Solutions 56 and 57 were used in vapor pressure measurements.

Discussion of Electromotive Force Measurements

The e. m. f. of our cells (for P_{H_2} , 1 atm.) is given by the expression

$$E = E_0 - \frac{RT}{2F} \log_e (a_{H^+}^2 a_{SO_4^{2-}})$$

If m_1 and C_1 are the molality and molarity, respectively, of sulfuric acid and if x_1 is the "normalized" mole fraction of SO_4^{2-} (*i. e.*, 55.51 times the actual mole fraction) calculated on the assumption that the sulfuric acid is completely ionized and that the acetic acid is completely un-ionized and unassociated, and if γ , γ_c and f are the mean activity coefficients of the sulfuric acid defined as usual with respect to molalities, molarities and mole fractions, respectively, then we may write

$$E = E_0 - \frac{3RT}{2F} \log_e 4^{1/2} m_1 \gamma \quad (1)$$

$$= E_0' - \frac{3RT}{2F} \log_e 4^{1/2} C_1 \gamma_c \quad (1')$$

$$= E_0'' - \frac{3RT}{2F} \log_e 4^{1/2} x_1 f \quad (1'')$$

We have also

$$E_0' = E_0 + \frac{3RT}{2F} \log_e \rho_0 \quad (2)$$

$$E_0'' = E_0$$

where ρ_0 is the density of pure water. If M_1 and M_2 be the formula weights of sulfuric acid and acetic acid, respectively, then

$$\log \gamma = \log f - \log \left[1 + \frac{3m_1 + m_2}{55.51} \right] \quad (3)$$

$$\log \gamma_c = \log f + \log \left[\frac{\rho_0 \left(1 + \frac{m_1 M_1 + m_2 M_2}{1000} \right)}{\rho \left(1 + \frac{3m_1 + m_2}{55.51} \right)} \right] \quad (3')$$

The calculation of the activity coefficient of sulfuric acid by means of equation (1) presupposes a knowledge of E_0 . A conceivable method of determining E_0 would consist in measuring E for an exceedingly dilute

(5) Randall and Cushman, *THIS JOURNAL*, **40**, 395 (1918).

solution of sulfuric acid for which we could make a fairly accurate estimate of the activity coefficient. This procedure, however, is not experimentally practicable. There remains the possibility that the e. m. f. of the solutions may be represented by means of an equation of the Debye and Hückel type, an equation partly theoretical and partly empirical. Applied to an aqueous solution of sulfuric and acetic acids, the equation of Debye and Hückel for a temperature of 25° may be written

$$\log_{10} f = \frac{-1.7476 C_1^{1/2}}{1 + AC_1^{1/2}} + \lambda_1 C_1 + \lambda_2 C_2 \quad (4)$$

$$\log_{10} \gamma = \frac{-1.7476 C_1^{1/2}}{1 + AC_1^{1/2}} - \log_{10} \left[1 + \frac{3m_1 + m_2}{55.51} \right] + \lambda_1 C_1 + \lambda_2 C_2 \quad (4')$$

In these equations, λ_1 and λ_2 may be looked on as purely empirical constants.

In terms of the theory of Debye, the constant A is equal to $0.5686 \times 10^8 a$, where a is an average ionic diameter. On substituting the value of γ given by (4') in equation (1), we obtain

$$\frac{E_0 - E}{0.088695} = 0.20069 + \log_{10} m_1 - \frac{1.7476 C_1^{1/2}}{1 + AC_1^{1/2}} - \log_{10} \left[1 + \frac{3m_1 + m_2}{55.51} \right] + \lambda_1 C_1 + \lambda_2 C_2 \quad (5)$$

This equation was fitted to the e. m. f. results for solutions (6), (8) and (10) which contain no acetic acid. We find: $E_0 = 0.6290$, $A = 0.8565$; $\lambda_1 = 0.2346$. This value of A corresponds to an ionic diameter $a = 1.506 \times 10^{-8}$ cm. Using these values of E_0 , A and λ_1 , the calculated values of the e. m. f. for solutions (7), (9) and (11) are 0.7285, 0.6935 and 0.6536 corresponding, respectively, to the observed values 0.7290, 0.6929 and 0.6555.

Equation (5) was tested further by calculating values of λ_2 , using the e. m. f. data for all the solutions which contained acetic acid and employing the values of E_0 , A and λ_1 derived from solutions containing sulfuric acid only. The variations in the calculated values of λ_2 were naturally greatest for solutions in which the concentration of acetic acid was low. For solutions in which the concentration of acetic acid was greater than 1 molar, the average value of λ_2 for the various concentrations ranged from 0.0312 to 0.0372 with a grand average of $\lambda_2 = 0.0339$ and an average deviation of 5% from the grand average.

