the resin absorbs water and swells, decreasing the concentration of the sulfonate groups ($[R^-]$ in equation 5a) and hence the selectivity of the resin for radium. This is what is observed experimentally, as shown in Fig. 4 where the plot for radium ion with the 2% DVB resin increases much less rapidly with decreasing hydrochloric acid concentration than that of radium and the highly cross-linked resin. A similar effect is observed for cesium, and likewise for sodium and strontium where the plots of *D* go through minima, but still increase less rapidly for the lower cross-linked resin than for the higher with decreasing acid concentration.

It may be noted that in 12 *M* HCl the values of *D* for the ions studied were greater with the 2% DVB resin than for the 16% DVB resin (not true for strontium with 12 *M* HCl, but from Fig. 4 indicated to be true at a slightly higher acid concentration) though at lower concentrations the reverse is true as would be expected from the lower sulfonate concentration in the 2% DVB resin. It is believed that this behavior is caused by the fifth factor mentioned earlier, the amount of non-exchange electrolyte present in the resin.[23] When the external solution is dilute, this is a negligible quantity and so has little effect on *D*, but as the external HCl concentration is increased, the amount absorbed by the resin phase increases rapidly. This non-exchange electrolyte consists of both HCl and MCl_2, and so, like the resin shrinkage itself, contributes to an increase in *D* with increasing electrolyte concentration in the contacting solution, as can be seen in equation 5a by increasing $_r[Cl^-]$. Since a less cross-linked resin takes up non-exchange electrolyte more readily than a highly cross-linked one, the values of *D* for the 2% DVB resin should show a slower decrease, or a faster increase, with increasing hydrochloric acid concentration than those for the 16% DVB resin, and if the excess of non-exchange electrolyte in the 2% DVB resin over that in the 16% DVB resin beomes large enough, the values of *D* for the former resin might become larger than those of the latter. In contact with 12 *M* HCl the 2% DVB resin becomes 10–11 *M* in HCl while the 16% DVB resin becomes only about 3–4 *M;* although the non-exchange MCl_2 in the two resins may not be in this same ratio, apparently the amount in the 2% DVB resin is enough in excess of that in the 16% DVB resin to cause a larger value of *D* at 12 *M* HCl than for the higher cross-linked resin.

CAMBRIDGE, MASS.

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[23] The author gratefully acknowledges helpful discussion on this topic with Dr. G. E. Boyd, Oak Ridge National Laboratory.

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Heat Capacities and Entropies of Sulfuric Acid Tri- and Tetrahydrates[1]

BY E. W. HORNUNG AND W. F. GIAUQUE

RECEIVED FEBRUARY 4, 1955

The heat capacities of sulfuric acid tri- and tetrahydrates have been measured from 15 to 300°K. The heats of fusion are 5736 and 7322 cal. $mole^{-1}$ at their respective melting points, 236.77 and 244.89°K. The peritectic temperature, where the trihydrate is in equilibrium with tetrahydrate and solution, was found to be 236.72°K. The unstable melting point was estimated to be 0.05° above this temperature. The values of the entropies at 298.16°K. are 82.55 cal. $deg.^{-1}$ $mole^{-1}$ for the trihydrate and 99.07 cal. $deg.^{-1}$ $mole^{-1}$ for the tetrahydrate. The entropies of formation of these two hydrates have been calculated from isothermal data and the values agree closely with those obtained by means of the third law of thermodynamics. This indicates that there is no residual disorder due to hydrogen bonding or other effects at limiting low temperatures. It has been shown that sulfuric acid tetrahydrate crystallizes as $H_2SO_4\cdot(4.0000 \pm 0.0001)H_2O$.

This is one of a series of investigations on the thermodynamics of the sulfuric acid–water system. We are concerned with the general problem of possible structural disorder, particularly hydrogen bond disorder, in crystals at limiting low temperatures as evidenced by residual entropy. It is important to know more about the extent and circumstances of such possible disorder, not only in connection with the application of the third law of thermodynamics, but also in connection with the interpretation of solid state phenomena at low temperatures. It has been shown previously[2,3] that ice retains hydrogen bond disorder at low temperatures. It is desirable to investigate a wide variety of chemical substances. The sulfuric acid–water system has been investigated partly because of the connection of these substances with many paramagnetic hydrated sulfates of interest at very low temperatures, and partly because of its widespread chemical importance.

