

Physics. — *On the Thermodynamics of Caoutchouc. II. Temperature-change of rubber under adiabatic stretching.* By Prof. Dr. L. S. ORNSTEIN, J. WOUDA and Miss J. G. EYMERS.

(Communicated at the meeting of March 29, 1930).

In our first communication ¹⁾ it has been shown that the heating-effect which takes place in stretched caoutchouc must be due to hysteresis, because from thermodynamic considerations it is obvious that a substance with a positive coefficient of elongation shows a cooling effect. If this is true, rubber without hysteresis must obey the laws of thermodynamics. We have tested this for rubber of the following composition :

First latex sheet	100	parts	}	vulcanised 30 minutes 147° C.
Sulpher	5	"		
D.P.G.	1	"		
Zincoxide	3	"		

which we got from Dr. v. ROSSEM of Rijksrubberdienst, whom we heartely thank for his kindness also on this occasion. It was examined whether this rubber is free from hysteresis by the following method :

A piece of rubber was successively loaded more and more, till the elongation was about 250 %, and than the load was gradually removed. No hysteresis was shown by the substance. When the rubber is submitted to a force which gives a change of length of this amount, the length of the rubber does not alter with the time. When however the elongation is more than 250 %, the length changes slightly with the time, up to an elongation of 370 %, beyond this elongation no alternation in length takes place again. When, in the case of these large extensions, the force is gradually decreased, the elongations come to much larger values than before, when the same force was acted to the rubber from its zero-state. However this is not an effect of hysteresis, for however great the force and however long the time might have been during which the force acted (even more than 24 hours), the rubber always momentarily takes the original length when the weight was removed at once. In fig. 1 the areas from *O* till *E* and from *B* till *C* must be ascribed to different phases, and the difference between the graph for increasing and decreasing force can be explained by a retardation of phase. Moreover, the slope of the curve *AB* can be much steeper as in this case, when a longer time between the application of different forces has been taken. Further the rubber in the region *DE* is not in a stable state,

¹⁾ These Proceedings 32, N^o. 9, p. 1235, 1929.

for a slight impulse affecting the rubber causes the elongation to decrease at once. Since the second phase already shows itself above an elongation of