It was found that the e. m. f.'s of all solutions in which the concentration of sulfuric acid was not greater than 1.09 could be calculated with a considerable degree of accuracy by means of equation (5), taking $\lambda_2 = 0.0339$ and using the values of E_0 , A and λ_1 previously mentioned. The average deviation of the calculated from the observed e. m. f. for twenty-four solutions was ± 0.0004 volt. The maximum deviation was 0.0012 volt.

Activity Coefficient of Sulfuric Acid.—The significance of the fact that equation (5) with definite values of the constants E_0 , A , λ_1 and λ_2 repre-

sents with some degree of accuracy the observed e. m. f. over a considerable range of concentration should not be overestimated. If we represent the E_0 and γ of equation (1) by E_0^* and γ^* , and retain the symbols E_0 and γ for the quantities defined in equations (5) and (4'), then the only indisputable conclusion is that

$$\log_{10} \gamma^* = \log_{10} \gamma + \frac{E_0^* - E_0}{0.088695} = \log_{10} \gamma + \frac{E_0^* - 0.6290}{0.088695} \quad (6)$$

for the validity of equation (5) over a limited range of concentration does not necessitate the identity of E_0 and E_0^* . It follows from equation (6) that if E_0 is not equal to E_0^* , then the values of γ calculated by means of equation (4') must be multiplied by a constant factor to give the true values which are symbolized by γ^* . If, however, we *assume* that equation (5) is valid also for solutions of low ionic strength, to which the theory of Debye is generally admitted to be applicable, then γ becomes identical with γ^* and equation (4') gives the true values of the activity coefficient of sulfuric acid for all solutions in which the concentration of

TABLE II
OBSERVED ACTIVITY COEFFICIENTS OF SULFURIC ACID

Basis: for solution (6), $f = 0.4817$; $\gamma_c = 0.4809$; $\gamma = 0.4804$

Solution	f	γ_c	γ	Solution	f	γ_c	γ
5	0.767	0.910	0.691	9	0.221	0.219	0.214
4	.669	.754	.623	24	.230	.232	.221
3	.575	.612	.554	31	.246	.253	.230
2	.529	.544	.518	38	.259	.277	.240
1	.488	.488	.485	45	.282	.315	.254
6	.482	.481	.480	52	.310	.362	.271
13	.476	.477	.474	18	.205	.203	.196
21	.493	.501	.486	10	.196	.192	.185
28	.523	.548	.508	25	.204	.204	.190
35	.553	.597	.528	32	.218	.224	.199
42	.608	.685	.565	39	.233	.247	.208
49	.666	.785	.602	46	.254	.281	.221
14	.382	.382	.379	53	.285	.329	.239
36	.432	.466	.411	11	.198	.192	.181
43	.472	.531	.437	19	.200	.195	.182
50	.520	.611	.468	26	.207	.205	.187
7	.343	.342	.341	33	.223	.227	.197
15	.337	.337	.334	40	.241	.254	.209
22	.357	.362	.350	47	.264	.290	.221
29	.377	.394	.364	54	.297	.341	.240
16	.300	.300	.297	12	.214	.206	.190
8	.271	.269	.267	27	.225	.221	.197
23	.281	.284	.274	34	.242	.245	.207
30	.297	.310	.285	41	.263	.275	.220
37	.316	.340	.298	48	.292	.321	.238
44	.343	.385	.315	55	.336	.382	.260
51	.375	.441	.334	20	.287	.274	.238
17	.241	.240	.235				

sulfuric acid is not much greater than 1 molar. It does not seem to be worth while to include in this paper the values of γ resulting from the application of equation (4') to all the solutions we have investigated. Since solutions (6), (8) and (10) have been used in this research as our standard reference solutions, it would seem to be a more useful procedure to calculate the activity coefficient for any one of these by means of equation (4') and then, on the basis of this value, to calculate the activity coefficients of all other solutions from the observed electromotive force. Applying equations (4'), (3) and (3') to solution (6), we find for the activity coefficients

$$f = 0.4817; \gamma_c = 0.4809; \gamma = 0.4804 \quad (7)$$

In Table II will be found the mean activity coefficients of sulfuric acid in all the solutions investigated, calculated on the basis of (7) and the observed e. m. f.'s. These will be called "observed" activity coefficients.

