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SPECIFIC HEAT AND INCREASES OF ENTROPY AND ENTHALPY OF THE SYNTHETIC RUBBER GR-S FROM 0° TO 330° K

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ABSTRACT

Specific heat measurements were made over the range 12° to 330° K on a sample of synthetic rubber GR-S (Buna S) by means of an adiabatic vacuum-type calorimeter. A Debye specific heat function was used to calculate values below 15° K. At about −61° C the material undergoes a transition of the second order, the specific heat increasing rapidly by about 40 percent. From −50° to +60° C, the specific heat values can be calculated to within 0.1 percent by the equation $C_p=0.4346+7.029\times10^{-4}\ t+1.156\times10^{-6}\ t^2$ in calories gram^{-1} degree Kelvin^{-1}. At 25° C the specific heat is 1.894 international joules gram^{-1} degree Kelvin^{-1} (0.4528 calorie gram^{-1} degree Kelvin^{-1}). The increase in entropy from 0° to 298.16° K is calculated to be 1.824 international joules gram^{-1} degree Kelvin^{-1} (0.4359 calorie gram^{-1} degree Kelvin^{-1}). Values of specific heat, and increases of entropy, enthalpy, and free energy are tabulated at 5-degree intervals. The experimental data indicate that values below the transition are dependent upon the thermal history of the sample. This phenomenon, as well as the temperature drifts observed, can be explained on the theory that the transition results from an increasingly slow approach to the equilibrium state at temperatures in the transition region and below.

CONTENTS

I. INTRODUCTION

In the present Government program for the production of synthetic rubber, the copolymer of butadiene and styrene is the type being manufactures in the largest quantities. It seemed important therefore to make this material, now known as GR-S (Government rubber-styrene type), the next on a research program started some years ago at the National Bureau of Standards 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 [1],[1] its monomer, isoprene [2], the equilibrium relationship between the two [3], Hycar OR-15 [4], and 1,3-butadiene [5]. In this paper specific heat measurements on a

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

sample of GR–S synthetic rubber are described, and the increases in entropy, enthalpy, and free energy from 0° to 330° K calculated from them, are included in a table at 5-degree intervals.

II. SAMPLE

The sample of GR-S was especially prepared by J. N. Street, Firestone Tire & Rubber Co., in a laboratory polymerization using a minimum quantity of materials other than butadiene and styrene. The monomers were polymerized in emulsion and coagulated from the latex by the addition of alcohol. An analysis [2] of the material showed that it contained the following:

	Percentage by weight	Estimated standard deviation of method
Carbon	88. 954	0. 018
Hydrogen	10. 2607	. 0036
Ash	0. 37	. 03
Soap as sodium oleate	. 42	. 01
Fatty acid as oleic acid	. 92	. 05
Modifier	. 44	. 05
Phenyl-beta-naphthylamine	. 50	--------
Amount soluble in ethanol-toluene azeotrope	5. 6	. 1

Soap was used as the emulsifying agent, some of which converted to fatty acid. The modifier was added to limit cross linking of the polymer chains, and phenyl-beta-naphthylamine was used as a stabilizer to prevent continued stiffening of the rubber. Ethanol-toluene soluble fractions contain polymer of low molecular weight, in addition to the fatty acid and stabilizer.

The weight percent of styrene units in the polymer was calculated to be 25.50 ±1.26 (the uncertainty assigned is twice the standard deviation). This calculation includes a correction for the carbon and hydrogen in the soap, fatty acid, phenyl-beta-naphthylamine, and modifier.

From the time the sample was received until it was put into the calorimeter for measurements, a period of about a month, it was kept at the temperature of dry ice and in an atmosphere of CO_2 to prevent oxidation or other reactions.

The sample was cut into pieces 10 to 40 mm^3 in volume which were packed between the vanes of the sample container and kept under vacuum for several hours to remove moisture and air. The container was then filled with helium at atmospheric pressure and room temperature and sealed with solder. The weight of the dried sample was 44.920 g corrected to vacuum.

III. CALORIMETER

The calorimeter was of the adiabatic vacuum type described by Southard and Brickwedde [6] (and similar to the one used to determine

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[2] Acknowledgment is made to Irving Madorsky and Max Tryon for the analysis of this sample.

the specific heat of natural rubber [1] and of Hycar OR–15 [4]). The apparatus for the measurement of temperature and energy input is described in a paper on butadiene [5].

The sample container used in this particular investigation was made of copper and weighed 80 g, including the platinum resistance thermometer. Eight vertical vanes were included to facilitate heat transfer. The inside surfaces of the container were tinned with Pb-Sn eutectic solder, which was also used for sealing the container.

