CALORIMETRIC INVESTIGATIONS OF DEFORMATION PROCESSES

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ABSTRACT

Heat effects by deformation are partly reversible and partly irreversible. The well known example for a reversible thermodynamic effect is the Joule Gough effect on stretched rubber. But these reversible effects exist as general phenomena and there is a thermodynamic relation to the linear thermal elongation coefficient.

By sufficient sensitive calorimetry the calorific effects by deformation can be investigated. There are given examples, one totally reversible, one completely irreversible (pure plastic) and one mixed case. Analysis of measurements furnishes quantitative information on the change of energy, but not on entropy changes for partial plastic deformation. This is due to the first law of thermodynamics, whereas the second law cannot be applied. The state at least at the end of processing is not thermodynamic equilibrium. Occasionally interesting indirect methods can be found to obtain information on the entropy.

Interesting fields are calorimetric investigations on rubberlike substances, because of the transition from the rubberlike behaviour (entropy elasticity) to the slow rubber and glassy state (energy elasticity) and studies of the time dependency and the quantity of crystallization by stretching. The latter becomes possible as a result of the demodulation of the distorted and retarded heat stream records.

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1. INTRODUCTION

Heat effects occurring by deformation are supposed to result from friction. Indeed viscosities in the plastic state are high enough to explain considerable heat-development even with slow rates of deformation. But there is for polymer scientists one well known case which shows that at least one other reason for heat effects during deformation processes exists: the Joule Gough Effect on rubber[1]. Sudden stretching of a rubber sample leads to heating, while unloading of a stretched sample leads to considerable cooling. When deformation is performed isothermally then heat must be deducted or added for loading or unloading of a rubber sample. These well known thermo-mechanical effects on rubber have nothing to do with friction. They are totally reversible. Also there are certain analogies to the behaviour of gas[2]; thus by elastic deformation the free energy of the material is changed so that changes of inner energy and of entropy take place. This results in changes of temperature, when deformation is performed adiabatically or

in calorific effects, when deformation occurs isothermally But this holds not only for the gaseous state and for rubberlike material, but also for every material in the solid state Metals, crystals, organic and inorganic glasses show these reversible thermomechanical effects[3].

These effects are related to thermal elongation by a thermodynamics equation Stretching of material of positive thermal elongation coefficient results in cooling[4] The warming up of rubber, therefore, is a consequence of the negative thermal elongation of stretched rubber samples[5]

Thus, we see there exist two kinds of calorific effects by deformation: 1) the irreversible effects by friction, 2) the reversible thermomechanical effect by change of entropy during elastic deformation In most cases, both can be observed

2. QUESTION OF EXPERIMENTAL PROCESSING

The question arises as to whether direct calorimetric investigation of deformation processes brings more information than mere mechanical measurements

This problem is primarily a question of technical equipment Heat effects to be expected should be of the order of the mechanical work done on a sample 1 m kp corresponds to 2·34 cal For reasons of operating stretching procedures the sample investigated should be relatively small Thus for example a sample may be stretched one cm by a force of one kp This equals 0·0234 cal In most cases, the heats to be measured will be even smaller, i e any calorimeter used for these investigations concerning heat by deformation must be very sensitive

During the period between 1955 to 1958 a very sensitive calorimeter was constructed at my institute which allows simultaneous recordings to be made of the mechanical work and the corresponding heat effects for any stress-strain process of any sample[6] This simultaneous measurement of work and heat I have called the *complete balance of energy by a deformation*[7] Such a complete balance of energy of any deformation process must yield more information than measurements of only mechanical work by deformation processing, even if the latter is performed at various temperatures However, maximum information would be attained if the heat could be separated into two parts: a reversible and an irreversible part We have discussed this possibility in detail But any decisive coordination of the heat towards entropy changes and friction is only possible in special cases (see later)[8]

3. SOME APPARATUS DETAILS

The above mentioned calorimeter works by means of electronic controls Without doubt, such an instrument may be constructed more efficiently today. But even today there are limitations to the precision of such an instrument One reason may be the sensitivity of the differential-manometer and another the noise level of the electronics A third and very important one may be the constancy of thermostatisation of the calorimeter cylinders

attained (higher than 10^{-5} °C and this in spite of an easy exchange of sample and rethermostatisation within a tolerable time interval).

