[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# The Heat Capacity and Entropy of Rhombic and Monoclinic Sulfur

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The only data at present available in the literature on the heat capacity at low temperatures of the two crystalline forms of sulfur are early measurements made in Nernst's laboratory.[1] As these are insufficient for the determination of entropy with the certainty now desirable, we have made a more complete investigation, the results of which are presented here.

## Experimental Details

The method of measurement of heat capacity was the standard one of electrical heating in vacuum now universally employed for such measurements at low temperatures, and conformed, in general practice, with that of numerous other investigations in this Laboratory at the date of these measurements, 1932–1933.

The calorimeter was constructed of gold, to enable measurements to be made near the transition temperature without danger of reaction of the metal with sulfur. It was welded from gold sheet of 1 mm. thickness in the form of a cylinder 7 cm. long and 5 cm. in diameter. Eleven radial vanes 0.2 mm. thick and extending nearly to the center were welded to the interior wall to promote thermal conduction. The opening to the calorimeter was provided by a tube of *einschmilzungsglas* sealed to a platinum tube which in turn was welded to the calorimeter. The materials of the calorimeter comprised 306 g. of gold, 3.66 g. of platinum and 5.52 g. of glass, together with small amounts of Bakelite lacquer and lens paper used in cementing and insulating the heater.

The calorimeter heater, which also served as a resistance thermometer, was of No. 40 B. and S. gage double silk insulated wire of gold alloyed with 0.1% silver, drawn in the manner described by Onnes and Clay.[2] Its resistance was 13.9 ohms at 15°K. and 248 ohms at 298°K. The procedure in attaching the heater-thermometer to the calorimeter was as follows. The surface of the calorimeter was first given a "hair" finish with fine emery paper. Two very thin coats of Bakelite lacquer were next applied, each dried in air and heated slowly in the course of a day or more up to 140–150°. This temperature was maintained until the color was a dark reddish-brown. A thickness of lens paper was then applied, the heater wound on, another thickness of lens paper applied and the whole soaked with Bakelite lacquer. This was baked as described above, and two or three more very thin coats of Bakelite applied. The surface was then covered with gold beaters leaf to cut down radiation interchange during the measurements.

The resistance thermometer on the calorimeter was standardized by comparison with a thermocouple which had been calibrated by Dr. R. T. Milner by comparison with laboratory standards, the temperature scale being that established by Giauque, Buffington and Schulze.[3] For the extension of this scale to higher temperatures the couple was calibrated at the transition temperature of sodium sulfate decahydrate and at the boiling point of water.

The timer described by Johnston[4] was used to measure the heating interval to less than one hundredth of a sec. The time of heating was from six to twenty minutes, the temperature increments varying from 1° at the lowest temperature to 6 or 8° near the transition.

A lead block of large heat capacity surrounded the calorimeter, making it possible to stabilize temperatures at points intermediate between those of the outer baths employed in different temperature ranges. For work above room temperature the metal can enclosing the block was provided with a heating coil for regulation of its temperature.

Helium at 75 cm. pressure at 20° was employed in the calorimeter to promote heat conduction to the sample. Measurements of the temperature head between the calorimeter wall and the sulfur showed it to be less than one-fifth the head between the heater and the wall (0.2 to 0.5°) under the same conditions.

Thermal equilibrium, except for a second order drift apparent between 200 and 300°K.,[5] was complete in the full calorimeter within ten or fifteen minutes after the heating period.

The calorimeter contained 113.41 ± 0.01 g. of sulfur prepared as follows. A pure crystallized commercial product was melted and maintained at 120° for several hours. It was then distilled in Pyrex glass and the distillate dissolved in freshly distilled carbon disulfide and recrystallized. Unbroken crystals, which passed a sieve opening of 3.5 mm. and were retained on a 2.0-mm. screen, were selected. These were freed of carbon disulfide by heating at 85 ± 5° at 1-mm. pressure for eight days. After this period, a test made by boiling a sample in a high vacuum resulted in the liberation of an amount of gas corresponding to less than 0.001% $CS_2$. All determinations on rhombic sulfur were made with this material. Monoclinic sulfur was obtained by holding the sample in the calorimeter at temperatures between the transition and melting points for a long period, as described later. The sample was never melted after the treatment above and could therefore have contained none of the "insoluble" sulfur, which differs considerably in heat capacity from monoclinic and is present in small amounts in material prepared by crystallization of the melt.

The data given below are based on the following constants: atomic weight of sulfur = 32.06, 1 cal. = 4.1833 int. joule, and 0 = 273.1°K.

