THE FREE ENERGY OF AQUEOUS SULFURIC ACID.

Thesis

by

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Previous Work and Outline of this Investigation

Though aqueous sulfuric acid is one of the most important acids, its free energy and its oxidizing power are very imperfectly known. In concentrated solution, especially when hot, sulfuric acid is strongly oxidizing while in dilute solution it oxidizes scarcely any of even the most strongly reducing substances.

The researches which may be used for calculating the free energy of aqueous sulfuric acid have recently been briefly discussed by Lewis and Randall.[2] The equilibria studied, however, were such that it is necessary to approximate the fugacities of the gases and the activities of the liquids involved, and to recalculate the results to standard temperature, which involves the use of uncertain heat data and a rather large extrapolation. Lewis and Randall[2] nevertheless give —176,500 calories as a "provisional value" for the free energy of $1H_2SO_4$ at 25° at hypothetical 1 molal.

The determinations here presented are based upon measurements of the equilibrium in aqueous solution at 80° of the reaction, $H_2SO_4 + 6HI = 3I_2 + 4H_2O + S_{rh}$. Equilibrium was attained with sulfuric acid at 5–7 *M*, hydriodic acid at 0.4–1.0 *M*, and iodine at 0.04–0.3 *M*. The concentrations of hydrogen iodide and iodine were kept as small as possible in comparison to that of the sulfuric acid, so that their presence would not largely change its activity. The reaction proceeds from either side

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[1] National Research Fellow in Chemistry.

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, pp. 552–555.

(Work done in conjunction with Dr. D.F.Smith
at this laboratory)

of the equilibrium at a rather slow rate even at a temperature of 80°, but equilibrium is nearly attained within a few weeks.

The difference in the free energies of the hydrogen iodide and iodine in the equilibrium solutions was determined by measuring the electromotive force of half-cells containing those solutions in contact with a platinum electrode and connected with a hydrogen-gas half-cell containing sulfuric acid and hydrochloric acid (in place of hydriodic acid) at the same concentrations.

The reaction accompanying the passage of 6 faradays through the cell is $3H_2(g) + 3I_2$ (in the equilibrium solution) = $6HI$ (in the equilibrium solution). Its electromotive force therefore gives a direct measure of the difference in the free energies of the hydrogen iodide and iodine in the equilibrium solution; and, hence, also of the equal change in free energy attending the reaction, $3H_2(g) + H_2SO_4 = 4H_2O + S_{rh}$, taking place under the conditions of concentrations prevailing in the equilibrium mixtures. The known vapor pressures of water over sulfuric acid solutions at 80° enabled the ratios of the activities of the water and hence of the sulfuric acid in the various equilibrium solutions to be calculated. And finally, by means of known heats of formation, heats of solution, and specific heats, the results could be recalculated to the standard temperature of 25°.

The authors are greatly indebted to Professor A. A. Noyes, the director of this Laboratory, for several valuable suggestions with regard to the experimental work, and especially for his criticism of our presentation of the data for publication.

Procedure in Making the Equilibrium Measurements

It was found that the hydriodic acid of commerce contains a small amount of some substance which immediately reduces sulfuric acid to hydrogen sulfide without formation of iodine. This substance is probably phosphonium iodide, which is formed during the process of manufacture by the phosphorus method. We therefore prepared all our hydriodic acid by direct combination of the pure elements as described by Bodenstein.[3]

Sulfur was made by acidifying a solution of pure sodium thiosulfate. The amorphous sulfur thus obtained was melted, cooled, and crystallized from carbon disulfide, from which it separated in the form of small crystals of rhombic sulfur.

Sulfur and iodine form liquid solutions; but it was found possible to keep the concentration of iodine in the aqueous solution low enough to avoid liquefaction of the sulfur.

