[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Heat Capacity of Sulfur from 25 to 450°, the Heats and Temperatures of Transition and Fusion[1,2]

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The heat capacity of sulfur (99.999% pure) has been determined from 25 to 405° with an accuracy of 0.1 to 0.2% using an adiabatic calorimeter. The heat of transition of rhombic to monoclinic sulfur is 401.7 j./g. atom at 95.31°, the transition temperature at saturation pressure. The heat of fusion is 1717.6 j./g.-atom at the triple point, 115.18°. The data indicate a previously unreported transition near 101° to which an enthalpy change of 1.6 j./g.-atom has been assigned. The behavior of the heat capacity of the liquid in the region of its maximum at 159.1° has been investigated in detail.

The thermodynamic properties of sulfur have received the attention of numerous investigators for more than a century, but, because of the difficulty of purifying the sulfur and of dealing with a material having so many forms and reaching equilibrium so slowly, the quality of the data has been considerably lower than that achieved with most other substances. The most recent heat capacity determinations have been reported for the temperature range 13 to 376°K. for both rhombic and monoclinic sulfur[3] and to 420° for liquid sulfur.[4-6] Calorimetric measurements on sulfur generally have given little attention to small amounts of impurity, which have a profound effect on at least some properties of the liquid.[7]

It was the purpose of this investigation to redetermine between 25 and 405° some of the thermodynamic properties of very pure sulfur using an adiabatic calorimeter which has a very low rate of heat loss and which has been checked for accuracy by measurements with a Calorimetry Conference sample of Al_2O_3.[8] The low rate of heat loss permits observation of slow rates of change in the calorimeter.

The Sulfur Sample.—The sample of sulfur was obtained from T. J. Murphy of the Inorganic Chemistry Section at the National Bureau of Standards. It was prepared by a method developed in that Section[9] in which the critical step of carbon removal is accomplished by oxidation with a mixture of hot concentrated nitric and sulfuric acids. The mole-fraction of liquid-soluble, solid-insoluble impurity of the sample *as used* was found to be 1.3×10^{-5} from analysis of the present measurements in the region below the melting point.

The sulfur sample was received sealed in a Pyrex glass ampoule with water and nitrogen. The water was removed by decanting and then melting the sulfur *in vacuo*. The sulfur was transferred to the container by gravity flow *in vacuo* just above the melting point. It was exposed to air only when at room temperature and for the short time required to seal the ampoule to the vacuum system. The system was constructed of Pyrex glass and aluminum, except that the crevice where the glass joined the aluminum was sealed on the outside with Teflon in a packing gland. Since liquid sulfur does not spread on clean glass, it seems likely that the sulfur did not penetrate to the packing. No sulfur was found in this space when the apparatus was disassembled.

The aluminum container was sealed by squeezing the aluminum filling tube with a special clamp, cutting the tube in a helium atmosphere, closing the end of the tube by arc-welding in helium and then removing the clamp. Tests prior to sealing had shown that the clamp was quite effective in maintaining a vacuum, so that the total gas in the container was the small amount of helium sealed between the clamp and the end of the filling tube. The maximum amount of helium is calculated to be about 4×10^{-6} mole. Sulfur was removed from the filling tube before welding by heating the tube with a flame while keeping the calorimeter container immersed in ice-water and connected to vacuum. Tight welds were impossible without this precaution.

The weight of the sulfur was taken as the difference between the weights of the full and empty container. Cutting and welding the aluminum tube was shown beforehand to introduce errors of, at most, a few milligrams. The weight of sulfur in the container was 114.122 g. corrected to vacuum. The gram atomic weight was taken to be 32.066.

After filling, the container was heated to about 440°, cooled to room temperature and again heated to 440°, but no leaks or bulges were detected. In spite of these precautions, the container bulged slightly (up to 0.015″ on a 1″ radius) during the measurements and could not be removed from the apparatus for emptying. A vacuum system was therefore attached to the container in place and the sulfur was removed by vaporization at 250°. Aluminum chips removed in making a hole for attaching the vacuum line were returned to the container for the measurements of the heat capacity with the empty container.

The cause of the bulging must be considered for the effect it might have on the results presented below. The bulge could not be caused by gas sealed in the container during the filling operation, since it did not occur in the testing described above. If it is postulated that gas is evolved in the container over a period of time, the pressure should increase the temperature of the triple point by 0.03°/atm. As the sulfur is melted its volume increases and reduces the volume of any gas in the container and increases the pressure. The temperature change to be expected in melting the last half of the sulfur is about 0.005°/atm. of total pressure. In Fig. 4, the equilibrium temperature is plotted against $1/F$ (F = fraction of sulfur melted). The temperature difference between $1/F = 2$ and $1/F = 1$ is 0.001°. Assuming for the moment that the impurity in the sulfur is negligible, the total pressure at 115° is calculated to be 0.2 atmosphere. At 400° this gas would exert a pressure of about 0.5 atmosphere, which is far too small to deform the aluminum. Discarding gas pressure as a cause of the bulging leaves the possibility of bulging due to volume changes accompanying changes of phase. Although melting could conceivably cause the bulging, melting first takes place along the metallic surfaces and, consequently, the liquid is probably not confined by the solid. However, the bulging may be the result of the change in volume at the rhombic–monoclinic transition. When liquid sulfur is cooled slowly, it can be supercooled well into the rhombic region. If the solid sulfur formed from this supercooled liquid is rhombic, the small volume change at the transition will expand the calorimeter. The observed bulging therefore seems likely to be the accumulated effect of numerous repetitions of this process.

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[1] This work was supported in part by the Allied Chemical and Dye Corporation and American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties."

[2] This paper includes material from a thesis submitted to the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

[3] E. D. Eastman and W. C. McGavock, THIS JOURNAL, **59**, 145 (1937).

[4] H. Braune and O. Möller, *Z. Naturforsch.*, **9a**, 210 (1954).

[5] F. Fehér and E. Hellwig, "Text of Lectures and Discussions," Colloquium of the Section for Inorganic Chem., International Union of Pure and Applied Chemistry, Münster, 1954.

[6] W. Oelsen and O. Oelsen, *Z. Elektrochem.*, **60**, 157 (1956).

[7] R. F. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

[8] E. D. West and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **60**, 309 (1958).

[9] T. J. Murphy, W. S. Clabaugh and R. Gilchrist, *ibid.*, to be published.

