Summary

1. The ultraviolet absorption spectra of 2-thiouracil, 2,4-dithiouracil, 4-thiouracil, 2-thiothymine, 2,4-dithiothymine and 4-thiothymine are given at pH values 1, 7 and 11.

2. Comparison is made between the spectra of these thio derivatives with the spectra of uracil and thymine and the anomalous position of the absorption bands of 4-thiouracil and 4-thiothymine is discussed.

Tuckahoe, N. Y.   RECEIVED JUNE 19, 1946

Low-Temperature Heat Capacities and High-Temperature Heat Contents of Al₂O₃·3H₂O and Al₂O₃·H₂O[1]

BY C. HOWARD SHOMATE[2] AND OSCAR A. COOK[2]

One of the recent programs of the Pacific Experiment Station of the Bureau of Mines has been the measurement of thermodynamic properties of aluminum compounds of interest in certain processes for extracting alumina from clay and alunite. Several previous papers[3] on this subject have been published. The present paper, the concluding member of this series, presents low-temperature heat-capacity and high-temperature heat-content data for two crystalline hydrates of alumina.

Materials

The tri-hydrate of alumina was prepared in this Laboratory by A. E. Salo[4] by dissolving aluminum wire in 0.2 N potassium hydroxide. The precipitated crystals of $Al_2O_3\cdot 3H_2O$ were washed with 4 N hydrochloric acid to remove iron resulting from the original impurity in the aluminum wire, washed finally with distilled water, and dried at 140°. Analysis was made by fusion with sodium bisulfate and precipitation by the 8-hydroxyquinoline method. Analysis gave 65.62% aluminum oxide (theoretical 65.35%). The sample used in the low-temperature heat capacity measurements weighed 86.36 g., and the high-temperature heat content sample weighed 4.129 g.

The mono-hydrate of alumina was prepared by heating the tri-hydrate at 220° for three days. The aluminum oxide content was found to be 3% too high, so the required amount of water was added and the mixture stabilized by heating at 80° for sixteen hours in an evacuated flask. Since the product was not readily fusible in sodium bisulfate nor satisfactorily soluble in any ordinary reagent, analysis was made by igniting to aluminum oxide in a platinum crucible over an oxygen-natural gas flame. Analysis gave 85.00% aluminum oxide (theoretical 84.90%). A 92.30-g. sample was used in the low-temperature measurements, and a 4.228-g. sample for the measurements at high temperatures.

X-Ray examinations showed the tri-hydrate to have the structure of gibbsite ($Al_2O_3\cdot 3H_2O$), and the mono-hydrate a structure similar to bayerite ($Al_2O_3\cdot 3H_2O$), differing from the latter principally in the intensities of the lines.

Low-Temperature Heat Capacities

The method and apparatus used in the low temperature heat-capacity measurements were

described previously.[5,6] The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[7] are listed in Table I and shown graphically in Fig. 1. The values of the heat capacities at 298.16°K., read from a smooth curve through the experimental points, are also included in Table I. The molecular weights are in accordance with the 1941 International Atomic Weights.

TABLE I

MOLAL HEAT CAPACITIES

Al₂O₃·3H₂O Mol. wt., 155.99		Al₂O₃·H₂O Mol. wt., 119.96	
T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
52.8	3.213	52.7	2.179
56.9	3.708	56.9	2.528
61.1	4.259	61.0	2.914
65.2	4.816	65.2	3.307
69.8	5.506	69.3	3.733
74.0	6.164	73.8	4.216
78.4	6.854	78.3	4.709
85.3	8.002	84.8	5.441
94.8	9.677	94.7	6.630
104.7	11.54	104.5	7.865
115.3	13.57	115.1	9.228
125.3	15.51	125.3	10.58
135.1	17.47	135.0	11.92
145.4	19.50	145.6	13.31
155.3	21.39	155.4	14.62
165.5	23.38	165.5	15.98
175.7	25.35	175.4	17.33
185.7	27.15	185.6	18.66
196.0	28.97	195.8	20.00
205.9	30.72	205.9	21.32
216.2	32.55	216.2	22.57
226.2	34.09	226.2	23.74
235.8	35.55	235.9	24.83
246.2	37.19	246.2	25.99
256.2	38.72	256.4	27.14
266.3	40.17	266.1	28.26
276.3	41.63	276.2	29.27
286.3	42.94	286.2	30.17
296.5	44.27	296.4	31.13
(298.16)	(44.49)	(298.16)	(31.37)

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) (a) Shomate and Naylor, THIS JOURNAL, 67, 72 (1945); (b) Young, ibid., 67, 257 (1945); (c) Shomate, ibid., 67, 765 (1945); (d) Young, ibid., 67, 851 (1945); (e) Shomate, ibid., 67, 1096 (1945).

(4) Metallurgist, Pacific Experiment Station, Bureau of Mines.

(5) Kelley, THIS JOURNAL, 63, 1137 (1941).

