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## ENTROPY OF ISOPRENE FROM HEAT-CAPACITY MEASUREMENTS

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### ABSTRACT

Measurements of heat capacity were made on a sample of isoprene of high purity from 20 to 300°K with an adiabatic vacuum-type calorimeter. At 20°K the heat capacity of the crystalline material was found to be 11.8 j/(mole·degree), and with increase in temperature the heat capacity increases, following the usual type of curve for crystalline substances. At 100°K the heat capacity of the solid is 64.7 j/(mole·degree), and at the melting point, 126.4°K, the heat of fusion is determined to be  $4,830 \pm 15$  j/mole. The heat capacity of the substance increases about 60 percent during the change from solid to liquid. Above the fusion temperature the curve is characteristic of liquids, and the heat capacity attains a value of 152.6 j/(mole·degree) at 298.2°K (25°C). Utilization of the data, according to the third law of thermodynamics, yields  $229.3 \pm 1.0$  j/(mole·degree) for the entropy of isoprene at this temperature.

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### I. INTRODUCTION

In a previous investigation [3]<sup>1</sup> the heat capacity, entropy, and free energy of the rubber hydrocarbon (C<sub>5</sub>H<sub>8</sub>)<sub>x</sub> were determined. Similar work has also been undertaken for substances related to rubber in order that thermodynamic relationships may be established among them. Isoprene, 2-methyl-1,3-butadiene, having the same empirical formula as rubber hydrocarbon, is produced in the destructive distillation of rubber as one of the two major constituents of the distillate [8]. It can be polymerized to form a product similar in many respects to natural rubber and is thought not only to be the substance from which rubber is formed in plants but also to play an important role in the growth of plant cells [1, 6, 16, 17]. Because of the chemical similarity and relationship between isoprene and the rubber hydrocarbon, a knowledge of the free energy of formation of isoprene from its elements would be useful in the study of the thermodynamics of reactions involving the two substances. A convenient method for obtaining this free energy or thermodynamic potential for isoprene involves determinations of the heat of combustion and of

<sup>1</sup> The numbers in the brackets here and elsewhere in the text refer to references at the end of this paper.

the entropy, the latter by means of the application of the third law of thermodynamics to data on low-temperature heat capacities and latent heats. From these are calculated the heat  $\Delta H$  and the entropy  $\Delta S$  of formation, which are combined according to the relation  $\Delta F = \Delta H - T\Delta S$  to obtain the free energy of formation  $\Delta F$ .

The present report gives, for the range 20 to 300°K, the results of measurements made in the Cryogenic Laboratory of this Bureau, of the heat capacities for both the liquid and crystalline solid and of the heat of fusion. From these a value of the entropy is calculated by means of the third law. The free energy in turn is calculated from the entropy and heat of combustion. Work on the heat of combustion is now in progress.

## II. SAMPLE INVESTIGATED

The sample of isoprene used was prepared by the cracking of dipentene vapors by means of the improved "isoprene lamp" [7, 18]. The details of its preparation and purification and many of its physical properties are described in a previous paper [4]. Immediately after purification the difference between the boiling and condensation temperatures of the sample was determined according to the method of Świątosławski [15] and found to be  $\Delta t = 0.002^\circ \text{C}$ , which in conjunction with the small freezing range [4] is indicative of high purity. Since isoprene is known to oxidize and polymerize on standing it was purified by distillation just previous to its introduction into the sample-container of the calorimeter. All the measurements on heat capacity were made within 2 weeks after the last distillation of the sample, and during most of this time it was kept at liquid-air temperatures in order to prevent polymerization. Also the sample practically filled the container and was hermetically sealed so that there was very little opportunity for oxidation. Repeated measurements of the heat capacity at various given temperatures showed no changes in the values with time. The weight of the isoprene sample was 34.175 g. This is equivalent to 0.5018 mole, the gram-molecular weight of isoprene being taken as 68.11.

## III. CALORIMETER AND ITS OPERATION

The calorimeter used for the measurements of the heat capacity and also the heat of fusion of the crystalline material was the same as that used for similar measurements on rubber [3, 14], the only change of any importance being the replacement of the old copper sample-container by one made of a platinum-iridium alloy. The resistance thermometer was rechecked at the ice point and was found to have the same value, within 0.001 ohm, as that obtained about 3 years previously. This change in resistance would be equivalent to less than  $0.004^\circ \text{C}$ , and the check was considered to be close enough so that a recalibration was not necessary. The method of operation of the calorimeter and accessory apparatus was the same as that previously described [3].