The heater, of No. 34 constantan wire, fibre glass insulated, was wound on the thermometer case before it was soldered into the reentry tube in the sample container. The heater had a resistance of 50 ohms at room temperature.

IV. DETERMINATION OF SPECIFIC HEAT

The methods of measurement and computation of data were similar to those described in the paper on butadiene [5]. The specific heat, C_p, of the sample was determined by measuring the heat capacity, G_b, of the container plus the sample and then the heat capacity, G_a, of the empty container. The specific heat of the sample is

$$C_p=\frac{G_b-G_a}{M},$$

where M is the mass of sample. A small correction varying from 0.37 percent at 15° to 0.01 percent at 330° K was necessary because of the helium in the filled container.

In order to make a comparison of the different series of observations, a mathematical function was chosen to give close agreement with the data over as wide a temperature range as possible, and deviations of the data from this function were plotted. It was possible when plotting the heat capacity of the empty calorimeter to use the same function (a modified Debye equation) over the entire range from 15° to 330° K. With the heat capacity of the filled calorimeter, however, it was necessary to use several functions over this temperature range. Parabolas have been found to be quite useful particularly at the higher temperatures. The data were usually plotted so that 0.1 percent of G was represented by at least one-half of an inch on the graph except at the lowest temperatures. Although agreement within 0.1 percent of the different runs was considered satisfactory, better results were obtained except below 40°K where the heat capacity is small and in the region just below the transition, as explained later.

Values of the specific heat are given at 5-degree intervals in table 2. The values at 5° and 10° K were calculated from the Debye function, $D(\beta\nu/T)$. The equation used was $C_p=0.03018\ D\ (87.5/T)$, with C_p in joules gram^{-1} degree Kelvin^{-1}. The numerical values were adjusted to obtain good agreement between the equation and the experimental values at 15°, 20°, and 25° K.

It was found that the values of specific heat between −50 °C and +60° C could be represented within 0.1 percent by the equation

$$C_p=0.4346+7.029\times10^{-4}t+1.156\times10^{-6}t^2,$$

in which C_p is in calories gram^{-1} degree centigrade^{-1}, and the temperature, t, is in degrees centigrade.

V. SECOND-ORDER TRANSITION

This sample of GR-S showed no evidence of the crystallization reported for natural rubber [1], but it exhibited a transition of the second order characterized by a sudden rise of about 40 percent in specific heat. In figure 1 the specific heat curve for GR-S is shown with the specific-heat curves of amorphous natural rubber hydrocarbon [1] and the synthetic rubber Hycar OR-15 [4]. The natural rubber hydrocarbon is a polymer of 2-methyl-1,3-butadine (isoprene), GR-S is a copolymer of 1,3-butadiene and styrene, and Hycar OR-15 is a copolymer of 1,3-butadiene and acrylonitrile. The amount of comonomer (styrene or acrylonitrile) is zero in natural rubber, about 25 weight percent in the GR-S used here, and considerably higher (40 percent or more) in Hycar OR-15. It is to be observed that here the higher amounts of comonomer correspond to the higher transition temperatures. Polystyrene has a second-order transition at about 80° C according to Patnode and Scheiber [7].

