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SPECIFIC HEAT OF THE SYNTHETIC RUBBER HYCAR O.R. FROM 15° TO 340° K

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ABSTRACT

Measurements of specific heat were made on a sample of Hycar O.R. synthetic rubber from 15° to 340° K by means of an adiabatic vacuum-type calorimeter. The experimental values of the specific heat between 15° and 22° K were well represented by the Debye specific-heat equation, using a $\beta\nu$ value of 80, and accordingly the values below 15° K were calculated with this equation. At about 250° K the material has a transition of the second order, the specific heat increasing by about 40 percent to a value of 1.84 Int. joules·gram⁻¹·degree⁻¹ just above the transition. From 250° to 340° K the specific heat-temperature curve is nearly linear, and the values can be calculated to within 0.2 percent from the formula $C_p = 0.00283T + 1.126$, in Int. joules·gram⁻¹·degree⁻¹. At 298.16° K (25°C) the specific heat is 1.971 Int. joules·gram⁻¹·degree⁻¹ (0.4712 calories·gram⁻¹·degree⁻¹). The increase in entropy resulting from heating from 0° to 298.16° K was calculated to be 1.743 ± 0.002 Int. joules·gram⁻¹·degree⁻¹ (0.4167 ± 0.0005 calories·gram⁻¹·degree⁻¹).

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I. INTRODUCTION

The determination of the specific heat of Hycar O.R. (oil-resistant) synthetic rubber is a continuation of a program started some years ago at the National Bureau of Standards, the object of which is to furnish thermodynamic data on various types of rubber, both natural and synthetic, and the monomers from which they are polymerized. Such data have been obtained for unvulcanized natural rubber [4]¹ and its monomer, isoprene [5], and the equilibrium relationship between the two has been studied [2]. In the present paper, specific heat measurements on synthetic rubber Hycar O.R. are described, and the increase in entropy from absolute zero to 25° C is calculated.

It has been found very useful in previous work to correlate thermal measurements with volume measurements. Anomalies in the enthalpy-

¹ Figures in brackets indicate the literature references at the end of this paper.

temperature relation or its derivative are found to be associated with similar changes in the volume-temperature relation or its derivative. Measurements of the volume-temperature relation by means of a dilatometer, therefore, furnish a relatively simple method of determining the location of transitions and a guide for thermal measurements.

Volumetric work on several samples of synthetic rubber has shown that they, as well as natural rubber, may undergo transitions [16]. Two types of transition are found. In first-order transitions, the fundamental properties, such as enthalpy, undergo large changes in a rather narrow temperature interval. Crystallization and fusion are first-order transitions. In second-order transitions, the derivatives of the fundamental properties, rather than the properties themselves, undergo the large changes. The changes therefore manifest themselves in the expansivity and in the specific heat, which are the derivatives of the fundamental quantities, volume and enthalpy.

Natural rubber has been shown, both by thermal measurements [4] and dilatometric measurements [3, 17] to exhibit both a first-order and a second-order transition. Many of the synthetic rubbers, however, unlike natural rubber, show no evidence of crystallization or fusion. Since the crystallization of a rubber-like substance may make the thermal investigation very complicated and time-consuming [6], it was thought advisable to make thermal measurements first on a synthetic rubber which does not crystallize. Volume measurements [16] with a mercury-filled dilatometer have failed to show any evidence of crystallization or fusion in Hycar O.R., and it was selected for the first thermal studies. The volume measurements showed a second-order transition at 250° K.

II. SAMPLE

Hycar O.R., for samples of which we are indebted to the Hycar Chemical Co. of Akron, Ohio, is an oil-resistant synthetic rubber which has been on the market since early in 1941. Its chemical composition has not yet been disclosed by the manufacturer, but it is reported to be a butadiene co-polymer, and to contain about 2 percent of phenyl-beta-naphthylamine as a stabilizer [1]. Some of the physical properties of the compounded Hycar are given by Garvey, Juve, and Sausser [8].