Sulfuric acid tetrahydrate has been investigated previously in this Laboratory by Rubin and Giauque.[4] Their experiments, which were completed in 1940, showed discordant thermal behavior in the region below the melting point. The effects, which could not be interpreted at that time, made it impossible to obtain a reliable value of the heat of fusion from their data. Later a freezing point investigation of Gable, Betz and Maron[5] disclosed the existence of a previously undiscovered trihydrate of sulfuric acid and it became evident that a small amount of this material had crystallized with the tetrahydrate and was responsible for the abnormal thermal behavior. For this reason the results were withheld from publication and the re-

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[1] This work was supported in part by the Office of Naval Research, United States Navy, and by the National Science Foundation.

[2] L. Pauling, THIS JOURNAL, **57**, 2680 (1935).

[3] W. F. Giauque and J. W. Stout, *ibid.*, **58**, 1144 (1936).

[4] T. R. Rubin and W. F. Giauque, *ibid.*, **74**, 800 (1952).

[5] C. M. Gable, H. F. Betz and S. H. Maron, *ibid.*, **72**, 1445 (1950).

search has now been repeated under circumstances which enable the investigation of 99.925 mole % tetrahydrate. The agreement of the earlier and present heat capacity measurements was quite good but the earlier heat of fusion was, as expected, inaccurate.

Sulfuric acid trihydrate, in the form of glass and also crystals, has recently been investigated by Kunzler and Giauque.[6] The trihydrate is unstable with respect to the tetrahydrate and equilibrium solution at 236.72°K., which may be estimated to be about 0.05° below the unstable melting point. This causes great difficulty in crystallizing the trihydrate and the particular sample on which most of the data were obtained was found by later thermal analysis of the data to contain over 3% in forms other than the trihydrate. Profitting by the previous experience we have succeeded in crystallizing a better sample for the present investigation which should be taken to supercede the previous results.

The present data will be combined with other results to provide evidence that the tetra-, tri- and dihydrates all approach zero entropy, and thus an ordered state at limiting low temperatures.

Apparatus.—The calorimeter used has been described previously.[7] It has had the laboratory designation Gold Calorimeter III. The calorimeter had two platinum thermocouple wells welded on the top and bottom, respectively. These wells contained Rose metal. Escape of Rose metal onto the gold caused diffusion along grain boundaries until a crack developed in the bottom. The calorimeter was rebuilt to the extent of a new gold top and bottom and carnauba wax was placed in the thermocouple wells. This was not as satisfactory as the Rose metal because of the poorer thermal conductivity. However, it did not lead to much additional inaccuracy in the calibration, since a correction could be applied for the effect of any temperature difference between the calorimeter and the heavy metal block which surrounded it. However, we believe that some solution of this problem other than the use of wax should be found. The volume of the rebuilt calorimeter was found to be 131.5 cm.^{3} at 25°.

Preparation of the Samples.—In preparing both the tetra- and trihydrates C.P. sulfuric acid was redistilled and adjusted to composition with distilled water. Analysis was by weight titration against 6 *N* NaOH which had been standardized against constant boiling sulfuric acid as outlined by Kunzler.[8]

A "tetrahydrate" sample containing 0.85989 mole H_2SO_4 + 3.43901 moles H_2O was placed in the calorimeter.

After the "tetrahydrate" was in the calorimeter the accidental breakage of a vacuum line led to the possibility that a very small but unknown amount of water had been added to the sample. We may use this accident to illustrate the possibilities of calorimetric analysis in making minor adjustments. The sample was stirred by heating the calorimeter in such a manner as to produce convection. The material was then crystallized and some preliminary calorimetric observations were made. These showed a small amount of the hexahydrate peritectic although the original composition had been slightly on the H_2SO_4 side of the tetrahydrate.