From Table II it follows that for aqueous solutions of sulfuric acid the activity coefficient f has a minimum value of 0.194 for $C_1 = 1.30$ or $m_1 = 1.37$; that γ_c has a minimum of 0.189 for $C_1 = 1.35$ or $m_1 = 1.43$; and that the minimum value of γ is 0.180 for $C_1 = 1.48$ or $m_1 = 1.57$.

Part II. Vapor Pressure Measurements

The dynamic method employed in determining the vapor pressures of the solutions was somewhat similar to that of Washburn and Heuse.⁶ However, a number of changes were made in the design of the apparatus. An extra alkali absorption bulb was added to collect the acetic acid vapor. Moreover, the air was bubbled through the liquids instead of over their surfaces. The saturators and absorbers were equipped with bubblers of the "petticoat" type. The exit tubes were wound with nichrome wire and maintained at a temperature of 30 to 35° to prevent condensation of vapor. The solution of barium hydroxide in the alkali absorbers was analyzed by weight titration with standardized hydrochloric acid.

To calculate the partial vapor pressure of the acetic acid from the results of our experiments, we need to know the average molecular weight of acetic acid vapor under the conditions of the experiment. This information we derived from a study of the vapor density data obtained by Ramsay and Young.⁷

Vapor Density of Acetic Acid.—If we assume that the vapor of acetic acid contains the two molecular species $C_2H_4O_2$ and $(C_2H_4O_2)_2$, we can readily calculate from the density determinations of Ramsay and Young the value of the equilibrium constant K_p , where

$$K_p = p_{HA}^2 / p_{H_2A_2} \quad (8)$$

Using the average values of K_p so obtained for each temperature, we have plotted in Fig. 1 the values of $-\log K_p$ against $1/T$. It should be emphasized that the individual values of K_p at any one temperature show

(6) Washburn and Heuse, *THIS JOURNAL*, **37**, 309 (1915).

(7) Ramsay and Young, *J. Chem. Soc.*, **49**, 790 (1886).

considerable deviations from the mean, amounting occasionally to 50%. The best straight line through the points of Fig. 1 leads to a value of $K_p = 0.325$ mm. at 25° . The possible error in this value is difficult to estimate but it may amount to 10 or 20%. Incidentally, from the slope of the line we find that the heat absorbed in the dissociation of one mole of $(C_2H_4O_2)_2$ is approximately 18,600 calories.

CALCULATION OF VAPOR PRESSURES FROM EXPERIMENTAL DATA

- B = average atmospheric pressure in mm. during a run
 M_1 = 60.03 = molecular weight of unassociated acetic acid
 M_{H_2O} = 18.016 = molecular weight of water vapor
 M_x = average molecular weight of vapor of acetic acid
 P_0 = vapor pressure of pure water, 23.773 mm.
 P_1 = partial water vapor pressure of solution
 P_x = partial acetic acid vapor pressure of solution
 $\Delta P_1, \Delta P_2$ = readings on the solution and water saturator manometers, respectively
 W_0 = mass of water vapor carried over from pure water
 W_1 = mass of water vapor carried over from solution
 W_x = mass of acetic acid vapor carried over from solution
 V_1, V_2 = volumes of gas leaving the solution and water saturators, respectively, during a run.

Among P_x, M_x, P_{HA} and P_{H_2A} , the following relations exist

$$M_x = M_1 \left[\frac{4P_x + K_p - \sqrt{K_p^2 + 4K_p P_x}}{2P_x} \right] \quad (9)$$

$$P_x = \frac{M_1(M_x - M_1)}{(2M_1 - M_x)^2} K_p \quad (9')$$

$$P_{HA} = \frac{(2M_1 - M_x)}{M_1} P_x \quad (9'')$$

$$P_{H_2A} = \frac{M_x - M_1}{M_1} P_x \quad (9''')$$

Assuming the validity of the ideal gas laws, we have

$$\frac{B - \Delta P_1 - p_1 - p_x}{B - \Delta P_2 - p_0} = \frac{V_2}{V_1} = \frac{p_1 W_0}{p_0 W_1} \quad (10)$$

Let us write

$$x = \frac{p_x}{p_1} = \frac{W_x M_{H_2O}}{W_1 M_x} \quad (11)$$

From equations (10) and (11) we obtain

$$p_1 = \frac{W_1 p_0 (B - \Delta P_1)}{W_0 (B - \Delta P_2 - p_0) + W_1 p_0 (1 + x)} \quad (12)$$

Equations (11) and (12) are solved for p_1 and p_x by repeated trials. Assuming an approximate value of M_x , we get from (11) an approximate value of x . Substituting this value of x in (12) gives a first approximation to p_1 . From these values of p_1 and x , we get from the equation, $p_x = X p_1$, a value of p_x which leads by means of equation (9) to a more accurate value of M_x . Repetition of this procedure finally gives values of p_1 and p_x which are consistent with equations (9), (11) and (12). Equations

(9'') and (9''') then give the partial vapor pressures of the associated and unassociated acetic acid vapor.