The density of a sample of unvulcanized Hycar O.R. was found to be 0.999 gram per cubic centimeter at 25° C. An analysis of the material showed that it contained the following:

Carbon.....	%
Hydrogen.....	80.1
Nitrogen.....	9.3
Ash.....	10.2
	0.1
Total.....	99.7

Since practically the whole weight of the material, within experimental error, was accounted for in this manner, analytical determinations for other elements were not made. The carbon and the hydrogen were

determined by the usual combustion technique and the nitrogen by the Kjeldahl method.

Both the high nitrogen content and the oil-resistant properties of the polymer would lead to the conclusion that the co-monomer used with the butadiene might be acrylonitrile. Since information is lacking as to the possible presence of other ingredients, and in view of the known ease of hydrolysis of nitriles, conclusions drawn from these figures as to the exact ratio of butadiene to acrylonitrile may be misleading.

The sample used for the specific-heat measurements was cut into small pieces averaging about 5 to 10 cubic millimeters in volume. These small pieces were placed in the sample container of the calorimeter and kept under vacuum for several days to remove moisture and air. The container was then filled with helium at atmospheric pressure and 25° C and sealed with solder. The weight of the dried sample was 30.030 grams.

III. SPECIFIC HEAT

The calorimeter used for the measurements of specific heat was of the adiabatic vacuum-type described by Southard and Brickwedde [15]. It was similar to the apparatus previously used to determine the specific heat of rubber [4] and of isoprene [5], with some alterations intended to increase the convenience and facility of the measurements.

The results of all the measurements of specific heat are given, in chronological order, in table 1. The temperatures given in the table are the mean between the beginning and end temperatures for each heating. The values of C_p were obtained from the equation given by Osborne, Stimson, Sligh, and Cragoe [11]:

$$[C_p]_{T_m} = \frac{\Delta Q}{\Delta T} - \left[\frac{\partial^2 C_p}{\partial T^2} \right]_{T_m} \frac{(\Delta T)^2}{24},$$

where ΔQ is the heat added per gram of sample, ΔT is the temperature rise, and T_m is the mean temperature of the heating. However, the second term of the right-hand member of this equation was not significant except at temperatures between 238° and 251° K, in which region the second derivative of the specific heat with respect to temperature was large. At its maximum the last term in the equation amounted to about 2 percent of the total. The temperature rise during a heating period was usually from 5 to 10 degrees, although this interval was considerably increased in a few instances where the specific heat-temperature curve was nearly linear, so that a larger temperature interval could be used without causing appreciable error. The rates of heating were varied from about 0.5° to 1.0° per minute. No consistent differences were observed between the data obtained from long heating intervals and those from short intervals, nor between the data obtained from rapid heating and those from slow heating.

TABLE 1.—*Specific heat values (observed)*

Run No.	T_m	C_p	Run No.	T_m	C_p
	$^{\circ}K$	$jl/g.^{\circ}C^a$		$^{\circ}K$	$jl/g.^{\circ}C^a$
I	89.80	0.5545	VI	213.79	1.1221
	96.00	.5965		223.42	1.1688
	101.99	.6250		230.76	1.2068
	107.84	.6527		235.84	1.2388
	113.58	.6782		240.88	1.2708
	119.21	.7070		245.80	1.3517
	129.13	.7505		250.19	1.6996
II	92.95	.5817	254.47	1.8482	
	104.84	.6382	258.52	1.8583	
	116.16	.6929	VII	15.18	0.0728
	127.06	.7437		19.51	0.1046
	137.65	.7914		23.72	.1383
	148.01	.8353		28.65	.1777
	158.19	.8806		33.35	.2193
	168.21	.9257		39.78	.2661
	178.08	.9683		47.68	.3215
	187.82	1.0113		55.08	.3695
197.45	1.0527	61.98		.4094	
206.98	1.0969	65.62		.4321	
216.39	1.1400	68.88	.4543		
III	201.45	1.0670	76.51	.4942	
	210.92	1.1117	84.26	.5364	
	220.27	1.1553	91.57	.5746	
	229.49	1.2024	98.59	.6065	
	238.58	1.2565	VIII	18.55	.0982
	247.26	1.4161		25.36	.1522
	255.08	1.8471		32.03	.2074
262.37	1.8698	38.57		.2588	
269.67	1.8903	42.66		.2865	
260.65	1.8621	45.76		.3075	
268.65	1.8841	55.11		.3690	
276.64	1.9126	65.05	.4305		
IV	283.35	1.9304	74.43	.4810	
	290.06	1.9478	84.46	.5368	
	296.78	1.9675	95.13	.5907	
	303.51	1.9861	IX	283.02	1.9262
	V	207.24		1.0932	303.28
228.42		1.1967		312.46	2.0042
237.71		1.2495		322.53	2.0406
X				333.52	2.0669
			310.85	2.0009	

^a Int. joules·gram⁻¹·degree⁻¹.