Rhombic sulfur which would give reproducible heat capacities could not be obtained merely by cooling the liquid until it solidified. Heat capacities measured six weeks after testing the container at 440° increased slightly from day to day. Apparently some non-equilibrium form, such as long chains from the liquid or possibly monoclinic sulfur, was slowly giving up its energy, decreasing the observed heat capacity by smaller amounts as its concentration decreased. The persistence of non-equilibrium forms far below their stable temperature ranges is well known. Monoclinic sulfur is sufficiently stable that its heat capacity has been measured at low temperatures[3] and plastic sulfur is a familiar example of the quenched liquid. However, the rate of conversion of monoclinic to rhombic has been measured as a function of temperature,[10] and it therefore seemed probable that a heat treatment could be found which would convert the sulfur to the stable rhombic form.

After trying numerous variations in heat treatment, the following procedure was adopted. After melting, the sulfur was cooled to room temperature overnight to overcome the tendency to supercool, heated in the monoclinic region at 105 to 110° for a day or two to allow conversion of any remaining chains to the stable S_8 rings,[11] cooled to room temperature to initiate the conversion of monoclinic to rhombic and then heated overnight at 60–70°, which is the range of the maximum rate of conversion of monoclinic to rhombic sulfur.[10] Sulfur treated in this way gave reproducible values for the heat capacity, in general somewhat higher than the preliminary values which showed a trend with time. This behavior was taken as evidence that measurements were being made on the equilibrium rhombic form.

Monoclinic sulfur was not obtained by crystallization from the liquid because of the strong tendency to supercool. At one point, heat capacities were measured in the monoclinic region which corresponded to the heat capacities of the liquid, although the sulfur had been held about 20° below the melting point for several days. Monoclinic sulfur was therefore obtained by conversion of the rhombic form prepared by the process just described. The conversions were carried out in connection with determinations of the heat and temperature of transition described later. In these experiments and also in a separate heating curve, the beginning of the transition was never observed much below 100°, although the rate was easily observed 0.1° above the transition temperature when about half the sulfur had been converted to the monoclinic form. The temperature of the sudden onset of the transition near 100° is very close to the temperature of a newly-found low-energy transition in the monoclinic region. In this connection, the low results obtained by Eastman and McGavock[3] from their second preparation of monoclinic sulfur may have been due to incomplete conversion of rhombic sulfur at "96 to 100°."

Calorimetric Procedure.—The calorimetric apparatus and method have been described in detail[8] along with results of measurements of the heat capacity of a Calorimetry Conference sample of Al_2O_3. Briefly, the method consists of determining the amount of the heat required to raise the temperature of the calorimeter and its contents by a small amount, usually 10°. In repeating experiments, initial and final temperatures are reproduced to a few hundredths of a degree and small corrections are applied to allow accurate intercomparisons. The calorimeter is surrounded by an adiabatic jacket, the temperature of which is maintained automatically at the temperature of the calorimeter so that there is very little heat exchange between the calorimeter and its jacket. This "heat leak," which is of the order of one joule per hour, sets the limit on the magnitude of the detectable rate of change in the calorimeter. Successive experiments are carried out to cover a considerable range of temperatures. This procedure gives the increase in enthalpy over the temperature interval. Dividing the increase in enthalpy by the temperature rise gives the average heat capacity over the interval.[11a] Subtracting the average heat capacity for the empty calorimeter from the average for the full calorimeter over the same temperature interval gives the average heat capacity of the contents. The true heat capacity at the average temperature of an interval differs from the average heat capacity over that interval by a small amount which depends on the behavior of the heat capacity over the interval. This difference is usually referred to as the curvature correction.

In the experiments with the empty calorimeter, the container was open to the CO_2 atmosphere in the calorimeter. Data in the tables have been corrected for the heat capacity of the gas. The correction amounted to 0.15% of the heat capacity of sulfur at 30° and decreased to 0.06% at 400°. The data for the full calorimeter have been corrected for the vaporization of sulfur by the method of Hoge[12] using the vapor pressure data of West and Menzies.[13] This correction ranged from 0.001% of the heat capacity of sulfur at 150° to 0.07% at 400°.

Container.—The material for the sulfur container had to be a good thermal conductor and inert to sulfur up to 450°. Commercially pure aluminum (alloy 1100, 99 + % Al) was selected largely on the basis of its use for years at the National Bureau of Standards in the apparatus for the calibration of platinum resistance thermometers at the normal boiling point of sulfur. To avoid welding thin aluminum vanes, the heat-distributing system for the container was made by drilling 125 holes 4 mm. in diameter and smaller in an aluminum cylinder, leaving a thin web of metal. An aluminum cover with filling tube was welded over the open end of the aluminum cylinder. The volume of the completed container was 79 cm.^{3}

Rhombic Sulfur.—The average heat capacities for the full and for the empty calorimeter were fitted by the method of least squares to a quadratic function of the temperature. The expression for the true heat capacity of sulfur was obtained by subtracting the function for the empty from that for the full calorimeter and dividing by the number of gram atomic weights of sulfur in the calorimeter, resulting in the equation

$$C_p = 22.0452 + 0.02561t - 3.4160 \times 10^{-5} t^2 \quad (35 \text{ to } 95°) \qquad (1)$$

C_p is the heat capacity at constant pressure in j. deg.$^{-1}$ g.-atom^{-1} and t is the temperature. In this equation and throughout this paper, energies are expressed in absolute joules and temperatures in degrees Celsius (International Temperature Scale of 1948).[14] The computed standard deviation is 0.021 j. deg.$^{-1}$ g.-atom.$^{-1}$ The data from which the equation is derived are given in Table I.

TABLE I

OBSERVED AVERAGE HEAT CAPACITIES IN RHOMBIC REGION

Temp. interval, °C.	Heat capacity, j./°C. Empty	Full	Temp. interval, °C.	Heat capacity, j./°C. Empty	Full
25–35	221.76	302.82	75–85	228.27	313.21
		302.81			313.19
35–45	223.05	304.95			313.14
	223.11	304.96			313.17
45–55	224.53	307.27			
	224.56	307.29	85–90		314.69
		307.30			
55–65	225.87	309.34	85–95	229.39	315.04
	225.86	309.34		229.42	315.08
		309.33			315.00
65–75	227.02	311.32			315.11
	227.02	311.32			
	227.08	311.32	90–95		315.61
		311.31			315.59
		311.31			

In Fig. 1 are shown deviations of experimental results from values calculated from equation 1. The circles were obtained by subtracting average values for the empty calorimeter from individual values for the full calorimeter. The

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(10) N. H. Hartshorne and M. H. Roberts, *J. Chem. Soc.*, 1097 (1951).