The solutions for the equilibrium measurements were made up from weighed quantities of sulfuric and hydriodic acids standardized through an alkali solution against constant-boiling hydrochloric acid made according to Foulk and Hollingsworth.[4] The solutions were placed in sealed glass tubes, the air being carefully displaced by carbon dioxide. These tubes were rotated at 80° on a horizontal shaft in a thermostat containing water covered with a layer of paraffin wax to prevent excessive evaporation. The iodine in the equilibrium mixtures was determined by titration against thiosulfate in the usual manner. The results were checked in some cases by titration of the total iodide by

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[3] Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894).

[4] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

the method of McLean and Van Slyke.[5] From the original concentrations and the change in the iodine concentrations the equilibrium concentrations of all the substances present were calculated.

The equilibrium tubes were provided with two sealed-on outlet tubes. Through one of these was passed a slow stream of carbon dioxide while the solutions were being introduced and while the sample for analysis was quickly removed by means of a pipet filled with carbon dioxide, and discharged into a weighed flask containing a considerable volume of cold water. The flask containing the sample was weighed again to determine the weight of the sample, the solution neutralized with the proper amount of sodium bicarbonate, and immediately titrated with thiosulfate.

Results of the Equilibrium Measurements

The time of rotation in the thermostat at 80° and the composition of the equilibrium mixtures are shown in Table I. In the first and fourth experiments the equilibrium was approached from the sulfur side; in the second and third from the sulfuric acid side. The first experiment was made in the early part of the work when great care was not taken to exclude air and is obviously not at equilibrium. The last three solutions represent our best experiments.

TABLE I

COMPOSITION OF THE EQUILIBRIUM SOLUTIONS

Expt.	Days rotated	Moles per kg. of water		
		I_2	HI	H_2SO_4
1	35	0.3110	0.8537	5.523
2	21	.1403	0.7592	5.441
3	21	.0403	0.4492	5.886
4	22	.2767	1.0063	6.811

Procedure for the Electromotive-Force Measurements

Measurements were made at 80° of the electromotive force of cells of the type, $Pt+H_2(g) \mid H_2SO_4(c_1) + HCl(c_2) \mid H_2SO_4(c_1) + HI(c_2) + I_2(c_3) \mid Pt$. The solutions in the second half-cell were separately made up of the same composition as the equilibrium solutions, but without sulfur, in a nitrogen-filled tube, the iodide and sulfuric acid solutions not being mixed, however, until they had been brought to 80°. The hydrochloric acid in the former half-cell was introduced at the same concentration in moles per 1000 g. of water as was the hydriodic acid in the iodine half-cell, for the purpose of reducing liquid potentials. Moreover, since the sulfuric acid was at the same concentration in the two half-cells, and since it carried most of the current, the liquid potential is doubtless negligible.

The cells were kept in an oil thermostat at 80°. The hydrogen half-cell and saturator were of the type described by Smith and Woods.[6] The iodine half-cell consisted of a tube fitted with a glass stopper carrying a piece of smooth platinum foil connected with a mercury cup through a sealed-in platinum wire. It was found that these iodine solutions slowly

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[5] McLean and Van Slyke, THIS JOURNAL, 37, 1128 (1915).

[6] Smith and Woods, *ibid.*, 45, 2632 (1923).

dissolved platinum black from platinized electrodes, the cells giving low readings. This may explain the low results obtained by Stegmüller[7] on iodine-iodide cells at the higher temperatures. No trouble was experienced with smooth platinum, however.

The cells came to equilibrium in about two hours, after which the electromotive force did not vary more than 0.1 mv. for many hours.

The measurements of the cell containing 6.811 *M* sulfuric acid were erratic, and obviously gave too low values. This led to the conclusion that the sulfuric acid had reached a concentration where it was being reduced by the hydrogen in the hydrogen half-cell at an appreciable rate. The electromotive force corresponding to this acid content was consequently obtained by using 5.500 *M* sulfuric acid (in place of 6.811 *M*) in the hydrogen half-cell and correcting for this difference in concentration, in a manner to be described later, with the aid of the electromotive force of the following cell, which measurements showed to have at 80° the value 0.0112 volt: $Hg(l) + Hg_2SO_4(s) \mid H_2SO_4\ (6.811\ M) \mid H_2SO_4\ (5.500\ M) \mid Hg_2SO_4(s) + Hg(l)$.

