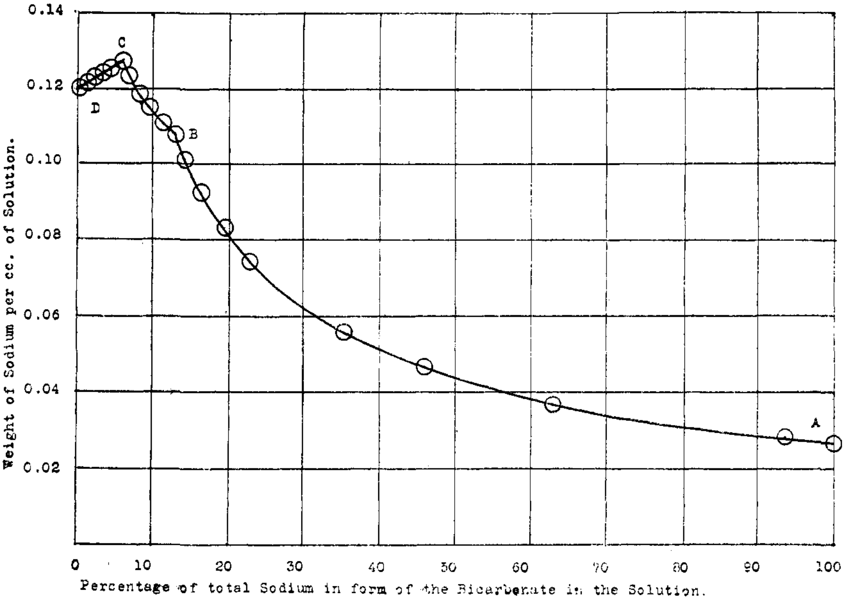
to the liquid and vapor phases, two solid phases: bicarbonate and sesquicarbonate. At C, the two solid phases are sesquicarbonate and normal carbonate decahydrate. Each of the three curves represents a three-phase system, each having a vapor, a liquid and a solid phase. Along AB the solid is the bicarbonate; along BC it is the sesquicarbonate; along CD the decahydrate of the normal carbonate. We have made preliminary determinations of the concentration of carbon dioxide in the vapor in equilibrium with solutions of various bicarbonate content. The concentration is high at A and decreases rapidly toward B. When air is drawn through a saturated solution of bicarbonate, in contact with an excess of the solid, the solution loses carbon dioxide: at first rapidly, later very slowly. In six weeks, at 25°, the composition of the solution changed along the curve AB until the solution contained only 18 per cent. of its sodium as bicarbonate. The rate of change was now very slow, but equilibrium had not been reached.



[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 66.]

THE HEAT CONTENT OF THE VARIOUS FORMS OF SULFUR.

BY GILBERT N. LEWIS AND MERLE RANDALL.

Received February 22, 1911.

In a systematic calculation of the free energy of the sulfur compounds, we have found it necessary to know, with some degree of precision, the energy changes involved in the conversion of the various forms of sulfur into one another, as well as the specific heat of the several forms. The specific heat of the two crystallin forms of sulfur and the heat of transformation of the one into the other have been determined with sufficient accuracy by previous investigators, but the data on the heat of fusion of the two crystallin modifications are in need of revision, and no reliable determinations of the specific heat of liquid sulfur are to be found in the literature. The present investigation, while undertaken primarily to provide necessary material for the calculation of free energy, possesses a certain interest of its own, on account of the very abnormal conditions which have been shown to exist in liquid sulfur.

It is well known that liquid sulfur is composed of two substances, the relative amounts of which, in equilibrium with each other at a given temperature, may be obtained by suddenly chilling the liquid under suitable conditions. One of the substances known as S_λ yields thus a product which is soluble in carbon bisulfide, and the other, S_μ, one which is insoluble, or rather, one which dissolves with no measurable speed. The relative amounts of these two, in equilibrium with each other at different temperatures, have recently been determined by Smith and his collaborators,[1] and their results have been plotted in Fig. 1. The percentage of S_μ, or insoluble sulfur, which is plotted from left to right, increases from about 4 per cent. at 120° to about 34 per cent. at 445°, the greater part of the change taking place within a comparatively narrow temperature range in the neighborhood of 160°.

