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HEAT CAPACITY, ENTROPY, AND FREE ENERGY OF
RUBBER HYDROCARBON

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ABSTRACT

Measurements of heat capacity were made on rubber hydrocarbon in its different forms from 14 to 320° K with an adiabatic vacuum-type calorimeter. At 14° K the heat capacity was found to be 0.064 j/g/°C for both the metastable amorphous and the crystalline forms. With increase in temperature, the heat capacity increases gradually up to a transition at about 199° K, the amorphous form having a little the greater value. At 199° K both forms undergo a transition of the second order, the heat capacity rising sharply. For the amorphous form above this transition the heat capacity rises gradually without discontinuity to the highest temperature of the measurements. The crystalline form undergoes fusion (a transition of the first order) at 284° K, the heat of fusion being 16.7 j/g. At 298.1° K the heat capacity of the rubber is 1.880 ± 0.002 j/g/°C. Utilization of the data according to the third law of thermodynamics yields 1.881 ± 0.010 j/g/°C for the entropy of rubber at 298.1° K. Combination of these with appropriate other data on entropies and heats of reaction yields 1.35 ± 0.10 kj/g for the standard free energy of formation at 298.1° K of rubber from carbon (graphite) and gaseous hydrogen.

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I. INTRODUCTION

The best method for obtaining the free energy of formation of rubber is by making use of the third law of thermodynamics. This makes necessary the determination of heat-capacity values of the rubber in the temperature range from that of room down to temperatures sufficiently low to apply an empirical formula for obtaining the values below this lower temperature. From these heat-capacity values the entropy may be obtained. Then from this latter value, along with the entropy values of carbon (graphite) and gaseous hydrogen and the heat of formation of rubber, a reliable value for the free energy of formation of rubber may be calculated.

Several investigators have previously determined the heat capacities of rubber, but their observations were not made at temperatures

sufficiently low to permit accurate extrapolation to the absolute zero in order to apply the third law. Furthermore, in the previous work the possibility that rubber at low temperatures might exist either as a metastable amorphous form or as a crystalline form was not clearly recognized. In the present investigation the aim was not only to extend the temperature range but also to obtain data of a higher order of accuracy than that previously reported.

II. RUBBER SAMPLE INVESTIGATED

The sample of rubber used in this investigation was prepared by the digestion of latex with steam at about 190° C and the subsequent extraction of the resins and the products of hydrolysis with alcohol and water [20].¹ Where the term rubber or rubber hydrocarbon is used without qualification in this paper, the foregoing product is understood. The sample, of mass 38.30 g, was cut into small pieces, roughly 10 mm³ each, before its introduction into the calorimeter. At that time it gave no indication of any oxidation having taken place. The air surrounding the rubber in the calorimeter container was replaced by helium so there would be no oxidation.

A complete set of values for the heat capacity of the amorphous form of rubber from 14 to 320° K and several values for the crystalline form were obtained within the first several months. During this time the sample container of the calorimeter can remained gastight and no oxidation of the rubber sample could have taken place. However, owing to a forced delay, no further measurements were made with the calorimeter for nearly two years, during which time the calorimeter can developed a leak and the helium was displaced by air. Oxidation of the sample was rapid, and by the time it was removed from the container it had a strong odor of oxidation products and had increased its weight to 39.38 g. The increase in mass was about 2.8 percent, and, if due to oxygen alone, would give an approximate empirical formula $C_5H_8O_{0.1}$ instead of C_5H_8 . During the several weeks previous to the removal of the sample from the calorimeter, a complete set of measurements was made on the crystalline form from 14 to 320° K and several measurements were repeated on the amorphous form. The air was pumped from the sample container during these observations, so it was assumed that this final weight of the sample was constant during these later runs. The larger mass was used for the calculations of the results of the latter experiments, while the original mass was used in the calculation of the results of the experiments performed two years before. When calculated in this manner, the heat capacity of the rubber after this oxidation had occurred appeared unchanged, within 0.2 percent, from its value before oxidation, the results on both forms at different temperatures showing no consistent deviation from the earlier values. This seems to indicate that the oxidation had no significant effect on the value of the heat capacity of the rubber as determined in these experiments.²

¹ The numbers in brackets here and elsewhere in the text refer to the "References" at the end of this paper.