Results of the Electromotive-Force Measurements

The results of the electromotive-force measurements are presented in Table II. The measurement upon the first solution is presented merely for the sake of completeness, since the last three solutions represent, as mentioned above, the most reliable results. The concentrations of the substances in the two half-cells are given in moles per 1000 g. of water. The vapor pressure, p_w, of water over the solution in the iodine half-cell was taken equal to that in a sulfuric acid solution at 80° of the same concentration, as determined by Burt.[8] The pressure, P_H, of hydrogen in the hydrogen half-cell was found by subtracting the so-obtained vapor-pressure of the water from the barometric pressure. The last column of the table gives the electromotive force corrected to a hydrogen pressure of one atmosphere by adding $(RT/2F)\ ln\ (760/P_H)$.

TABLE II

OBSERVED ELECTROMOTIVE FORCES AT 80°

	Hydrogen half-cell		Iodine half-cell			E.m.f.			E.m.f.
Cell	H_2SO_4	HCl	H_2SO_4	HI	I_2	obs.	p_w	P_H	corr.
1	5.523	0.8537	5.523	0.8537	0.3110	0.3576	247.6	492.3	0.3642
2	5.441	0.7592	5.441	0.7592	.1403	.3486	249.5	487.9	.3553
3	5.886	0.4492	5.886	0.4492	.0403	.3475	239.2	489.7	.3542
4	5.500	1.0063	6.811	1.0063	.2767	.3475	218.2	489.7	.3542
4a	6.811	1.0063	6.811	1.0063	.2767	(.3539)	218.2	489.7	.3606

The electromotive force of Cell 4 in Table II may now be corrected for the difference in the concentration of the sulfuric acid in the hydrogen half-cell and that in the equilibrium solution in Expt. 4 in Table I. When

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[7] Stegmüller, *Z. Elektrochem.*, **16**, 85 (1910).

[8] Burt, *J. Chem. Soc.*, **85**, 1339 (1904).

two faradays are passed from left to right through the mercurous sulfate cell formulated above, the cell reaction is the transfer of τ_H formula weights of sulfuric acid from the 6.811 *M* to the 5.500 *M* solution, τ_H being the average transference number of the hydrogen ion for the two solutions. On the other hand, when two faradays are passed through the cell, H_2(1 atm.) | H_2SO_4 (6.811 *M*), H_2SO_4 (5.500 *M*) | H_2 (1 atm.) there are so transferred $(1 - \tau_H)$ formula weights of sulfuric acid. The electromotive force of the hydrogen cell therefore stands to that of the mercury cell in the ratio $(1 - \tau_H)/\tau_H$, and the former value could be computed from the latter if the value of τ_H were known. This value can, however, be derived from the activity values obtained below and recorded in Table III; for from the activities a_1 and a_2 of the sulfuric acid in the 6.811 *M* and 5.500 *M* solutions, through the relation $-\Delta F = RT\, ln\, (a_1/a_2)$, there can be derived the free-energy decrease $-\Delta F$ attending the transfer of $1H_2SO_4$ from the first to the second solution. This free-energy value is found to be 3390 joules, which corresponds to 0.0176 volt (since $-\Delta F = 2$ EF). Since the electromotive force of the mercury cell was 0.0112 volt, the value of τ_H is 0.636, and the electromotive force of the hydrogen-cell formulated above is 364/636 times that of the mercury cell, or 0.0064 volt. If it be assumed that this electromotive force would not be substantially altered by the presence of the relatively small and equivalent quantities of hydrochloric and hydriodic acids in the two sulfuric acid solutions, we shall evidently get the electromotive force of Cell 4a, for which the compositions are recorded in the last row of Table II, by adding this value (0.0064 volt) to the electromotive force of Cell 4 in that table. In this way the value 0.3606, recorded as the corrected electromotive force of Cell 4a, was computed.