From the form of this curve, it is evident that in case the change from S_λ to S_μ is associated with a considerable energy change, the specific heat of liquid sulfur, when it is heated in such a way as to maintain equilibrium between the two forms, must vary with the temperature in a very unusual manner. Wigand[2] has attempted to calculate the heat associated with the change from S_λ to S_μ by introducing the data which we have reproduced in Fig. 1 in the van't Hoff equation,[3]

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[1] Smith and Holmes, *Z. physik. Chem.*, 54, 257 (1905); Carson, THIS JOURNAL, 29, 499 (1909). A comprehensive bibliography of the earlier work on this subject is given by Kruyt, *Z. physik. Chem.*, 64, 513 (1908).

[2] Wigand, *Z. physik. Chem.*, 63, 273 (1908).

[3] This procedure was first suggested by Schaum, *Ann.*, 308, 23 (1899). Smith and Holmes, *Z. physik. Chem.*, 54, 267 (1905), attempted to apply this method of calculating the heat of reaction but concluded that it was incorrect, giving as their reason that the equation of van't Hoff, being derived from the laws of dilute solutions, could not be expected to hold in a system containing only the two reacting substances and no other solvent. This is not identical with the explanation which we offer here, for the equation of van't Hoff would be rigorously applicable to this case, no matter what the relative amounts of the two varieties of sulfur might be, if these formed perfect solutions with each other. For a discussion of the definition of a perfect solution see Lewis, THIS JOURNAL, 30, 668 (1908).

$$\frac{d \ln K}{dT} = \frac{U}{RT^2}.$$

In this equation K is the ratio of S_μ to S_λ, in equilibrium, and U is the heat absorbed when eight gram-atoms of sulfur pass from the soluble to the insoluble form (the formula of both forms of liquid sulfur is assumed to be S_8). From the rate of change in the relative amounts of S_μ and S_λ, at 130°, Wigand obtains at this temperature 21.1 cal. per gram for the heat of the reaction in question. That this value is not