(11) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

(11a) The average heat capacities of the full and empty calorimeter are actually in error by a small undetermined amount due to unknown temperature gradients during the heating period. The apparatus is designed so that the error for the empty calorimeter cancels the error for the full calorimeter and gives the correct average heat capacity for the contents. See reference 8 for a more complete discussion.

(12) H. J. Hoge, *J. Research Natl. Bur. Standards*, **36**, 111 (1946).

(13) W. A. West and A. W. Menzies, *J. Phys. Chem.*, **33**, 1880 (1929).

(14) H. F. Stimson, *Am. J. Phys.*, **23**, 614 (1955).

latter values have greater uncertainties, especially above 80° because of the time required to obtain equilibrium in the sulfur. Many of the points have been displaced horizontally to avoid confusion. The squares show deviations of individual measurements of Eastman and McGavock.[3] Deviations of their smooth equation are given by the dotted line, which generally lies below their data in this range. Their smoothed values agree with the NBS smoothed values to about their assigned tolerance of 0.5%.

As a check on the measurements and on the equation for the heat capacity of the full calorimeter, the enthalpy difference ($H_{95} - H_{35}$) for the calorimeter plus sulfur between 35 and 95° has been measured in two experiments each covering the 60° interval. A comparison of this enthalpy increase obtained in various ways is shown in Table II. The agreement between the integral of the equation and the summation of the short experiments is quite good, indicating a good fit. The difference between these two values and the two determined directly is only 0.026%.

TABLE II

ENTHALPY OF FULL CALORIMETER BY VARIOUS METHODS

Method	$H_{95} - H_{35}$, joules
Integration of eq. 1	18,612.0
Summation of short expt.	18,611.1
Single experiment, 9–6–56	18,616.7
Single experiment. 9–12–56	18,616.1

The Rhombic to Monoclinic Transition.—Because of the slow rate of the transition near the equilibrium temperature, the procedure for obtaining the heat of transition was to measure the total enthalpy increase between 95 and 110° and correct to the transition temperature using the heat capacity data from other experiments. The results of three experiments are shown in Table III.

TABLE III

HEAT OF TRANSFORMATION OF RHOMBIC TO MONOCLINIC SULFUR

Initial temp., °C.	Final temp., °C.	Date	Total energy, j.	ΔH, j./g.-atom
95.207	110.016	9–7–56	6164.55	402.5
94.996	110.207	9–12–56	6289.33	401.6
95.014	110.063	10–18–56	6235.84	401.1

The average of these three values is 401.7 j./g.-atom, which is estimated to be accurate within ± 2 j./g.-atom. For comparison, this average value is tabulated with the data of earlier observers in Table IV. Where applicable, the older values have been corrected to the transition temperature by use of the data of Eastman and McGavock.[3] In 1937, these authors, after a critical review of the literature, selected the value 397 ± 42 j./g.-atom for the heat of transition.

TABLE IV

COMPARISON OF VALUES FOR HEAT OF TRANSFORMATION

Observer and date	ΔH, j./g.-atom	Method
National Bureau of Standards (1957)	401.7 ± 2	Adiabatic calorimeter
Neumann (1934)[15]	439 ± 52	Vapor pressure
Mondain-Monval (1926)[16]	362	"Drop" calorimeter
Lewis and Randall (1911)[17]	470	"Drop" calorimeter
Tammann (1903)[18]	420	Pressure dependence of transformation temp.
Brønsted (1906)[19]	436	Direct measurement in an ice calorimeter

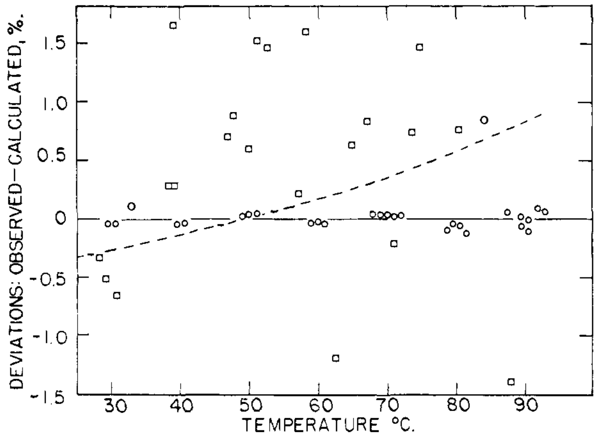

Fig. 1.—Heat capacity of rhombic sulfur: deviations from equation 1,. □, Eastman and McGavock,[3] experimental; – – –, Eastman and McGavock, smoothed; ○, NBS, experimental.

The method of locating the temperature of transition involves a variation of the method usually used. Ordinarily, one can exceed a transition temperature until the process gets a good start, then turn off the power and let the energy absorbed in the transition cool the substance to the transition temperature. Because of the slow rate of conversion of rhombic to monoclinic sulfur, this procedure would require very long equilibrium times. For example, with the temperature 0.1° below equilibrium, the rate of transition is such that about three days would be required to reach equilibrium, providing the rate did not decrease, as it must. To circumvent this difficulty, the rhombic sulfur was heated until the transformation started at about 100°. The power was then shut off and the calorimeter was cooled by heat transfer to the jacket to a temperature thought to be slightly below the transition temperature. The adiabatic jacket was then brought up to temperature and the rate of change of the calorimeter temperature was observed for 0.5 hr. The calorimeter was then heated for a short time and the new rate observed. This procedure was repeated, approaching equilibrium from both higher and lower temperatures and obtaining both positive and negative rates. The results are plotted in Fig. 2, numbered in chronological order. From this graph, the temperature at which the rate of transformation is zero is 95.31°. This temperature of transition is believed to be accurate within ± 0.01°, allowing for the fact that the adiabatic jacket is not perfect and may alter the true rate of temperature change due to the transition. Based on density data at room temperature,[20] the transition temperature at one atmosphere is calculated to be 0.08° higher than at saturation pressure, which brings it into surprisingly good agreement with the value of 95.4° given in recent summaries of sulfur data.[21,22] After these experiments were completed, the sulfur was

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(15) K. Neumann, *Z. physik. Chem.*, *A* **171**, 416 (1934).

(16) P. Mondain-Monval, *Bull. soc. chim.*, *France*, **39**, 1349 (1926).

(17) G. N. Lewis and M. Randall, THIS JOURNAL, **33**, 476 (1911).

(18) G. Tammann, "Kristallizieren und Schmelzen," J. A. Barth, Leipzig. 1903.

(19) J. N. Brønsted, *Z. physik. Chem.*, **55**, 371 (1906).

(20) "American Institute of Physics Handbook," McGraw-Hill Book Co., Inc., New York, N. Y., 1957.