The specific-heat data given in table 1 are plotted in figure 1. The broken line at the lowest temperatures is calculated from the Debye equation [10, 14] for specific heats, with a value of 80 for the parameter $\beta\mu$. This value was selected because it was found to give the best agreement with the three lowest experimental points.

The data from table 1 were also used to prepare a large graph in which C_p/T values were plotted as a function of the temperature. Since in the temperature range 18° to 340° K the values of C_p/T lie between 0.0052 and 0.0073 Int. joule·gram⁻¹·degree⁻², it was not difficult to plot the values on a scale sufficiently large to do justice to the accuracy of the data. From the best smooth curve drawn through the plotted values of C_p/T , values of C_p were obtained at integral temperatures and are presented in table 2.

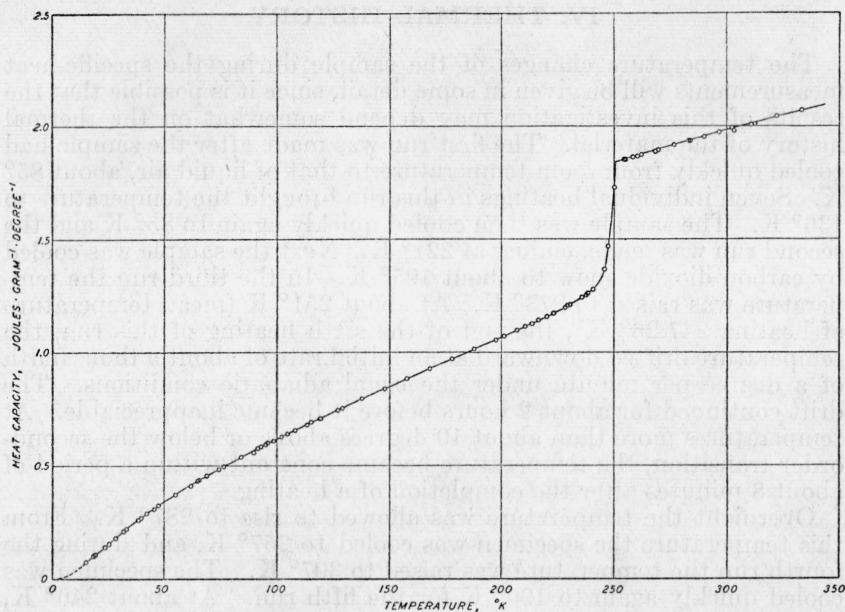


FIGURE 1.—Relation between the heat capacity of Hycar O.R. and temperature.

The dotted part of the curve is calculated from the Debye equation.

TABLE 2.—Specific heat values (from graph)

T	C_p	T	C_p	T	C_p
$^{\circ}K$	$j/g \cdot ^{\circ}C^a$	$^{\circ}K$	$j/g \cdot ^{\circ}C^a$	$^{\circ}K$	$j/g \cdot ^{\circ}C^a$
0	b 0.000	125	0.733	246	1.358
5	b .004	130	.756	247	1.402
10	b .030	135	.778	248	1.466
15	.071	140	.800	249	1.562
20	.108	145	.823	250	1.678
25	.149	150	.845	251	1.838
30	.191	155	.867	255	1.849
35	.232	160	.890	260	1.863
40	.268	165	.912	265	1.878
45	.303	170	.934	270	1.892
50	.336	175	.955	275	1.905
55	.369	180	.977	280	1.919
60	.400	185	.998	285	1.933
65	.429	190	1.020	290	1.946
70	.458	195	1.041	295	1.960
75	.486	200	1.063	298.16	1.969
80	.514	205	1.085	300	1.973
85	.540	210	1.107	305	1.986
90	.566	215	1.130	310	2.000
95	.591	220	1.154	315	2.013
100	.615	225	1.179	320	2.028
105	.639	230	1.205	325	2.042
110	.663	235	1.233	330	2.055
115	.687	240	1.265	335	2.071
120	.710	245	1.329	340	2.087

^a Int. joules · gram⁻¹ · degree⁻¹.