² These results indicate, however, that at room temperature the oxygen taken up by the rubber must have a heat capacity contribution of about 7 cal per oxygen atom if the addition causes no change in the heat capacity per gram of total sample. This value of 7 cal is considerably larger than that usually derived from organic compounds by Kopp's rule.

It was not necessary to remove the sample from the container in order to convert it from one form to another. The procedure for obtaining the crystalline form of rubber was to cool the calorimeter to about -40°C , allow it to warm up slowly over a period of several days to 0°C , and then to hold it at this latter temperature for several more days. Previous work [3] has indicated that this is sufficient time to obtain complete conversion into the crystalline form. Incomplete conversion would liberate heat in the temperature range from -40 to 0°C , which would easily be noticed from the behavior of the calorimeter during the heat-capacity measurements, as was actually found to be the case on several occasions.

III. CALORIMETER AND ITS OPERATION

The calorimeter used for the measurements of the heat capacities and the heat of transition was of the adiabatic and vacuum type described by Southard and Brickwedde [33], which is an improvement on the type originated by Eucken [8]. The object of the vacuum surrounding the sample container is to minimize the exchange of heat between the container and its surroundings as caused by gaseous conduction and convection. The calorimeter was made adiabatic by surrounding the sample container with a shield which, by means of controlled electrical heating, could be kept the same temperature as the sample, thus minimizing heat leakages to and from the sample. The calorimeter is described in detail by Southard and Brickwedde and only a few general statements need be made here. After the introduction of the sample into its container, the remaining air in the container was replaced by helium at about 1 atmosphere pressure before the container was sealed. Air could not be left inside because it would permit oxidation of the rubber and also because it would liquefy at low temperatures. A vacuum in place of the helium would not be as suitable because the lack of thermal conducting qualities would necessitate too long a time for the sample to reach temperature equilibrium, which was found to be the case in the latter experiments.

Measurements of temperature were made by means of a resistance thermometer of platinum containing 10 percent of rhodium, the resistance of which was about 150 ohms at room temperature. From 14 to 90°K its calibration was made against a helium gas thermometer described by Southard and Milner [34]. Above 90°K it was calibrated against a standard platinum resistance thermometer in a precision cryostat designed and built by Scott and Brickwedde [30]. Resistances were measured by means of a Wenner potentiometer [2, 37], potentials being obtained across the thermometer and also across a 100-ohm standard coil in series with the thermometer when a current of about 1 milliampere was passing through the circuit. This current was supplied by a 2-volt lead storage battery. The precision of the temperature measurements was within 0.002°C above 90°K and within 0.01°C at lower temperatures.

This thermometer was also used as a heater. The current and voltage during the heating were also measured with the same potentiometer, using a 1-ohm standard resistance coil and a volt-box with a ratio of 150:1. Lead storage cells of 120 volts were the source of the heating current. The time of heating was regulated by an automatic switch connected to time signals, which gave a measure of time to

within 0.01 second. The time of heating was varied from 5 to 30 minutes, the heating current from 0.03 to 0.1 ampere, and the temperature from 0.5 to about 15° C. The amount of heat added could be measured to within 1 part in 10,000, which is greater precision than is necessary, since the temperature rise could sometimes be measured only to about 1 part in 1,000. It was not found difficult to control the shields so that the sample would remain constant in temperature within 0.002° C for an hour, even when its temperature was many degrees above that of the surrounding external bath. An actual test of the heat exchange to and from the sample was made with an external bath of liquid hydrogen at about 20° K, the sample and its container at about 90° K, with the shields a little more than a degree higher. Here the temperature of the sample rose 0.15° C per hour. With the shields only 0.4° C higher, the rate of temperature rise was 0.04° C per hour. In actual operation of the calorimeter, the temperature of the shields was kept within 0.01° C of that of the sample, and these deviations were not consistent in either direction but tended to balance each other.