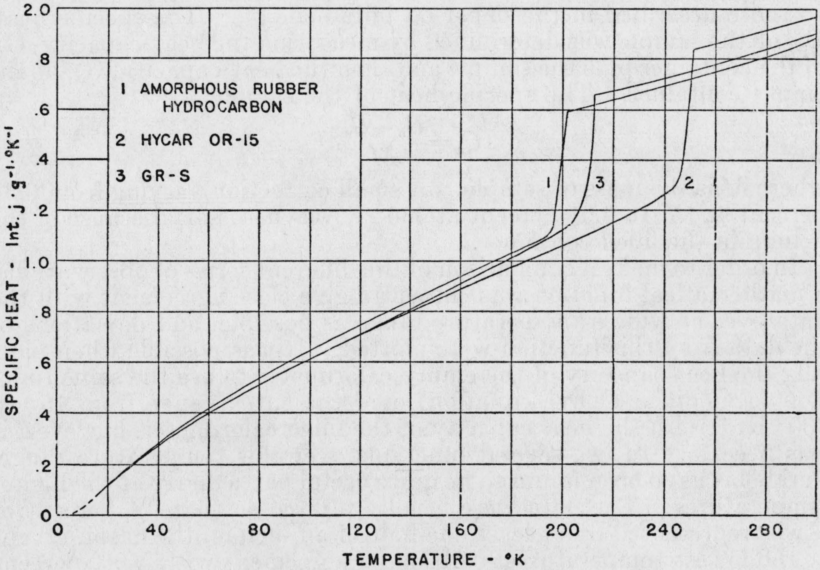

FIGURE 1.—*Specific-heat curves.*

The experimental data for GR-S indicate that the sharply rising section of the specific heat curve in the transition region intersects the line representing specific heats at higher temperatures, as indicated in figure 1. Although the temperature of the intersection of these two curves is spoken of as the transition temperature, the position of the sharply rising curve is rather uncertain because of wide differences (explained below) between the values of specific heat obtained in the several series of observations in this region. The maximum difference under extreme conditions was 14 percent and the transition temperature varied between −64° and −59° C. Some experimental points at the transition were found to lie above the smooth line representing the specific heat at higher temperatures. This no doubt resulted from the fact that temperature equilibrium was not realized in the transition region.

In order to get a clearer idea of what was happening in the transition region, a plot of cumulative energy input versus temperature was made for one of the series of observations through this region. With this curve as reference, the other experimental runs were plotted on the same graph, and at least one of the points above the transition from each run was made to fall on the reference curve by shifting the energy-input axis of each. The observations on the upper side of the transition were lined up because it was assumed that the heat content was always the same at any given temperature above the transition temperature. In this graph the transition appears as a slight change in the slope of the curve. In order to magnify this change in slope, a linear equation in T and the total energy added to raise the temperature of the calorimeter was fitted to the region above the transition, and deviations of the experimental data from this equation were plotted versus T, as shown in figure 2.

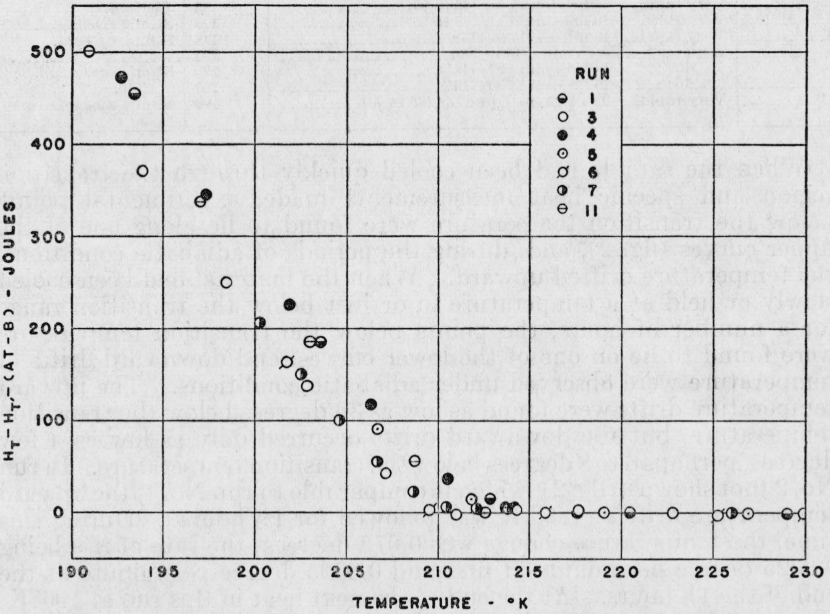

FIGURE 2.—*A sensitive plot of differences between the enthalpies, H, of the filled calorimeter in the transition region for several runs differing in the immediate past history of the sample, i.e. in the length of time the filled calorimeter remained in the transition region.*

Ordinates are differences $H_T - H_{220°} - (103.134T - 22{,}690)$.

This plot indicates that the points below the transition are dependent upon the thermal history of the sample between the time it is cooled below and the time it is heated up to the transition temperature. Table 1 gives a record of the thermal treatment before each run and the direction of temperature drifts between heats in the transition region when adiabatic conditions are realized. A "very rapid" rate of cooling indicates that the material was in the transition region for only several minutes while cooling; a "very slow" rate, that it was in this region for several hours. The starting temperature is the temperature to which the GR-S was heated before heat-capacity measurements were started.