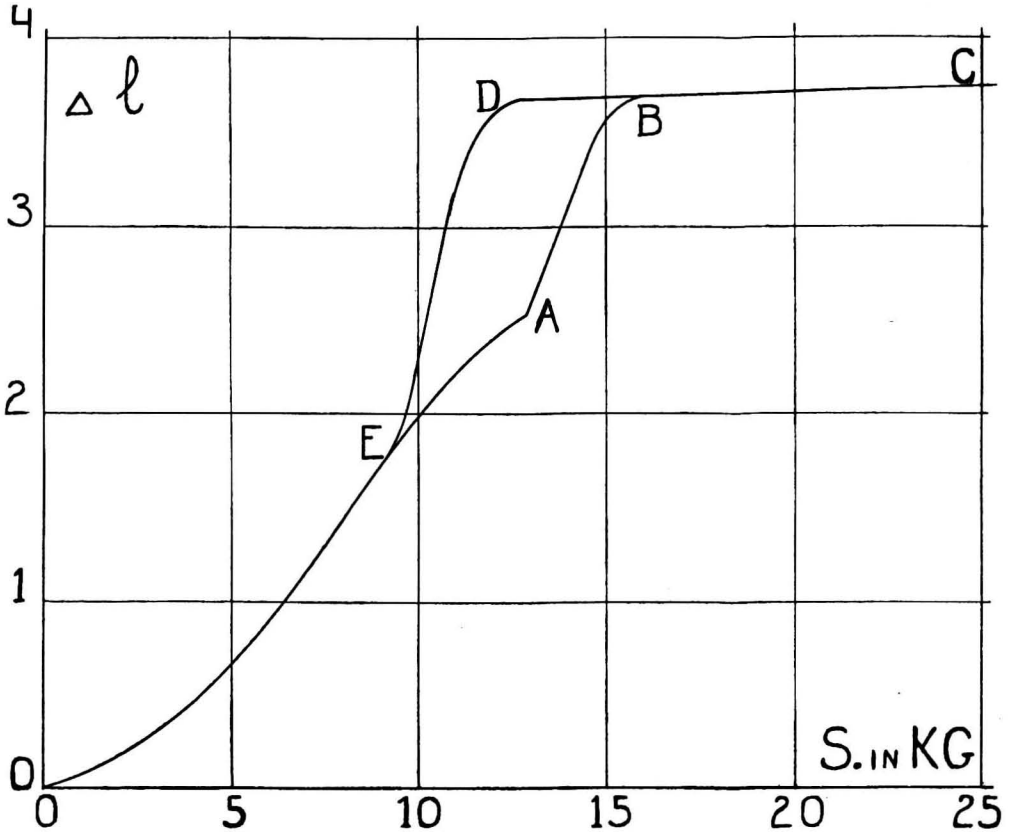


Fig. 1.

200 %, we have taken all our readings for thermodynamic relation below that elongation. It is known that from thermodynamical considerations one can get the formula for the change in temperature :

$$\Delta T = -T \int_0^{\Delta l} \frac{\left(\frac{\partial S}{\partial l}\right)_T \cdot \left(\frac{\partial l}{\partial T}\right)_S}{\left(\frac{\partial \varepsilon}{\partial T}\right)_l} dl,$$

where T is the absolute temperature during the measurement (ΔT is small compared with T), S is the force and ε , the energy and thus $\left(\frac{\partial \varepsilon}{\partial T}\right)_l$ the specific heat by constant length per cm^3 rubber. In order to test this relation the length must be measured as a function of the force at different temperatures. From the curves, giving this (fig. 2), we can deduce $\left(\frac{\partial S}{\partial l}\right)_T$ and

$\left(\frac{\partial l}{\partial T}\right)_S$; besides the dynamical qualities, the specific heat as a function of the elongation has been measured (fig. 3). The $S-l$ curves were determined

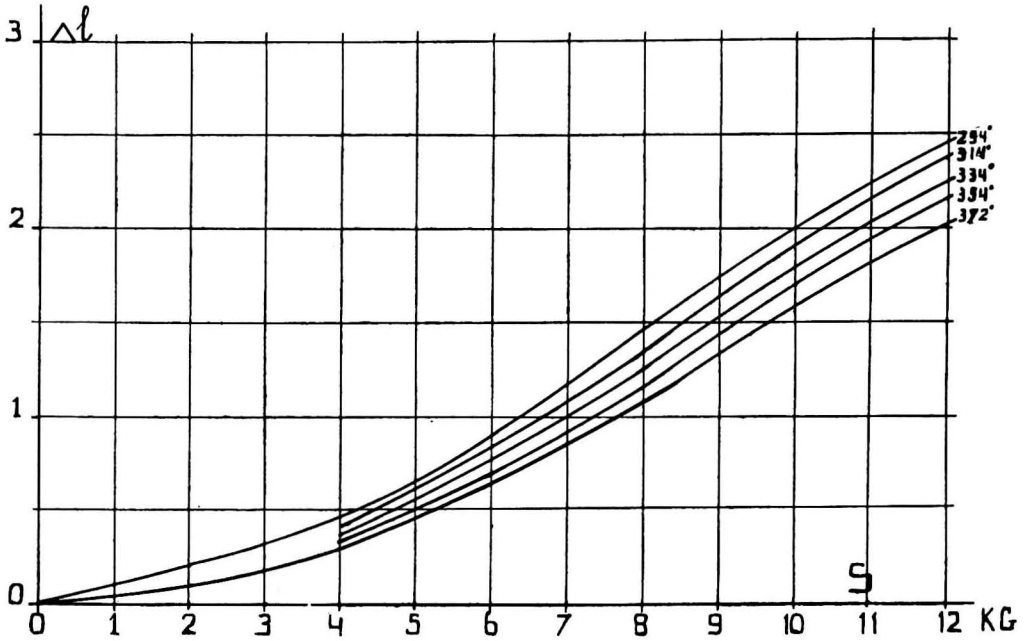


Fig. 2.