## IV. HEAT CAPACITY

The results obtained in the measurements of heat capacity are represented by graphs in figures 1 and 2, which give the relation

between heat capacity and temperature. Table 1 gives the heat capacity values for all observed points. The temperature ranges of heating varied from 3 to 10° C, except in the region of the melting point. Table 2 gives the heat-capacity values at 5° intervals taken from a large-scale drawing of the curve. All quantities of heat in this paper are expressed in international joules. The factor for conversion into calories is 4.1833 j/cal [12]. The method of calculation of the results from the data will not be shown here since it is the same as that previously described in detail [3].

TABLE 1.—Heat capacity of isoprene

Temperature	Heat capacity	Temperature	Heat capacity	Temperature	Heat capacity
°K	j/(mole-degree)	°K	j/(mole-degree)	°K	j/(mole-degree)
23.41	15.87	120.71	123.82	203.32	127.74
28.66	21.85	123.29	251.76	206.77	128.02
34.17	27.22	123.52	308.00	211.61	129.29
39.29	31.61	125.31	706.8	216.11	129.97
45.40	35.67	126.10	2,062	222.98	131.82
52.57	40.45	126.41	4,441	225.46	131.84
59.83	44.85	126.59	5,312	234.35	134.31
67.36	48.99	127.15	856.0	234.81	134.21
74.36	52.66	130.17	122.96	244.14	135.54
81.82	56.60	133.05	123.54	245.71	137.12
85.80	57.94	140.15	122.88	253.46	138.83
89.78	60.52	140.37	123.12	257.05	139.79
92.07	61.42	146.12	123.14	262.79	141.62
92.62	61.44	152.05	123.04	268.46	143.27
97.40	64.33	160.22	123.10	272.04	144.41
99.97	65.40	161.97	123.68	278.55	146.48
100.24	64.53	169.61	123.90	281.22	147.34
105.50	71.20	178.79	124.53	287.61	149.31
107.55	70.26	188.02	125.69	290.40	149.91
109.99	72.89	196.20	126.72	296.65	152.14
114.43	81.10	198.53	126.29	298.46	153.29
115.76	86.12	200.23	127.28		

TABLE 2.—Heat capacity of isoprene

Temperature	Heat capacity	Temperature	Heat capacity	Temperature	Heat capacity
°K	j/(mole-degree)	°K	j/(mole-degree)	°K	j/(mole-degree)
20	11.8	120	<sup>a</sup> 73.2	215	129.7
25	17.9	125	<sup>a</sup> 75.3	220	130.7
30	23.2	126.4	<sup>b</sup>	225	131.8
35	27.9	130	123.0	230	133.0
40	32.0	135	123.0	235	134.3
45	35.6	140	123.0	240	135.5
50	38.9	145	123.0	245	136.7
55	42.0	150	123.0	250	137.9
60	44.9	155	123.1	255	139.3
65	47.7	160	123.3	260	140.7
70	50.3	165	123.6	265	142.2
75	52.9	170	123.9	270	143.7
80	55.3	175	124.2	275	145.2
85	57.7	180	124.6	280	146.8
90	60.1	185	125.2	285	148.3
95	62.5	190	125.8	290	149.9
100	64.7	195	126.4	295	151.6
105	<sup>a</sup> 66.9	200	127.0	298.2	152.6
110	<sup>a</sup> 69.0	205	127.7	300	153.3
115	<sup>a</sup> 71.1	210	128.7		

<sup>a</sup> Extrapolated values, taken from dotted curve in figure 1.

<sup>b</sup> Fusion.