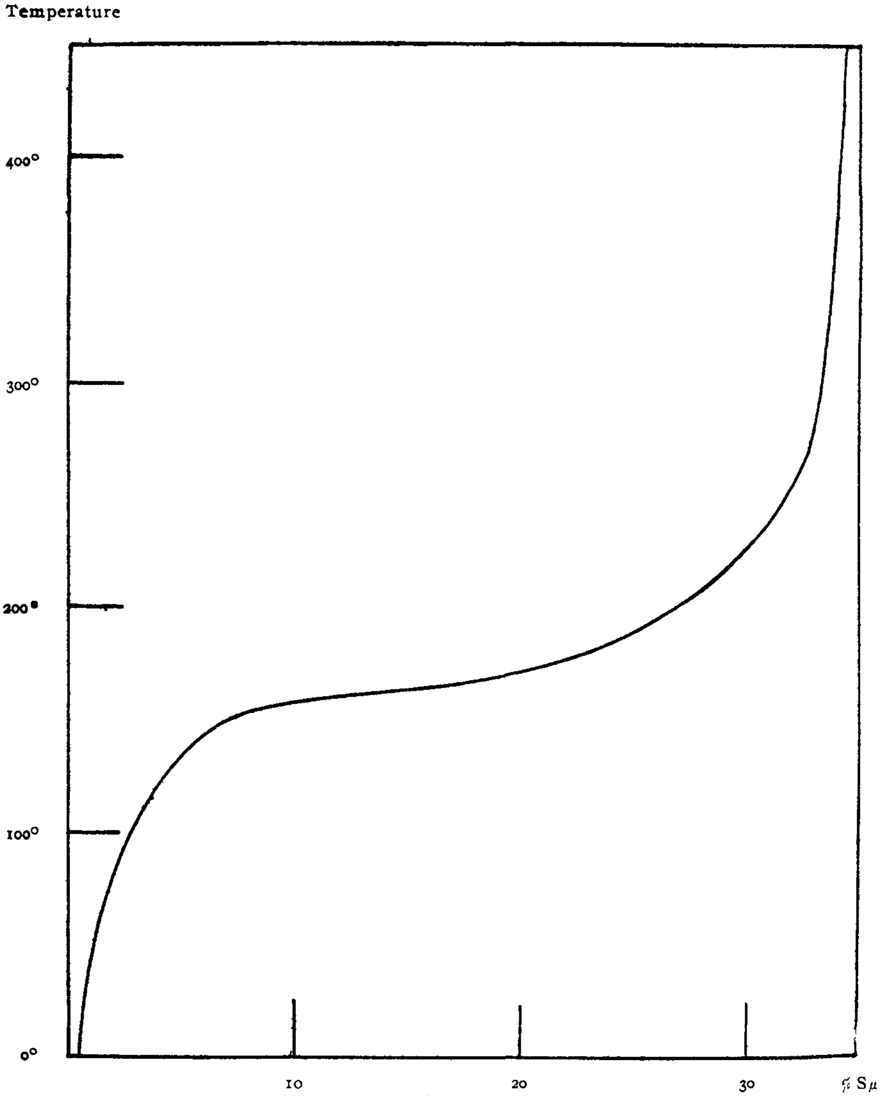

Fig. 1.

far from the one which will be obtained below from calorimetric measurements is the merest accident, for if Wigand had used other temperatures, his method would have given far different results, ranging from 2 or 3 cal. to a maximum value of 146 cal. per gram at 159.5°. Of course, the true heat of the reaction can hardly change much in so small a temperature range, and the calculation of Wigand must, therefore, be erroneous. This is due to the fact that the above equation of van't Hoff is only true in such a case as this, when the substances entering into the reaction obey the laws of the perfect solution. That a mixture of S_μ and S_λ is not a perfect solution may be deduced from the fact that these two liquids are not under all conditions completely miscible. We may, therefore, regard the heat of this reaction as completely unknown.

The Total Heat of Sulfur between 23° and the Temperatures 100°, 140°, 184° and 390°.

In order to determin the specific heat of liquid sulfur and the effect upon it of the transformation of one form of liquid sulfur into the other, molten sulfur was dropped from a constant-temperature bath into a calorimeter at about 23°. The sulfur was of the best quality obtainable from Kahlbaum and was prepared for use in the following manner: A suitable quantity of the crystals was melted in a glass tube and a current of dry ammonia was bubbled through it. It was then allowed to cool, and solidify. The glass tube above the sulfur was then drawn out and attached to a high-vacuum pump. After exhaustion dry ammonia gas was allowed to enter from a bulb containing a solution of ammonium nitrate in liquid ammonia (Divers' solution). The tube containing the sulfur was then sealed off and weighed. The presence of ammonia was shown by Smith, Holmes and Hall,[1] and by Carson[2] to catalyze not only the conversion of one form of liquid sulfur into the other, but also the formation of crystallin sulfur from the insolubl sulfur at room temperatures.

The tube containing sulfur was suspended from a fine wire and introduced[3] into the heating apparatus shown in Fig. 2, and constructed as follows:[4] The concentric iron tubes AA and CC and the plate BB were welded together in the oxy-acetylene flame, forming an annular vessel to contain a boiling liquid. Into the upper end of CC was likewise welded a very small tube, D, through which runs the wire E supporting the sulfur

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[1] Smith, Holmes and Hall, *Ber.*, 35, 2992 (1902); THIS JOURNAL, 27, 797 (1905); *Z. physik. Chem.*, 52, 602 (1905).

[2] Carson, *loc. cit.*

[3] In order to prevent the bursting of the tube, owing to the expansion of the sulfur, it was melted cautiously with a free flame before its introduction into the bath.

[4] An apparatus which in several features is not unlike the one which we have employed has been described by White (*Physik. Rev.*, 31, 670 (1910)) while our investigation was under way.

tube I. The tubes H and J served as condensers and were surrounded by coils of metal tubing carrying running water. A portion of this tubing also passed for a certain distance inside the tubes H and J, making the condensation more efficient. The tube AA was wrapped with mica, around which nickel-steel wire was wound, the number of turns being greater at the lower end of the tube. A current of electricity through