TABLE 1.—*Thermal treatment before runs shown in figure 2*

Run No.	Rate of cooling through transition region	Time held at the given temperature before heating	Starting temperature of specific heat measurements	Temperature drift in transition region
		°*K*	°*K*	
1	Very rapid	16 hr—liquid air (85 to 90)	85	*Upward.*
3	Very slow	40 hr—liquid air (85 to 90)	125	Strong *downward.*
4	Very rapid	10 min—(215 to 175)	178	Strong *upward.*
5	Rapid	8-10 min (215 to 200)	200	
6	do	18 hr—solid CO_2 (195)	200	Strong *downward.*
7	do	16 hr—solid CO_2 (195)	200	Do.
11	Very rapid	3 to 4 days—liquid air (85 to 90)	190	Strong *upward.*

When the sample had been cooled quickly through the transition region and specific heat measurements made, experimental points below the transition temperature were found to lie along one of the upper curves (fig. 2), and, during the periods of adiabatic conditions, the temperature drifted upward. When the material had been cooled slowly or held at a temperature in or just below the transition range for a number of hours, the points below the transition temperature were found to lie on one of the lower curves, and downward drifts of temperature were observed under adiabatic conditions. The upward temperature drifts were found as low as 30 degrees below the transition temperature, but the downward drifts occurred only as low as a few degrees, perhaps 6 to 8 degrees below the transition temperature. In run No. 2 (not shown in fig. 2), which is comparable to run No. 1, the upward temperature drift at 186° K was followed for 1½ hours. During this time, the temperature change was 0.075 degrees; the rate of rise being 0.0025 degree per minute at first and 0.0005 degree per minute at the end of the 1½ hours. At the end of the next heat in this run at 196°K, the rate of temperature rise was about 0.003 degree per minute after 7 minutes. After the following heat the rate of rise at 206° was about 0.008 degree per minute after 7 minutes. In all of the observations shown in figure 2, the temperature was measured 7 minutes after the time the heating current was shut off. This is the time ordinarily required for the calorimeter to come to temperature equilibrium.

The observed drifts in temperature and the observed dependence of the specific heat in the transition region on the previous history of the sample are explainable on the basis of a slow approach to a state or condition of lower energy when the sample is in or below the transition region. (See also the paper on Hycar OR–15 [4].) The equilibrium condition evidently changes with the temperature, and the approach to equilibrium becomes slower the lower the temperature, so that at more than a few degrees below the transition region the time required to reach complete equilibrium becomes inordinately long. From this viewpoint the transition temperature depends on the rate of cooling, and at any temperature below the transition the material is essentially in an unstable state. Jenckel [8] studied the second-order transition of selenium by volume measurements and obtained results which were similar in many ways to observations made.in this investigation. He was able to keep the temperature constant and measure the volume change over the long periods of time necessary to reach equilibrium in the region just below the transition temperature. In a recent paper, Alfrey, Goldfinger, and Mark [10] have studied the second-order transition of polystyrene by volume measurements. They drew many of the same conclusions which had been reached independently in this work from thermal measurements.

From all of these papers it is evident that:

1. The second-order transition temperature depends on the rate of cooling; the faster the cooling, the higher the temperature of transition.
2. If the material is cooled in such a manner that it unedergoes a second-order transition, it is no longer in a stable state.
3. The further the temperature of the material is below thibtransition temperature, the slower is its approach to the equilsi um condition, and at temperatures somewhat below the transsrion temperature, the times required for equilibrium exceed those potiible in ordinary laboratory experiments.

VI. DERIVED VALUES

The increases of entropy $(S-S_0)$ and enthalpy, or heat content, $(H-H_0)$ from 0° to 330° K of this sample of GR–S were calculated by performing tabular integrations of $\int(C_p/T)dT$ and $\int C_p dT$, using Simpson's rule except between 212° and 215°K, where the trapezoidal rule was used. The integrations from 0° to 15° K were calculated from values of specific heat tabulated at 1.25-degree intervals obtained from the Debye equation mentioned previously. The entropy and enthalpy changes from 15° to 200° K and from 215° to 330° K were calculated from values at 5-degree intervals and from 200° to 212° K from values at 1-degree intervals. The results are given at 5-degree intervals in table 2.

The increase in entropy of this sample from the absolute zero of temperature to 25° C is calculated to be

$$S_{298.16}-S_0=1.824 \text{ international joules gram}^{-1} \text{ degree Kelvin}^{-1}$$
$$(\text{or } 0.4359 \text{ calorie gram}^{-1} \text{ degree Kelvin}^{-1}).$$

The increase in free energy $(F-F_0)$ from 0° to 330° K was calculated by the equation

$$F-F_0=(H-H_0)-T(S-S_0),$$

and values at 5-degree intervals are included in table 2.