A vacuum was applied to the acid until 0.00125 mole of H_2O was removed. This could be determined accurately from the heat effect since the heat of vaporization of water from the solution was accurately known. Subsequent calorimetric analysis is given below and it could be calculated that 0.00104 mole H_2O was added by the accident. The final composition was 0.85989 mole H_2SO_4 + 3.43880 moles H_2O corresponding to $H_2SO_4 \cdot 3.999H_2O$. As a check on these procedures the material was analyzed after removal from the calorimeter and the result checked to 0.006%.

In addition to the thermal analysis in terms of heats of fusion at the di-tetra eutectic and the tri-tetra peritectic, the heat effects due to premelting were measured. Usually, such premelting heat effects are interpreted in terms of ideal solution laws, but in the present case all of the necessary partial molal heat quantities were available. Long equilibrium periods were allowed during the premelting measurements to insure equilibrium, which is particularly difficult in such measurements, since they involve diffusion.

The results of the calorimetric analysis made during the two series of heat capacity measurements are given in Table I. The excellent agreement of the excess acid determined by the two types of observation is shown.

TABLE I

CALORIMETRIC ANALYSIS OF SULFURIC ACID "TETRAHYDRATE"

Units are moles per mole of "tetrahydrate."

	Anal. from eutectic heats of fusion		Anal. from premelting
Series	Crystalline hydrate	Total expressed as excess H_2SO_4	Total expressed as excess H_2SO_4
1	0.00005 dihydrate		
	0.0007 trihydrate	0.00020	0.00023
2	0.00045 dihydrate	.00023	.00024

The trihydrate analysis gave exactly $H_2SO_4 \cdot 3.000H_2O$. 1.10709 moles of this material was used for the measurements. The calorimetric analyses at the two eutectics with the trihydrate showed 0.0002 mole mono- and 0.0070 mole of dihydrate per mole of trihydrate. The premelting heat immediately above these temperatures gave 0.0072 mole expressed as dihydrate compared to the value 0.0074 calculable from the eutectic results. The above results imply that 0.0074 mole of tetrahydrate per mole of trihydrate was present during the low temperature heat capacity measurements. As may be seen from a phase diagram the presence of this solid tetrahydrate would not disclose itself by a heat effect below the melting point of the trihydrate.

The defined calorie was taken as 4.1840 absolute joules. 0°C. = 273.16°K.

Proof that $H_2SO_4 \cdot 4H_2O$ Crystallizes Accurately at that Composition.—We may use the above data to show that $H_2SO_4 \cdot 4H_2O$ corresponds to this composition very exactly. After the accidental addition of water mentioned above the substance was melted and stirred by convection. After freezing the substance, a calorimetric investigation indicated 0.00047 mole of excess water in the form of $H_2SO_4 \cdot 6H_2O$ at the peritectic. After removal of the 0.00125 mole of water and subsequent stirring and freezing there was a deficiency of 0.00076 mole of water below that required to make tetrahydrate as indicated in Table I. If there were a solid solution on the hexahydrate side of the tetra and another on the trihydrate side they must have essentially the same composition because 0.00047–0.00125 gives a deficiency of 0.00078 compared to the observed 0.00076 mole mentioned above assuming no contribution from the solids.

Since it is theoretically impossible to have a pure compound in equilibrium with a solution of different composition, and since the solutions on the hexa- and tri-sides of the tetrahydrate must be in equilibrium with solid solutions of different compositions, a small discrepancy must exist. The discrepancy of 0.00002 (0.000025 in 4.00000 mole H_2O) corresponds to 0.0006%. This is well within the limit of error and is in fact in the opposite direction from expectation. However considering sources of error we believe it is safe to conclude that the solid tetrahydrate is $H_2SO_4 \cdot (4.0000 \pm 0.0001) H_2O$.

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(6) J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 707 (1952).

(7) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(8) J. E. Kunzler, *Anal. Chem.*, **25**, 93 (1953).

The Melting Point of $H_2SO_4 \cdot 4H_2O$.—The temperature–composition curve near the melting point of $H_2SO_4 \cdot 4H_2O$ is so flat that the 0.006% excess acid produces a very small depression of the temperature. The results, shown relatively to 0.001°, are given in Table II.

TABLE II

MELTING POINT OF $H_2SO_4 \cdot 4H_2O$

Melted, %	Resist. therm.	Thermocouple
25	244.890	244.886
50	244.889	244.893
75	244.889	244.890

Accepted value 244.89°K.