Two operators were necessary for conducting experiments with the calorimeter. One made the measurements on the temperature of and the heat energy added to the sample and container, while the other controlled the temperatures of the shields. The latter was done by regulating the current flowing through the heating wires of the shields. After the sample had shown a constant temperature over a period of several minutes, the electrical switch was thrown for the addition of heat. This necessitated a corresponding increase in the quantity of heat to the shields in order to maintain them at the temperature of the sample. The heat to the shields, of course, was not measured. The heat delivered to the sample was determined from current and voltage readings made at definite time intervals. When the heating interval was complete the automatic switch was again thrown, this time to stop the heating current. When temperature equilibrium was again established, which generally took from 5 to 10 minutes, the temperature was again measured, and then another heating period started. During these heating periods resistances of the current leads from the heater to the shield were measured. The assumption was made that half the heat produced in these leads went to the sample and container and the other half to the shields. Corrections for this additional current were found to be about 3 parts in 10,000 at room temperature and less at lower temperatures.

IV. HEAT CAPACITIES

The curves in figures 1 and 2 give the relation between heat capacity and temperature, the solid line indicating the amorphous form of rubber and the broken line the crystalline form. The curve is shown in sections so that a larger scale may be used. Figure 3 gives the same curves on a smaller scale, the only points of observation shown being those in the transition range, which are not indicated in figures 1 and 2 because of the scale used. Table 1 gives the heat-capacity values at 5° intervals obtained from the curve. All quantities of heat in this paper are expressed in international joules. The factor for conversion into cal₁₅ is 4.1833 [25].

TABLE 1.—Heat capacities of the rubber hydrocarbon

Temperature	Form of the rubber hydrocarbon		Temperature	Form of the rubber hydrocarbon	
	Crystalline	Amorphous		Crystalline	Amorphous
°K	j/g/°C	j/g/°C	°K	j/g/°C	j/g/°C
15	0.073	0.073	175	0.995	1.009
20	.117	.117	180	1.018	1.032
25	.161	.161	185	1.041	1.054
30	.202	.204	190	1.064	1.078
35	.240	.243	195	1.086	1.102
40	.276	.282	200	1.200	1.440
45	.310	.317	205	1.397	1.603
50	.343	.352	210	1.474	1.615
55	.374	.387	215	1.506	1.628
60	.405	.418	220	1.534	1.641
65	.437	.450	225	1.560	1.655
70	.467	.480	230	1.587	1.668
75	.497	.510	235	1.616	1.682
80	.524	.537	240	1.644	1.696
85	.552	.566	245	1.664	1.710
90	.579	.596	250	1.684	1.723
95	.605	.622	255	1.704	1.737
100	.629	.646	260	1.723	1.750
105	.656	.673	265	1.743	1.764
110	.681	.697	270	1.763	1.777
115	.707	.723	275	1.783	1.790
120	.733	.748	280	1.804	1.805
125	.757	.772	• 284	(^o)	(^o)
130	.781	.796	285	-----	1.822
135	.805	.820	290	-----	1.840
140	.829	.844	295	-----	1.865
145	.853	.868	300	-----	1.890
150	.877	.892	305	-----	1.915
155	.901	.916	310	-----	1.940
160	.925	.939	315	-----	1.965
165	.948	.963	320	-----	1.990
170	.972	.986			

• Heat of fusion at 284° K is 16.7 J/g.

With the exception of the range of temperature where the crystals are melting, the heat capacities of the crystalline form of rubber are in general lower than those of the amorphous form. This is to be expected because of less randomness of the positions of the molecules in the crystalline form.

Tables 2 and 3 give the data and results of the calculation of one observation on the heat capacity of the crystalline form of the rubber hydrocarbon. Current reversals were made and the values obtained in the two directions were averaged in order to compensate for any stray currents which may have been present in the system. The mean temperature and the rise in temperature were obtained directly from the data in table 2. In order to obtain the amount of heat added, the values of the current passing through the heater and also the potential across the heater (table 3) were plotted as a function of time, and the values at the half-period of heating (6.5 minutes) were taken as the average. Both the current and the voltage show straight-line relationships with time over short intervals such as this unless the sample is undergoing a transition, in which case there will appear a change of slope of the voltage curve with time.