Calculation of the Free Energies at 80°

The relative activities of sulfuric acid at the concentrations involved may first be calculated from the vapor-pressure measurements of Burt at 80° with the aid of the Duhem equation. This equation leads[9] to the following expression for the relation between the activities a_1 and a_2 of the sulfuric acid and the vapor pressures p_1 and p_2 of the water in two solutions, and the mole-ratio n of the water to the acid in any solution:

$$\log \frac{a_2}{a_1} = \int_{p_2}^{p_1} n\, d \log p.$$

The integration was carried out graphically by plotting n against log p/p_0 (where p_0 is the vapor pressure of pure water), and measuring with a planimeter the area below the graph. The results are shown in Table III. The concentrations of sulfuric acid are here given in moles per 1000 g. of water.

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[9] Ref. 2, p. 332.

TABLE III

ACTIVITIES OF SULFURIC ACID AT 80° REFERRED TO THAT AT 5.441 MOLAL

Molality	3.500	4.000	4.5000	5.000	5.441	5.500
Activity	0.1328	0.2347	0.3993	0.6580	1.000	1.065
Molality	5.523	5.886	6.000	6.500	6.811	7.000
Activity	1.086	1.524	1.538	2.363	3.373	4.018

In order to compare the results of the four combinations of equilibrium and electromotive-force measurements, and to derive from them a best average value, we will calculate from each of them the free-energy decrease attending the change in state (corresponding to Expt. 2 of Table I, and Cell 2 of Table II) expressed by the equation, $3H_2$ (1 atm.) + H_2SO_4 (5.441 M) = $4H_2O$ (249.5 mm.) + S_{rh}. To do this we multiply the "corrected electromotive forces" given in the last column of Table II by 6 × 96,494/4.182; and subtract from the resulting free energies in calories the values of the expressions $RT\ ln\ a$ and $-4\ RT\ ln\ (p_w/249.5)$, using for a the values of the activities of sulfuric acid given in Table III and for p_w the values of the vapor pressure of water given in Table II.

There are thus obtained the following free energies in calories for the change in state as just formulated at 80°: 50,340; 49,188; 48,621; 48,692.

It may be recalled that in the first and fourth experiments the equilibrium was approached from the sulfur side, which would tend to make the calculated free energy too high, and in the second and third experiments, from the sulfuric acid side, which would have the opposite effect. The direction of the deviation of the first value corresponds to the conclusion stated above that in the first experiment equilibrium was probably not fully attained. We adopt, therefore, the mean of the last three values, namely, **48,830** calories, as the best final value.

Using the temperature function for the free energy of water vapor given by Lewis and Randall,[10] the free energy of $1H_2O(g)$ at one atm. and at 80° is found to be —53,889 cal. Subtracting from this the amount $RT\ ln$ (760/249.5), the free energy of $1H_2O$ (249.5 mm.) at 80° is found to be —54,671 cal. Multiplying this value by four and adding to it **48,830** cal. as derived above, gives **—169,854** cal. which is the free-energy decrease accompanying the following reaction at 80°: H_2SO_4 (at 5.441 M) = H_2 (1 atm.) + $2O_2$ (1 atm.) + S_{rh} and is thus the free energy content of $1H_2SO_4$ in 5.441 M solution at 80°. With the aid of the activity ratios at round concentrations presented in Table III the free-energy values for sulfuric acid at these concentrations can be readily calculated.

Calculation of the Free Energies at 25°

Probably the best value for the heat of formation of sulfuric acid from its elements is that obtained from the data quoted by Bichowsky,[11] who

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[10] Ref. 2, p. 485.