In accordance with the third law of thermodynamics, the entropy of amorphous GR–S at 0° K is greater than zero. The difference between the entropy of the natural rubber hydrocarbon in its crystalline and amorphous states at 0° K is less than 1 percent of the value of the entropy at 25° C [1]. It is probable that the entropy of random orientation of amorphous GR–S, for each polymerization unit, is of the same order of magnitude as for the natural rubber hydrocarbon. However, the GR–S also has entropy resulting from the randomness of the mixture of butadiene and styrene units, and like natural rubber, randomness of chain lengths.

TABLE 2.—*Specific heat, and increases in entropy, enthalpy, and free energy of GR–S*

[The units of energy and mass are the international joule and the gram, respectively]

T	C_p	$S-S_0$	$H-H_0$	$-(F-F_0)$	T	C_p	$S-S_0$	$H-H_0$	$-(F-F_0)$
$^{\circ}K$	$j\,g^{-1}\,{}^{\circ}K^{-1}$	$j\,g^{-1}\,{}^{\circ}K^{-1}$	$j\,g^{-1}$	$j\,g^{-1}$	$^{\circ}K$	$j\,g^{-1}\,{}^{\circ}K^{-1}$	$j\,g^{-1}\,{}^{\circ}K^{-1}$	$j\,g^{-1}$	$j\,g^{-1}$
0	0	0	0	0	175	.9876	1.0103	91.64	85.16
5	.0036[a]	.0012	.0046	.0015	180	1.0137	1.0385	96.65	90.28
10	.0275[a]	.0095	.0712	.0242	185	1.0394	1.0666	101.78	95.54
15	.0704	.0285	.3124	.1152	190	1.0658	1.0947	107.05	100.94
20	.1127	.0545	.7702	.3195	195	1.0931	1.1227	112.44	106.49
25	.1550	.0842	1.439	.6664	200	1.124	1.1508	117.97	112.19
30	.1958	.1161	2.317	1.166	205	1.182	1.1791	123.71	118.02
35	.2349	.1493	3.395	1.829	210	1.338	1.2092	129.95	124.03
40	.2715	.1830	4.662	2.660	212.3[b]	1.661	1.2248	133.26	126.72
45	.3058	.2170	6.107	3.659	215	1.667	1.2458	137.75	130.05
50	.3380	.2509	7.716	4.829	220	1.678	1.2843	146.11	136.44
55	.3690	.2846	9.477	6.176	225	1.689	1.3221	154.53	142.97
60	.3989	.3180	11.404	7.676	230	1.701	1.3594	163.00	149.66
65	.4277	.3511	13.471	9.350	235	1.713	1.3961	171.54	156.58
70	.4554	.3838	15.679	11.187	240	1.726	1.4323	180.14	163.65
75	.4822	.4161	18.023	13.184	245	1.738	1.4680	188.80	170.86
80	.5091	.4481	20.50	15.348	250	1.752	1.5032	197.52	178.30
85	.5360	.4798	23.11	17.669	255	1.766	1.5381	206.31	185.92
90	.5623	.5112	25.86	20.15	260	1.780	1.5725	215.18	193.65
95	.5879	.5423	28.74	22.78	265	1.794	1.6065	224.11	201.62
100	.6120	.5730	31.74	25.56	270	1.808	1.6402	233.11	209.75
105	.6365	.6035	34.86	28.51	275	1.823	1.6735	242.19	218.01
110	.6612	.6336	38.10	31.60	280	1.838	1.7065	251.35	226.52
115	.6860	.6636	41.47	34.84	285	1.853	1.7391	260.57	235.04
120	.7110	.6933	44.96	38.24	290	1.869	1.7715	269.88	243.84
125	.7363	.7228	48.58	41.77	295	1.884	1.8036	279.26	252.76
130	.7613	.7522	52.32	45.47	298.16	1.894	1.8237	285.24	258.51
135	.7864	.7814	56.19	49.30	300	1.900	1.8354	288.72	261.92
140	.8114	.8105	60.19	53.28	305	1.917	1.8669	298.27	271.10
145	.8364	.8394	64.31	57.40	310	1.933	1.8982	307.89	280.54
150	.8612	.8681	68.55	61.66	315	1.950	1.9293	317.60	290.13
155	.8860	.8968	72.92	66.08	320	1.966	1.9601	327.39	299.83
160	.9109	.9253	77.41	70.64	325	1.983	1.9907	337.26	309.68
165	.9363	.9537	82.03	75.33	330	2.001	2.0211	347.22	319.76
170	.9618	.9820	86.77	80.17					

[a] Calculated from the Debye function.

[b] This temperature was chosen for the transition only for the purpose of calculation.

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