An estimate of the accuracy of the experiments may be made from a consideration of the following results. Nine runs with one apparatus were made using pure water instead of a solution. The values of the vapor pressure of water so determined ranged from 23.73 to 23.83 mm. with an average value of 23.79. A second series of seven runs with a different apparatus gave values ranging from 23.70 to 23.78 with an average value of 23.73 mm. For solution (24) in which the concentrations of sulfuric acid and acetic acid were $C_1 = 0.5453$ and $C_2 = 0.5483$, respectively, the values found for $p_{\text{H}_2\text{O}}$ were 22.93, 23.05, 23.02 and 22.92; and for p_x , 0.129, 0.117, 0.120, 0.120. For solution (50), with $C_1 = 0.1086$ and $C_2 = 4.368$, the values found for $p_{\text{H}_2\text{O}}$ were 21.76, 21.71, 21.74 and 21.70; and for p_x , 1.050, 1.046, 1.041 and 1.046. These results may, we think, be taken as representative.

In Table III, we give the average values of $p_{\text{H}_2\text{O}}$, p_x (vapor pressure due to both species of acetic acid), p_{HA} and $p_{\text{H}_2\text{A}_2}$, together with p_{total} , the total vapor pressure of the liquid investigated.

Thermodynamic Calculation of the Partial Vapor Pressure of Acetic Acid.—For the thermodynamic treatment we have in mind, it is necessary to know the activity coefficient of the sulfuric acid, the partial water vapor pressure and the partial acetic acid vapor pressure, P_{HA} , for a series of solutions of constant molality in sulfuric acid and varying molality in acetic acid as well as for a series of solutions of constant molality in acetic acid and varying molality in sulfuric acid. This information was obtained graphically from a series of plots and is assembled in Table IV.

Representing by a_0 , a_1 and a_2 the activity of water, sulfuric acid and acetic acid in a given solution in which the molalities of the acids are m_1 and m_2 , respectively, we have the following thermodynamic relation, valid for any changes in composition at constant temperature and pressure, *viz.*

$$55.51 d \log a_0 + m_1 d \log a_1 + m_2 d \log a_2 = 0 \quad (13)$$

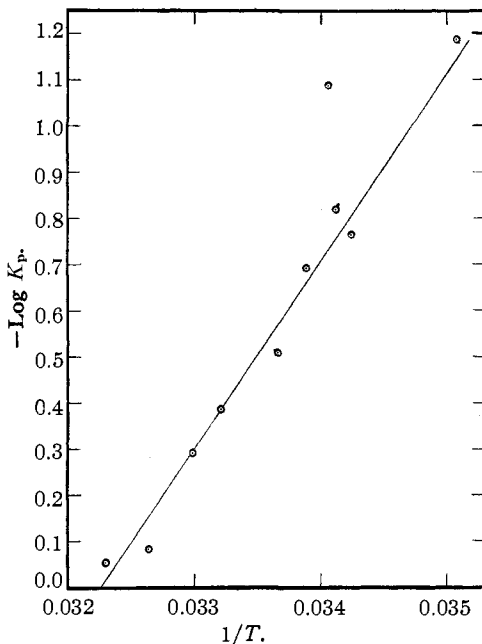


Fig. 1.—Reaction in gas phase: $\text{H}_2\text{A}_2 \rightleftharpoons 2\text{HA}$.