[11] Bichowsky, THIS JOURNAL, 44, 130, 131 (1922).

has reviewed the best thermochemical data. Using these data, the increase in heat content ΔH for the reaction $2H^+ + SO_4^=$ (at infinite dilution) = H_2 (1 atm.) + $2O_2$ (1 atm.) + S_{rh} is found to be 209,790 cal. at 291° K. If there is added to this heat effect that for the change in state H_2SO_4 (at 5.441 M) = $2H^+ + SO_4^=$, which by interpolation of the data compiled by Lewis and Randall[12] is found to be —7170 cal., there is obtained the value 202,620 cal., which is the sum of the increases in heat content for the removal of $1H_2SO_4$ from an infinite quantity of its 5.441 M solution, and the dissociation of it into its elements at 291° K. This quantity (202,620 cal.) is then the value of ΔH for the reaction for which we have the free-energy change at 80°, namely for H_2SO_4 (at 5.441 M) = H_2 (1 atm.) + $2O_2$ (1 atm.) + S_{rh}.

To express this heat effect as a temperature function we make use of the following molal heat-capacity values:[13] for H_2, $C_p = 6.50 + 0.0009\ T$; for O_2, $C_p = 6.50 + 0.0010\ T$; for S_{rh}, $C_p = 4.12 + 0.0047\ T$; and for the partial molal heat capacity of $1H_2SO_4$ in 5.441 M solution (at mole fraction 0.0893), $C_p = 15.86$. The values of ΔH and ΔF at any temperature T for this reaction are therefore given by the expressions: $\Delta H = 200{,}040 + 7.76\ T + 0.0038\ T^2$; $\Delta F = 200{,}040 - 7.76\ T\ ln\ T - 0.0038\ T^2 + IT$. From the value of $\Delta F = 169{,}850$ cal. as derived above for this reaction at $T = 353.1°$ K. the value of I is calculated to be —38.62. Solving this equation for ΔF at 298.1° K. we find its value to be 175,010 cal., which with negative sign is the free energy content of $1H_2SO_4$ in 5.441 M solution.

In order to compare this result with the values of the free energy of sulfuric acid previously derived, it is best to recalculate it to hypothetical 1 M. This may be done with the aid of the activity values derived by Lewis and Randall.[14] By interpolation from a plot of their values we find for the molality 5.441 an ion-activity coefficient of 0.237. Since this coefficient γ is defined[15] by them by the equation $4\ m^3\gamma^3 = a_H^2 a_{SO_4} = a_{H_2SO_4}$ where the a's represent the activities at molality m, we find the activity of the sulfuric acid at 5.441 M to be $4 \times (5.441)^3 \times (0.27)^3$ or 13.1. Now, by subtracting the value 298.1 $R\ ln$ 13.1, which is equal to 1525 cal., from —175,010 cal. we find **—176,535** cal. as the free energy of 1 H_2SO_4 at 25° at hypothetical 1 M (that is, when H^+ is 1 M and $SO_4^=$ is 1 M and these ions have activity-coefficient unity).[16]

This value agrees closely with the "provisional value" —176,500 adopted by Lewis and Randall.[17] This confirmation was desirable, since without

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[12] Ref. 2, p. 95.

[13] Ref. 2, pp. 80, 86 and 531.

[14] Ref. 2, p. 357.

[15] Ref. 2, p. 328.

[16] It may be noted that an error of 1% in the estimated activity of the acid at 5.441 M makes an error of only 20 calories in the result.

[17] Ref. 2, p. 554.

giving the separate values the authors state that their result is the average, obtained by three independent methods, of values differing by 1000 cal.

The uncertainty in our value due to error in the measurements at 80° probably does not exceed 240 cal., which is the average deviation of the three independent determinations from the mean. It is impracticable, however, to estimate the error involved in the correction of about 5000 cal. in recalculating the result to 25° with the aid of the heat data, or the uncertainty introduced by neglecting the activation effect of the hydriodic acid present with the sulfuric acid in the equilibrium mixtures. Whatever be the accuracy of our final value, it is hoped that the results presented in this research may facilitate a more extensive investigation by the same method, which lack of time prevented us from carrying out.