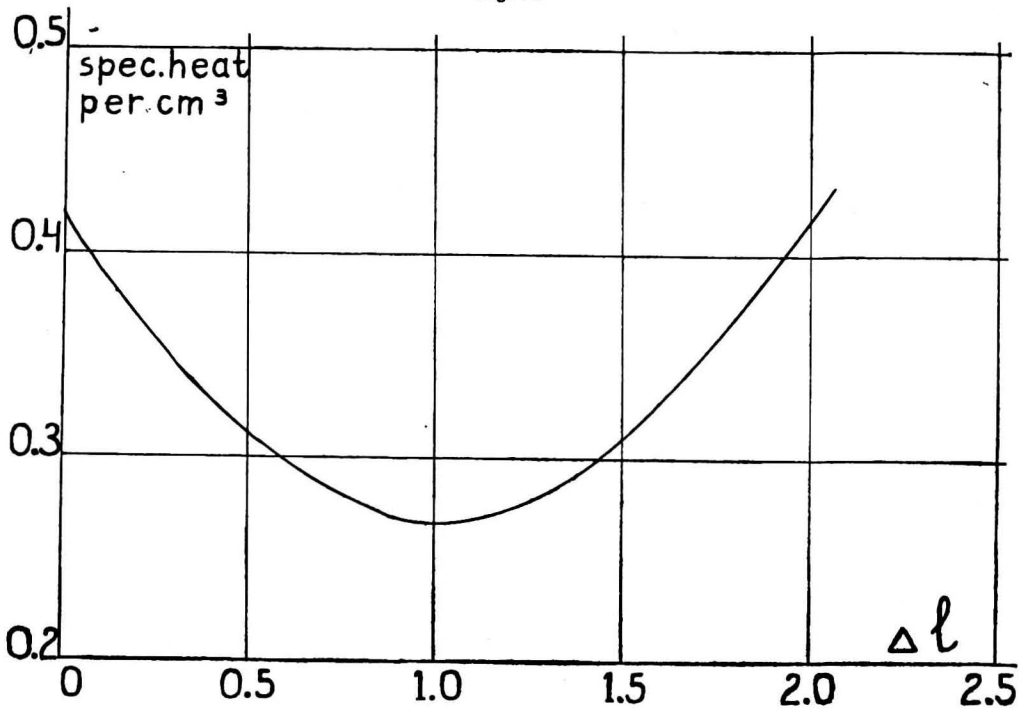


Fig. 3.

in the same way described in our first communication, loading a piece of rubber with different weights and measuring the length with a cathetometer. The rubber is placed in a furnace which could be brought to the desired temperature by electric heating. During a series of measurements the oscillations of temperature were less than 2° . The results are plotted in fig. 2. The temperatures used are 294° , 314° , 334° , 354° and 372° K.

The measurement of the specific heat was somewhat more difficult, as a result of the very bad conduction of heat by the rubber. Finally the following method was adopted: small rings are stamped with a diameter of about 2 cm and a breadth of $1 \text{ à } 1\frac{1}{2}$ mm. This form of the pieces of rubber is chosen for two reasons, first in order to make the surface as great as possible (in this way we get a better conductivity of heat with the same mass of rubber) and further in order to get a simple way for measuring the stretched rubber. The rings could be stretched on plates of brass of different lengths, which were bent in the form of a cylinder, to occupy as small a space as possible. The cylinder of brass with rubber was heated in an electric furnace up to about 80° C (the furnace was kept at this temperature during an hour) and then brought into a calorimeter turning the furnace quickly. The calorimeter is constructed as follows: a vacuum tube of *U*-form is placed in a water-bath of constant temperature. The lower part of the tube is filled with mercury. In the small branch a thermometer is placed in the mercury, which can be read off to a fiftieth part of a degree through the unsilvered portion of the tube, by means of an eyepiece.