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[1] (a) Nernst, Koref and Lindemann, *Sitzb. kgl. preuss. Akad. Wiss.*, 247 (1910); (b) Nernst, *Ann. Physik*, [4] **36**, 395 (1911).

[2] Onnes and Clay, *Leiden Communications*, **99c**, 21 (1907).

[3] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[4] Johnston, *J. Opt. Soc. Am.*, **17**, 381 (1928).

[5] We suspect the glass sealing tube, because of its low thermal conductivity, to have been in part responsible for this drift. The large radiating and absorbing power is an additional unfavorable property of this material. We now consider all metal construction preferable.

## Heat Capacity of Rhombic Sulfur

The results of the heat capacity measurements for rhombic sulfur are listed in Table I and shown graphically in Fig. 1. The figure also includes certain points from Table V, to be explained later.

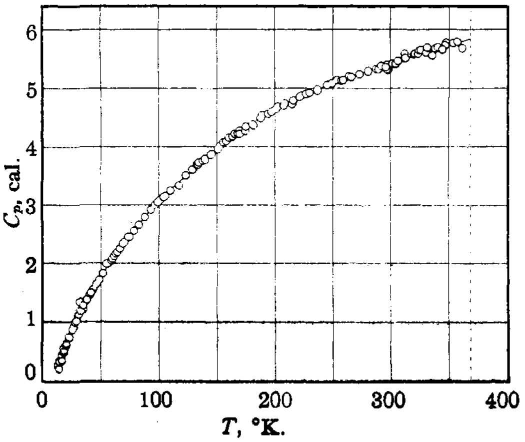

**Fig. 1.—Atomic heat capacity of rhombic sulfur.**

The individual measurements show fluctuations larger than can be attributed to instrumental errors, which in general were of the order of 0.1%. The very large differences among the points at the lowest temperatures result from inaccuracies in three separate calibrations[6] of the resistance thermometer in different series of experiments. These calibrations permit measurements of temperature differences in very close agreement over most of their range but deviate in the region of extremely small resistances. The remaining variations we believe to be due to imperfect drift and heat exchange corrections. At the highest temperatures employed, the method of measurement is inherently defective in this regard for precise work. In the intermediate range the difficulty attributed above to the glass tube on the calorimeter is important. To ensure the absence of constant errors from these sources in the final results, the conditions of approach to thermal equilibrium were varied systematically in making measurements. This, together with the large number of observations, gives us confidence in the accuracy of the averaged results, within the limits estimated below.

Representative values of the heat capacity read from the smoothed curve of Fig. 1 are given in Table II. The uncertainty connected with these smoothed values varies with the temperature. We estimate it to be about 8% at 15°K., 1.5% at 20°K., 1.0% at 30°K., and 0.5% at 40°K. From 60 to 290°K. it is of the order of 0.3%. Above 290°K. it averages about 0.5%. These figures are limits of error, which we think should not be exceeded in any values listed in Table II, with the possible exception of those very near the extremes of the temperature range.