Examination of the 1940 data books of Rubin and Giauque[4] shows 244.90°K. as the melting point in good agreement with the present value.

Transition Temperature of $H_2SO_4 \cdot 3H_2O$.—Sulfuric acid trihydrate decomposes to form a very small amount of tetrahydrate and equilibrium solution. The temperature was found to be 236.72°K. in exact agreement with the value of Kunzler and Giauque.[6] From the shape of the temperature–composition curve of Gable, Betz and Maron[5] the unstable melting point may be estimated as about 0.05° above the transition temperature. Thus we estimate the unstable melting point of $H_2SO_4 \cdot 3H_2O$ as 236.77°K.

The Heat Capacity Measurements.—The heat capacity measurements were made in the usual manner, except that in the range between 200°K. and the melting points of both tetra- and trihydrates, strain developed in the resistance thermometer. In this region the temperature measurements were made directly by means of a standard copper–constantan thermocouple with the laboratory designation W-25. At other temperatures this thermocouple was used as a reference standard for the resistance thermometer. The strain was probably caused by crystallization of the small amounts of other hydrates which may have undergone considerable supercooling before they crystallized. During warming this process could not be exactly reversed. We do not believe that the strain was due to the tetra- or trihydrates because after they had been crystallized from the supercooled liquids, they were partly remelted to relieve any strain. The tetrahydrate was melted to about 98% liquid before recrystallization; however, in the case of the trihydrate, which decomposes before melting, the small amount of premelting due to the other hydrates present should have released strain.

The observed data are given in Tables III and IV.

The measurements from about 220°K. to the respective melting points include heat effects due to eutectic fusion and premelting. The observations in Tables III and IV are not corrected for the small amounts of other hydrates present. This can easily be done by means of the known heat capacities of the other hydrates. The corrected results in the form of smoothed tables will be presented in a summarizing paper which will include all of our thermodynamic data on aqueous sulfuric acid and its several hydrates.

TABLE III

THE HEAT CAPACITY OF "$H_2SO_4 \cdot 3.999H_2O$"

Cal. deg.$^{-1}$ mole^{-1}, mol. wt. H_2SO_4 = 98.082, mol. wt., H_2O = 18.016.

T, °K.	C_p	ΔT	T, °K.	C_p	ΔT
		Series 1			
14.90	1.84	1.71	167.80	34.38	6.87
16.84	2.46	1.39	181.94	36.69	7.55
18.92	3.15	2.02	189.34	37.92	7.15
21.36	3.95	2.41	196.72	39.13	7.47
24.39	5.07	3.24	204.08	40.31[a]	7.09
27.72	6.22	3.32	211.42	41.59[a]	7.39
31.42	7.50	3.90	218.72	42.79[a]	7.03
35.38	8.80	3.78	224.65	43.86[a]	4.72
39.91	10.20	5.14	230.71	44.83[a]	7.11
45.03	11.75	5.15	236.74	47.02[a]	4.93
50.71	13.40	6.16	241.60	49.14[a]	4.95
56.96	15.04	6.33	260.63	90.49	6.59
63.29	16.56	6.22	267.46	90.86	6.93
69.93	18.04	7.03	274.70	91.24	7.27
76.69	19.41	6.47	282.07	91.58	7.05
83.44	20.64	7.00	289.49	91.90	7.41
90.36	21.87	6.83	297.07	92.30	7.18
97.21	23.07	6.84	305.06	92.59	7.53
103.99	24.18	6.70		Series 2	
110.92	25.30	7.15	208.02	35.30[a]	8.80
118.12	26.46	7.27	217.40	36.71[a]	9.75
125.31	27.57	7.03	224.96	38.20[a]	5.38
132.44	28.68	7.21	231.08	38.76[a]	6.76
139.53	29.82	6.96	236.98	39.64[a]	5.00
146.62	30.94	7.17	241.87	42.53[a]	4.67
153.69	32.08	6.90	250.96	90.14[a]	6.63
160.75	33.26	7.14	257.61	90.47[a]	6.46

[a] Temperatures measured directly by thermocouple.