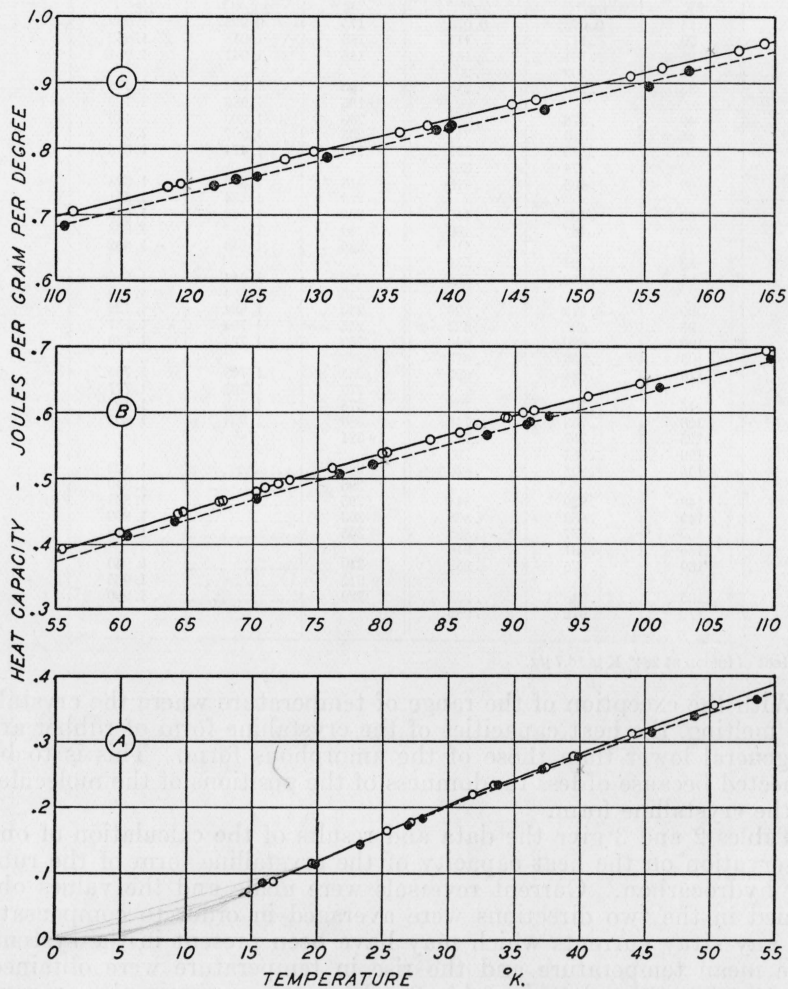


FIGURE 1.—Relation between heat capacity of rubber hydrocarbon and temperature.

The dotted line represents the crystalline form and the solid line the amorphous. (See fig. 2 for other half of curve.)

