[CONTRIBUTION FROM THE U. S. DEPARTMENT OF INTERIOR, BUREAU OF MINES, PACIFIC EXPERIMENT STATION, UNIV. OF CALIFORNIA]

Specific Heats at Low Temperatures of Calcium Sulfite, Sodium Sulfite, and Manganese Dithionate Dihydrate[1]

BY K. K. KELLEY[2] AND G. E. MOORE[3]

As part of its program of supplying fundamental thermochemical data for substances of metallurgical interest, the Bureau of Mines has reported previously on the low-temperature specific heats and entropies of manganese[4] and eleven of its inorganic compounds.[4,5] The present paper adds another compound to this list, the dithionate-dihydrate, and also presents similar data for calcium and sodium sulfites, as these substances are of interest in connection with certain hydrometallurgical methods of extracting manganese.

This work represents the first measurements of low-temperature specific heats of any members of the two classes of substances concerned—sulfites and dithionates—and is of some interest from this viewpoint alone.

Materials

Calcium sulfite was prepared from C. P. calcium carbonate, low in alkali. The fine carbonate was suspended in a flask of water, previously boiled to remove air, and allowed to react with a rapid stream of sulfur dioxide at 80° in a system protected from contact with air. The reaction was continued until virtually all the carbonate was decomposed, as shown by intermittent tests. (The carbonate test consisted of removing a sample from the flask, acidifying with strong acid, and leading the evolved gas slowly through a concentrated iodine–potassium iodide solution to remove sulfur dioxide and then through barium hydroxide solution to detect carbon dioxide.) When the reaction was considered complete, the temperature was raised and the flask boiled dry while the sulfur dioxide stream was continued. At this point the product gave no test for sulfate. It was transferred to a high-vacuum system and heated five hours at 155°, after which a direct test for water gave 7.1%. (Röhrig's[6] claim that calcium sulfite may be dehydrated to hemihydrate at 80° and to the anhydrous salt at 100° is incorrect.) Heating was continued several hours longer at temperatures up to 245°, with but little additional removal of water. At about 275° water removal again commenced, and the temperature was raised slowly to 310° and held for two hours until evolution of water stopped. At this point 0.5% water remained in the material, and it was still free of sulfate. Seven hours of heating and pumping at 390–400° was finally required before the water content was reduced to a negligible quantity. During the latter process some sulfate was formed and some sulfite decomposed. Analyses were made for CaO, $SO_4^=$, CO_2, and H_2O. The results corresponded to 98.75% calcium sulfite, 0.9% calcium sulfate, 0.24% calcium oxide, 0.07% calcium carbonate, and 0.02% water, and it was felt that this product was about as good as could be obtained in any reasonable time. A 117.96-g. sample was used in the measurements.

Reagent-grade anhydrous sodium sulfite was used without further purification. Analyses gave 98.8% sodium sulfite and 0.90% sodium sulfate. It required 158.82 g. to fill the calorimeter.

Manganese dithionate is difficult to prepare in pure form, and after some preliminary experiments the following procedure was adopted. A suspension of reagent-grade manganese dioxide in a flask of water was cooled with ice–salt mixture and sulfur dioxide passed from a cylinder until reaction was complete. The sulfur dioxide flow was maintained slow enough to prevent the temperature in the flask from rising above 7°. The solution, containing mainly manganese dithionate but also some manganous sulfate, was filtered, diluted with water and treated with enough barium hydroxide solution to precipitate the sulfate and all the manganese. After filtering, the solution contained mainly barium dithionate, of which a fraction was crystallized out after low-temperature evaporation. The crystalline barium dithionate then was filtered off, redissolved in water, and titrated with reagent-grade manganous sulfate to precipitate barium sulfate and leave manganese dithionate in solution. This final solution was evaporated slowly under vacuum at 35° until a satisfactory yield of hydrated crystalline manganese dithionate was obtained. It was originally intended to dry these crystals to anhydrous form, but this was found to be impossible without considerable sacrifice of purity, because of the instability of manganese dithionate with respect to manganous sulfate and sulfur dioxide. Prolonged drying, for several weeks, at 35° in a warmed desiccator, first over concentrated sulfuric acid and then over phosphorus pentoxide, and finally under 10^{-4} mm. pressure at 45° for several hours, resulted in a sample of manganese dithionate-dihydrate that had decomposed only slightly. Under these conditions, dehydration ceased at the dihydrate point. Experiments on further dehydration at higher temperatures (up to 100°) resulted in too much decomposition. The product used in the measurements was analyzed and found to contain 99.0% $MnS_2O_6\cdot 2H_2O$, 0.58% BaS_2O_6, and 0.42% $MnSO_4$. In computing the analytical results it was assumed that all $SO_4^=$ was present as manganous sulfate from decomposition of manganese dithionate, as the latter is much less stable than barium dithionate. The odor of sulfur dioxide was detectable over the preparation after standing in a sealed container, but the decomposition at room temperature is quite slow. This was shown by analyses for sulfate made before and after the specific heat measurements, which indicated no significant change. The specific heat measurements were made using a 123.18-g. sample.[7]