TABLE III
 VAPOR PRESSURES OF SOLUTIONS
 For Concentration Data, see Table I

No. of solution	No. of runs averaged	$p_{\text{H}_2\text{O}}$	p_x	p_{HA}	$p_{\text{H}_2\text{A}_2}$	p_{total}
Pure water	9	23.79				23.79
Pure water	7	23.73				23.73
2	4	23.23	0.179	0.128	0.051	23.41
3	4	22.90	.366	.219	.147	23.27
4	4	22.30	.731	.351	.380	23.03
5	4	21.80	1.075	.449	.626	22.88
6	5	23.67				23.67
7	4	23.55				23.55
8	3	23.47				23.47
9	3	23.18				23.18
10	4	22.64				22.64
11	2	21.94				21.94
12	5	20.91				20.91
21	4	23.41	0.109	0.086	0.023	23.52
22	3	23.29	.108	.085	.023	23.40
23	4	23.15	.118	.092	.026	23.27
24	4	22.98	.122	.095	.027	23.10
25	4	22.31	.134	.102	.032	22.44
26	4	21.56	.149	.111	.038	21.71
27	4	20.67	.164	.120	.044	20.83
28	4	22.97	.278	.179	.099	23.25
29	4	22.83	.294	.187	.107	23.12
30	4	22.67	.304	.191	.113	22.98
31	2	21.84	.354	.213	.141	22.20
33	2	20.90	.443	.251	.192	21.34
34	2	19.80	.497	.271	.226	20.30
35	8	22.60	.456	.255	.201	23.06
36	4	22.65	.460	.256	.204	23.11
37	4	22.44	.479	.264	.215	22.92
38	4	22.11	.523	.280	.243	22.63
39	4	21.33	.611	.311	.300	21.94
41	4	19.38	.824	.379	.445	20.21
42	3	22.30	.708	.344	.364	23.01
43	4	22.27	.733	.351	.302	23.00
44	3	21.96	.781	.366	.415	22.74
45	5	21.58	.850	.386	.464	22.43
46	4	20.80	.999	.429	.570	21.80
47	4	19.72	1.180	.477	.703	20.90
48	4	18.58	1.374	.524	.850	19.95
49	4	21.82	1.041	.441	.600	22.86
50	4	21.73	1.046	.442	.604	22.77
51	4	21.54	1.105	.457	.648	22.65
52	4	21.09	1.217	.486	.731	22.30
53	4	20.23	1.371	.523	.848	21.60
54	4	18.92	1.714	.600	1.114	20.63
56	4	23.25	0.195	.137	0.058	23.45
57	4	22.85	.430	.245	.185	23.28

Since the partial vapor pressures, $P_{\text{H}_2\text{O}}$ and P_{HA} are proportional to a_1 and a_2 , respectively, and since the activity a_1 of sulfuric acid is proportional to $(m_1\gamma)^3$, where γ is the mean activity coefficient of sulfuric acid, we may rewrite equation (13) in the form

$$d \log P_{\text{HA}} = - \frac{55.51}{m_2} d \log P_{\text{H}_2\text{O}} - \frac{3m_1}{m_2} d \log (m_1\gamma) \quad (14)$$

Representing any two solutions by the symbols 1 and 2, we have for the case in which the two solutions have the same molality of acetic acid, m_2

$$\log (P_{\text{HA}})_2 - \log (P_{\text{HA}})_1 = - \frac{55.51}{m_2} [\log (P_{\text{H}_2\text{O}})_2 - \log (P_{\text{H}_2\text{O}})_1] - \frac{3}{m_2} \int_1^2 m_1 d \log (m_1\gamma) \quad (15)$$

Similarly for any two solutions of equal molality, m_1 , in sulfuric acid, integration of (14) gives the expression

$$\log (P_{\text{HA}})_2 - \log (P_{\text{HA}})_1 = - 55.51 \int_1^2 \frac{1}{m_2} d \log P_{\text{H}_2\text{O}} - 3m_1 \int_1^2 \frac{1}{m_2} d \log (m_1\gamma) \quad (16)$$

Careful plots were made, using the data of the first four columns of Table IV for the appropriate series of solutions, of m_1 and $1/m_2$ as functions of