TABLE IV

THE HEAT CAPACITY OF "$H_2SO_4 \cdot 3.000H_2O$"

Cal. deg.$^{-1}$ mole^{-1}, mol. wt. H_2SO_4 = 98.082, mol. wt., H_2O = 18.016.

T, °K.	C_p	ΔT	T, °K.	C_p	ΔT
14.36	0.99	2.34	144.58	26.40	7.33
17.12	1.63	2.53	152.15	27.50	7.44
19.79	2.32	2.48	159.42	28.55	6.97
22.69	3.10	3.15	166.60	29.61	7.13
25.98	4.00	3.46	173.54	30.65	6.74
29.62	4.98	3.89	180.42	31.66	6.92
33.96	6.14	4.52	187.44	32.77	7.06
38.55	7.30	4.58	194.48	33.84	6.72
43.34	8.52	5.01	201.69	35.01[a]	7.33
48.78	9.85	5.88	209.01	36.28[a]	6.96
54.52	11.17	5.66	215.75	37.36[a]	6.13
60.33	12.50	5.89	220.86	38.47[a]	3.93
66.72	13.91	6.87	225.56	39.02[a]	5.23
74.37	15.45	8.49	229.74	57.81[a]	3.11
81.98	16.88	6.82	233.18	53.11[a]	3.65
88.45	17.89	6.16	244.31	74.54	6.72
94.82	18.94	6.62	251.48	74.64	7.49
101.45	19.99	6.61	258.93	74.83	7.29
108.31	21.06	7.05	266.52	74.90	7.56
115.40	22.15	7.12	274.09	75.11	7.37
122.57	23.23	7.22	281.52	75.48	7.18
129.82	24.30	7.30	288.94	75.66	7.41
137.12	25.33	7.26	296.42	76.21	7.29

[a] Temperatures measured directly by thermocouple.

Smooth curves through the corrected data should be accurate to 3% near 15°K., 1% near 20°K., 0.2% at 35°K. and 0.1% at 60°K. and above.

Most of the uncertainty arises from difficulty in establishing absolute values of dR/dT of the resistance thermometer which loses sensitivity at the lower temperatures. However, it should be noted that the nature of the problem is such that a high value of dR/dT at one point must be compensated by a low value at another temperature not far removed, so that compensation gives entropy or energy function values of higher accuracy. The detailed composition of "$H_2SO_4 \cdot 3.999H_2O$" is given in Table I.

The detailed composition of "$H_2SO_4 \cdot 3.000H_2O$" referred to in Table IV was 0.9854 mole tri, 0.0074 mole tetra, 0.0070 mole di and 0.0002 mole mono.

Heats of Fusion of Sulfuric Acid Tetra- and Trihydrates.—The heats of fusion were measured in the usual manner of starting somewhat below the melting point and ending somewhat above. However in the present work it was necessary to make corrections for the small amounts of other hydrates present as disclosed by calorimetric analysis of eutectic fusion or premelting effects or both. The results are given in Table V. The values given have been corrected for premelting and the eutectic due to the small amounts of other hydrates.

TABLE V

HEATS OF FUSION OF $H_2SO_4 \cdot 4H_2O$ AND $H_2SO_4 \cdot 3H_2O$, CAL DEG.$^{-1}$ MOLE^{-1}

Tetrahydrate m.p. 244.89°K.		Trihydrate m.p. 236.77°K.	
Series	ΔH	Series	ΔH
1	7320	1	5733
2	7321	2	5738
3	7324		
Mean	7322	Mean	5736

As mentioned above the previous work[4] on the tetrahydrate could not be used for an accurate calculation of the heat of fusion so that the above value is the only reliable determination.[9]

Kunzler and Giauque[6] give 5786 cal. mole^{-1} as the heat of fusion of $H_2SO_4 \cdot 3H_2O$. We have re-examined their data books in an attempt to reinterpret the complex heat effects in the region covered by eutectic melting to the melting point. A recalculation gives a considerably lower result for the heat of fusion but leads to no values which can be given any weight in comparison with the present value 5736 cal. mole^{-1}. The earlier work also contains calculation errors which led to an over estimate of the premelting heat effects.