We now can measure heats down to 0.001 cal with an accuracy of 5 per cent with a thermostatisation period of change of sample of only about 6 hours Also, we can operate the calorimeter in a temperature range between about 0° and 50°C The latter was not easy to achieve. In any case the instrument as well as the room must be thermostatically controlled.

A few points regarding the principle of this calorimeter[9] need explaining in detail for specific reasons which will be seen later (*Figure 1*): The ribbon
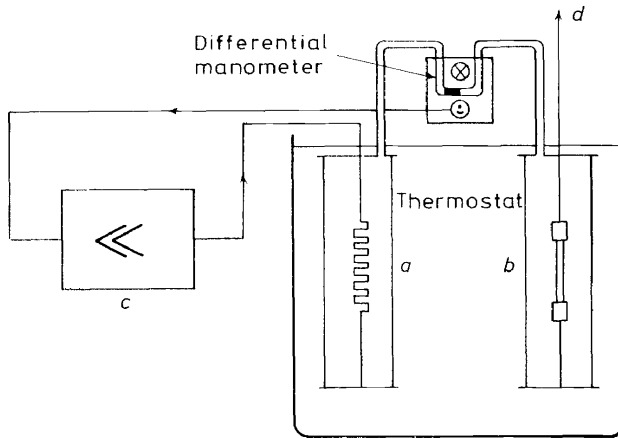

Figure 1. Principle of the calorimeter. (*a*) phantom cylinder. (*b*) measuring cylinder. (*e*) amplifier. (*d*) stretching device.

or threadlike sample is strained in the middle of a cylinder by means of a wire through a hollow in the cap The cylinder is made air-tight by a drop of mercury When the sample changes the temperature due to strain, a logarithmic gradient of temperature between the sample and the wall of the cylinder is built up As long as a heatstream $\dot{Q}$ is flowing, the mean temperature of the gas in the cylinder is changed. There is a second cylinder (phantom cylinder) connected with the first one by a differential manometer The change of pressure coupled with the heat flow operates the differential manometer which, by electronics, heats a wire in the phantom cylinder, corresponding exactly to the heat effect in the cylinder containing the sample.

Mechanical work, performed on the sample and heat emanating from or absorbed by the sample. is thus recorded From this recording of force F and $\dot{Q}$ as function of time, work and heat can be attained by integration. Recordings are reproducible within narrow limits. Calibrations of both, heat and work, must be so precise, that any conclusion from the difference of work and heat are valid 1 wish to emphasize this point because decisive conclusions follow from the difference of two absolutely and not relatively measured quantities This demands a high claim on the accuracy of the absolute values obtained, easy for mechanical work Fortunately, due to the reversible thermomechani-

cal effects the absolute operating as far as heat values are concerned can be well controlled[10].

The record of force as a function of time (this is with a constant elongation rate identical to a function of stress) shows exactly the input of mechanical work to be used as a function of time for the deformation. But this does not hold for the heat effect. The heat needs time when leaving the sample, and the calorimetric equipment needs time too to record the heat. Therefore, as far as time dependency is concerned the $\dot{Q}$ values are recorded with delay and modifications[9].

It would be very desirable, however, if an appropriate demodulation of $\dot{Q}$-curves could be achieved. But, fortunately, nearly all the interesting conclusions can already be drawn from the integrated values of heat balances for the complete cycle from loading to disloading. However, additional detailed information could be gained if demodulation of time for the heat flow could be effected. In the last section I will refer to this matter.