(6) Shomate and Kelley, ibid., 66, 1490 (1944).
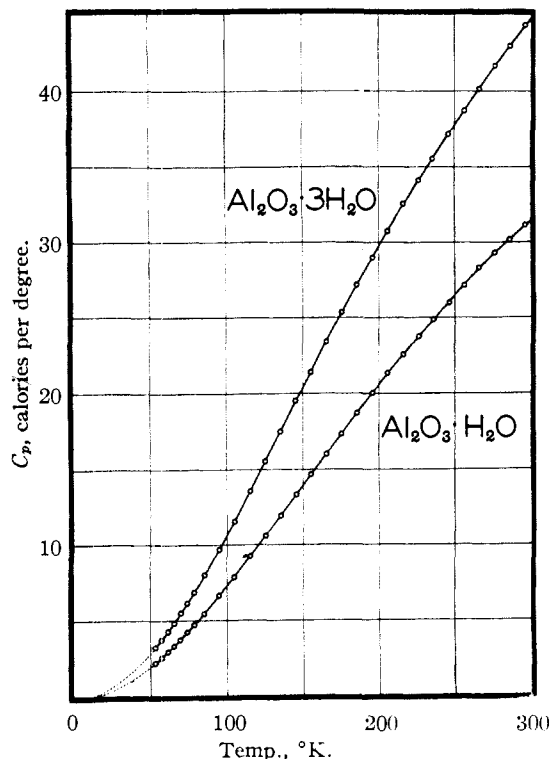
(7) Mueller and Rossini, Am. J. Physics, 12, 1 (1944).

Fig. 1.—Molal heat capacities.

All weights were corrected to vacuum using the following densities: $Al_2O_3 \cdot 3H_2O$, 2.45; and $Al_2O_3 \cdot H_2O$, 2.83 g./cc., respectively. These values were determined in this Laboratory by A. E. Salo.[4]

The two hydrates exhibited normal behavior, there being no thermal anomalies in the temperature range studied.

Entropies at 298.16°K.

Evaluation of the entropies at 298.16°K. is obtained by numerical integration of a plot of C_p against $\log T$. This necessitates the extrapolation of the heat-capacity curve from the temperature of the lowest measurement down to absolute zero of temperature. It was found that the following function sums adequately represent (within 1%) all the measured heat capacities

$$Al_2O_3 \cdot 3H_2O: \quad D\left(\frac{223}{T}\right) + 4E\left(\frac{440}{T}\right) + 7E\left(\frac{964}{T}\right)$$

$$Al_2O_3 \cdot H_2O: \quad D\left(\frac{265}{T}\right) + 4E\left(\frac{550}{T}\right) + 6E\left(\frac{1380}{T}\right)$$

The symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the heat-capacity curves to 0°K. (broken lines in Fig. 1).

TABLE II

ENTROPIES AT 298.16°K. (E.U./MOLE)

	$Al_2O_3 \cdot 3H_2O$	$Al_2O_3 \cdot H_2O$
0–52.00°K. (extrapolated)	1.40	0.94
52.00–298.16°K. (measured)	32.11	22.21
	33.51 ± 0.1	23.15 ± 0.1

Table II summarizes the entropy calculations for the two hydrates.

High-Temperature Heat Contents

The heat-content measurements were made by the "drop" method. The experimental procedure and apparatus have been described previously.[8] During the measurements the samples were contained in platinum–rhodium alloy capsules, the heat contents of which had been determined separately. After being filled with sample, the cap-

TABLE III

MOLAL HEAT CONTENTS ABOVE 298.16°K.

$Al_2O_3 \cdot 3H_2O$ Mol. wt., 155.99		$Al_2O_3 \cdot H_2O$ Mol. wt., 119.96	
T, °K.	$H_T - H_{291.16}$, cal.	T, °K.	$H_T - H_{298.16}$, cal.
322.2	1056	321.7	688
323.0	1095	341.0	1255
349.1	2322	366.2	1969
373.2	3594	416.2	3669
423.5	6312	445.4	4690
		473.0	5746
		500.4	6901
		520.1	7914

sules were evacuated of air, filled with helium, and quickly sealed. The results are listed in Table III and shown graphically in Fig. 2.
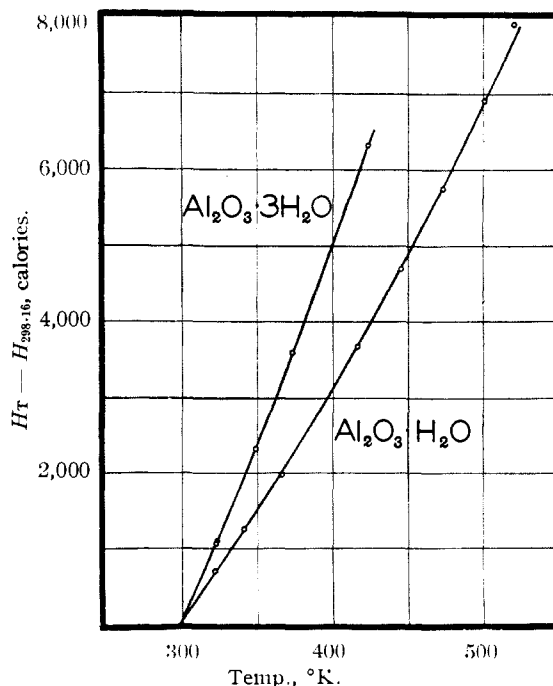

Fig. 2.—Molal heat contents above 298.16°K.