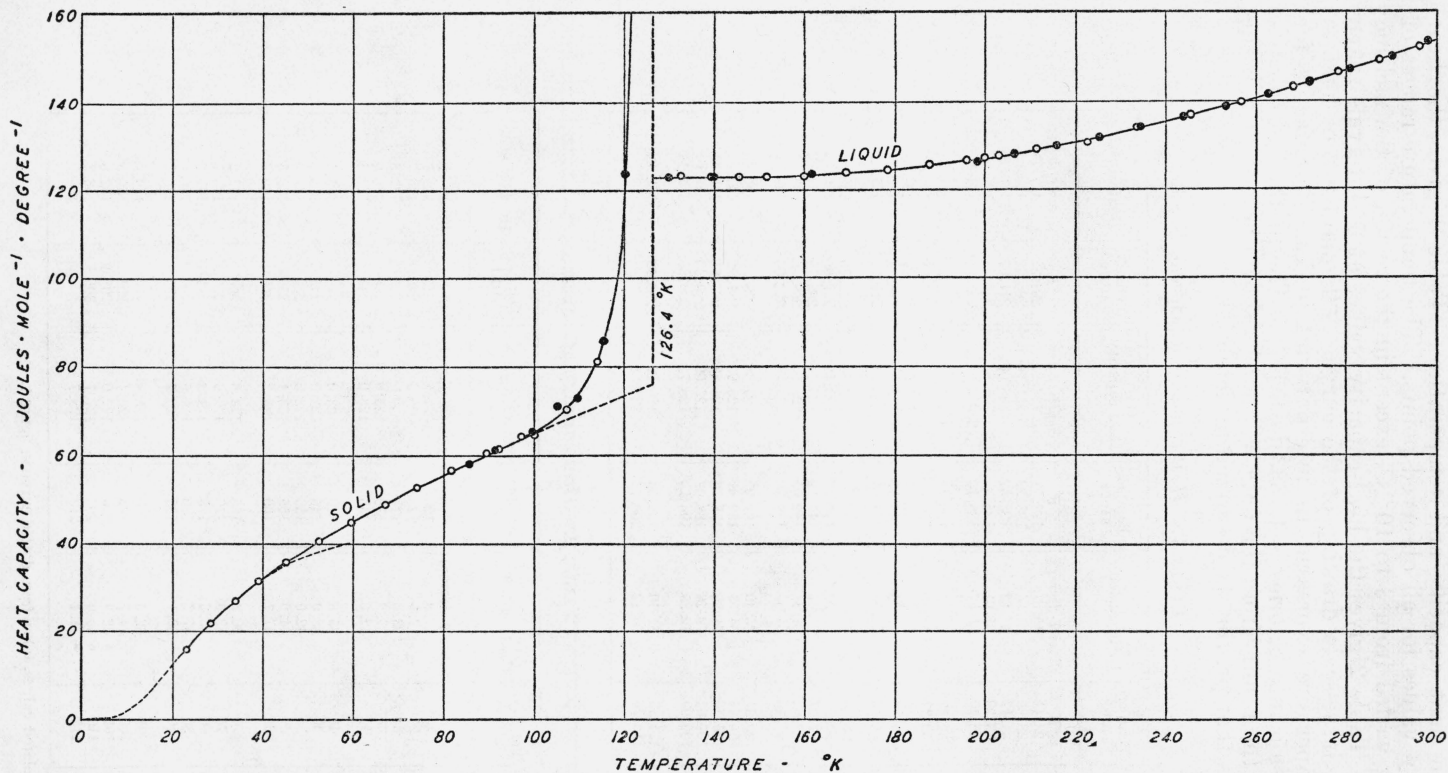


FIGURE 1.—Relation between heat capacity of isoprene and temperature.

The dotted curve at the extreme low temperatures represents values of the heat capacity taken from tables of Debye for a  $\beta_v$  value of 127. The dotted curve just below the melting temperature indicates a heat-capacity curve for the solid isoprene extrapolated to its melting point at 126.4° K. The points represented by the open and by the solid circles are for two distinct sets of observations.

When the sample of isoprene was cooled rapidly through its freezing point to liquid-air temperatures it did not become completely crystallized. This was evident from the fact that there was an evolution of heat when the sample was heated to  $115^{\circ}\text{K}$  while measurements of heat capacity were being made. Without the further addition of external heat the temperature of the sample continued to rise until conversion to the crystalline state was complete, or until the melting point was reached. This phenomenon occurs with many other organic substances including the rubber hydrocarbon [2, 3], in which the freezing is slower and has been studied in more detail. Complete crystallization of the isoprene, like that of many other substances, can be obtained by a very slow cooling through the freezing point, or by holding the temperature not more than a few degrees below the freezing point for several hours. However, if the temperatures are too low, the same supercooling occurs as in the case of rubber. All the observations reported here were taken after the sample had been cooled so slowly that on warming no evolution of heat caused by crystallization could be observed.