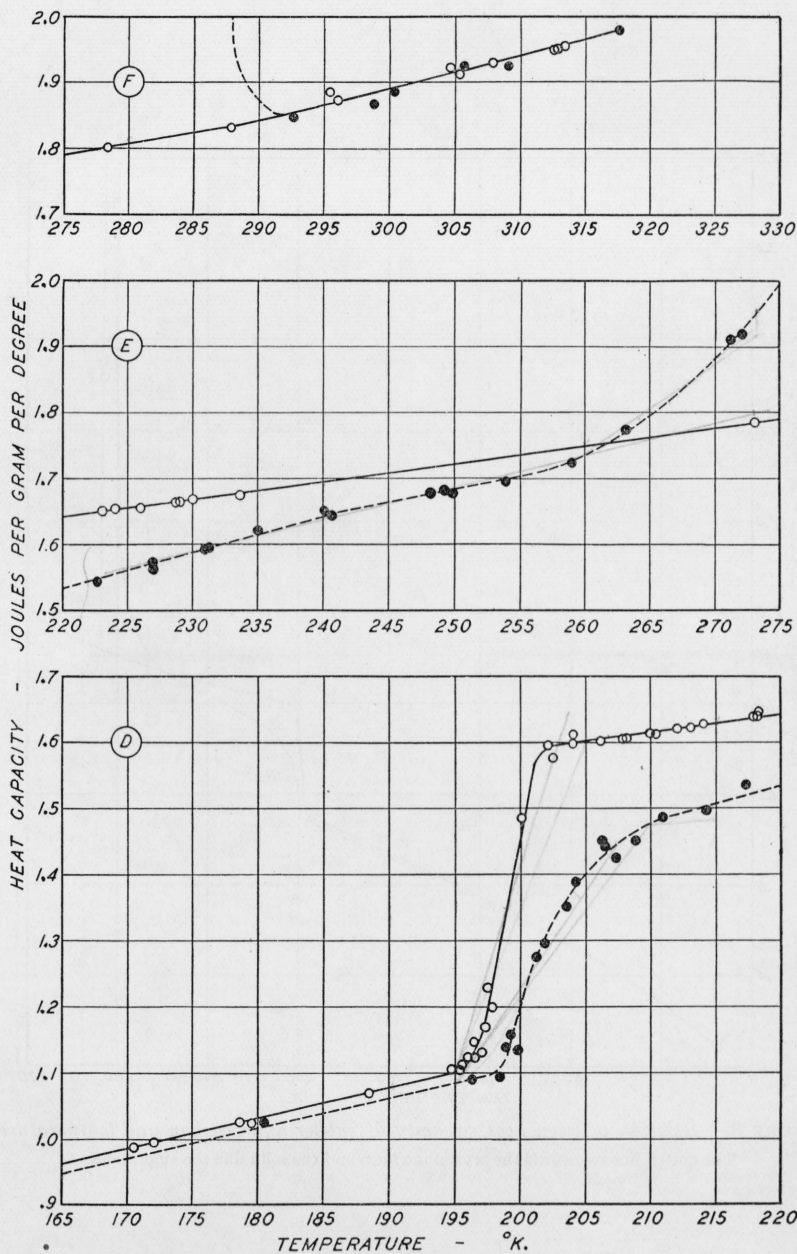


FIGURE 2.—Relation between heat capacity of rubber hydrocarbon and temperature. The dotted line represents the crystalline form and the solid line the amorphous. (See fig. 1 for other half of curve.)