(21) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956.

(22) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffee, National Bureau of Standards Circ. 500, 1952.

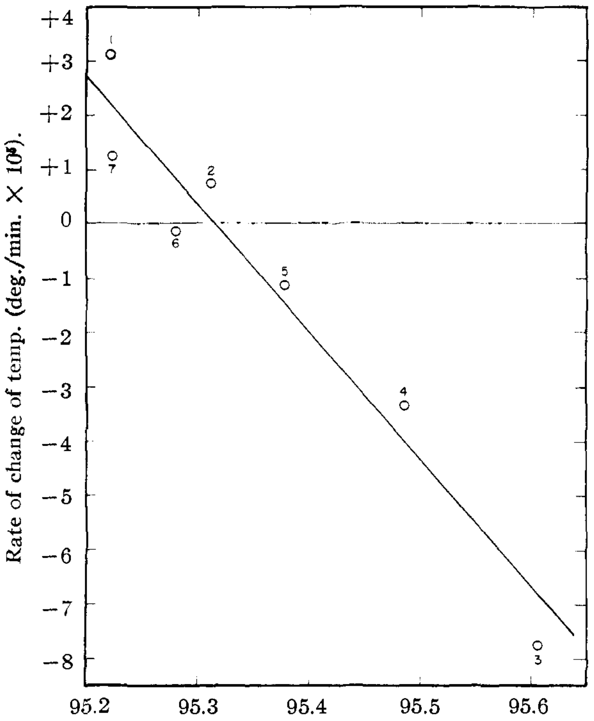

Fig. 2.—Temperature of the transition of rhombic to monoclinic sulfur (total pressure about 1 mm.). Experimental data, O, are numbered in chronological order.

converted completely to the monoclinic form and the amount of heat required was measured. The heat required indicated that, during these experiments, the sulfur was about half rhombic and half monoclinic.

From their low temperature data on both rhombic and monoclinic sulfur, Eastman and McGavock[3] calculate the entropy of transition at 95.3° to be 0.90 ± 0.21 j. deg.$^{-1}$ g. atom^{-1}. The entropy of transition calculated from the data in Table III is 1.090 j. deg.$^{-1}$ g.-atom^{-1}, which is estimated to be accurate to ±0.005 j. deg.$^{-1}$ g.-atom^{-1}. The discrepancy between these two values is equivalent to what would have been observed if Eastman and McGavock had made their monoclinic measurements on a mixture containing 18% rhombic sulfur.

Monoclinic Sulfur.—Measurement of the heat capacity of sulfur in the temperature range between 95 and 115° presents many difficulties. In this short range, equilibrium is attained slowly, most experiments are subject to corrections for premelting of sulfur due to slight impurities, and there is an abrupt change in the heat capacity near 101°. Figure 3 shows the behavior of the data in this temperature range. The experimental points are average heat capacities over 2 to 5° intervals plotted at the mean temperatures.

The data between 95 and 101° were smoothed using a three-constant equation fitted by the method of least squares. (Although measurements were made virtually at saturation pressure, the correction to constant pressure is insignificant in this range.) The estimated standard deviation is 0.064 j. deg.$^{-1}$ g.-atom^{-1} (0.026%). The apparent heat capacity C (including the heat of premelting) between 101 and 115.18° is given by the equation

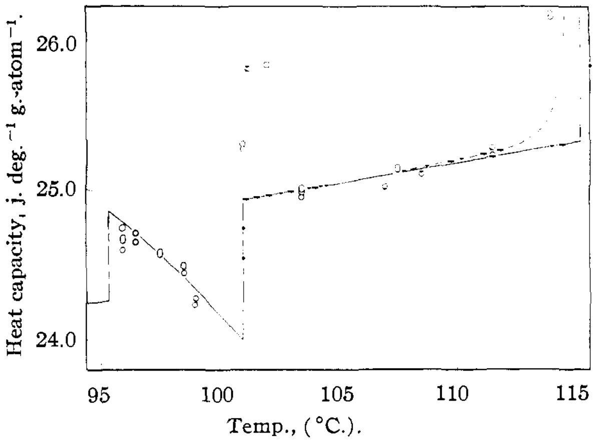

Fig. 3.—Heat capacity of monoclinic sulfur: O, NBS experimental (data plotted at 101° include the small heat of transition): ———, NBS smoothed heat capacity; - - - -, heat capacity + premelting; □, Eastman and McGavock,[3] experimental.

$$C = 22.0210 + 0.02869t + \frac{0.33635}{(115.176 - t)^2} \qquad (2)$$

The third term on the right represents the energy due to melting small amounts of solid. The computed standard deviation is 0.032 j. deg.$^{-1}$ g.-atom^{-1} (0.013%).

Following a suggestion of W. S. Connor,[23] the constants in equation 2 were obtained by fitting the observed average heat capacities using the method of least squares to an equation of the form

$$\frac{\int C\,\mathrm{d}t}{t_2 - t_1} = a + b\,\frac{t_2 + t_1}{2} + \frac{c}{(115.176 - t_2)(115.176 - t_1)} \qquad (3)$$

This method eliminates the need for approximating curvature corrections after first fitting a curve to the average heat capacities. a procedure which is often followed. The use of equation 3 gives a better estimate of the standard deviation when an equation is fitted to data of different temperature intervals. If curvature corrections are made after the equation is fitted, the difference in the curvature corrections between long and short experiments increases the estimated standard deviation.

From 95 to 101° the heat capacity of sulfur decreases with increasing temperature. To make certain that these measurements were not affected by proximity to the transition at 95.31°, the experiments at 96 and 96.5° were subjected to a variety of preliminary treatments after the conversion to monoclinic sulfur had been carried out at a higher temperature. One was held at 96° overnight and cooled to 95° to start, two were cooled to 85° and heated back to 95° to start after being held at about 95° overnight, four were held at 89 to 92° for 12 at 36 hours before the experiment. The agreement among the data is nevertheless about that expected for low-energy experiments which require long periods for equilibration. The

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(23) W. S. Connor, Statistical Engineering Laboratory, Natl. Bur. Standards, private communication.

downward trend of the heat capacity is also shown by points at 98.5 and 99°, which start well above the transition temperature.