Measurements

The method and apparatus[8] used previously again were employed. The results of the specific heat measurements are listed in Table I and shown plotted against temperature in Fig. 1. The defined calorie (1 calorie = 4.1833 int. joules) is used throughout, and the molecular weight values in the headings of Table I are in accord with the 1941 international atomic weights. The calcium sulfite data have been corrected for the impurities previously listed, assuming the specific heats to be additive. The cor-

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[4] Kelley, THIS JOURNAL, **61**, 203 (1939).

[5] (a) Millar, *ibid.*, **50**, 1875 (1928); (b) Anderson, *ibid.*, **53**, 476 (1931); (c) Anderson, *ibid.*, **56**, 849 (1934); (d) Kelley, *ibid.*, **63**, 2750 (1941); (e) Moore and Kelley, *ibid.*, **64**, 2949 (1942); (f) Kelley and Moore, *ibid.*, **65**, 782 (1943); (g) Kelley and Moore, *ibid.*, **65**, 1264 (1943); (h) Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.

[6] Röhrig, *J. prakt. Chem.*, **37**, 232 (1888).

[7] The authors wish to acknowledge the assistance of Mr. A. R. Fox, formerly Assistant Chemist, Bureau of Mines, who carried the preparation of this product up to the final dehydration stage.

[8] Kelley, THIS JOURNAL, **63**, 1137 (1941).

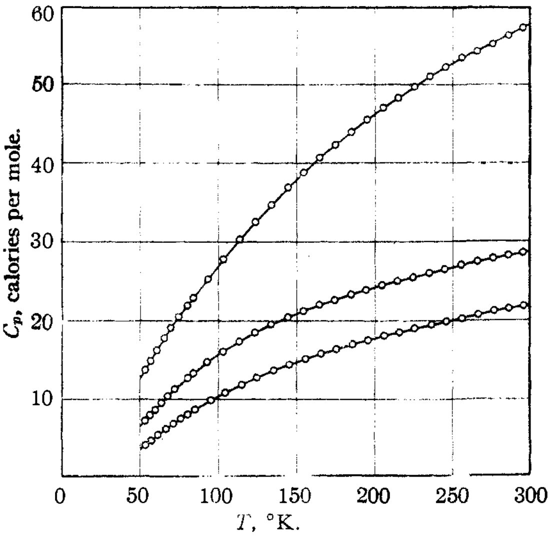

Fig. 1.—Specific heats of $CaSO_3$, Na_2SO_3, and $MnS_2O_6 \cdot 2H_2O$: upper curve, $MnS_2O_6 \cdot 2H_2O$; middle curve, Na_2SO_3; lower curve, $CaSO_3$.

rection amounted to 0.00 to 0.14%, depending on the temperature. Likewise, the sodium sulfite results were corrected for the 0.9% sodium sulfate content. In this instance, the correction varied from 0.07 to 0.16%. The impurity correction of the manganese dithionate-dihydrate data was the largest, on the average, of the three substances under consideration, 0.04 to 0.39%, depending on the temperature.

TABLE I

SPECIFIC HEAT OF $CaSO_3$ (MOLE WT. = 120.14 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
53.2	4.180	114.9	11.96	215.8	18.56
57.1	4.753	124.5	12.85	225.6	19.06
61.7	5.473	135.3	13.75	236.1	19.47
66.7	6.246	145.2	14.47	245.9	19.94
71.4	6.933	155.9	15.22	255.9	20.34
76.0	7.567	165.7	15.88	266.2	20.80
80.4	8.164	175.4	16.43	276.3	21.25
85.2	8.767	185.9	17.05	286.0	21.56
95.2	9.953	195.7	17.60	295.3	21.82
104.3	10.93	206.0	18.09		

SPECIFIC HEAT OF Na_2SO_3 (MOLE WT. = 126.05 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
53.2	7.292	113.1	17.40	214.3	25.05
56.5	7.991	123.3	18.54	224.1	25.53
59.9	8.746	133.6	19.55	234.7	26.04
63.8	9.592	144.1	20.48	244.6	26.53
67.7	10.44	154.0	21.26	255.1	27.03
72.2	11.35	164.4	22.06	265.7	27.48
80.4	12.81	174.1	22.67	275.9	27.92
84.0	13.41	184.7	23.36	285.8	28.28
92.8	14.80	194.4	23.97	295.1	28.62
103.0	16.18	204.5	24.54		