TABLE IV
CALCULATION OF P_{HA} AND SUMMARIZED DATA ON ACTIVITY COEFFICIENT OF
SULFURIC ACID

m_1 H_2SO_4	m_2 acetic acid	$P_{\text{H}_2\text{O}}$ 23.773	γ for H_2SO_4	P_{HA} (mm.), observed	P_{HA} calcd.	m_1 H_2SO_4	m_2 acetic acid	$P_{\text{H}_2\text{O}}$ 23.773	γ for H_2SO_4	P_{HA} (mm.), observed	P_{HA} calcd.
2.5	6.0	0.7961	0.245	0.595	0.567	2.5	1.5	0.8440	0.206	0.257	0.292
2.0	6.0	.8216	.239	.567	.560	2.0	1.5	.8750	.199	.242	.245
1.5	6.0	.8497	.239	.538	.527	1.5	1.5	.9013	.195	.230	.238
1.0	6.0	.8740	.253	.507	.506	1.0	1.5	.9243	.205	.217	.230
0.5	6.0	.8973	.306	.477	(.477)	0.5	1.5	.9465	.244	.199	.203
.25	6.0	.9090	.389	.461	.460	.25	1.5	.9578	.305	.190	.184
.10	6.0	.9158	.540	.453	.450	.10	1.5	.9653	.414	.184	.169
.0506	6.0	.9178	.691	.448	.447	.0506	1.5	.9683	.539	.179	.160
2.5	4.0	.8111	.227	.471	.516	2.5	0.5	.8695	.197	.114	.090
2.0	4.0	.8423	.226	.445	.470	2.0	.5	.8981	.190	.099	.084
1.5	4.0	.8703	.220	.422	.434	1.5	.5	.9236	.185	.089	.097
1.0	4.0	.8950	.232	.396	.411	1.0	.5	.9463	.195	.086	.095
0.5	4.0	.9183	.278	.371	.381	0.5	.5	.9670	.232	.080	.082
.25	4.0	.9303	.351	.357	.362	.25	.5	.9775	.277	.077	.076
.10	4.0	.9374	.484	.348	.350	.10	.5	.9840	.380	.076	.067
.0506	4.0	.9396	.623	.343	.347	.0506	.5	.9863	.493	.073	.063
2.5	2.5	.8278	.214	.350	.420	2.5	.0	.8826	.192		
2.0	2.5	.8580	.207	.332	.379	2.0	.0	.9098	.185		
1.5	2.5	.8860	.204	.313	.351	1.5	.0	.9358	.180		
1.0	2.5	.9110	.215	.294	.320	1.0	.0	.9576	.186		
0.5	2.5	.9340	.256	.273	.289	0.5	.0	.9776	.221		
.25	2.5	.9463	.325	.263	.265	.25	.0	.9879	.278		
.10	2.5	.9539	.441	.256	.251	.10	.0	.9941	.379		
.0506	2.5	.9563	.572	.252	.246	.0506	.0	.9957	.480		

$\log(m_1\gamma)$ and of $1/m_2$ as a function of $\log P_{\text{H}_2\text{O}}$. The values of the definite integrals occurring in (15) and (16) were determined by graphical integration using a planimeter. It should be noted that equations (15) and (16) do not give the value of P_{HA} for one solution but the ratio of the vapor pressures for two solutions. Equation (15) was applied to each of the groups for which m_2 is constant, namely, for $m_2 = 6, 4, 2.5, 1.5$ and 0.5 , respectively. This procedure gives the relative values of P_{HA} within each group. A possible method of comparing calculated with observed values of P_{HA} would consist in selecting arbitrarily some one observed value of P_{HA} in each group and then calculating by means of the ratios determined for each group by means of equation (15) the values of P_{HA} for the other members of the group. This method has the advantage of improving the chances for agreement between observed and calculated values. We preferred to make only one arbitrary selection of P_{HA} . We selected as our standard the observed value, $P_{\text{HA}} = 0.477$, for the solution in which $m_1 = 0.5$ and $m_2 = 6.0$. The passage from the group for which $m_2 = 6.0$ to the groups for which $m_2 = 4.0, 2.5, 1.5$ and 0.5 was made by applying equation (16) to the series for which m_1 was constant and equal to 1.5 and for which m_2 varied from 0.5 to 6.0 . In the sixth column of Table IV are given the values of P_{HA} calculated by this method. The agreement with the observed values of column five must be admitted to be, in general, excellent.

Activity Coefficients of Unassociated and Associated Acetic Acid in Solution and the Equilibrium between the Two Forms.—The theory of Debye⁸ considers the effect of a change in the dielectric constant of a solution on the activity coefficients of the various solutes. On the assumption that the dielectric constant decreases linearly with the concentration of the dissolved substances as given by the expression

$$D = D_0(1 - C_1\delta_1 - C_2\delta_2) \quad (17)$$

where C_1 is the concentration of electrolyte and C_2 the concentration of non-electrolyte, Debye and McAulay find the equivalent of the following expression for a temperature of 25°

$$\frac{\log_{10} f}{S} = \frac{0.4343 N e^2 \delta_2}{D_0 R T b} = \frac{3.072 \times 10^{-8}}{b} \delta_2 \quad (18)$$

In equation (18), f is the mole fraction activity coefficient of the non-electrolyte, S is the ionic strength, N is Avogadro's number and b is an average ionic radius. Equation (18) is derived for solutions of low ionic strength, but an extension of the considerations to more concentrated solutions leads to the conclusion that a fairly constant value of $\log f/S$ even for moderate ionic strengths, is not inconsistent with the theory. Randall and Failey,⁹ in an extended test of equation (18), using, however, the

(8) Debye and McAulay, *Physik. Z.*, **26**, 22 (1925).