^b Calculated from the Debye equation.

IV. THERMAL HISTORY

The temperature changes of the sample during the specific-heat measurements will be given in some detail, since it is possible that the results of this investigation may depend somewhat on the thermal history of the material. The first run was made after the sample had cooled quickly from room temperature to that of liquid air, about 85° K. Seven individual heatings in this run brought the temperature to 136° K. The sample was then cooled quickly again to 85° K and the second run was made, ending at 221° K. Next the sample was cooled by carbon dioxide snow to about 195° K. In the third run the temperature was raised to 273° K. At about 251° K (mean temperature of heating 247.26° K), the end of the sixth heating of this run, the temperature drifted downward at an initial rate of about a thousandth of a degree per minute under the usual adiabatic conditions. The drift continued for about 2 hours before it became inappreciable. At temperatures more than about 10 degrees above or below the second-order transition, the temperature became constant within a period of about 8 minutes after the completion of a heating.

Overnight the temperature was allowed to rise to 287° K. From this temperature the specimen was cooled to 257° K, and during the fourth run the temperature was raised to 307° K. The specimen was cooled quickly again to 196° K for the fifth run. At about 246° K, the temperature at the end of the fourth heating of the run, a downward drift of temperature again took place. Before the temperature became constant, more heat was added until the temperature was 250° K.

The temperature was then allowed to decrease slowly by discontinuing the heating of the thermal shields around the sample container. The temperature fall was at the average rate of about 2.4° per hour. At 209° K the sixth run was started. Downward drifts of temperature were again observed at the ends of the fifth, sixth, and seventh heatings of this run, although only the normal time was required for equilibrium in all the other heatings. The approximate times required for a constant temperature to be reached after each of the three heatings just mentioned were 0.5 hour at 243° K, 1.5 hours at 248° K, and 1 hour at 252° K. From 260° K where the run ended, the temperature was reduced slowly, reaching about 241° K in 16 hours. When subjected to adiabatic conditions after this treatment, the sample was found to drift upward slowly in temperature. The initial upward drift was about the same as the previous downward drifts, about a thousandth of a degree per minute. After about 2 hours no further change in temperature could be observed. The specimen was next heated to 254° K, and a downward drift of temperature was again observed.

The specimen was then allowed to come to room temperature and remained at that temperature for several days. The temperature was next quickly lowered to 12.5° K, and the seventh run brought it up to 102° K. An immediate cooling brought the temperature to 21° K in preparation for the eighth run. After this run the specimen was warmed to 217.5° K and a 50-minute heating, to be discussed in more detail later, raised the temperature to 270.2° K. After the sample had remained at room temperature overnight, the ninth run

was made from 299° to 339° K. The tenth run included only one heating, which was from 299° to 323° K.

The 50-minute heating of the specimen from 217.5° to 270.2° K, mentioned in the previous paragraph, required 2.4 percent less heat than that indicated by the curve of figure 1. The third and sixth runs, upon which the section of the curve near the transition is based, differed from each other by only 0.21 percent over the range mentioned. If this 2.4-percent discrepancy is real and not due to experimental error, it is probably connected with the time effect near the transition. The long drift in temperature before equilibrium near the transition should cause no error, since adiabatic conditions were maintained.

V. ENTROPY

The entropy increase of Hycar O.R. from 0° to 20° K was calculated from the Debye equation, using a $\beta\nu$ of 80. The value so obtained was

$$S_{20} - S_0 = 0.056 \text{ Int. joule}\cdot\text{gram}^{-1}\cdot\text{degree}^{-1}.$$

The entropy change from 20° to 298.16° K was obtained from graphical integration of the curve C_p/T against T , and gave

$$S_{298.16} - S_{20} = 1.687 \text{ Int. joules}\cdot\text{gram}^{-1}\cdot\text{degree}^{-1}.$$

This value was also checked within experimental error by the integration of the C_p versus $\log T$ curve. The increase in entropy resulting from heating from the absolute zero of temperature to 25° C is calculated to be

$$S_{298.16} - S_0 = 1.743 \pm 0.002 \text{ Int. joules}\cdot\text{gram}^{-1}\cdot\text{degree}^{-1}.$$

(or 0.4167 ± 0.0005 calorie $\cdot\text{gram}^{-1}\cdot\text{degree}^{-1}$).² This value, with its probable error of 0.002, refers to the particular sample used under the conditions described.