TABLE I

ATOMIC HEAT CAPACITY OF RHOMBIC SULFUR

| $T$, °K. | $C_p$, cal./deg. | $T$, °K. | $C_p$, cal./deg. | $T$, °K. | $C_p$, cal./deg. |
|---|---|---|---|---|---|
| 12.68 | 0.254 | 122.76 | 3.508 | 249.02 | 5.081 |
| 13.85 | .204 | 128.63 | 3.608 | 253.63 | 5.145 |
| 14.26 | .331 | 132.02 | 3.684 | 257.12 | 5.130 |
| 16.13 | .424 | 133.29 | 3.693 | 258.85 | 5.141 |
| 16.33 | .341 | 134.02 | 3.728 | 263.79 | 5.202 |
| 17.99 | .494 | 137.45 | 3.758 | 265.98 | 5.190 |
| 18.16 | .505 | 139.32 | 3.790 | 272.91 | 5.240 |
| 20.26 | .617 | 139.63 | 3.774 | 280.15 | 5.284 |
| 20.27 | .631 | 144.50 | 3.863 | 280.47 | 5.296 |
| 22.23 | .741 | 145.01 | 3.869 | 287.32 | 5.333 |
| 22.61 | .732 | 150.39 | 3.953 | 289.12 | 5.325 |
| 25.18 | .863 | 150.40 | 3.957 | 289.26 | 5.320 |
| 26.38 | .917 | 150.40 | 3.957 | 290.17 | 5.382 |
| 28.66 | 1.012 | 152.21 | 4.013 | 295.48 | 5.361 |
| 30.71 | 1.114 | 155.44 | 4.079 | 296.46 | 5.323 |
| 32.62 | 1.182 | 157.92 | 4.095 | 296.55 | 5.401 |
| 34.68 | 1.274 | 160.16 | 4.155 | 297.71 | 5.314 |
| 37.70 | 1.374 | 163.26 | 4.176 | 298.28 | 5.362 |
| 41.10 | 1.494 | 165.08 | 4.210 | 301.40 | 5.419 |
| 45.79 | 1.642 | 165.31 | 4.219 | 302.32 | 5.414 |
| 51.39 | 1.826 | 167.75 | 4.227 | 303.97 | 5.415 |
| 55.93 | 1.966 | 169.16 | 4.274 | 306.13 | 5.466 |
| 58.95 | 2.045 | 169.50 | 4.217 | 311.46 | 5.508 |
| 59.82 | 2.078 | 174.26 | 4.267 | 311.95 | 5.586 |
| 62.54 | 2.167 | 174.76 | 4.342 | 312.42 | 5.513 |
| 63.99 | 2.189 | 180.25 | 4.378 | 319.98 | 5.577 |
| 66.33 | 2.250 | 181.33 | 4.361 | 320.92 | 5.593 |
| 68.84 | 2.336 | 187.56 | 4.492 | 323.17 | 5.590 |
| 70.04 | 2.357 | 188.86 | 4.543 | 324.37 | 5.648 |
| 70.34 | 2.367 | 194.00 | 4.562 | 325.87 | 5.653 |
| 73.22 | 2.453 | 196.67 | 4.598 | 330.34 | 5.608 |
| 74.04 | 2.455 | 200.83 | 4.642 | 331.32 | 5.690 |
| 74.61 | 2.452 | 202.25 | 4.688 | 335.76 | 5.558 |
| 78.12 | 2.554 | 207.38 | 4.701 | 338.11 | 5.674 |
| 82.44 | 2.654 | 208.25 | 4.740 | 340.22 | 5.697 |
| 87.66 | 2.791 | 214.59 | 4.730 | 344.16 | 5.657 |
| 92.81 | 2.915 | 215.69 | 4.794 | 346.87 | 5.728 |
| 96.29 | 2.989 | 220.99 | 4.851 | 347.86 | 5.773 |
| 98.83 | 3.045 | 222.50 | 4.868 | 353.74 | 5.765 |
| 100.83 | 3.086 | 226.56 | 4.900 | 357.23 | 5.789 |
| 103.92 | 3.136 | 229.53 | 4.925 | 361.21 | 5.681 |
| 105.25 | 3.154 | 236.46 | 4.959 | 364.02 | 5.935[a] |
| 109.80 | 3.248 | 236.51 | 4.984 | 364.59 | 5.672[a] |
| 117.13 | 3.346 | 244.79 | 5.056 | 365.60 | 5.944[a] |

[a] In each of these runs the average temperature of the heater on the calorimeter was above the transition point of sulfur during a portion of the run. These points are not plotted in Fig. 1.

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(6) Necessitated by changes in resistance resulting from the thermal treatment.

TABLE II

ATOMIC HEAT CAPACITY OF RHOMBIC SULFUR, SMOOTHED VALUES

| $T$, °K. | $C_p$, cal./deg. | $T$, °K. | $C_p$, cal./deg. |
|---|---|---|---|
| 15 | 0.311 | 200 | 4.639 |
| 20 | .605 | 210 | 4.743 |
| 25 | .858 | 220 | 4.841 |
| 30 | 1.075 | 230 | 4.927 |
| 40 | 1.452 | 240 | 5.010 |
| 50 | 1.772 | 250 | 5.083 |
| 60 | 2.084 | 260 | 5.154 |
| 70 | 2.352 | 270 | 5.220 |
| 80 | 2.604 | 280 | 5.286 |
| 90 | 2.838 | 290 | 5.350 |
| 100 | 3.060 | 298.1 | 5.401 |
| 110 | 3.254 | 300 | 5.412 |
| 120 | 3.445 | 310 | 5.474 |
| 130 | 3.624 | 320 | 5.535 |
| 140 | 3.795 | 330 | 5.598 |
| 150 | 3.964 | 340 | 5.660 |
| 160 | 4.123 | 350 | 5.721 |
| 170 | 4.269 | 360 | 5.783 |
| 180 | 4.404 | 368.6 | (5.837) |
| 190 | 4.526 | | |

Comparison with the data of Nernst[1] shows our results in Table II to be lower by amounts varying from 6 to 28% between 20 and 30°K. and from 1 to 5% between 70 and 90°K. and near 200°K. The remaining data in the literature are all mean specific heats over large temperature intervals above room temperature due to Regnault,[7] Kopp,[8] Bunsen,[9] Wigand,[10] Koref,[1,11] Lindemann,[1] and Mondain-Monval.[12]

Our values are higher by amounts averaging about 2% than those of Kopp, Bunsen, and Mondain-Monval, and lower by about the same amount than those of the other observers.