Above the mercury in the wider arm are 40 cm^3 of distilled water, into which the warm cylinder of rubber is brought. A wire is fixed to the cylinder, which can be moved up and down by a small motor; the rubber itself thus acting as a stirrer. The chosen form of the calorimeter has the advantage that the volume of liquid is as small as possible in comparison to the mass of the rubber and therefore the rise of temperature in the calorimeter as large as possible. We got in this way maximal a rise of the temperature of two degrees. Before and after the rubber was brought into the calorimeter the change of temperature was observed during about an hour, in order to determine the corrections necessary for the gain or loss of heat to the surroundings. The effective waterequivalent of the calorimeter was determined as a function of the volume of the material, with which it was filled; is appeared to increase with that volume. The change of the specific heat per cm^3 as a function of the elongation is given in fig. 3. Apart from the investigation of the thermodynamical equation the form of the curve for the specific heat is most interesting, as the strong variation of this quantity with the elongation must be of utmost importance for the understanding of the molecular state of rubber. The specific weight of this rubber, necessary to calculate the specific heat per cm^3 , appears to be 0.915. From the results given in fig. 2, we can calculate $\left(\frac{\partial S}{\partial l}\right)_T$ and $\left(\frac{\partial l}{\partial T}\right)_S$ as a function of the extension. These curves obtained are multiplied with each other and divided

by the curve giving the specific heat per cm^3 as a function of the elongation, where all functions are expressed in C. G. S. units. The resulting curve is given in fig. 4.

$$I = - \frac{\left(\frac{\partial S}{\partial l}\right)_T \times \left(\frac{\partial l}{\partial T}\right)_S}{\left(\frac{\partial \varepsilon}{\partial T}\right)_l}$$

The area between this curve and the axis is measured with a planimeter

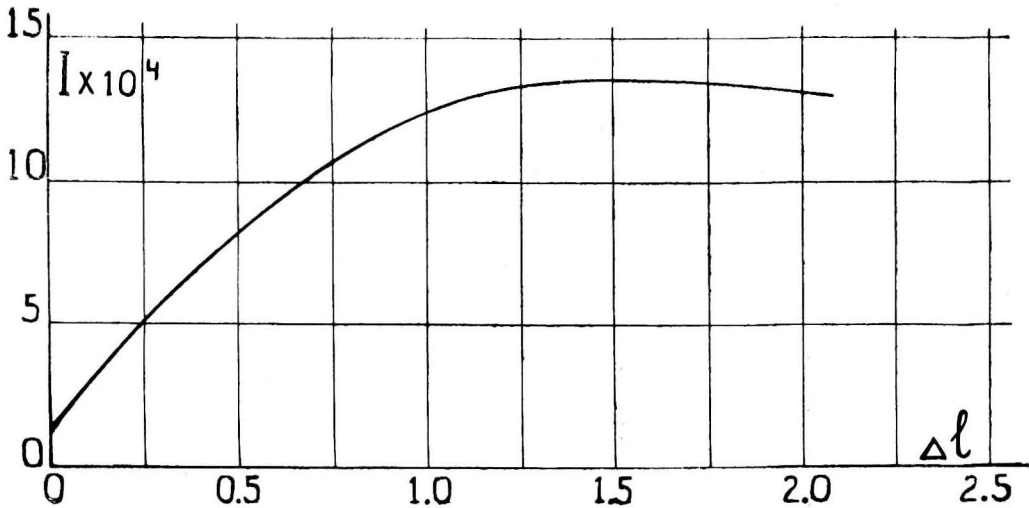


Fig. 4.

for different elongations and multiplied with the absolute temperature at which the generation of heat has been measured (ΔT is positive because $\left(\frac{\partial l}{\partial T}\right)_S$ is negative). In order to test the thermodynamics, the generation of heat itself ought to be measured, which has been done by the method described below.