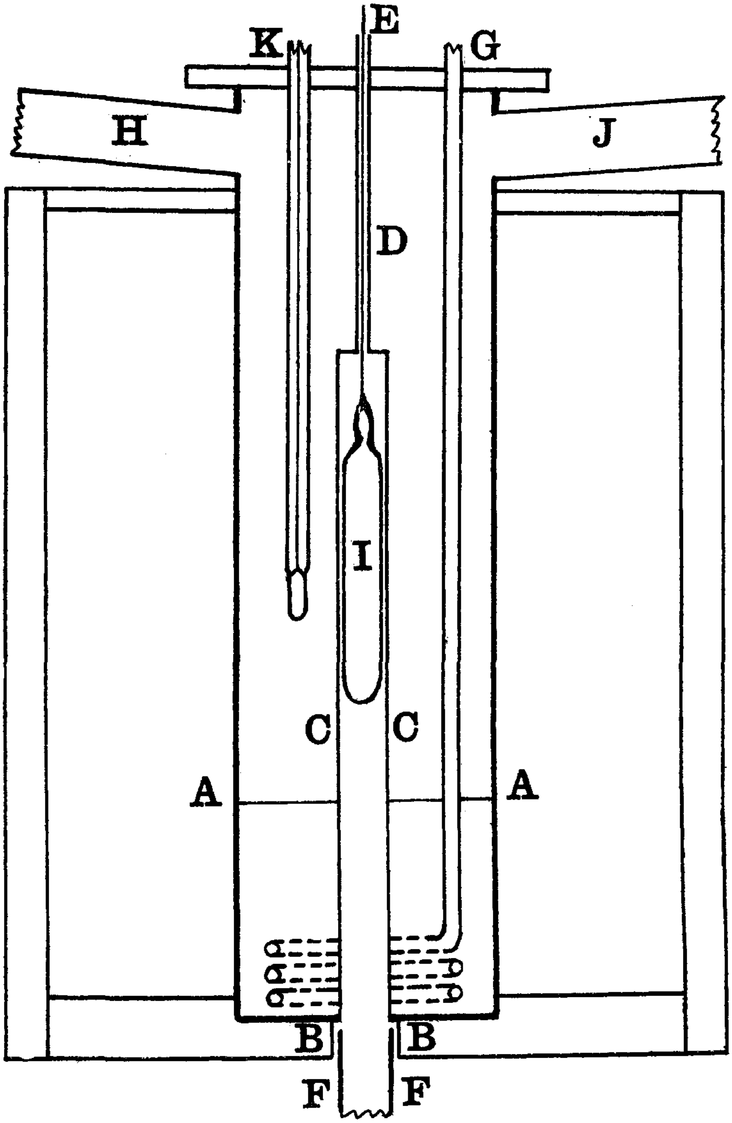

Fig. 2.

this wire helped to maintain the desired temperature, while the main heating was furnished by an electrical heater, G, of the "Simplex"[1] form. The bath was well lagged with asbestos and furnished with an asbestos cover supporting the thermometer K. The temperature was constant throughout the tube CC, except for a few centimeters at the bottom, as was shown by a thermometer introduced from below. In order to avoid any draft through the small tube D its upper end was joined to a rubber tube which was closed by a pinchcock except at the moment when the wire E was to be released.

This whole apparatus was placed upon a wooden support 45 cm. above the top of the calorimeter, and the tube CC was continued by a glass tube, FF, of the same size which extended to within 2 cm. of the top of the calorimeter. The latter consisted of a Dewar tube of about 800 cc. capacity in which were placed a Beckmann thermometer, a vigorous rotary stirrer, operated by a motor, and a nearly cylindrical metal cage composed of a number of vertical wires connected at the bottom through a brass plate, and fastened at the top to the calorimeter cover of vulcanite. A circular hole in this cover was situated just above the metal cage and below the tube FF. This hole was itself covered by a disk of vulcanite except at the moment when the sulfur tube was lowered into the cage of the calorimeter. The calorimeter was conveniently mounted on a sort of sliding track so that it could be removed from under the heater between experiments.

The experiments were conducted in the customary way, the calorimeter containing a weighed quantity of water was placed under the heater, the stirrer started, and after a suitable time the temperature was read every minute for 6 to 10 minutes. The substance contained in the heating bath was then dropped.[2] The temperature readings were then continued at intervals of a minute until a constant rate of cooling was reached.

The first experiments were made with a bath of boiling xylene at temperatures ranging from 139.6° to 140.2°, depending upon the atmospheric pressure.

In order to calibrate the calorimeter and thermometer, several tubes containing water were first dropped from the xylene bath into the calorimeter. Ten experiments were made with three different tubes of water. In two cases the tube containing water burst on striking the calorimeter, a third experiment was lost through faulty lowering of the tube. Of the remaining seven, two gave results which were obviously inconsistent with the others and were doubtless due to our lack of experience with the apparatus. The remaining five gave results in which the average

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[1] Manufactured by the Simplex Elec. Heating Co., Cambridge, Mass.

[2] The substance was not actually dropped but was rapidly lowered into the calorimeter. The time of fall was from two- to three-fifths of a second.

deviation from the mean was 0.3 per cent. This figure probably gives a fair measure of the reproducibility of determinations with this calorimeter.