The heat capacity at constant volume as a function of temperature is of some interest, and is approximately calculable in the case of rhombic sulfur. For this purpose the thermodynamic relation

$$C_p - C_v = \alpha^2 VT/\beta \qquad (1)$$

is employed. Based on the work of Kopp,[13] Russner,[14] and Schrauf,[15] we take the cubic coefficient of expansion at 20° as $\alpha = (18.1 \pm 1) \times 10^{-5}$ deg.$^{-1}$. The compressibility, $\beta$, from the work of Richards[16] and an extrapolation of Bridgman's data,[17] is $(13.0 \pm 0.2) \times 10^{-6}$ cm.$^2$/kg. at 20°. The atomic volume is 15.60 ± 0.05 cc. These values substituted in equation 1 give $C_p - C_v = 0.270 \pm 0.03$ cal./deg. at 20°. The value of $C_p$ at this temperature from the smoothed curve of Fig. 1 is 5.37 ± 0.03. $C_v$ at 293.1°K. is therefore 5.10 ± 0.05. Data required for application of equation 1 at lower temperatures are lacking. We have therefore resorted to an approximate empirical equation proposed and discussed by Grüneisen,[18] namely

$$C_p - C_v = kTC_p^2 \qquad (2)$$

From the datum above, $k$ in this equation is found to be $3.20 \times 10^{-5}$. Employing this constant with figures for $C_p$ from our work we obtain values of $C_p - C_v$ and $C_v$ shown at regular intervals in log $T$ in Table III.

TABLE III

CALCULATED ATOMIC HEAT CAPACITY AT CONSTANT VOLUME OF RHOMBIC SULFUR

| Log $T$ | $C_p - C_v$ cal./deg. | $C_v$ cal./deg. |
|---|---|---|
| 2.500 | 0.308 | 5.21 |
| (2.4672) | (.270) | (5.10) |
| 2.400 | .208 | 4.88 |
| 2.300 | .137 | 4.49 |
| 2.200 | .085 | 4.00 |
| 2.100 | .051 | 3.50 |
| 2.000 | .0297 | 3.02 |
| 1.900 | .0170 | 2.56 |
| 1.800 | .0095 | 2.16 |
| 1.700 | .0050 | 1.77 |
| 1.600 | .0027 | 1.45 |

We may mention at this point that the values of $C_v$ in Table III (and at lower temperatures where $C_v$ is nearly identical with $C_p$) may be represented approximately up to $C_v = 3.0$ by the function

$$C_v = f(T/\Theta)^n \qquad (3)$$

proposed by Lewis and Gibson,[19] if log $\Theta = 1.992$ and $n = 0.5025$. Above $C_v = 3.0$ deviations begin, $C_v$ at 293°K. falling about 0.45 cal./deg. above the typical curve of these authors. Applying the values of $n$ and $\Theta$ adopted by Lewis and Gibson to our data, we find that the experimental points fall above their curve at low temperatures and below it in the upper range by amounts much greater than the experimental error. No values of the constants applied to our

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(7) Regnault, *Pogg. Ann.*, **51**, 225 (1840); **62**, 50 (1844); *Ann. chim. phys.*, [2] **73**, 50 (1840); [3] **9**, 322 (1843).

(8) Kopp, *Liebigs Ann. Chem. Supp.*, **3**, 1 (1864–65).

(9) Bunsen, *Pogg. Ann.*, **141**, 1 (1870).

(10) Wigand, *Ann. Physik*, [4] **22**, 64 (1907).

(11) Koref, *ibid.*, [4] **36**, 49 (1911).

(12) Mondain-Monval, *Bull. soc. chim.*, [4] **39**, 1349 (1926).

(13) Kopp, *Ann.*, **93**, 129 (1855).

(14) Russner, *Carl Repert.*, **18**, 152 (1882).

(15) Schrauf, *Z. Kryst.*, **12**, 322 (1887).

(16) Richards, THIS JOURNAL, **37**, 1643 (1915).

(17) Bridgman, *Proc. Am. Acad. Arts Sci.*, **62**, 207 (1927).