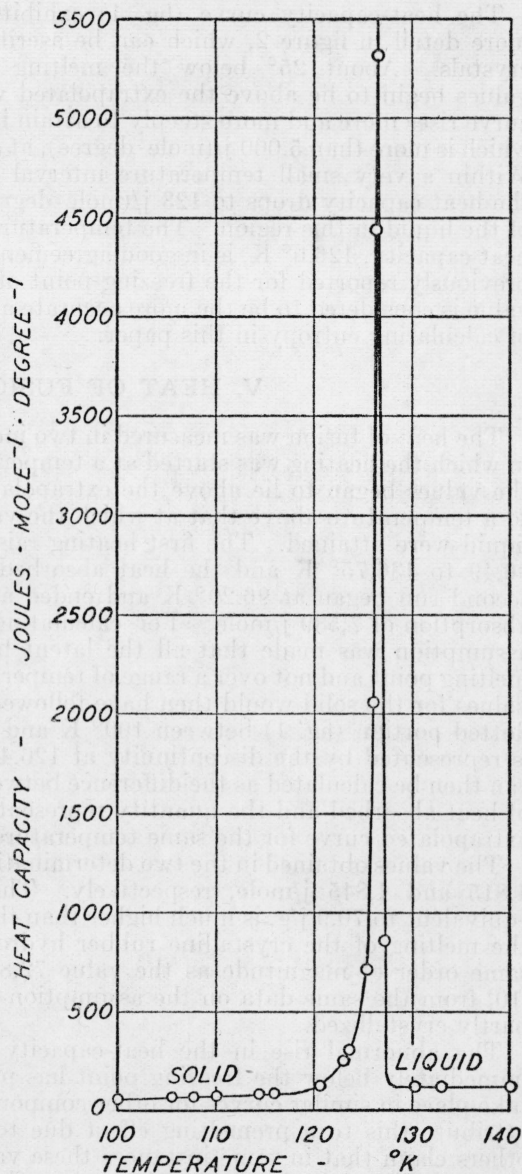


FIGURE 2.—Relation between heat capacity of isoprene and temperature in the region of the transition from the solid to the liquid state.

The heat-capacity curve (fig. 1) exhibits an anomaly, shown in more detail in figure 2, which can be ascribed to the melting of the crystals. About  $25^\circ$  below the melting point the heat-capacity values begin to lie above the extrapolated values for the solid. The curve rises more and more steeply to attain its highest observed value, which is more than  $5,000$  j/(mole·degree), at a temperature of  $126.6^\circ$  K. Within a very small temperature interval above this highest value the heat capacity drops to  $123$  j/(mole·degree), a value characteristic of the liquid in this region. The temperature at this highest observed heat capacity,  $126.6^\circ$  K, is in good agreement with the value  $126.4^\circ$  K previously reported for the freezing point of isoprene [4]. The latter value is considered to be the more accurate and is used for the purpose of calculating entropy in this paper.

## V. HEAT OF FUSION

The heat of fusion was measured in two independent determinations in which the heating was started at a temperature below that at which the values began to lie above the extrapolated curve, and continued to a temperature above that at which the values characteristic of the liquid were attained. The first heating raised the temperature from  $96.49$  to  $136.75^\circ$  K and the heat absorbed was  $8,183$  j/mole. The second run began at  $96.29^\circ$  K and ended at  $131.15^\circ$  K, with a heat absorption of  $7,539$  j/mole. For calculating the heat of fusion the assumption was made that all the latent heat was absorbed at the melting point and not over a range of temperature. The heat-capacity values for the solid would then have followed the curve shown by the dotted portion (fig. 1) between  $100^\circ$  K and the melting point, which is represented by the discontinuity at  $126.4^\circ$  K. The heat of fusion can then be calculated as the difference between the observed quantity of heat absorbed and the quantity represented by the area below the extrapolated curve for the same temperature range.