In order to compare these results with one another and to determin the constant of the calorimeter, it was necessary to know the specific heat of water and of the glass used. The specific heat of water has been taken from the formula of Callender[1] which is based chiefly on the experiments of Barnes and of Regnault. This gives for the total heat of one gram of water from 23° to 140°, 117.46 cal.[2] The specific heat of the particular specimen of glass tubing employed, which was a common soft sodium glass made in Germany, we determined directly in three experiments which gave as a mean for the specific heat of this glass between 23° and 140°, 0.2057.[3]

From these data we find that when the calorimeter contains 690 grams of water, 736.1 cal. produce a rise of one degree in the Beckmann thermometer, showing that the heat capacity of the calorimeter is about 47 cal. per degree.

Experiments were next made with a number of tubes of the same glass containing sulfur. The weight of the sulfur ranged from 25 to 35 grams and that of the glass from 15 to 20 grams. The sulfur was kept in the bath from one and a half to three hours. The results of five experiments with three different tubes are given in Table I. The third column shows the total heat given to the calorimeter per gram of sulfur, after allowance is made for the heat of the glass.

TABLE I.—140–23°.

No. of expt.	No. of tube.	Total heat: cal. per gram sulfur.
1	1	37.76
2	2	38.42
3	2	37.93
4	2	38.08
5	3	38.00
	Average,	38.04

A fourth tube gave results quite inconsistent with the others, namely, 34.01, 33.31, 32.23. This discrepancy is far too great to be due to any calorimetric error. Since some of these tubes were prepared before the best means of treating the sulfur with ammonia had been found it seemed likely that an insufficiency of ammonia in the fourth tube might be respon-

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[1] Callender, *Trans. Roy. Soc.*, *A.* **199**, 55 (1902).

[2] We shall use throughout the common calorie, that is, the heat required to raise one gram of water from 15° to 16°.

[3] This is very near to the value 0.2040 obtained by White, *Am. J. Sci.*, [4] **28**, 334 (1909), over the same range for a similar glass. At other temperatures, therefore, we have used the temperature coefficient obtained by White.

sible for the results obtained. In order to test this hypothesis two other tubes were prepared which were previously treated with sulfur dioxide instead of ammonia, since Carson[1] has shown that sulfur dioxide has an effect opposit to that of ammonia, retarding the establishment of equilibrium conditions. These two tubes gave for the total heat of sulfur, 32.74 and 33.04, respectively. Since both of these tubes broke in the calorimeter the experiments are probably not entirely conclusive but appear to show the correctness of our theory of the discrepancy in the case of tube four. The sulfur in the first three tubes appeared after each experiment to be in the form of rhombic sulfur and this view was corroborated by some experiments which will be described below. One of these tubes after being dropped into the calorimeter was broken and the sulfur was found to be almost completely soluble in carbon disulfide. We will therefore take 38.04 cal. per gram as the difference in internal energy between liquid sulfur at 140°, and rhombic sulfur at 23°.

The next experiments were made with a bath of aniline, boiling at 184°. The first five experiments gave for the total heat of sulfur per gram between 184° and 23°, the values 47.59, 50.74, 48.64, 50.99 and 48.55. In every case but the second the glass-containing tube broke, and the sulfur flowed to some extent into the calorimeter cage before solidifying. Here also the differences are too great to be regarded as calorimetric errors.

Before studying this matter further several experiments were made in a bath of boiling water at 100°. Sulfur when once liquefied is readily supercooled and the tubes could be kept at 100° for any desired time without crystallization. The first two experiments gave the total heat between 100° and 23° as 29.00 and 29.04 cal. In both cases a distinct change was noticed in the cooling curve, due apparently to a process evolving heat which began when the contents of the calorimeter had nearly reached uniform temperature, and lasted for five or ten minutes, after which a constant rate of cooling was again obtained. This phenomenon was so marked in the third experiment that a constant rate of cooling had been reached before the secondary reaction began, so that the total heat evolved in the calorimeter could be divided into two distinct portions. The sum of the two per gram of sulfur was 28.34 cal. while the first portion was only 25.85 cal. The same tube was again heated and dropped, and as soon as it reached its first constant cooling rate it was removed from the calorimeter and found to contain a form of sulfur entirely different in appearance from the yellow, opaque substance obtained previously. It was amber-colored, translucent and showed the long prismatic crystals characteristic of monoclinic sulfur. Presently at one end of the tube the sulfur began to change to the yellow, opaque form, and this change