(18) Grüneisen, *Ann. Physik*, **26**, 211, 393 (1908).

(19) Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

data will reproduce this curve over the full range of our investigation.

## Heat Capacity of Monoclinic Sulfur

After completion of the runs with rhombic sulfur, the sample was transformed to monoclinic by maintaining the temperature of the calorimeter between 96 and 100° for a period of twenty-four hours. The first measurement recorded in column 4 of Table IV was then made, the calorimeter held for an additional twenty-four hours above the transition point and the second measurement made. During these runs the conditions appeared as nearly ideal as could be obtained, and they were therefore considered sufficient to establish the heat capacity of the monoclinic form in the rather narrow range of temperature within which it is stable. After the second run, the calorimeter was cooled as rapidly as possible to 60°K. The initial rate of cooling was 10° per minute, and in thirty minutes the temperature was reduced to 200°K., below which transition is very slow. Runs numbered 3 to 16 in Table IV were then made in sequence. The total *time* elapsing from the beginning of the initial cooling to the start of the run is shown in each case in the second column of the table. After completion of run 15 the temperature was raised to about 218°K. and maintained there for fifty-three hours before the start of run 16. Following this the calorimeter was again cooled, and run 17 completed at 92°K. Immediately before run 18 the calorimeter was heated from this temperature to about 153°K.

TABLE IV

ATOMIC HEAT CAPACITY OF MONOCLINIC SULFUR, AND ITS DIFFERENCE FROM THAT OF RHOMBIC SULFUR

| Run no. | Time, hours | Temp., °K. | $C_p$, cal./deg. | $\Delta C_p$, cal./deg. | $(\Delta C_p/T) \times 10^4$ cal./deg. |
|---|---|---|---|---|---|
| 1 | ... | 376.16 | 6.175 | 0.292 | 7.76 |
| 2 | ... | 375.14 | 6.167 | .291 | 7.76 |
| 3 | 3 | 64.83 | 2.242 | .0198 | 3.05 |
| 4 | 7 | 68.82 | 2.330 | .0045 | 0.66 |
| 5 | 9 | 72.82 | 2.431 | .0045 | 0.62 |
| 6 | 24 | 80.12 | 2.622 | .0220 | 2.75 |
| 7 | 27 | 84.76 | 2.744 | .0265 | 3.13 |
| 8 | 96 | 94.31 | 2.976 | .0330 | 3.50 |
| 9 | 97 | 98.25 | 3.069 | .0435 | 4.43 |
| 10 | 139 | 102.55 | 3.150 | .0401 | 3.91 |
| 11 | 144 | 110.08 | 3.293 | .0381 | 3.46 |
| 12 | 161 | 119.59 | 3.481 | .0404 | 3.38 |
| 13 | 180 | 127.24 | 3.642 | .0599 | 4.71 |
| 14 | 193 | 147.42 | 4.028 | .1118 | 7.59 |
| 15 | 211 | 172.41 | 4.404 | .0972 | 5.64 |
| 16 | 264 | 219.80 | 4.930 | .0895 | 4.07 |
| 17 | 288 | 91.98 | 2.641 | .0282 | 3.07 |
| 18 | 334 | 154.91 | 4.158 | .1136 | 7.33 |

The results shown in Table IV lie consistently above the smoothed curve for the rhombic form. Runs 18 and 19, at 92 and 155°K., respectively, which were made after the calorimeter had been held for a long period at 220°K., agree within the experimental error with the preceding runs near these temperatures. We have taken this as evidence that no appreciable reversion to the rhombic form occurred in this series after the initial cooling. Run 17 at 220° appears to be rather lower than should correspond to the monoclinic form at this temperature. We have indications from later runs, however, that this is due to an unusually large fluctuation rather than to transition, and consequently attach less weight to this point than to the others.

In an attempt to confirm and extend the data on the monoclinic form, the sample, which had been allowed to warm and stand for some days at room temperature, was again heated and held above the transition point, and then cooled rapidly, this time to 12°K. A second series of measurements ranging from 13.5 to 205°K. was then made. At temperatures where the two forms differ appreciably in heat capacity, as shown by the earlier measurements, this series gave results only a little higher than those with rhombic. We believe that the repetition of the transformation had produced more reactive crystals, in which the transformation could not be so completely inhibited on cooling as with those which had undergone only the single change. (It should be mentioned that during the "annealing" period preceding the cooling an accidental drop below the transition temperature occurred, which may have had some influence on the subsequent behavior.) In connection with this point, the appearance of the sample after removal from the calorimeter may be noted. The crystals, which had been subjected to several transitions, had maintained their original form, but had become opaque, indicating the presence of small crystals in mosaic form.