The Reduction Potentials of Sulfur Compounds at 25°

Now that the free energy of the sulfate ion has been determined with greater certainty, it seems worth while to compute and tabulate the free-energy decreases and the corresponding molal reduction potentials for the electronic reactions that are of direct practical importance in determining the oxidation-reduction behavior of sulfur compounds in aqueous solution. This has been done from the free energies by combining the new value (—176,540 cal.) for the sulfate ion with the free energies of other sulfur compounds given by Lewis and Randall.[18] The corresponding reduction potentials have been found by multiplying the resulting free energies by 4.182 (to reduce them to joules) and then dividing by 96,494 and by the number of faradays involved in the electronic reaction.

The results are presented in Table IV, of which the headings are in the main self-explanatory. The electronic reaction is understood to involve as its counterpart the reaction N ($H^+ = {}^1/_2H_2$) for which the free-energy change is regarded as zero and to imply that all the substances, except the (solid) sulfur and (liquid) water, are at 1 *M*.

TABLE IV

MOLAL REDUCTION POTENTIALS OF SULFUR AND ITS COMPOUNDS AT 25°

Reduced state	Oxidized state	Free-energy decrease	Reduction-potential
$H_2S + 2\oplus$	$S(s) + 2H^+$	− 6,490	−0.141
$H_2S + 2H_2O(1) + 6\oplus$	$SO_2 + 6H^+$	−49,840	− .360
$H_2S + 4H_2O(1) + 8\oplus$	$SO_4^= + 10H^+$	−56,190	− .304
$S(s) + 2H_2O(1) + 4\oplus$	$SO_2 + 4H^+$	−43,350	− .470
$S(s) + 4H_2O(1) + 6\oplus$	$SO_4^= + 8H^+$	−49,700	− .359
$SO_2 + 2H_2O(1) + 2\oplus$	$SO_4^= + 4H^+$	− 6,350	− .138

Some interesting conclusions to be drawn from these results may be pointed out. When all the substances involved are at 1 *M* the reducing powers of hydrogen sulfide and sulfur dioxide are nearly the same, though

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[18] Ref. 2, p. 608.

that of the former becomes relatively greater at higher hydrogen-ion concentrations. Sulfuric acid should from the equilibrium standpoint be capable of reduction to sulfur and hydrogen sulfide by very mild reducing agents, the fact that this does not occur in practice being doubtless due to marked passivity or slow reactivity of the sulfate ion. Any reducing agent strong enough to reduce sulfuric acid to sulfurous acid should be capable of reducing it completely to hydrogen sulfide, thus showing that it is impossible to realize at 25° stable equilibrium conditions between these two acids. Sulfuric or sulfurous acid may, however, be reduced to sulfur, without producing hydrogen sulfide; but the formation of the latter is favored by large hydrogen-ion concentration.

Summary

The equilibrium conditions of the reaction H_2SO_4 (5.4–6.8 *M*) + $6HI$(0.4–1.0 *M*) = $3I_2 + 4H_2O + S_{rh}$ at 80° have been determined. The electromotive force of cells consisting of the equilibrium mixtures and a platinum electrode as one half-cell, and of sulfuric acid at the same molality, hydrochloric acid at the same concentration as the hydriodic acid, and of a hydrogen electrode as the other half-cell, have also been measured at 80°. By combining these data the partial free energy of $1H_2SO_4$ at 5.441 *M* was calculated to be —169,850 cal. at 80°. With the aid of known heat data the corresponding value at 25° was computed to be —175,010 cal.

By means of the activity data of Lewis and Randall the free energy of $1SO_4^{=}$ at hypothetical 1 *M* at 25° was found to be —176,540 cal., thus confirming the provisional value —176,500 cal. derived by Lewis and Randall.

By combining this new value for the free energy of sulfate ion with the values given by Lewis and Randall for other sulfur compounds, the reduction potentials of various combinations that are of much practical significance in determining the oxidation chemistry of sulfur compounds in solution have been worked out and tabulated (see Table IV).

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