4. THREE EXAMPLES

(a) Reversible case.

Now I would like to consider three typical examples: one for the reversible effect, another for the pure plastic deformation and a third for the case of partial plastic flow. These examples are recordings by Ad. Engelter[11] with the first type of calorimeter. The galvanometers record corresponding values on the same strip of paper. The force and heat flow are still coordinated in a very comprehensive manner. *Figure 2* is a direct reproduction of such a record. The upper curve gives the heat stream as function of time and the lower curve the force. Today we have two different types of recorders, therefore curves must be redrawn before coordination becomes evident.
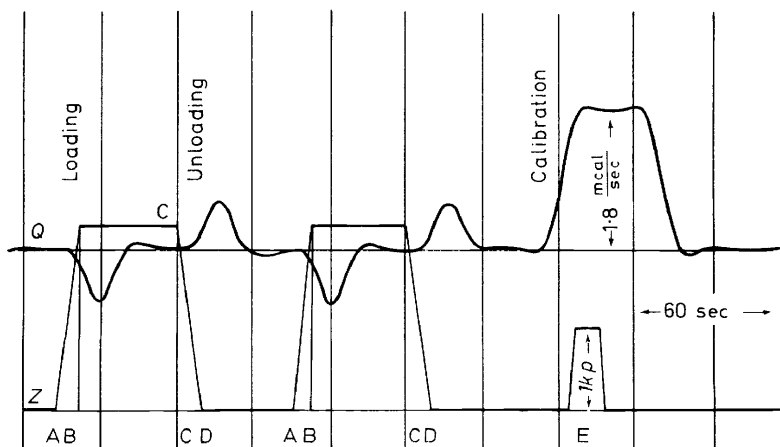

Figure 2. Reproduction of original records of an investigation of steel wire (V 2a). Lower curve: force Z, upper curve: heat stream $\dot{Q}$ both as a function of time (distance between two vertical lines = 30 sec). On the right-hand side: calibrations.

There is still another fundamental difference betwen the two records. The force is presented correctly for every moment. The heat stream $\dot{Q}$ is recorded with a certain retardation, caused by the time constant of the apparatus. Thus conclusions, drawn from the integral against time are true in every case. But details, concerning the time dependency of produced $\dot{Q}$ need a demodulation of the $\dot{Q}$-curve.

Figure 2 gives the reversible thermodynamic effect on steelwire. From the lower curve and the elastic module the mechanical work can be calculated. From the integral over the upper curve there follows the heat input or output from the sample. The heat quantities for loading and unloading must be identical in this case. The repetition of the procedure must show the reproducibility of the process. The peaks at the right refer only to calibrations of the equipment.

The modulation of the heat curves is caused by the retarded record of the heat stream. Thus $\dot{Q}$-curves show final values after stress is already applied or already removed from the sample. We have something that resembles the method of ballistic measurements[12], e.g. a quantity of electric charge e:

$$e = \int_0^\infty i(t)\, dt. \quad \text{corresponding } Q = \int_0^\infty \dot{Q}(t)\, dt.$$

In the reversible case there exists the above mentioned thermodynamic relationship

$$dQ = - T\, \beta l\, dZ \tag{1}$$

dQ = heat, T = abs. temperature, l = length of sample, dZ = change of force and β = thermal elongation coefficient.

By this formula a severe control of the calorimeter is possible (*Figure 3*). In *Figure 4* the records of invar are shown. This allows a second control.
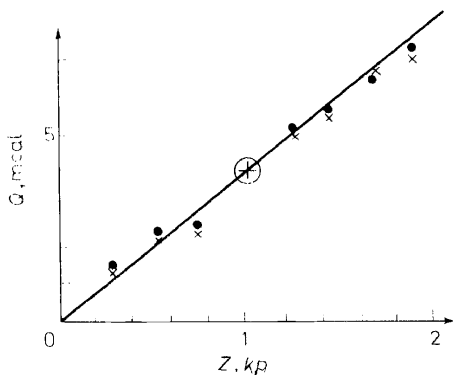

Figure 3. ● × = Measured heat as a function of Z (for Cronifer steel); ⊕ = point according formula [1] calculated from the measured value of linear thermal elongation coefficient β.