Of the measurements of this series, only those below 65°K., which are useful in supplementing the data on rhombic sulfur, with which they are identical within the errors in this range, will be recorded here. These are given in Table V, and plotted in Fig. 1.

A third "annealing" above the transition tem-

TABLE V

ATOMIC HEAT CAPACITY OF A MIXTURE OF MONOCLINIC AND RHOMBIC SULFUR

| $T$, °K. | $C_p$ |
|---|---|
| 13.51 | 0.217 |
| 15.41 | .326 |
| 17.75 | .549 |
| 18.65 | .538 |
| 20.27 | .621 |
| 22.72 | .739 |
| 25.38 | .874 |
| 27.73 | .993 |
| 29.99 | 1.106 |
| 32.33 | 1.199 |
| 34.66 | 1.213 |
| 36.55 | 1.338 |
| 39.86 | 1.446 |
| 43.04 | 1.550 |
| 48.17 | 1.717 |
| 54.19 | 1.994 |
| 61.43 | 2.127 |

perature was next made, followed by a series of runs extending from 110 to 345°K. The results of these measurements in the lower temperature range fell consistently between the rhombic curve and the first series of points for the monoclinic. From their position relative to these two, it appeared that the sample consisted in this case of about 60% of the monoclinic form. The corresponding difference in heat capacity persisted up to 255°K. Within the period of ten hours intervening between the run at this temperature and the next at 268°K., the sample was apparently entirely transformed to rhombic, since its heat capacity fell to the rhombic curve and remained there in all succeeding runs. No further attempts to secure measurements on monoclinic sulfur were made.

The evidence cited above convinces us that no appreciable conversion of monoclinic to rhombic occurred after the initial cooling in any of the three series of experiments at temperatures below about 250°K. During the cooling itself there was marked conversion in the second and third series. We believe that if any such effect occurred in the first series it could have affected only a small fraction of the sample. The approximate agreement of our results, discussed below, for the difference in heat capacity of the two forms with those of Nernst near 200°K. supports this belief, since Nernst's observations were made on relatively large crystals of monoclinic sulfur which were known not to transform appreciably on cooling.

We consider it advantageous for the present purposes in dealing with the data on monoclinic to treat the difference, $\Delta C_p$, of monoclinic from rhombic, rather than $C_p$ itself. Values of $\Delta C_p$ (and of $\Delta C_p/T$) from our work are therefore included in Table IV. These are computed from the difference in heat capacity of the full calorimeter in individual runs with monoclinic sulfur from the smoothed curve for the full calorimeter containing rhombic sulfur at the same temperature. We have secured smoothed values of $\Delta C_p$, and at the same time obtained a plot for use in a later calculation, by treating $\Delta C_p/T$ as a function of temperature.

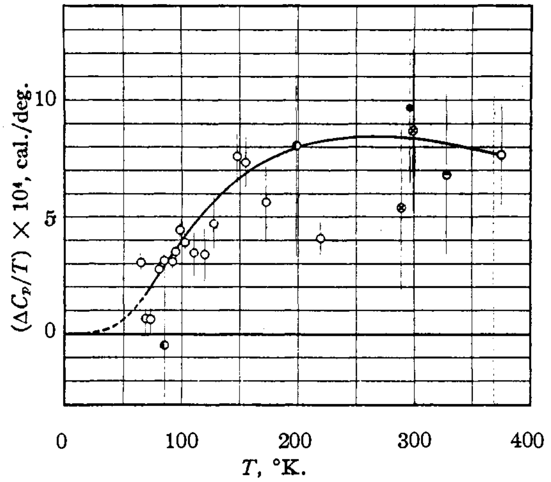

Fig. 2.—Difference of atomic heat capacities of monoclinic and rhombic sulfur: Regnault, ⊖; Wigand, ⊗; Nernst, ◐; Koref, ●; this research, ○.

In Fig. 2, $\Delta C_p/T$ is plotted against $T$. The vertical strokes attached to points representing our measurements are intended to give an idea of the experimental uncertainty. They represent the average deviation of three or four determinations on rhombic sulfur from the smoothed curve for rhombic immediately above and below the temperature of the monoclinic run in question. The uncertainty in particular cases may therefore exceed considerably that indicated as normal. For comparison with our results, and to supplement them, values of $\Delta C_p$ obtainable from the work of other observers are also plotted in Fig. 2. These data represent small groups of points at neighboring temperatures for the two forms which have been corrected to a common mean temperature, averaged separately, and the difference of the averages plotted against the mean temperature. Our estimate of the uncertainty is also indicated for these points in the plot.