VI. SUMMARY AND DISCUSSION

The specific-heat curve of figure 1 shows a transition of the second order at about 250° K. During this transition the specific heat increases abruptly by about 40 percent without the evolution or absorption of any heat. The transition first makes itself evident at about 225° K, where the specific-heat curve begins to deviate from the almost-linear increase which it has shown for over 100° below this temperature. Above 225° K the specific heat increases at an accelerated rate through the region of the transition. About half the change of specific heat seems to occur between 249° and 251° K. The curve is drawn with a discontinuous slope at 251° K, since the results from several heatings which were begun just above 251° K showed no evidence of the transition, the points determined from them falling exactly on the linear curve.

A similar second-order transition is found in natural rubber at about 200° K, as has already been mentioned. Second-order transitions at widely different temperatures are found in many other substances of high molecular weight, such as styrene polymers [12], isobutene polymers [7], and methyl rubber [13]. Of the materials which have been studied, all which have rubber-like properties have been found to have a second-order transition, and it is only above this transition temperature that such rubber-like properties have been observed. It

² 1 calorie = 4.1833 Int. joules.

seems likely that at temperatures below that of the transition no substance exhibits the extensibility and elasticity associated with natural rubber at normal temperatures.

The occurrence of a second-order transition of this type has been explained as resulting from a very slow approach to the equilibrium state at temperatures below the transition. On this view the location of the transition depends on the rate of temperature change; and at temperatures more than a few degrees below the transition, the times required for equilibrium are beyond the range of accessibility. Consequently at these temperatures one deals with a substance in an unstable state. Jenckel [9] studied the second-order transition in selenium at 30° C by volume measurements. He extended the measurements over the long periods of time which were necessary to reach equilibrium. Thus he was able to measure the rate of approach to equilibrium over a range of about 7° below the temperature at which the second-order transition occurs when the cooling is at the rate of more than a few tenths of a degree per minute. The drifts in temperature under adiabatic conditions, as described under the section on thermal history, may quite likely be explained on the basis of the slow approach to equilibrium. However, this point will not be discussed further, since it was not considered advisable at this time to make a detailed calorimetric study of the phenomenon.

Crystallization, a transition of the first order, is well known in natural rubber. In Hycar O.R., however, no evidence of it was found at any temperature. The failure of the atoms in this case to become part of an ordered crystalline structure is probably connected with the attachment of the nitrile groups to the main chain of the carbon atoms. Perhaps it is because of the size of the nitrile group, or perhaps it is because of the randomness of its position of attachment.

The specific-heat curve from 250° to 340° K is almost linear, so that the values of the specific heat for any temperature in this range may be calculated to within 0.2 percent by means of the formula

$$C_p = 0.00283 T + 1.126,$$

in which C_p is in Int. joules·gram⁻¹·degree⁻¹ and T is the absolute temperature. The value at 298.16° K (25° C) is 1.971 Int. joules·gram⁻¹·degree⁻¹ (0.4712 calorie·gram⁻¹·degree⁻¹). This value is only slightly higher than that for natural rubber hydrocarbon, which is given as 1.880 Int. joules·gram⁻¹·degree⁻¹ [4].

The increase in entropy resulting from heating from the absolute zero of temperature to 298.16° K was found to be 1.743 Int. joules·gram⁻¹·degree⁻¹ for the Hycar, as compared with 1.881 for the natural rubber hydrocarbon.

Since the Hycar O.R. was not in a crystalline state, it cannot be assumed without further evidence that the entropy at the absolute zero of temperature has a value of zero. However, since no significant difference in entropy could be found in the previously mentioned comparison of the amorphous and crystalline states of the natural rubber, it is possible that the same may be the case for the synthetic material.

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