A thermocouple of copper-constantan is sewed in a piece of rubber in the direction in which the displacement of the material along the thermoelement is as small as possible when the rubber is stretched, in that way the generation of heat caused by friction is reduced to a minimum. The other contact of the thermocouple was plunged in a thermoflask filled with water, the temperature of which was absolutely constant during each measurement. The thermoelectric force was measured with a Moll-galvanometer in the circuit of which was placed an arrangement for measuring, the sensitivity for changes of potential. The rubber was clamped in a box between a fixed and a moveable clamp. To the moveable clamp was fixed a drawing rod, the end of which projected from the side of the box and to which was also fixed a stop, by means of which the rubber could be stretched to a given

length. The elongation was determined with a cathetometer, just as in the case of the measurements for the $S-l$ curves. The time of elongation was small compared with the time the galvanometer took for its deflection. This deflection of the galvanometer was registered during the adiabatic strain and also for a few minutes after. By extrapolation the influence of inertia of the galvanometer and loss of heat to the surroundings could be eliminated. The time necessary for the thermocouple to assume 99 % of the temperature increase of the rubber was calculated to be of the order of $\frac{1}{6}$ sec. i.e. it can be neglected in comparison to the time necessary for the galvanometer to come to its maximum deflection. The maximum error due to losses of energy by the thermocouple itself is, as calculated, 4 %. The values for the increase on temperature got from experiment and from the theoretical formula have been plotted in fig. 5. The observed and calculated points are indicated

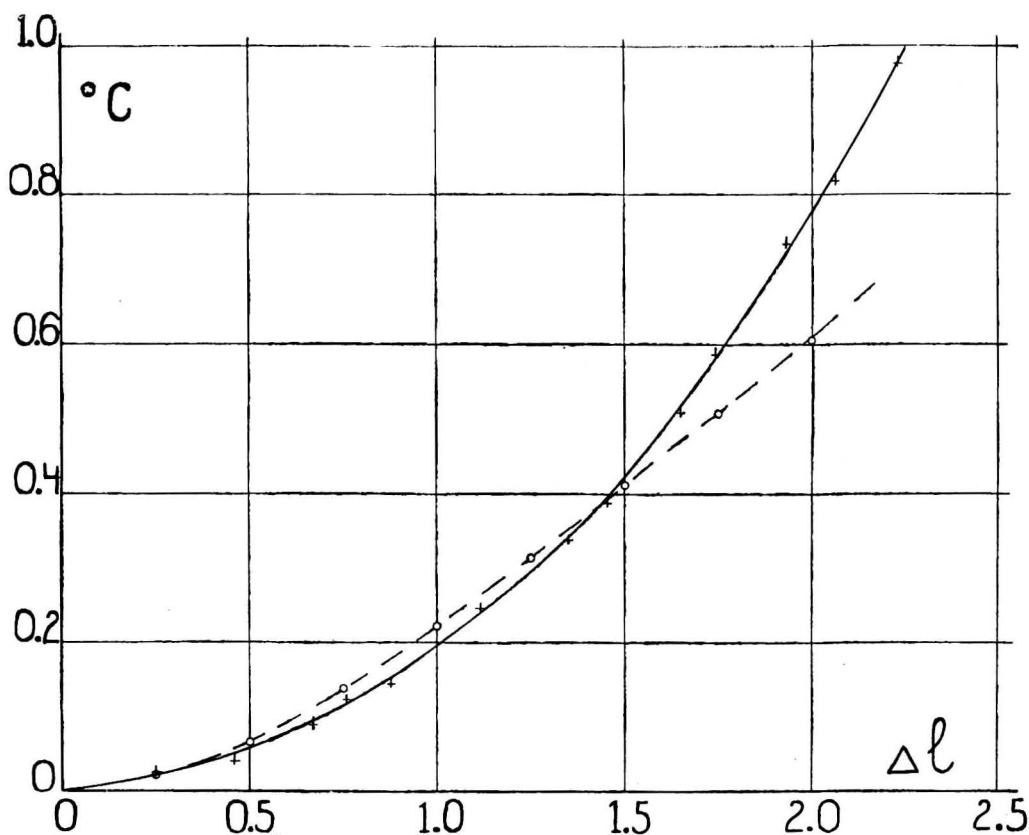


Fig. 5.