The heat capacity exhibits an abrupt increase between 100 and 102°. This transition may involve another of the known monoclinic forms in addition to the common one.[24] Whether an enthalpy change is to be assigned to this transition depends on the treatment of the data above 100°. If the constants of equation 2 are determined assuming that there is no heat of transition and accordingly including the two points at 101°, the net heat capacity, exclusive of the heat of fusion correction, decreases with increasing temperature. If the two points at 101° are omitted, the net heat capacity increases and the equation fits the data better. The latter treatment therefore seems more plausible. The value assigned to this heat of transition on this basis is the difference between the average of the two experiments at 100–102° and the heat capacity extrapolated and integrated over the interval. As is evident from Fig. 3, the value of this heat of transition depends on the temperature of transition. If this temperature is taken to be 100°, ΔH = 0.70 j./g.-atom; if it is taken to be 102°, ΔH = 2.56. The value at 101°, the mid-point of these two experiments, is 1.6 j./g.-atom.

The data for the heat capacity of the full calorimeter from which Fig. 3 is derived are shown in Table V. The heat capacity of the empty calorimeter was obtained from an equation fitted by the method of least squares to measurements over ten-degree intervals between 85 and 125°. Average heat capacities of the empty calorimeter not included in other tables of experimental data are: at 95 to 105°, 230.50 and 230.52; at 105 to 115°, 231.55 and 231.57.

TABLE V

OBSERVED AVERAGE HEAT CAPACITIES IN MONOCLINIC REGION

Temp. interval, °C.	Heat capacity full, j./°C.	Temp. interval, °C.	Heat capacity full, j./°C.
95–97	317.64	100–102	320.55
	317.88		320.68
	317.90		
	317.90	100–105	320.16
	318.14		320.06
			320.15
95–98	317.87		
	318.08	102–105	320.00
95–100	317.74	104–110	320.42
	317.63		
		105–110	320.80
97–100	317.30		320.77
	317.46		
	317.48	107–110	320.76
98–100	316.63	110–113	321.51
	316.79		321.69
		113–115	325.07
			325.14

As a check on the heat capacity measurements on the monoclinic sulfur, four experiments were carried out with the full calorimeter, each measuring directly the change in enthalpy between 95 and 113°. The average value is 5759.09 j. with a standard deviation of 1.39 j. The comparable enthalpy change for the full calorimeter calculated from the smoothed sulfur heat capacity below 101°, equation 2, the small heat of transition and the heat capacity of the empty calorimeter is 5756.70 j., a difference of 0.04%.

In Fig. 3 are shown two heat capacity values (squares) determined by Eastman and McGavock.[3] These two values are several per cent. higher than the values obtained in the present work. just as their experimental values in the upper part of the rhombic region tend to be higher.

From the third constant in equation 2 and the heat of fusion given below, the liquid-soluble, solid-insoluble impurity is estimated to be 2.2×10^{-6} mole fraction. A more reliable estimate will be made subsequently in connection with the determination of the triple point.

Heat of Fusion, Triple Point and Purity.—Two determinations were made of the heat of fusion of monoclinic sulfur by measuring the enthalpy change between 113 and 125° and subtracting the integrals of heat capacity over this range. The values obtained are 1718.2 and 1716.9 j./g.-atom. Considering the reproducibility of heat capacity measurements in this temperature region, the average value 1717.6 is believed to be accurate within ± 2.2 j./g.-atom. For comparison, experimental values for the heat of fusion obtained by various observers are given in Table VI.

TABLE VI

HEAT OF FUSION OF SULFUR

Observer	ΔH, j./g.-atom	Method
National Bureau of Standards	1717.6 ± 2.2	Adiabatic calorimeter
Neumann[15]	1300	Vapor pressure
Mondain-Monval[16]	1250	From enthalpy curve
Lewis and Randall[17]	1650	"Drop" calorimeter
Tammann[18]	1680	Pressure dependence of melting curve
Oelsen and Oelsen[6]	1960 ± 40	Cooling curve
Wigand[25]	1400	Isothermal jacket calorimeter
Iitaka[26]	1770	"Drop" calorimeter
Stratton and Partington[27]	1190	

In making the calculation of the heat of fusion, the heat capacity of monoclinic sulfur is taken from equation 2. The integral of the last term in equation 2 has been applied as a correction to the heat of fusion. If the points at 101° are included in determining the monoclinic heat capacity, the heat capacity will decrease instead of increase with temperature, resulting in a different enthalpy integral to be applied as a correction. Such a treatment would increase the heat of fusion by about 1.4 j./g.-atom.

As an over-all check on the measurements of heat capacity and the heats of transition and fusion, the enthalpy change in the full calorimeter between 75 and 135° was determined in a single experiment to be 27,171.7 j. By integration and sum-

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(24) "Gmelins Handbuch der anorganischen Chemie," 8. Auflage, System Nummer 9, Teil A, Verlag Chemie, Weinheim, 1953.

(25) A. Wigand. *Z. physik. Chem.*, **63**, 273 (1908).

(26) I. Iitaka, *Science Repts.*, *Tohoku Imp. Univ.*, 1 **8**, 99 (1919).

(27) K. Stratton and J. R. Partington, *Phil. Mag.*, [6] **43**, 436 (1922

mation of the quantities given in this paper added to the integrated heat capacity of the empty calorimeter, the value for this enthalpy change is 27,176.9, a difference of 0.02%.

The melting point has been determined under a very small pressure of helium, so that the temperature obtained is virtually the triple point. Since the material is not absolutely pure, the observed melting point will be less than the true equilibrium triple point. By adding known fractions of the heat of fusion in the melting range and measuring the equilibrium temperature for each fraction one obtains the equilibrium temperature as a function of the amount of solvent (liquid sulfur). If this temperature is plotted against $1/F$, the reciprocal of the fraction melted, and extrapolated to $1/F = 0$ (corresponding to infinite solvent), the triple point of sulfur is obtained. In Fig. 4 are shown results of three series of experiments. The data represented by the circles were taken after approximately 4 hr. waiting for equilibrium, the squares after 8 hr. and the triangles after 6 hr. The first two series were taken during the early part of the work in the liquid range; the last at the completion of the work to detect any progressive contamination. The data were fitted to a straight line by the method of least squares and extrapolated to give a triple point of 115.176°, which is believed to be accurate within 0.010°. From the slope of the line and the calculated freezing point depression constant, the mole-fraction of liquid-soluble, solid-insoluble impurity is 1.3×10^{-5}.