A principal advantage of the present work is due to the fact that the substance was cooled and heated several times over the range between 80°K. and somewhat below the melting point. Since small amounts of other hydrates crystallize by chance, the above treatment was designed to stabilize the distribution and crystallization of any hydrates resulting from their unavoidable chance occurrence. This treatment did reduce the amount of other hydrates present by recombining higher and lower hydrates to form the trihydrate. This could be shown by a progressive decrease in eutectic heat of fusion. Since this recombination occurs principally in the region between eutectic melting and the melting point of the trihydrate, it is particularly important not to have such a process in operation during calorimetric determinations. This type of behavior is one of the most difficult problems we have encountered in the measurement of heat capacities. In the present work at least 0.5 hour was allowed for equilibrium in measurements involving premelting, and heat leak corrections were made from known heat leak constants of the apparatus, rather than in terms of observed temperature drifts which are complicated by the rapidly changing heat capacity.

The Entropies of $H_2SO_4 \cdot 4H_2O$ and $H_2SO_4 \cdot 3H_2O$.—The calculation of the entropies is summarized in Table VI. The heat capacity data in Tables III and IV were corrected for the presence of the small amounts of other hydrates before the entropy computations were made.

TABLE VI

THE ENTROPIES OF $H_2SO_4 \cdot 4H_2O$ AND $H_2SO_4 \cdot 3H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

$H_2SO_4 \cdot 4H_2O$	
0–15°K., extrapolation	0.69
15–244.89°K., graphical	50.56
Fusion 7322/244.89	29.90
244.89–298.16°K., graphical	17.92
Entropy at 298.16°K.	99.07
$H_2SO_4 \cdot 3H_2O$	
0–15°K., extrapolation	0.40
15–236.77°K., graphical	40.62
Fusion 5736/236.77	24.23
236.77–298.16°K., graphical	17.30
	82.55

Kunzler and Giauque[6] obtained 82.90 cal. deg.$^{-1}$ mole^{-1} for the entropy of trihydrate but this value should be given no weight because of the type of difficulty mentioned above. The larger part of the difference is due to error in their calculation of the heat of fusion. A somewhat similar situation led to high (but unpublished) values of the heat of fusion and entropy of the tetrahydrate when an attempt was made to reinterpret the unpublished tetrahydrate data of Rubin and Giauque[4] after the trihydrate was recognized as a complication some years ago.

The entropy values may be checked against the third law of thermodynamics by means of the reactions

$$H_2SO_4 \cdot 2H_2O + H_2O(l) = H_2SO_4 \cdot 3H_2O \qquad (1)$$

and

$$H_2SO_4 \cdot 2H_2O + 2H_2O(l) = H_2SO_4 \cdot 4H_2O \qquad (2)$$

$$\Delta S = (\Delta H - \Delta F)/T$$

The values of ΔF may be calculated by means of the partial pressure of water over sulfuric acid solutions. The available data have been discussed by Hornung and Giauque.[10] The values of ΔH may

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[9] Rubin made a personal communication of some results of preliminary calculations of the properties of sulfuric acid and its hydrates to D. M. Yost and H. Russel. These should not have been published but were included in their book "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 337. Some of these values were considerably in error.

[10] E. W. Hornung and W. F. Giauque, THIS JOURNAL, **77**, 2744 (1955).

be calculated from the data of Kunzler and Giauque.[11]

The entropy of liquid water[12] is 16.71 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. and the entropy of sulfuric acid dihydrate[4] is 66.04 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

For equation 1, $\Delta S_{298.16} = (-1788 + 1720)/298.16 = -0.23$ cal. deg.$^{-1}$ mole^{-1}. From the third law of thermodynamics, $\Delta S_{298.16} = 82.55 - 66.04 - 16.71 = -0.20$ cal. deg.$^{-1}$ mole^{-1}.

For equation 2, $\Delta S_{298.16} = (-2978 + 2857)/298.16 = -0.41$ cal. deg.$^{-1}$ mole^{-1}. From the third law of thermodynamics $\Delta S_{298.16} = 99.07 - 66.04 - 2\,(16.71) = -0.39$ cal. deg.$^{-1}$ mole^{-1}.

The close agreement of the results indicates that the above hydrates of sulfuric acid approach zero entropy and thus have no hydrogen bond or other type of disorder as the absolute zero of temperature is approached.