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[1] Carson, THIS JOURNAL, 29, 499 (1909).

progressed rapidly through the tube until in a few minutes the conversion was complete. The total heat per gram given to the calorimeter in this experiment was 25.50 cal., and of course did not include, as in the other cases, the heat of transition from the amber-colored sulfur to the yellow sulfur. Further experiments showed that the amber-like sulfur changed to the other form more rapidly at higher temperatures, but when a tube in which the conversion was partially completed was plunged into boiling water the transformation ceased and did not recommence until the tube was partially cooled. This experiment showed conclusively that the two forms of sulfur under consideration were the rhombic and monoclinic, of which the transition point is 95°.

In four experiments the values for the total heat per gram from liquid sulfur at 100° to rhombic sulfur at 23° were 29.00. 29.04, 28.34 and 28.24 with an average of 28.65. Two experiments gave as the total heat per gram between liquid sulfur at 100° and monoclinic sulfur at 23°, the values 25.97 and 25.50 with an average of 25.74.

The difference between these two means, namely 2.91 cal., should be the heat of transition of monoclinic to rhombic sulfur at 23°, although, of course, this is not an accurate method for the determination of this quantity, since the heat of transition appears as a small difference between the two quantities experimentally determined. This heat of transition has been determined directly and therefore more accurately by Brönsted[1] at 0° and by Tammann[2] at 95° and their results are in close agreement. From Brönsted's value and the known specific heats[3] of rhombic and monoclinic sulfur the heat of transition at 23° is 2.54 cal. Assuming this value to be correct we may add it to the total heat obtained in the two cases where monoclinic sulfur was the final product, and thus obtain two additional values for the total heat between liquid sulfur at 100° and rhombic sulfur at 23°, namely 28.51 and 28.04 cal. These values, averaged with the four given above, give a final mean of 28.53.

From the specific heat of rhombic sulfur the total heat of this substance between 23° and 100° is 13.66 cal. By subtracting this value from the one we have just obtained above we find 14.87 cal. as the heat of fusion of rhombic sulfur at 100°. The heat of transition between rhombic and monoclinic sulfur at this temperature from the data previously mentioned is 3.36 cal. and therefore 11.51 cal. is the heat of fusion of monoclinic sulfur at 100°.

It must be borne in mind that these are the heats of fusion when the solid is converted into liquid sulfur in which S_λ and S_μ are in equilibrium.

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[1] Brönsted, *Z. physik. Chem.*, 55, 371 (1906).

[2] Tammann, *Kristallisieren und Schmelzen*, 275 (1903).

[3] The specific heat of rhombic sulfur is taken as $0.168 + 0.00015t$, and of monoclinic sulfur as $0.174 + 0.00022t$ where t is temperature centigrade. The complete data from which these values are taken will be discussed in another paper.

These values are therefore higher than those which would be obtained by merely fusing the crystallin substances to form pure S_λ. The difference is the heat of conversion of about 0.03 gram of S_μ into S_λ. From the calculations which we give below this proves to be 0.4 cal. The heats of fusion of rhombic and monoclinic sulfur to form pure S_λ at 100° are therefore 14.5 and 11.1 respectively. For the latter quantity Wigand[1] gives a résumé of the results of previous investigators. His own value is 10.4 cal. at 119° which is equivalent to 9.8 cal. at 100°. Although Wigand used a direct method, his four values show an average deviation from the mean of 5.7 per cent., and his highest value agrees with ours. It is hardly likely that our value can be in error by more than 2, or perhaps 3 per cent.

Returning now to the experiments at 184°, two more experiments were made in which the sulfur was examined as soon as possible after the calorimeter came to a constant rate of cooling. In both cases the glass containing tube broke in the calorimeter. In the first experiment the greater part of the sulfur appeared in a form which we have not seen described hitherto. It was glassy, brittle, almost colorless, and appeared to be noncrystallin. Inside of the glassy shell was a considerable amount of rhombic sulfur. This experiment gave for the total heat per gram 47.86 cal. The next experiment was similar except that the percentage of glassy sulfur was relatively small, the greater part being rhombic. The total heat per gram for this experiment was 49.93 cal. These results entirely corroborated a view to which we had been led by the preceding experiments, namely that the two experiments in which the result was high, 50.74 and 50.99, were the only ones in which pure rhombic sulfur was the end product. In one of these the glass containing tube remained intact and there can be no question that the product was pure rhombic sulfur. In the other cases the values were smaller, apparently by an amount dependent upon the percentage of glassy sulfur which was formed. We shall therefore take the average of 50.74 and 50.99, namely, 50.86, as the total heat per gram between liquid sulfur at 184° and rhombic sulfur at 23°.