(9) Randall and Failey, *Chem. Rev.*, **4**, 285 (1927).

molality activity coefficient in place of f , were able to show that in many cases $\log \gamma/S$ was approximately constant. On the basis of our vapor pressure measurements we have been able to determine the activity coefficient of acetic acid as a function of the concentration of sulfuric acid. We have also investigated the equilibrium between unassociated and associated acetic acid in aqueous solution.

In a solution in which the stoichiometric concentrations of sulfuric acid and acetic acid are C_1 and C_2 , respectively, let C_u and C_a be the respective concentrations of unassociated and associated acetic acid. Assuming that the associated acid consists of double molecules, we have

$$C_2 = C_u + 2C_a \quad (19)$$

For the equilibrium $2 \text{HA} \rightleftharpoons \text{H}_2\text{A}_2$, we have

$$K_c = \frac{a_{\text{H}_2\text{A}_2}}{a_{\text{HA}}^2} = \frac{C_a \gamma_a}{C_u^2 \gamma_u^2} \quad (20)$$

where γ_a and γ_u are molarity activity coefficients. Since $P_{\text{HA}} = k_1 a_{\text{HA}} = k_1 C_u \gamma_u$, we find from equations (19) and (20)

$$C_2 = \frac{1}{k_1 \gamma_u} P_{\text{HA}} + \frac{2K_c}{k_1^2 \gamma_a} P_{\text{HA}}^2 \quad (21)$$

$$= B_1 P_{\text{HA}} + B_2 P_{\text{HA}}^2 \quad (21')$$

where $B_1 = 1/k_1 \gamma_u$ and $B_2 = 2K_c/k_1^2 \gamma_a$. We have also the relation

$$\frac{B_2}{2B_1^2} = \frac{K_c \gamma_u^2}{\gamma_a} = \frac{C_a}{C_u^2} \quad (22)$$

In Table V we have assembled values of P_{HA} for round concentrations of sulfuric acid and of acetic acid. A cursory examination of this table will show that: (a) for a given concentration of acetic acid, the value of P_{HA} increases with the ionic strength; in other words, the activity of the acetic acid in solution increases with the ionic strength; (b) for a given ionic strength, the value of P_{HA} increases with, but not so rapidly as, the concentration of acetic acid; this points to an increasing degree of association of the acetic acid with the concentration.

TABLE V
VAPOR PRESSURES AT ROUND CONCENTRATION

C_2 acetic acid	P_{HA} for $C_{\text{H}_2\text{SO}_4} = 2.0$	P_{HA} $C_1 = 1.5$	P_{HA} $C_1 = 1.0$	P_{HA} $C_1 = 0.5$	P_{HA} $C_1 = 0.25$	P_{HA} $C_1 = 0.0$
4.0	0.570	0.524	0.479	0.433	0.411	0.389
3.5	.510	.468	.427	.384	.366	.344
3.0	.456	.419	.380	.340	.326	.306
2.5	.401	.369	.335	.295	.287	.269
2.0	.345	.317	.289	.257	.246	.231
1.5	.284	.260	.237	.214	.203	.190
1.0	.203	.188	.174	.160	.150	.143
0.5	.106	.100	.091	.085	.080	.077

Let us assume that the activity coefficients of the two forms of acetic acid are functions of the ionic strength only and that they are approxi-

mately unity for solutions of low ionic strength. If the values of P_{HA} given in any one of the vertical columns of Table V be divided by the corresponding values of P_{HA} in the last column ($C_1 = 0.0$), it will be found that for each column an approximately constant ratio is obtained. This is shown in Table VI. It follows from this, as can be readily shown, (a) that C_a/C_u^2 is constant and equal to K_c , independently of the ionic strength; (b) that, therefore, $\gamma_a = \gamma_u^2$; (c) that the value of γ_u for a solution of any ionic strength is given by the value of R in the appropriate column of Table VI.