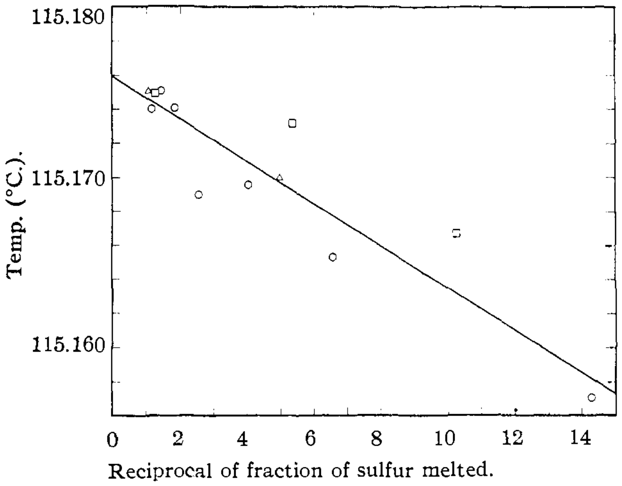

Fig. 4.—The triple point, monoclinic–liquid–vapor: ○, data taken 4 hours after heating; □, data taken 8 hours after heating; Δ, data taken 6 hours after heating (after completion of heat capacity measurements).

The use of the freezing point depression to calculate the impurity needs to be explained for the special case of sulfur. Liquid sulfur consists mainly of S_8 rings near the melting point, but there are also present a few per cent. of rings and chains other than S_8 which makes the equilibrium melting point lower than the equilibrium temperature between S_8 (monoclinic) and S_8 (liquid).[11,28] The concentration of these other molecular species is also a function of temperature, so that the effect of this "self" impurity depends on the concentration of the true impurity. The relation between the freezing point lowering θ and the other factors involved can be derived, starting with the familiar equation for freezing point lowering

$$\theta = k(N_2 + N_3) \qquad (4)$$

where θ is the difference between the observed temperature and the temperature of the equilibrium between S_8 (monoclinic) and S_8 (liquid), k is the freezing point lowering constant, N_2 is the mole fraction of non-sulfur impurity and N_3 is the "self" impurity. If the equilibrium concentration of sulfur other than S_8 is assumed to vary linearly over the narrow temperature region, N_3 can be expressed by the relation

$$N_3 = (a - b\theta) \qquad (5)$$

The mole fraction of non-sulfur impurity in the liquid is a function of the amount of sulfur melted

$$N_2 = \frac{N_2^*}{F} \qquad (6)$$

where F is the fraction of sulfur melted and N_2^* is the mole fraction of true impurities when all the sulfur is melted. Combining these equations and solving for θ gives the equation

$$\theta = \frac{k}{1 + bk}\left(a + \frac{N_2^*}{F}\right). \qquad (7)$$

On the basis of data given for the concentration of sulfur other than S_8 in the liquid[28] the value of the product bk is about 0.07. This correction has been applied to arrive at the estimate of impurity, although the applicability of these concentration data to very pure sulfur may be of questionable validity.

The "approximate mean" value of the cryoscopic constant obtained by direct measurement is given in Gmelins Handbuch[24] as 665 deg. C./mole for one gram-atom of sulfur. The cryoscopic constant computed from data presented in this paper is 730, but, if allowance is made for the decrease in "self" impurity as the temperature is lowered, the constant which would be observed experimentally is calculated to be 686, which agrees rather well with the "approximate mean."

The melting point at one atmosphere calculated from densities of solid[18] and liquid[29] and the triple point given above is 115.21°, which is 0.71° higher than the summary of old values given in Gmelins Handbuch.[24] This corresponds to a mole fraction of impurity in the older measurements of 0.1%, either as true impurity or as excess of "self" impurity over the equilibrium concentration.

Liquid Sulfur.—The heat capacity of liquid sulfur exhibits rather extraordinary behavior, especially in the vicinity of 159°. In Fig. 5, the heat capacity is plotted as a function of temperature. There is a rapid increase to a maximum heat capacity about 50% greater than the heat capacity at 120°. This maximum is quite sharply defined, as is apparent from the detailed plot in the upper right corner of the figure. The temperature of the maximum is found by short extrapolations to be 159.1°, which is believed to be accurate to ± 0.3°.

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(28) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1944.

(29) A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

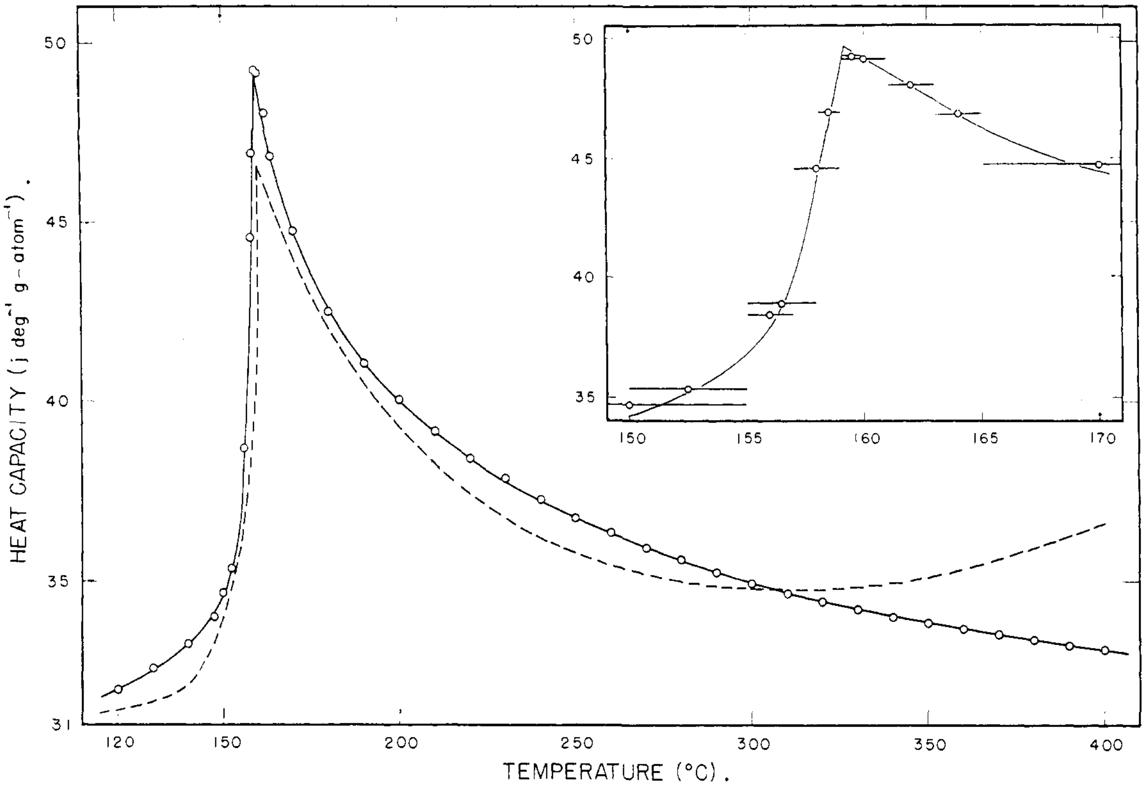


Fig. 5.—Heat capacity of liquid sulfur: ———, NBS smoothed; O, NBS, experimental (each circle represents several determinations); – – – –, Braune and Möller,[4] smoothed. The insert shows the behavior of the heat capacity near its maximum. (Horizontal lines indicate the length of experiments.)