It seemed advisable to make a few experiments with a bath at a much higher temperature, and for this bath we chose a substance known as retene, the boiling point of which was 391°, according to a standardized mercury thermometer, and 388°, according to a calibrated copper-constantan thermocouple. The average was assumed to be correct and as the temperature varied slightly in the different experiments the results were all calculated to 390°. We hoped to avoid the breaking of the containing tubes by using a special borosilicate glass[2] of very small coefficient of

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[1] Wigand, *Z. physik. Chem.*, 63, 273 (1908).

[2] Known as HH glass, and manufactured by the Corning Glass Works, Corning, N. Y.

expansion, but partly perhaps because the glass was old this precaution did not suffice. Since a smaller amount of sulfur was dropped in these experiments, it was necessary to attach to the tube a gold weight of 43 grams, to make the tubes sink rapidly into the calorimeter.

In order to allow for the specific heat of this glass and the gold, as well as for any constant error due to loss of heat in dropping the tube, two blank experiments were made with glass tube and gold weight alone. The gold weight of 43 grams and glass tube weighing 13.81 grams gave 1694 cal. to the calorimeter at 23°. The experiments with sulfur were not altogether satisfactory, owing to the breaking of the glass. The consequent sudden heating of the calorimeter caused an appreciable quantity of steam to be evolved. In several experiments a yellow, rubber-like form of sulfur was obtained, concerning the energy of which we have no information. The first experiment gave only glassy and rhombic sulfur about as in the last two experiments at 184°. The total heat per gram of sulfur was 100.0 cal. The second gave a similar sulfur with a small amount of the rubber-like form. It also gave the value 100.0 cal. The next two experiments gave larger amounts of rubbery sulfur and the values were 99.9 and 95.3 cal. Only the first two experiments deserve much consideration. That they agree so closely is pure accident, for in both cases steam was evolved which we roughly estimate as equivalent to 3 cal. Moreover, the sulfur formed was of the sort which we have previously found to differ in energy from rhombic sulfur by about 2 cal. We shall therefore take 105 cal. per gram as the total heat between liquid sulfur at 390° and rhombic sulfur at 23°.

The values for 390° and 184° will need revision. We believe that with no other change in our procedure except the substitution of quartz for glass tubes extremely satisfactory results could be obtained.

The Specific Heat of Liquid S_λ and the Heat of Transformation of S_λ to S_μ.

We have found for the total heat per gram between liquid sulfur at four different temperatures and rhombic sulfur at 23° the values given in column 2 of the following table. The first column gives the temperatures of the liquid sulfur. The third column gives the changes in total heats between the successive temperature intervals. The fourth column gives this change divided by the temperature interval; in other words, the mean specific heat of the liquid sulfur in each interval. The fifth column shows the percentage of S_μ in the liquid at each temperature, as taken from the plot reproduced in Fig. 1. The sixth column shows the change in this percentage in the successive intervals, and the last column these changes divided by the temperature intervals, or in other words the average change per degree in the percentage of S_μ.

TABLE II.

t.	Total heat.		Mean sp. heat.	Per cent. S_μ.		Change in per cent. S per degree.
100	28.53			3.1		
		9.51	0.238		2.4	0.060
140	38.04			5.5		
		12.82	0.292		18.2	0.414
184	50.86			23.7		
		54.14	0.263		10.2	0.050
390	105.0			33.9		

The effect of the heat of transformation from S_λ to S_μ on the specific heat is very evident, the specific heat being larger in that interval in which the transformation is taking place most rapidly. In order to form an estimate of the heat of this transformation, we will make the assumption that this heat is nearly independent of the temperature, at least throughout the region of most rapid change, and that the specific heat of S_λ is a linear function of the temperature. We will write then for the specific heat of liquid sulfur at any temperature the equation

$$c = a + bt + q\,dx/dt,$$

where t is the centigrade temperature, a is the specific heat of liquid S_λ at the centigrade zero, b is the change of this quantity with the temperature, q is the heat absorbed when one gram of S_λ is completely converted to S_μ, and x is the fraction of the sulfur which exists as S_μ at the temperature in question. We have evidently in the above table sufficient data for the calculation of the constants of this equation, and we find that $a = 0.21$, $b = 0.00016$ and $q = 13$. In other words we find for the specific heat of liquid S_λ,

$$c = 0.21 + 0.00016\,t,$$

and 13 cal. for the heat of transformation per gram from S_λ to S_μ. This estimate of the heat of transformation is not accurate and may easily be in error by 10 or 15 per cent.