TABLE VI
RATIO, R , OF VAPOR PRESSURE, P_{HA} , OF A SOLUTION TO THAT OF A SOLUTION OF THE SAME ACETIC ACID CONCENTRATION BUT CONTAINING NO SULFURIC ACID

C_2 acetic acid	R $C_{H_2SO_4} = 2$	R $C_1 = 1.5$	R $C_1 = 1.0$	R $C_1 = 0.5$	R $C_1 = 0.25$
4.0	1.465	1.347	1.231	1.113	1.057
3.5	1.483	1.360	1.241	1.116	1.064
3.0	1.490	1.369	1.242	1.111	1.065
2.5	1.491	1.372	1.245	1.097	1.067
2.0	1.494	1.372	1.251	1.113	1.065
1.5	1.495	1.368	1.247	1.125	1.068
1.0	1.420	1.315	1.217	1.119	1.049
0.5	1.377	1.299	1.182	1.104	1.039
Average	1.466	1.350	1.232	1.112	1.059

These conclusions have been checked as follows. For each value of C_1 , the best values of B_1 and B_2 of equation (21') were found by applying the method of least squares to the data in Table V. For a given value of C_1 , we have the two equations

$$\Sigma C_2 P_{HA} = B_1 \Sigma P_{HA}^2 + B_2 \Sigma P_{HA}^3 \quad (23)$$

$$\Sigma C_2 P_{HA}^2 = B_1 \Sigma P_{HA}^3 + B_2 \Sigma P_{HA}^4 \quad (23')$$

from which we determine the values of B_1 and B_2 as given in Table VII, which also contains the values of γ_u and γ_a calculated from B_1 and B_2 . We see that these values of γ_u and γ_a satisfy, roughly, the relation: $\gamma_u^2 = \gamma_a$. Moreover these values of γ_u agree approximately with the corresponding ratios of Table VI which are more accurate values of γ_u . These latter values are given by the equation

$$\gamma_u = 1 + 0.233 C_1 = 1 + 0.0777 S \quad (24)$$

whence we find that approximately

$$\begin{aligned} \log_{10} \gamma_u &= 0.101 C_1 - 0.0118 C_1^2 \\ &= 0.0337 S - 0.00131 S^2 \end{aligned} \quad (25)$$

and hence that

$$\frac{\log_{10} \gamma_u}{S} = 0.0337 - 0.00131 S \quad (26)$$

This result may be compared with equation (18). The stoichiometric activity coefficient of acetic acid, γ_2 , satisfies the relation

$$C_2 \gamma_2 = C_u \gamma_u \quad (27)$$

Hence the value of γ_2 for solutions of acetic acid and sulfuric acid can be determined for any value of C_2 from equation (24) and the value of K_c , which, according to Table VII, is approximately 0.185 liter/mole.

TABLE VII

C_1	B_1	B_2	$B_2/2B_1^2 = K_c$	γ_u	γ_a
2.0	3.95	5.52	0.177	1.49	2.19
1.5	4.15	6.89	.200	1.41	1.74
1.0	4.64	8.08	.188	1.27	1.49
0.5	5.25	9.78	.178	1.12	1.23
.25	5.35	11.17	.195	1.10	1.08
.00	5.87	12.00	.174	1.00	1.00

Average .185

Summary

1. We have measured the e. m. f. of cells of the type H_2 , HA, H_2SO_4 , Hg_2SO_4 , Hg at 25°.

2. We find $E_0 = 0.6290$.

3. The e. m. f. over a considerable range can be represented by an equation of the Debye and Hückel type.

4. The activity coefficients of sulfuric acid have been determined from the e. m. f. data.

5. The vapor pressures of aqueous solutions of sulfuric acid and acetic acid have been determined by a dynamic method.

6. The data of Ramsay and Young on the vapor density of pure acetic acid have been employed to study the equilibrium between single and double molecules in the gas phase. The value of $K_p = P_{HA}^2/P_{HA_2}$, found in this way is 0.325 mm. at 25°. This value of K_p was used in calculating the various partial vapor pressures.

7. From the observed values of the activity coefficient of sulfuric acid (derived from the e. m. f. data) and from the observed partial vapor pressures of water, the partial vapor pressures of acetic acid were calculated thermodynamically and compared with the observed values.

8. The equilibrium between single and double molecules of acetic acid in aqueous solution was investigated.

9. It was found that $K_c = \frac{C_a \gamma_a}{C_u^2 \gamma_u^2} = \frac{C_a}{C_u^2} = 0.185 \frac{\text{liter}}{\text{mole}}$.

10. It follows that $\gamma_a = \gamma_u^2$, independent of the concentration of sulfuric acid.

11. It was found that the activity coefficient of unassociated acetic acid, γ_u , is given by the equation (where $C_1 =$ concentration of sulfuric acid), $\gamma_u = 1 + 0.233 C_1$.

12. This result is in approximate agreement with the equation of Debye and McAulay.