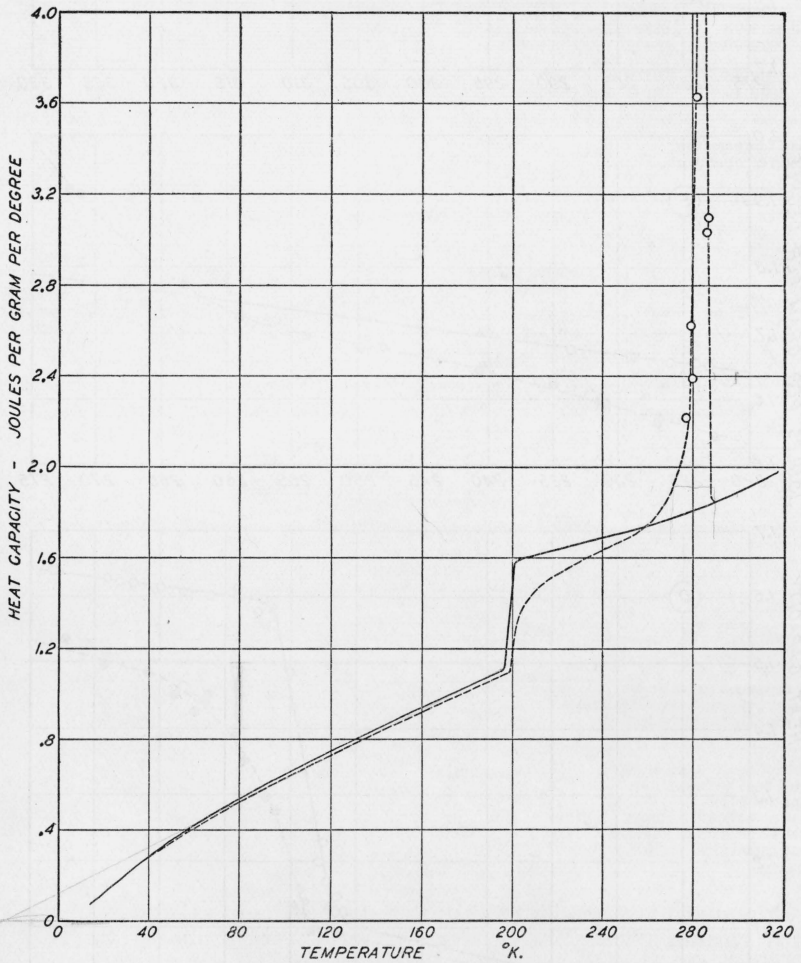


FIGURE 3.—Relation between heat capacity of rubber hydrocarbon and temperature. The dotted line represents the crystalline form and the solid line the amorphous.

TABLE 2.—Measurements of temperature before and after heating

Potential measurements across—		Direction of thermometer current	Current in thermometer	Resistance of thermometer	Temperature of sample	
100-ohm resistance	Thermometer				Before heating	After heating
<i>Volt</i> 0.099 999 5 .099 999 0	<i>Volt</i> 0.088 902 0 .088 901 2	Normal..... Reverse.....	<i>Ampere</i> 0.000 999 995 .000 999 990	<i>Ohms</i> 88.902 4 88.902 0	} 65.662	} -----
.100 014 5 .100 014 5	.091 500 0 .091 497 5	Normal..... Reverse.....	.001 000 145 .001 000 145	91.486 7 91.484 3		
Mean temperature.....					70.281° K	
Rise in temperature.....					9.238° K	

TABLE 3.—Measurement of heat added

Time	Potential measurements across—		Direction of battery current to potentiometer	Current in heater	Potential across heater
	1-ohm resistance	Volt-box			
<i>Minutes</i>	<i>Volt</i>	<i>Volt</i>		<i>Ampere</i>	<i>Volt</i>
0 (begin).....					
1.....	0.058 393		Normal.....	0.058 393	
2.....	.058 393		Reverse.....	.058 393	
3.....		0.034 657	Normal.....		5.198 9
4.....		.034 729	Reverse.....		5.209 7
5.....	.058 374		Normal.....	.058 374	
6.....	.058 374		Reverse.....	.058 374	
7.....		.034 938	Normal.....		5.241 0
8.....		.035 006	Reverse.....		5.251 2
9.....	.058 355		Normal.....	.058 355	
10.....	.058 353		Reverse.....	.058 353	
11.....		.035 217	Normal.....		5.282 9
12.....		.035 283	Reverse.....		5.292 8
13 (end).....					
Mean values (from curve).....				.058 370	5.235 5
Current through the 3,000-ohm volt-box.....				.001 745	
Current through the heater.....				.056 625	
Time of heating, seconds.....					780
Total heat added, joules.....					230.46
Heat added, j/°C.....					24.95
Heat absorbed by empty calorimeter, j/°C.....					6.45
Heat absorbed by 39.38 grams of sample, j/°C.....					18.50
Heat capacity of sample at 70.28° K, j/g°C.....					.4698

Previous investigators have determined the heat capacities of rubber with various results. Gee and Terry [9] were probably the first to measure the specific heat and obtained a mean value of 2.00 j/g/°C on raw rubber between about 20 and 100° C. This compares fairly favorably with the results at the higher temperatures obtained in the present investigation. LeBlanc and Kröger [19] made measurements from -70 to +40° C on various samples of smoked sheet rubber. While not very smooth in most cases, their curves gave an average value of about 2.2 j/g/°C at 25° C, which is considerably higher than the value 1.88 indicated in figure 2. Ruhemann and Simon [29] obtained a value of about 2.1 j/g/°C for smoked sheet at 25° C. Boström [5] reported an average value of 1.55 j/g/°C at 17° C, which is lower than the 1.85 value obtained in the present investigation. Ruhemann and Simon's value for the specific heat at -80° C was

about 1.2 j/g/°C as compared with 1.09 for that temperature as indicated in figure 2. In an earlier investigation on the heat of vulcanization of rubber [21], mean heat-capacity values were obtained between 25 and 175° C. The average mean value obtained for both crude and purified rubber was 2.17 j/g/°C, which seems quite reasonable from the trend of the curve of the present investigation.