The values obtained in the two determinations of this difference were  $4,815$  and  $4,845$  j/mole, respectively. The average,  $4,830$  j/mole, equivalent to  $70.9$  j/g, is much higher than the value  $16.7$  j/g found for the melting of the crystalline rubber hydrocarbon [3], and is of the same order of magnitude as the value  $72.8$  j/g calculated by Parks [10] from the same data on the assumption that the rubber was only partly crystallized.

The abnormal rise in the heat-capacity curve at a temperature immediately below the freezing point has previously been noticed to take place in similar curves for other compounds. Some investigators attribute this to a premelting effect due to impurities [9, 19] while others claim that in some instances these values are characteristic of the pure material [5]. As previously mentioned, the isoprene for this investigation was purified to a very high degree, but other tests indicate that isoprene may absorb moisture from the atmosphere. Since there was some possibility of this occurrence during the introduction of the sample into the calorimeter, it is not known whether this abnormal rise in the curve immediately below the melting point is due to the presence of water or whether it is characteristic of the pure material.

## VI. ENTROPY

From the definition of entropy, the value  $S_{298.2}^{\circ}$  of the entropy of a substance in the liquid state at the standard temperature of 298.2° K (25° C) is given by the equation:

$$S_{298.2}^{\circ} = S_0 + \int_0^{T_{mp}} C_p d \ln T \text{ (crystals)} + \frac{\Delta H_f}{T_{mp}} + \int_{T_{mp}}^{298.2} C_p d \ln T \text{ (liquid)}$$

Here  $S_0$  denotes the entropy of the substance at the absolute zero of temperature,  $C_p$  the heat capacity at constant pressure,  $\Delta H_f$  the heat of fusion, and  $T_{mp}$  the absolute temperature of the melting point. According to the third law of thermodynamics, all pure substances in a perfect crystalline arrangement at absolute zero have the same value of entropy, which is conventionally taken as zero, so that  $S_0 = 0$ .

Curves were prepared by plotting the values of  $C_p$  for isoprene as a function of the logarithm of the temperature, and the entropy differences were obtained by graphic integration. As a check a similar integration was made on a graph in which the  $C_p/T$  values were plotted as a function of  $T$ . Since no heat-capacity values were obtained below 20° K, graphical integration could not be continued below this point. The Debye approximation formula gave values which agree very well with those found experimentally in the range from 20 to 40° K for a  $\beta\nu$  value of 127. For comparison the Debye curve is shown in figure 1 as a dotted line from 0 to 60° K. It can be seen that it begins to deviate from the experimental curve at about 40° K. With the assumption that these values are valid in the range from 0 to 20° K, entropy tables [13] of the Debye function were used to calculate the entropy increase in this range. The value obtained in this manner was

$$S_{20} - S_0 = 4.55 \text{ j/(mole-degree)}$$

This amounts to only about 2 percent of the total value of the entropy at 25° C. Graphic integration of the curves yielded the following values:

$$S_{126.4} - S_{20} = \int_{20}^{126.4} C_p d \ln T \text{ (crystals)} = 74.73 \text{ j/(mole-degree)}.$$

$$S_{298.2} - S_{126.4} = \int_{126.4}^{298.2} C_p d \ln T \text{ (liquid)} = 111.80 \text{ j/(mole-degree)}.$$

The entropy of fusion of the crystals at 126.4° K is

$$S_{126.4} \text{ (fusion)} = \frac{\Delta H_f}{T_{mp}} = 38.2 \text{ j/(mole-degree)}.$$

The entropy of isoprene at 298.2° K, assuming  $S_0$  to be zero, is then equal to the sum of these four terms, or 229.3 j/(mole-degree) (54.8 cal/(mole-degree)).<sup>2</sup> This value is believed to be correct within 1.0 j/(mole-degree) (0.2 cal/(mole-degree)).

The authors express their appreciation to the staff of the Cryogenic Laboratory for their generous assistance.

<sup>2</sup> It is interesting to note that equations of Parks and Huffman [11], who have developed a method for the calculation of entropies of organic compounds on the basis of their structural formulas, predict an estimated value of 53.6 cal/(mole-degree) for the entropy of liquid isoprene at 25° C.

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