The well known material invar has an extremely low thermal elongation. In this case, therefore, only a very slight calorific effect is noticed, corresponding to formula 1.
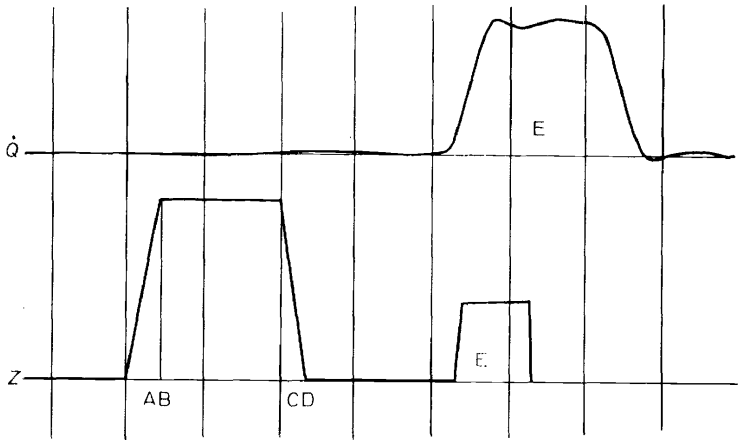
Figure 4. Same records as *Figure 2*, with the exception of material: invar β; ~ 1/20 β of V 2a-steel.

(b) Pure plastic case.

The other extreme is pure plastic deformation, shown in *Figure 5* with a tin-wire. The force rises up to the point B at the end of the stretching procedure. The rise of force is nonlinear in spite of a constant rate of stretching. But this fact does not influence the evaluation.

After the end of deformation at point B for a constant elongation a relaxation of stress takes place. We cannot state for sure whether there is any heat effect coupled with this stress relaxation as a part of the total heat recorded
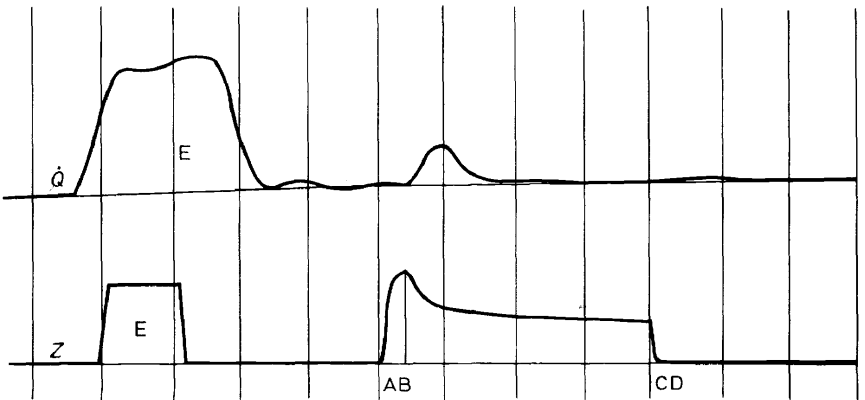

Figure 5 Recorded curves for pure plastic deformation of a tin-wire (on the right side), on the left are the calibrations E.

for the stretching procedure. We see only a very small effect of heat after the unloading of the sample at point C by reversing the stretching equipment. What we can definitely state is that for the total cycle of loading and unloading

heat and work are equal within 3 per cent of the total amounts. And this behaviour is quite different from the pure elastic case.