We thank W. P. Cox for assistance with the measurements on sulfuric acid tetrahydrate and R. H. Sherman and M. N. Papadopoulos for assistance with the measurements on sulfuric acid trihydrate.

BERKELEY, CALIFORNIA

[11] J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 3472 (1952).

[12] M. N. Papadopoulos and W. F. Giauque, *ibid.*, **77**, 2740 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Heat of Formation of Molybdenum Dioxide and Molybdenum Trioxide[1]

BY BERNARD A. STASKIEWICZ, JAMES R. TUCKER AND PAUL E. SNYDER

RECEIVED JANUARY 8, 1955

A study has been made of the heats of combustion of molybdenum and molybdenum dioxide. The metal was used in the form of purified wire while the dioxide was a powder obtained by hydrogen reduction of purified trioxide. It was found that oxidation of the combustible was only 70–80% complete. In the case of the metal both dioxide and trioxide were formed. The data obtained in the two sets of experiments were sufficient to calculate three heat values: the standard heat of formation of MoO_3 of −744.6 ± 0.4 int. kjoules; the standard heat of formation of MoO_2 of −589.4 ± 0.5 int. kjoules; and the standard heat of combustion of MoO_2 to MoO_3 of −155.3 ± 0.13 int. kjoules.

In line with the program of this Laboratory to attempt to obtain more reliable values for the heat of formation of metallic oxides, a study has been made of such data for molybdenum dioxide and molybdenum trioxide. A survey of the literature yielded several previous determinations with the usual wide spread in the values reported. These data are listed in Table I.

TABLE I

Investigators	Date	$-\Delta H_f$, kcal./mole
Of MoO_3		
Delépine[2]	1903	167
Mixter[3]	1910	181.5
Moose and Parr[4]	1924	175.6
Neumann, Kröger and Kunz[5]	1934	180.4
This work	1953	178.0
Of MoO_2		
Mixter[3]	1910	142.8
Chaudron[6]	1921	134.0
Tonosaki[7]	1940	131.7
This work	1954	140.9

The values shown for MoO_3 were obtained by means of the oxygen bomb with the exception of that by Mixter who used the Na_2O_2 bomb on both MoO_3 and MoO_2. On the other hand, the data of Chaudron and Tonosaki were obtained by means of equilibrium studies involving Mo, H_2O, MoO_2 and H_2. Ignoring the earliest work of Delépine, it is seen that a spread of about 3% exists in the other three values for MoO_3. While this is not nearly as bad as is usually the case in connection with the literature values for the heat of formation of a given compound, it was felt that another determination was worthwhile. As will be indicated below, it was found necessary to investigate the heat of combustion of MoO_2 as well.

Experimental

Apparatus.—The apparatus employed in this investigation has been in use for a number of years in this Laboratory and has been previously described.[8] The model G-1 bridge that was formerly in use has been replaced by a Leeds and Northrup model G-2 in order to obtain better precision and more convenient operation of the calorimetry. Calibration of the several parts of the system was carried out in the usual way as has been described in the earlier publication.

Material.—The molybdenum used in this investigation consisted of 20 mil wire. It was wound into coils and purified electrically in a vacuum in the same way that tungsten[9] was treated some years ago. As before, the purification yielded a material of very high purity. Analysis by methods suitable for the element in question showed the following amounts of impurities: 0.004% carbon; 0.0057% oxygen; 0.004% nitrogen; 0.006% silicon; and less than 0.001% each of Fe, Cu, and Mg. Purity of the wire by difference was 99.98%.

The MoO_2 was prepared in the usual way by the reduction of highly purified MoO_3 with purified hydrogen gas. Spectrographic analysis showed only trace (0.001%) amounts of Fe, Cu, Mg and Ca with 0.01% W. The question of these minor impurities is not the important one, however. The method of preparation carries along with it an uncertainty concerning the amount of MoO_3 left unchanged and the amount of Mo that might be produced. Unfortunately, there is no elegant way by which MoO_2 may be determined in such a mixture. Recourse was had to two methods for

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[1] From a thesis submitted by Bernard H. Staskiewicz to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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