The curve obtained by Ruhemann and Simon for the heat capacities of smoked sheet from -100 to about -20° C, which includes a transition of the second order [3, 7], which they called the α anomaly, is similar to the one obtained in the present investigation. At 0° C they obtained a hump in the curve which they called the β anomaly, but this break in the curve could not be found in the present investigation. Figure 3 shows that at 284° K a transition of the first order takes place in which there is melting of rubber crystals. This transition was named the γ anomaly by Ruhemann and Simon, but was found by them to take place at a temperature several degrees higher.

The transition obtained at 199° K in this investigation is probably the same as that shown in some previous work on the thermal expansion and dielectric constant of rubber [3], and there reported to take place at approximately 200° K. The temperature of fusion obtained in the present investigation also agrees with that obtained from data on the coefficient of thermal expansion.

V. HEAT OF FUSION

At above 255° K the curve for the heat capacity of the crystalline form begins to rise, owing to the premelting of some of the crystals. Although the fusion temperature is 284° K, there is a great tendency for the rubber to premelt with respect to the average temperature of the calorimeter. The higher local temperature near the heating coil produces a small amount of melting which does not reverse itself when temperature equilibrium is established below the fusion temperature, because the rate of transition from the crystalline to the amorphous form is much greater than that in the reverse direction [3]. This, however, will have no appreciable effect on the value obtained for the heat of melting.

With the rubber in the crystalline form a heating was begun at a temperature of 253.73° K, continued through the transition, and ended with an equilibrium temperature of 291.90° K. The heat required to raise the rubber through this temperature range was 102.605 j/g. On the heat capacity-temperature diagram, a smooth curve was drawn from some point on the curve of the crystalline form just below the beginning of the melting of the rubber (about 250° K) to the curve above the temperature of the transition. The energy required to bring the rubber from 253.73 to 291.90° K, assuming no transition, was obtained by measuring the area under this curve between these two temperatures, and was found to be 85.894 j/g. The difference between these two energy values is 16.71 j/g, which is the heat of fusion of the rubber. This value is in agreement with that obtained in a similar manner by Ruhemann and Simon [29] for frozen smoked sheet. Van Rossem and Loticius [35] report a value of 21.1 j/g for latex sheet at 0° C, obtained from the difference between the heats of swelling of frozen and thawed rubber.

VI. ENTROPY

According to the third law of thermodynamics, the entropy of a substance in the liquid state at 298.1° K is given by the equation

$$S^0_{298.1} = \int_0^{T_{mp}} C_p(\text{crystals}) d\ln T + \frac{\Delta H_{\text{fusion}}}{T_{mp}} + \int_{T_{mp}}^{298.1} C_p(\text{liquid}) d\ln T.$$

Curves were prepared plotting the values of the heat capacities at constant pressure, C_p , of the rubber hydrocarbon both in the crystalline and the amorphous forms as functions of the logarithm of the absolute temperature T . Since C_p values were obtained only as low as 14° K, the graphic integration of these curves could not be made below this point. Here the Debye approximation formula [6] was used. From tables [31] of the heat capacities and Debye functions, $\beta\nu$, the latter was found to be constant with a value of 120 from 14 to 35° K. From tables [31] of the Debye functions and entropies with a $\beta\nu$ value of 120, the entropy change of the rubber from 0 to 14° K, $\int_0^{14} C_p d\ln T$, was found to be 0.015 ± 0.001 j/g/°C for both the amorphous and the crystalline forms.