SPECIFIC HEAT OF $MnS_2O_6 \cdot 2H_2O$ (MOLE WT. = 251.08 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
53.1	13.81	113.4	30.31	215.0	48.30
56.8	14.96	123.6	32.56	225.5	49.71
60.9	16.26	133.9	34.74	235.4	51.03
65.4	17.79	144.3	36.90	245.3	52.22
69.7	19.15	154.3	38.80	255.8	53.47
74.4	20.52	164.7	40.67	265.7	54.23
80.0	21.98	174.5	42.35	275.6	55.20
83.8	22.94	184.8	43.99	285.7	56.30
93.0	25.30	195.0	45.58	294.9	57.30
103.0	27.82	205.2	47.05		

The two sulfites were measured in our best calorimeter, while the dithionate was measured in an older one that had been in use previously. This was considered advisable because of the possibility of the decomposition pressure of the dithionate reaching a value that would burst the container. This appears theoretically possible, according to available thermochemical data, but it did not occur because of the slowness of decomposition. It is believed that the measurements of calcium and sodium sulfites are accurate on the average to within 0.3% and those of the manganese dithionate-dihydrate to within 0.5%, the difference being attributable to the use of the older calorimeter for the last substance. The average deviation of the results from a smooth curve is considerably smaller than the error claimed, being less than 0.1%.

As is seen from Fig. 1, no abnormal behavior was noted for these compounds, and the course of their specific heat curves needs no discussion. There are no previous data with which to compare any of the present measurements.

Entropies at 298.16°K.

The entropies at 298.16°K. were calculated in the usual manner. Between 50.12° and 298.16°K., graphical integrations were made under the C_p against log T curves, $\int_{50.12}^{298.16} C_p \, d \ln T$. The entropy increments lying below 50.12°K. were obtained by extrapolation. This was accomplished by fitting the experimental data over the entire experimental range by the following series of Debye and Einstein functions

$$CaSO_3:\ C_p = D\left(\frac{201}{T}\right) + 2E\left(\frac{322}{T}\right) + E\left(\frac{720}{T}\right) + E\left(\frac{1316}{T}\right)$$

$$Na_2SO_3:\ C_p = D\left(\frac{175}{T}\right) + 3E\left(\frac{256}{T}\right) + 2E\left(\frac{860}{T}\right)$$

$$MnS_2O_6 \cdot 2H_2O:\ C_p = D\left(\frac{91.7}{T}\right) + 4E\left(\frac{197}{T}\right) + 4E\left(\frac{501}{T}\right) + 2E\left(\frac{857}{T}\right) + 2E\left(\frac{1205}{T}\right)$$

Only the first two functions are of significance in each instance in computing the extrapolated portion of the entropy. The results are listed in Table II.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	$CaSO_3$	Na_2SO_3	$MnS_2O_6 \cdot 2H_2O$
0–50.12°K. (extrap.)	1.68	2.65	7.15
50.12°–298.16°K. (graph.)	22.55	32.23	59.51
$S^\circ_{298.16}$	24.2 ± 0.3	34.9 ± 0.4	66.7 ± 1.0

The entropy of calcium sulfite is 1.3 to 1.6 unit less than that of calcium sulfate,[9] depending on the variety of calcium sulfate, and the entropy of sodium sulfite is 0.8 unit less than that of

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(9) Kelley, Southard, and Anderson, Bureau of Mines Tech. Paper 625, 1941, 73 pp.

sodium sulfate.[10] Thus, in these two instances, the effect on the entropy of removing one oxygen atom from a sulfate group to form a sulfite group is a decrease of about 1 unit. A difference of this order of magnitude reasonably may be expected between sulfates and sulfites of other metals, and this offers a means of estimating the entropy of the sulfite when that of the sulfate is known or *vice versa*.

The entropy of manganese dithionate-dihydrate may be subject to some correction because of unextracted magnetic entropy; but sufficient information on this point is not available at present, and it is not taken account of in the error assigned to the entropy value in Table II. In view of recent observations[11] on the approximate constancy of the entropy of water of crystallization, one would estimate the entropy of anhydrous manganese dithionate to be about 45 units at 298.16°K. and that of the hexahydrate to be about 110 units.

Summary

Low-temperature specific heat measurements, throughout the temperature range 51 to 298°K., have been made of calcium sulfite, sodium sulfite, and manganese dithionate-dihydrate.

The respective entropies at 298.16°K. are 24.2 ± 0.3, 34.9 ± 0.4, and 66.7 ± 1.0.