These materials were not well adapted to high temperature heat content determinations. Their temperature ranges of stability were too low to permit the usual accuracy of measurement. In addition, difficulty was encountered in evolution of

(8) Southard, THIS JOURNAL, **63**, 3142 (1941).

water which was irreversible in the calorimetric process; i.e., evolved water condensed as liquid in the capsule during cooling and did not recombine with alumina. For these reasons the data of Table III may be uncertain by as much as a few

TABLE IV

MOLAL HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	$Al_2O_3 \cdot 3H_2O$		$Al_2O_3 \cdot H_2O$	
	$H_T - H_{298.16}$, cal.	$S_T - S_{298.16}$, E. U.	$H_T - H_{298.16}$, cal.	$S_T - S_{298.15}$, E. U.
325	1180	3.79	770	2.47
350	2390	7.37	1515	4.68
375	3680	10.3	2295	6.83
400	5010	14.6	3115	8.95
425	6390	17.31	3970	11.02
450			4860	13.05
475			5810	15.11
500			6850	17.24

per cent. They are adequate, however, for ordinary heat-balance calculations.

Heat-content values read from smooth curves at 25°-intervals and the corresponding graphically computed entropy increments are given in Table IV.

Summary

The heat capacities of $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot H_2O$ were measured in the temperature range 52 to 298°K.

The following molal entropies at 298.16°K. were computed: $Al_2O_3 \cdot 3H_2O$, 33.51 ± 0.1; and $Al_2O_3 \cdot H_2O$, 23.15 ± 0.1 E.U.

High-temperature heat contents above 298.16°K. were measured for the two hydrates. These data have been summarized by a table of heat contents and entropies above 298.16°K. at 25° intervals.

A New Type of Precision Capillarimeter

BY JOSEPH J. JASPER AND KERMIT D. HERRINGTON

During the investigation of the molar surface energies and the related properties of a series of addition compounds in this Laboratory, it became evident that truly comparable values could be obtained only from high precision surface tension measurements of pure compounds. To obtain data restricted to these requirements plans were made to prepare the compounds in a high vacuum system and to subsequently transfer them to a capillarimeter sealed into the line. The capillarimeter was then to be sealed off from the line and the surface tension measurements carried out under orthobaric conditions. In this way the effects due to moisture and other impurities are eliminated.

This method, however, is by its nature restricted to relatively small quantities of liquids. The primary problem, therefore, was to design and construct a capillarimeter embodying all known features which contribute to the precision of the measurements, and which required a small volume of liquid.

Although the capillary rise method is generally recognized as the ultimate standard for the determination of surface tension, high precision is obtained only by conforming rigorously to certain structural and dimensional specifications in designing the capillarimeter. These specifications arise from the necessity of eliminating, or reducing to negligible proportions, uncertainties introduced by (a) the mathematical theory in the treatment of curved liquid surfaces, and (b) the difficulties attending the measurement of radii of curvature. The uncertainties, however, are reflected in the

capillary constant, rh, and equations for its calculation have been derived by Rayleigh,[1] Verschaffelt,[2] and other earlier workers, giving approximations within the range of their applicability.

Results from the exact experiments of Richards and Carver[3] show that the major error in the capillary constant can be reduced to a minimum if (a) the radius of the capillary is constant and of such value that the curvature of the liquid meniscus approaches closely that of a hemisphere for liquids which wet the tube, and (b) if the reference surface varies but slightly from that of a geometric plane. It is evident, therefore, that the structural and dimensional specifications of a precision capillarimeter are largely determined by these fundamental requisites.

A capillarimeter, conforming to the precision and volume requirements outlined above, was designed by one of us. It was later constructed and tested with compounds of known purity and surface tensions under orthobaric conditions. In the design additional features were added which eliminate, or minimize, several possible sources of error. Since the experimental details of the capillary rise method have been worked out by Richards and his co-workers,[3,4,5] and by Harkins and Brown,[6] it seemed expedient to follow their

(1) Lord Rayleigh, Proc. Roy. Soc. (London), **A92**, 184 (1915).

(2) J. E. Verschaffelt, Proc. Koninkl. Akad. Wetenschappen Amsterdam., **21**, 357, 836 (1919).

(3) T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 827 (1921).

(4) T. W. Richards and J. W. Shipley, ibid., **36**, 1828 (1914).

(5) T. W. Richards and L. B. Coombs, ibid., **37**, 1656 (1915).

(6) W. D. Harkins and F. E. Brown, ibid., **41**, 499 (1919).