The data upon which Fig. 5 is based are shown in Table VII. The data were smoothed by fitting empirical equations over three temperature regions by the method of least squares, except that graphical methods were used between 155 and 165°. The computed standard deviation is 0.025 j. deg.$^{-1}$ g.-atom^{-1} except between 155 and 165°. The short experiments between 155 and 165° were corrected to make their sum equal to the enthalpy change determined in a ten-degree experiment. These corrections total 0.35% of the enthalpy increase in this interval. Included in Table VII are three experiments (of somewhat inferior accuracy) made with the supercooled liquid. From these experiments the heat capacity is calculated to be 31.3 j. deg.$^{-1}$ g.-atom^{-1} at 102.5° and 31.5 at 107.5°.

TABLE VII

OBSERVED AVERAGE HEAT CAPACITIES IN LIQUID REGION

Temp. interval, °C.	Heat cap. full, j./°C.	Heat cap. empty, j./°C.	Temp. interval, °C.	Heat cap. full, j./°C.	Heat cap. empty, j./°C.
100–105	342.2[a]		225–235	377.17	242.56
	342.5[a]			377.13	242.54
105–110	343.3[a]		235–245	376.07	243.41
115–125	346.44	232.58		376.03	243.39
	346.37	232.60	245–255	374.99	244.18
116–125	346.61			375.00	244.17
125–135	349.40	233.59	255–265	374.36	245.06
	349.35	233.66		374.45	245.03
	349.35		265–275	373.80	245.89
135–145	352.96	234.57		373.78	245.88
	352.85	234.59	275–285	373.44	246.69
145–150	356.35			373.35	246.69
145–155	358.88	235.48	285–295	372.93	247.54
		235.48		373.04	247.49
150–155	361.54		295–305	372.91	248.37
	361.55			372.78	248.37
155–157	373.00			372.83	
155–158	374.53		305–315	372.65	249.15
157–159	394.92			372.68	249.17
158–159	403.39			372.62	
159–160	411.72		315–325	372.60	250.00
159–161	411.37			372.69	249.98
155–165		236.49		372.64	249.94
		236.48	325–335	372.78	250.80
161–163	407.59			372.75	250.79
163–165	403.55		335–345	372.90	251.68
165–175	396.64	237.42		372.85	251.59
		237.44	345–355	373.00	252.50
175–185	389.61			372.94	252.36
	389.54	238.30	355–365	373.09	253.24
	389.58	238.32		373.17	253.22
	389.59		365–375	373.58	254.15
185–195	385.47	239.21		373.62	254.17
	385.43	239.23			254.18
	385.41		375–385	373.90	255.03
	385.38			373.97	255.04
195–205	382.52	240.03	385–395	374.29	256.08
	382.56	240.09		374.37	255.90
205–215	380.29	240.92			255.94
	380.19	240.93	395–405	374.72	256.91
215–225	378.54	241.76		374.86	256.79
	378.54	241.78			256.84

[a] Supercooled liquid. Less reliable than other data.

Also shown in Fig. 5 is the smooth curve of the heat capacity of the liquid determined by Braune and Möller.[4] Although the authors believed their data were accurate to about 1.5%, there is a difference of about 10% at 400° between their data and those presented in this paper. In this connection, three comments can be made. (1) They obtained data from a continuous heating curve, with no waiting for equilibrium. Although they state that they found no trend with the rate of heating, it is apparent from the present work that equilibrium is often attained only after several hours at a constant temperature. (2) The calorimeter was not checked using a substance of known heat capacity. (3) The sulfur was prepared by recrystallization from carbon disulfide and doubtless contained significant impurities.[7,9] Although the heat capacity data do not agree very well, the increase in enthalpy obtained by integrating the data of Braune and Möller over the liquid range is only 1.5% higher than that obtained from the present work.

A further comparison with published data can be made by calculating the increase in enthalpy from the NBS data and comparing with data obtained from the heat of cooling sulfur from known temperatures in calorimeters at about room temperature.[16,17,26] Such experiments quench the sulfur, which then approaches equilibrium very slowly. The enthalpy values so obtained therefore tend to be too low. However, the data of Lewis and Randall[15] are lower by only 0.2% at 140°, 1.2% at 184° and 1.7% at 390° than enthalpies calculated from the data in Table VII.

The Thermodynamic Functions.—The standard-state values of enthalpy, entropy and the heat capacity are listed in Table VIII. These values were computed from heat capacity equations fitted to the data by the method of least squares, except that graphical methods were used between 155 and 165°. Linear interpolation below the melting point and above 220° will not introduce errors greater than the estimated uncertainty.

The tabulated values for the heat capacity are believed to be accurate to 0.1% below 95°, 0.5% from 95 to 101° (with additional uncertainty near 101° because of the uncertainty of the transition temperature), 0.2% above 101°, with a somewhat larger tolerance in the vicinity of 159°. The difference between C_p at experimental pressures and C_p^0 has been neglected. The enthalpy values are more reliable than the heat capacity values because the separate, longer "enthalpy" experiments were carried out in regions where the heat capacity was difficult to measure. The entropy is also more reliable than the heat capacity. This follows from the fact that the heat capacity data sum to the enthalpy. (Between 155 and 165° they were *corrected* to sum to the enthalpy.) For example, an error in entropy due to a heat capacity value which is 0.5% low at one temperature will be offset by higher values at other nearby temperatures. The values given for the enthalpy and entropy are believed to be accurate to 0.1% below 95° and 0.2% above that temperature. Above 405° the table is based on the extrapolation of the fourth degree heat capacity equation for the upper liquid region and is therefore less reliable.