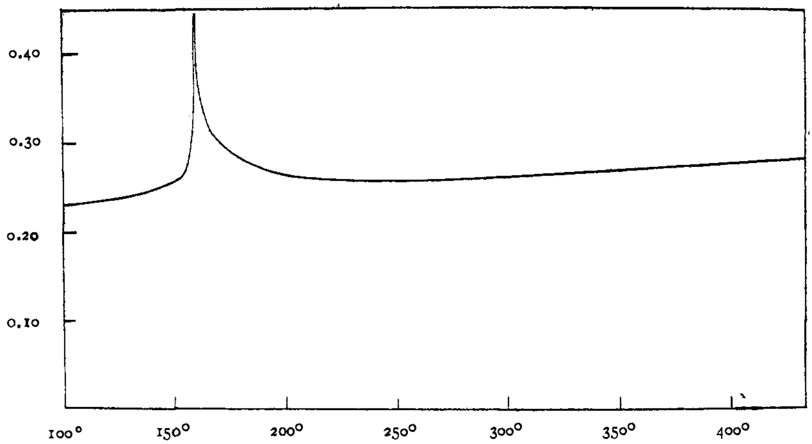

Fig. 3.—Specific heat of liquid sulfur.

Knowing the value of γ and the fraction of S_μ at different temperatures we may obtain a rough idea of the change of the specific heat with the temperature, from the above equation. We thus obtain the results plotted in Fig. 3, in which the abscissas represent centigrade temperature, and the ordinates actual specific heats. It will be seen that the specific heat changes very remarkably with the temperature, with a maximum value of 0.44 at about 160°.

It should be noted that all of these results refer to the specific heat of liquid sulfur in the presence of a suitable catalyzer. It is not therefore possible to compare them directly with the values obtained by other observers using sulfur of unknown character. We may refer to the value 0.234 between 119° and 147° obtained by Person,[1] the value 0.232 between 116° and 136° obtained by Classen[2] and several determinations by Dussy.[3]

Summary.

The total heat change is determined between rhombic sulfur at 23° and liquid sulfur (in a state of equilibrium) at the temperatures 100°, 140°, 184° and 390°. From the results obtained the following data are calculated in small calories per gram of sulfur. The heat of fusion at 100°, to form liquid sulfur in a state of equilibrium: from rhombic sulfur 14.9, from monoclinic sulfur 11.5. For the heat of fusion to form pure liquid S_λ: from rhombic sulfur 14.5, from monoclinic sulfur 11.1. For the heat of transformation in the liquid state from S_λ to S_μ, about 13. For the specific heat of pure liquid S_λ about $0.21 + 0.00016\,t$.

A diagram is given showing the approximate values of the specific heat of liquid sulfur, in the equilibrium state, over a range of temperature from 100° to 450°.

YTTRIUM POTASSIUM OXALATE.

By L. A. Pratt and C. James.

Received February 20, 1911.

The fact that the rare earth oxalates carry down the alkali oxalates is an interesting subject to those working on the rare earths.

In 1873, Cleve and Hoeglund,[4] in their articles on the compounds of yttrium and erbium, described two double salts of yttrium and potassium with oxalic acid, and assigned the following formulas (recalculated):

$$Yt_2(C_2O_4)_3.4K_2C_2O_4.12H_2O \text{ and } Yt_2(C_2O_4)_3.K_2C_2O_4.H_2O.$$

In 1906, Baxter and Griffen[5] studied the occlusion of ammonium

[1] Person, *Ann. chim. phys.*, 21, 295 (1847).

[2] Classen, *Z. Instrumentenkunde*, 11, 301 (1891).

[3] Dussy, *Compt. rend.*, 123, 305 (1896).

[4] *Bull. soc. chim.*, 193–201, 289–297.

[5] This Journal, 28, 1684.