From the graphic integration of the curves the following values were obtained:

$$\int_{14}^{298.1} C_p d\ln T \text{ (amorphous form)} = 1.860 \text{ j/g/°C,}$$

$$\int_{14}^{284} C_p d\ln T \text{ (crystalline form)} = 1.717 \text{ j/g/°C,}$$

$$\int_{284}^{298.1} C_p d\ln T \text{ (amorphous form)} = 0.090 \text{ j/g/°C.}$$

The entropy of fusion of the crystalline form of rubber at 284° K,

$$\frac{\Delta H_{284}(\text{fusion})}{T} = 0.059 \text{ j/g/°C.}$$

Following the curve for the amorphous form, one obtains

$$S_{298.1} - S_0 = \int_0^{14} C_p d\ln T + \int_{14}^{298.1} C_p d\ln T = 1.875 \pm 0.004 \text{ j/g/°C.}$$

From the data on the crystalline form one obtains

$$S_{298.1} - S_0 = \int_0^{14} C_p d\ln T + \int_{14}^{284} C_p d\ln T + \frac{\Delta H_{284}(\text{fusion})}{T} + \int_{284}^{298.1} C_p d\ln T = 1.881 \pm 0.010 \text{ j/g/°C.}$$

The third law of thermodynamics states that a pure substance in the crystalline state has zero entropy at the absolute zero of temperature. Any other form may not have zero entropy, as has been found by several investigators [11, 16, 17, 23, 24, 32]. The entropy of rubber at 298.1° K is obtained from the last equation by setting the entropy

of the crystalline form equal to zero at 0° K. Then for rubber at 298.1° K, $S_{298.1} = 1.881 \pm 0.010$ j/g/°C.³

The above data give for the difference between the entropies for the crystalline and amorphous forms at 0° K the value $(1.881 \pm 0.010) - (1.875 \pm 0.004) = 0.006 \pm 0.011$ j/g/°C. This indicates, within the accuracy of the present experimental data, that S_0 (amorphous) - S_0 (crystalline) is not greater than 0.017 j/g/°C, or 0.28 cal/°C/C₅H₈ unit.

VII. FREE ENERGY OF FORMATION

Various investigators [4, 12, 15, 18, 22, 36] have determined the heat of combustion of rubber, but the results of Jessup and Cummings [15] are probably the most nearly accurate. Their value for steam-purified rubber at 30° C is 45,239 ± 90 int. j/g. Using the values of specific heats of 1.89 j/g/°C for rubber at 27.5° C as determined in this investigation, 8.9 cal/mole/°C for CO₂ [13], 7.0 cal/mole/°C for O₂, and 17.5 cal/mole/°C for H₂O [1], the heat of combustion of the rubber hydrocarbon at 298.1° K is calculated to be 45,250 ± 90 int. j/g.

Using the heats of formation at 298.1° K of gaseous CO₂ taken as -94.24 ± 0.10 kcal/mole [28, 27] and of liquid H₂O -68.313 ± 0.010 kcal/mole [26], the heat of formation of the rubber from its elements, $\Delta H_{298.1}$ is -507 ± 100 j/g. Likewise, from the entropies of carbon (graphite) taken as 1.36 ± 0.03 cal/mole/°C [14] and H₂ 31.23 ± 0.00 cal/mole/°C [10], the entropy of formation of the rubber hydrocarbon at 298.1° K, $\Delta S_{298.1}$, is -6.215 ± 0.014 j/g/°C. Then, from the thermodynamic formula $\Delta F = \Delta H - T\Delta S$, the thermodynamic potential or free energy of formation of the rubber hydrocarbon at 298.1° K, $\Delta F_{298.1} = (-507 \pm 100) - (298.1)(-6.215 \pm 0.014) = 1,345 \pm 100$ j/g, or 1.35 ± 0.10 kJ/g, or 21.9 ± 1.6 kcal/C₅H₈ unit.

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³ It is of interest to note here that from a calculation of the entropy of the rubber hydrocarbon at 298.1° K from a table on page 210 of Parks and Huffman's "The Free Energy of Some Organic Compounds" (Chemical Catalog Co., Inc., New York, N. Y.), a value of 1.92 j/g/°C is obtained. This assumes a long chain rubber molecule having 1 CH₃ branch chain and 1 double bond per C₅H₈ unit.

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