The curve shown in Fig. 2 fits all of the points within the experimental uncertainty, and is correct in general form. The approximate position and shape of the theoretically required maximum in the curve we have inferred from the position of our points above the transition temperature relative to the fairly well defined course of the curve at low temperatures, and also from the points of the third series of measurements mentioned above. From the curve as shown we have obtained smoothed values of $\Delta C_p$. These, in conjunction with the data of Table II on rhombic, yield smoothed values of $C_p$ for monoclinic sulfur shown in Table VI over the temperature range in which the difference in heat capacity of the two forms is significant. The uncertainty in $C_p$ in this table is of the order of 1.5% in the upper temperature range, and approaches that previously estimated for rhombic at lower temperatures.

TABLE VI

ATOMIC HEAT CAPACITY OF MONOCLINIC SULFUR ("BEST VALUES")

| $T$, °K. | $\Delta C_p$, cal./deg. | $C_p$ monoclinic, cal./deg. |
|---|---|---|
| 60 | 0.007 | 2.091 |
| 80 | .020 | 2.624 |
| 100 | .040 | 3.100 |
| 120 | .063 | 3.508 |
| 140 | .087 | 3.882 |
| 160 | .112 | 4.235 |
| 180 | .136 | 4.540 |
| 200 | .159 | 4.798 |
| 220 | .180 | 5.021 |
| 240 | .199 | 5.209 |
| 260 | .217 | 5.371 |
| 280 | .234 | 5.520 |
| 298.1 | .248 | 5.649 |
| 300 | .250 | 5.662 |
| 320 | .264 | 5.799 |
| 340 | .276 | 5.936 |
| 360 | .286 | 6.069 |
| 368.5 | .289 | 6.126 |

## Calculations of Entropy

The entropy difference between 15°K. and any higher temperature up to the transition point for rhombic sulfur is obtainable by graphic integration on a suitable plot of the data of Table II. For the entropy difference between 0 and 15°K., we find by similar integration under an extrapolated curve of $C_p/T$ against $T$, and by calculation from a Debye function fitted to our points up to 40°K., 0.12 ± 0.02 e. u. For the total entropy of rhombic sulfur we obtain 7.624 ± 0.05 e. u. at 298.1°K. and 8.827 ± 0.06 at the transition point (368.6°K.).

The entropy of transition of rhombic to monoclinic sulfur is determined by integration under the curve in Fig. 2 to be 0.157 ± 0.04 e. u. at 298.1°K. and 0.215 ± 0.05 at 368.6°K. By combination of these figures with the values for the rhombic form, the entropy of monoclinic sulfur is 7.78 ± 0.1 e. u. at 298.1°K. and 9.04 ± 0.1 e. u. at 368.6°K.

These results are in agreement with those of Lewis and Gibson,[19] 7.6 and 7.8 e. u. at 298.1°K., for the two forms. The closeness of this agreement is in part fortuitous, in view of our earlier remarks in the discussion of $C_v$. Equally well justified calculations of the type of Lewis and Gibson's might introduce discrepancies of the order of 0.5 e. u. To this degree of approximation, however, their method is justified in the case of sulfur.

For comparison of the above value of $\Delta S$ obtained by application of the third law with one based solely on the second law, existing data on the heat of transition may be employed. Numerous measurements of $\Delta H$, by widely different direct and indirect methods, due to Mitscherlich,[20] Reicher,[21] Tammann,[22] Brönsted,[23] Mondain-Monval,[12] and Neumann[24] are available. After a critical review of the work of these investigators, into which we cannot enter here, we have adopted 95 ± 10 cal. as the value of $\Delta H$ at the transition point. This corresponds to 0.258 ± 0.027 e. u., compared with the value based on the third law of 0.215 ± 0.05 at the same temperature.

It appears from this comparison that the third law is accurately applicable, without complications of the types that sometimes occur, to the sulfur transition. The uncertainty of 0.05–0.1 e. u. in this "check" of the law is smaller[25] than that in many others, and permits the assumption of no significant discrepancy. This case, as is well known, has often been cited in support of the third law. The experimental basis for this claim is greatly strengthened by the data discussed here.

## Summary

Measurements of the heat capacity of rhombic and monoclinic sulfur have been made over the temperature range 15–375°K., and from them the

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(20) Mitscherlich, *Pogg. Ann.*, **88**, 328 (1852).

(21) Reicher, *Z. Kryst.*, **8**, 593 (1884).