TABLE VIII

THERMODYNAMIC FUNCTIONS OF SULFUR

Temp., °C.	C_p^0, j. deg.$^{-1}$ g.-atom^{-1}	$H_t^0 - H_{25}^0$, j. g.-atom^{-1}	$S_t^0 - S_{25}^0$, j. deg.$^{-1}$ g.-atom^{-1}
30	22.783	113.6	0.3779
40	23.015	342.6	1.1211
50	23.240	573.9	1.8480
60	23.459	807.4	2.5596
70	23.671	1043.0	3.2565
80	23.875	1280.8	3.9394
90	24.073	1520.5	4.6088
95.39	24.177	1650.6	4.9643
95.39	24.74	2052.3	6.0545
100	24.18	2165.2	6.3591
101	24.00	2189.3	6.4235
101	24.919	2190.9	6.4278
110	25.177	2416.3	7.3957
115.207	25.326	2547.8	7.9482
115.207	31.710	4265.4	12.371
120	31.983	4418.1	12.762
130	32.534	4740.6	13.572
140	33.203	5069.1	14.376
150	34.454	5406.4	15.183
156	38.28		
157	40.97		
158	44.45		
159	48.50		
160	49.24	5798.6	16.099
161	48.68		
162	48.03		
163	47.34		
164	46.81		
170	44.603	6265.1	17.188
180	42.453	6699.2	18.156
190	41.097	7116.6	19.068
200	40.025	7522.0	19.934
210	39.144	7917.7	20.761
220	38.415	8305.4	21.556
230	37.804	8686.4	22.320
240	37.272	9061.8	23.059
250	36.774	9431.8	23.773
260	36.349	9797.3	24.465
270	35.956	10159	25.137
280	35.596	10517	25.790
290	35.267	10871	26.425
300	34.969	11222	27.043
310	34.700	11570	27.645
320	34.459	11916	28.233
330	34.242	12260	28.807
340	34.048	12601	29.369
350	33.873	12941	29.918
360	33.712	13279	30.456
370	33.562	13615	30.983
380	33.417	13950	31.500
390	33.272	14283	32.007
400	33.121	14615	32.504
410	32.957	14946	32.991
420	32.774	15274	33.469
430	32.564	15601	33.937
440	32.319	15925	34.395
444.60	32.193	16074	34.602

Summary.—The heat capacity of highly purified sulfur has been measured with an adiabatic calorimeter having a low rate of heat exchange with its surroundings. This apparatus, with its automatic temperature control system, makes it possible for the first time to hold sulfur in a calorimeter for long periods of time at virtually constant temperatures and observe the approach to equilibrium by observing the accompanying thermal effects. Many of the experiments described have involved waiting from 2 to 6 hr. before the rate of change of the calorimeter temperature reached the level of uncertainty.

The data obtained indicate the existence of a second stable "monoclinic" modification.

The heat capacity of the liquid at equilibrium is established, showing the λ-shaped maximum in detail. Differences from older data may be largely calorimetric, but the possibility remains that impurities may affect the shape of the heat capacity curve.

The measurements have been made with sufficient care to establish the values for the thermodynamic functions of sulfur between room temperature and the normal boiling point with an acccuracy acceptable for thermochemical calculations.

Acknowledgments.—The continual interest and encouragement of Professor W. J. Svirbely are gratefully acknowledged. Thanks are due to Mr. M. L. Reilly for the use of the computer code which he is developing for treating heat capacity data and to Mr. C. H. Hochgesang for constructing the container. The author is especially indebted to Dr. D. C. Ginnings for many valuable discussions regarding the vagaries of calorimetric and electronic apparatus.

WASHINGTON, D. C.

[CONTRIBUTION NO. 866 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Kinetics and Mechanism of the Periodate Oxidation of α-Diketones

BY V. J. SHINER, JR., AND C. R. WASMUTH[1]

RECEIVED JULY 17, 1958

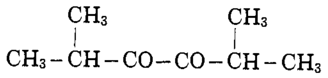
The rates of oxidation of diacetyl, diisobutyryl, benzil and camphorquinone by periodate solutions over a range of *p*H have been measured and correlated with the changes in concentration of the various ionized species of periodate present in these solutions and the separate rates of reaction of each of the periodate species with the α-diketones. The concentrations of the various species of periodate present in solution were determined spectrophotometrically using the general method of Crouthamel[5] with the important exception that the third stage of ionization is found to take place around *p*H 12.0 as indicated by a change in the optical density of the periodate solutions at 250 mμ in the *p*H range 11–13. The results are interpreted in terms of a nucleophilic attack of each of the six-coördinated periodate species on the carbonyl carbon atoms of the glycol to form a transient intermediate which undergoes spontaneous decomposition to the products, iodate and two molecules of carboxylic acid. The reaction rate is first order in periodate and first order in α-diketone over a fairly wide range of concentration and the rate of attack of the periodate increases as the degree of ionization increases.

A rather extensive body of work on the kinetics and mechanism of the oxidation of α-glycols by periodic acid has been accumulated through the efforts of several groups of authors[2] with the result that these reactions seem now to be fairly well understood. The evidence seems best explained in terms of the prior formation of a kinetically appreciable concentration of a cyclic complex through coordination of the oxygen atoms of the glycol with the iodine atom of the periodate. This complex, in the singly negatively charged state of ionization, then undergoes electronic rearrangement and decomposition into the products, iodate and two organic fragments containing new carbonyl groups.

The periodate oxidation of α-diketones however has received relatively little attention. The only kinetic observations reported have been by Clutterbuck and Reuter[3] who found that diacetyl was oxidized much more rapidly than benzil, and by Taylor, Soldano and Hall,[4] who reported that the oxidation of diacetyl proceeded *via* an initial fast reaction followed by a subsequent slower one, which showed a negative salt effect and a low activation energy. Because of its relationship to the glycol oxidation and because of the various possibilities for reaction between the several different species of both periodate and α-diketone that exist in solution, it seemed that a more thorough investigation of the α-diketone oxidation would be of interest. The present paper reports studies on the kinetics of the periodate oxidation of diacetyl (I), diisobutyryl (II), benzil (III) and camphorquinone (IV). Initial kinetic studies indicated that the reactions were strictly second order, first order in total periodate concentration and first order in α-diketone, and that there was formed no kinetically detectable concentration of an intermediate complex. The kinetic studies then were extended to include measurements over a considerable range of *p*H to determine which of the species of periodate originating from the dissociation of the acid were reactive in the oxidation. The concentrations of the various per-

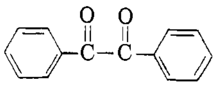
$CH_3COCOCH_3$

I

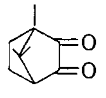


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CO-CO-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

II



III



IV

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(1) Abstracted in part from a thesis submitted by C. R. Wasmuth to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree.

(2) For detailed information on this reaction see G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 4580 (1957), and references cited therein.

(3) P. W. Clutterbuck and F. Reuter, *ibid.*, 1467 (1935).

(4) J. E. Taylor, B. Soldano and G. A. Hall, THIS JOURNAL, **77**, 2656 (1955).