by the signs $+$ and o respectively. Up to an elongation of 150 % the agreement is satisfactory. Above this elongation the observed rises in temperature are higher than those calculated from the thermodynamical formula. This difference can easily be explained by the influence of the

second phase, which shows itself appreciable above an elongation of 150 %, as fig. 1 shows.

As was pointed out in our former publication, the generation of heat by stretching raw caoutchouc was measured. It was expected that the generation of heat at the transition point would show an anomaly owing to the heat of transition. For this reason an amplifier-method was used to measure the temperature with a greater accuracy.

The copper-constantan thermocouple was placed between two pieces of raw caoutchouc. New pieces were used for each measurement in order to eliminate the influence of hysteresis as much as possible. The measurement took place as described above for the measurements with vulcanised rubber. The results are plotted in fig. 6. This curve has the same form as the curves

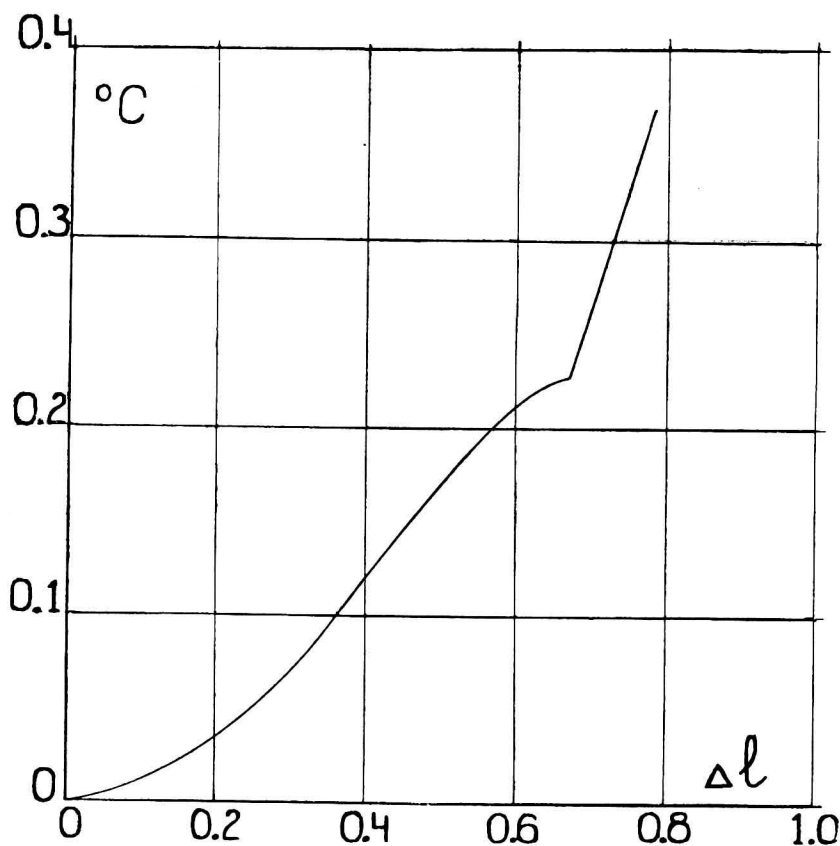


Fig. 6.

for double refraction and elongation as a function of the tension, given in our former paper. Beyond the transition-point, that occurs at an elongation of ca. 70 %, the rise in temperature increases linearly with the length. Further measurements are planned in order to find the relation between hysteresis and heat development.