(22) Tammann, "Kristallisieren und Schmelzen," Barth, Leipzig, 1903, p. 274.

(23) Brönsted, *Z. physik. Chem.*, **55**, 371 (1906).

(24) Neumann, *ibid.*, **A171**, 416 (1934).

(25) It is, of course, the absolute rather than the percentage figure which is important in such tests.

entropy of both forms determined. The entropy difference of the two forms obtained from the heat capacities agrees, within the small experimental uncertainty, with that from the heat of transition, as expected from the third law.

The heat capacity at constant volume has been calculated for rhombic sulfur, and its variation with temperature compared with the "*n* formula" of Lewis and Gibson.

BERKELEY, CALIF. RECEIVED NOVEMBER 10, 1936

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# The Reaction of Titanium Tetrachloride with Hydrogen Peroxide in Dry Ethyl Acetate

BY DOUGLAS G. NICHOLSON AND M. ANTOINE REITER

Several references concerning addition compounds of titanium tetrachloride and neutral molecules have appeared in recent chemical literature.[1–4] In view of these references, it seemed quite probable that titanium tetrachloride would unite with hydrogen peroxide in a non-aqueous medium to form a similar addition compound. Since both substances have an appreciable solubility in dry ethyl acetate, this material was selected as the solvent in the investigation.

## Experimental

The solution of hydrogen peroxide in dry ethyl acetate was prepared in a manner previously described.[5] This peroxide solution was added slowly to an ice cold solution of titanium tetrachloride in ethyl acetate. As it was added, the titanium solution became orange to orange-red in color, and, with continued addition of the peroxide, a white crystalline precipitate formed. After thoroughly washing this precipitate with cold dry ethyl acetate, samples were analyzed in an effort to determine the chlorine to titanium, as well as the hydrogen peroxide to titanium, ratios present. Efforts to determine the actual composition of the white precipitated material proved unsatisfactory, because of its extremely unstable nature.

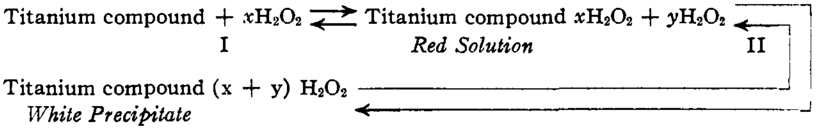
## Data

Analysis of fourteen different samples of the material showed the average ratio of chlorine to titanium content to be 1 to 1.05 with an average deviation of 0.01 and a maximum deviation of 0.03. The average hydrogen peroxide to titanium ratio obtained from the same sample was 1 to 1.01 with an average deviation of 0.022 and a maximum deviation of 0.05.

## Discussion

The color change encountered, as the solution of hydrogen peroxide in acetate was added to the titanium tetrachloride solution, followed by the formation of the white precipitate, seemed to indicate that more than one compound of these two substances had been formed. If some of the red colored solution was allowed to remain in an open vessel for some time the intensity of the color gradually faded.

In view of these facts the following equilibria are postulated:



$$\text{Titanium compound} + x\text{H}_2\text{O}_2 \underset{\text{I}}{\rightleftharpoons} \underset{\textit{Red Solution}}{\text{Titanium compound } x\text{H}_2\text{O}_2} + y\text{H}_2\text{O}_2 \underset{\text{II}}{\rightleftharpoons} \underset{\textit{White Precipitate}}{\text{Titanium compound } (x+y)\,\text{H}_2\text{O}_2}$$

The presence of a trace of moisture caused the white precipitate to become orange-red in color. Thus, it seems quite probable that moisture tends to shift the right-hand equilibrium (II) toward the left. All attempts to remove the last traces of acetate solution from the white precipitate resulted in its partial decomposition, in which the surface of the material became yellow to orange in color. This white precipitate was very soluble in water, producing the yellow to orange typical peroxytitanate solutions.

Analysis of the titanium tetrachloride used showed it to be very pure. The apparent loss of three atoms of chlorine per molecule of titanium tetrachloride can be attributed to either or both of two factors: namely, (1) oxidation to free chlorine by the hydrogen peroxide present, and

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[1] Chrétien and Varga, *Compt. rend.*, **201**, 558 (1935).

[2] Ralston and Wilkinson, THIS JOURNAL, **50**, 258 (1928).

[3] Holtje, *Z. anorg. allgem. Chem.*, **190**, 241 (1930).

[4] Karantassis, *Compt. rend.*, **194**, 461 (1932).

[5] Nicholson, THIS JOURNAL, **58**, 2525 (1936).