It is suggested that the difference in entropy between a sulfate and a sulfite group in a solid compound is about 1 unit at 298.16°K.

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[10] Pitzer and Coulter, THIS JOURNAL, **60**, 1310 (1938).

[11] Kelley and Moore, *ibid.*, **65**, 2340 (1943).

[CONTRIBUTION FROM STEELE CHEMICAL LABORATORY, DARTMOUTH COLLEGE]

The Crystal Structure of Potassium Silver Carbonate, $KAgCO_3$[1]

BY JERRY DONOHUE[2] AND LINDSAY HELMHOLZ

Introduction.—The determination of the structure of potassium silver carbonate, which is colorless, was undertaken in conjunction with that of silver carbonate,[3] which is yellow, for the purpose of establishing the character of the silver-oxygen bond in those crystals, and discussing the difference in color in terms of the rule suggested by Pitzer and Hildebrand,[4] which states that the color of a compound formed from colorless ions is related to the amount of "covalent character" in the bond between these ions. Since the electronic structure of the carbonate group can readily be interpreted in terms of single bond double bond resonance, any effect of silver to oxygen covalent bond formation on the normal ionic configuration could be discussed in a relatively straightforward manner. Unfortunately an accurate structure of silver carbonate, in which appreciable covalent bond formation is suggested both by approximate distances and the rule of Pitzer and Hildebrand, is not yet available.

Experimental.—Potassium silver carbonate was prepared by the method of de Schulten.[5] Silver nitrate solution (0.25 *m*) was added dropwise to 50% potassium carbonate saturated with potassium bicarbonate. The yellow precipitate first formed turned white on standing. Complete solution takes place on heating. Slow cooling of this hot solution in a Dewar flask gives needle-like crystals, elongated in the *c* direction. The crystals prepared in this manner had all the properties described by de Schulten. Goniometric examination showed the crystals to be possibly orthorhombic, there being well-developed (100) and (110) faces ($a:b = 3.54:1$). Laue photographs showed the Laue symmetry D_{2h}-mmm, this establishing the orthorhombic symmetry.

Oscillation photographs were taken with the *c* axis vertical, using CuKα radiation. One oscillation photograph using Mo Kα radiation was taken for the purpose of obtaining more layer lines. The dimensions of the unit cell, as determined by indexing those photographs, were found to be $a_0 = 20.23$ Å., $b_0 = 5.75$ Å., $c_0 = 5.95$ Å. (all ±0.5%) ($a:b:c = 3.521:1:1.036$). Indexing of symmetric and asymmetric Laue photographs ($\lambda_{\min.} = 0.24$ Å.) showed no first order reflections requiring a larger unit cell.

The number of molecules in the unit cell (using de Schulten's density value of 3.77 g./cc.) is calculated to be 7.66. Assumption of eight molecules in the unit cell gives a calculated density of 3.94 g./cc. de Schulten's value is low probably due to the fact that potassium carbonate clings tenaciously to the surface of the crystals as prepared. Attempts to measure the density also gave low values.

The intensities of the reflections on the oscillation photographs were estimated by means of the multiple film technique,[6] and by taking pictures of different exposure times over the same range. It was found necessary to correct the intensities for absorption; the correction factor was derived by integrating the expression for the path of beam through the crystal (assumed to be bathed by the beam) in accordance with the relation $I = I_0K|F|^2\, e^{-\mu p}\, dp$ where I = the corrected intensity, I_0 = the incident intensity, K = the product of the Lorentz, polarization and temperature factors, F = the structure factor, μ = the absorption coefficient, and P = the path length of the beam through the crystal. The path length is expressed as function of: A, the width of the crystal; α, the angle through which the crystal has been rotated; and φ, the azimuthal scattering angle. Two cases are considered: (1) the incident and the emergent rays pass through the same crystal face, and (2) these two rays pass through different crystal faces. For case (1), the simplified expression is $I = I_0K|F|^2 \frac{A \sin\alpha}{\mu c}$, where $c = 1 + \frac{\sin\alpha}{\sin(\alpha - \varphi)}$. For case (2), the simplified expression is $I = I_0K|F|^2 \left(\frac{\sin(2\alpha - \varphi)}{\mu^2}\right)$. In

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[1] Abstracted from a thesis submitted by Jerry Donohue to Dartmouth College in partial fulfillment of the requirements for the degree of Master of Arts.

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[3] John E. Eldridge, Thesis, 1943, Dartmouth College.

[4] K. S. Pitzer and J. H. Hildebrand, THIS JOURNAL, **63**, 2472 (1941).

[5] A. de Schulten, *Compt. rend.*, **105**, 811 (1887).

[6] J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).