(c) Plastic–elastic case

The usual behaviour is the plastic-elastic deformation. The calorimeter was originally developed for investigations of this deformation process, especially for the process of cold stretching with necking[13]
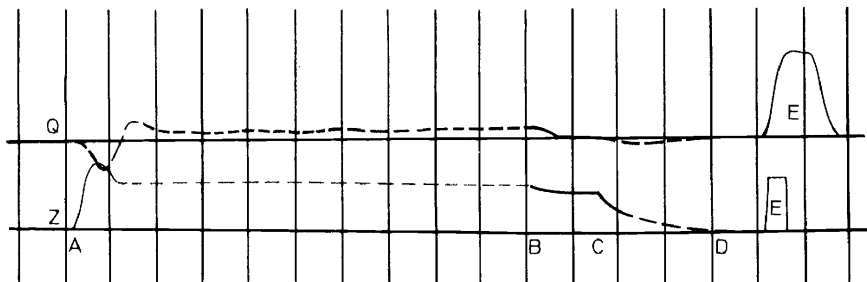

Figure 6. Recorded curves for the cold drawing of a polyamide rod: A beginning, B end of stretching with constant rate $v = 0.032$ cm/sec; C beginning, D end of unloading of drawn sample: calibrations E on the right.

In *Figure 6* you see the record of the cold-drawing of a polyamide sample. The stress-strain-curve shows at the beginning the well known peak according to the development of the necking zone[14] As long as elongation takes place the force is constant. At point B elongation is over and a certain stress relaxation is noticed Unloading follows At the end of the procedure the sample is some 100 per cent elongated.

The record of $\dot{Q}$ shows a cooling effect at the very beginning which corresponds to the pure elastic strain and the positive thermal elongation coefficient. Later, flow processes begin and heat production starts, partially produced by
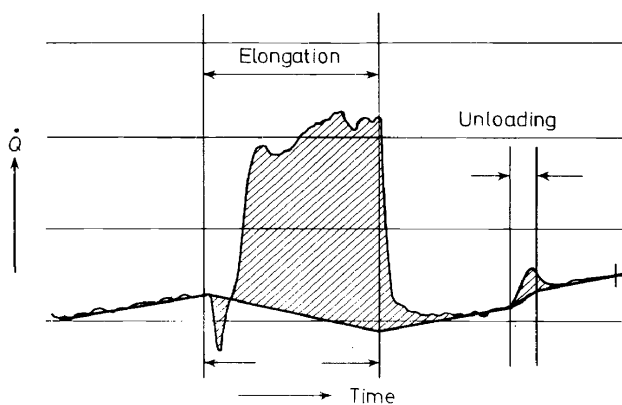

Figure 7 Example of heat record for polycarbonate with the later and still more sensitive apparatus by N. Weimann.

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friction and partially be entropy change with stretching. It lasts as long as stretching continues· However, it is registered with the usual retardation and modulation in the vicinity of point B. The unloading is coupled with a number of complex processes which will not be discussed here in detail.

These results can be discussed by comparing heat stream and mechanical work per time if a well defined range of constant force and constant heat stream is recorded. In other cases, it is possible to integrate over the time the work and the heat put in and taken out with different signs respectively (*Figure* 7)[15]. Taking the total balance we can make use of the first law of thermodynamics and find a change of inner energy of the sample as the difference of work and heat over the complete cycle of deformation:

$$\Delta U = A - Q \tag{2}$$

5. CHANGE OF STATE BY DEFORMATION

(a) Inner energy (enthalpy)
In all cases investigated, we found, after stretching, an increase of inner energy according to formula (2). This corresponds to a decrease in specific heat. For coldstretched polycarbonate for instance this difference amounts to 0.035 cal/g[15]; for plastic deformed copper the difference is much smaller, naturally in the right proportion.

(b) Entropy change
It is not only the inner energy of the sample which varies by deformation but also the entropy of the material. Coldstretching of polymers for example means a certain orientation of molecular chains and/or crystallites. This increase of orientation causes a decrease of entropy. The question is, can any information on the quantities of the entropy change be obtained?
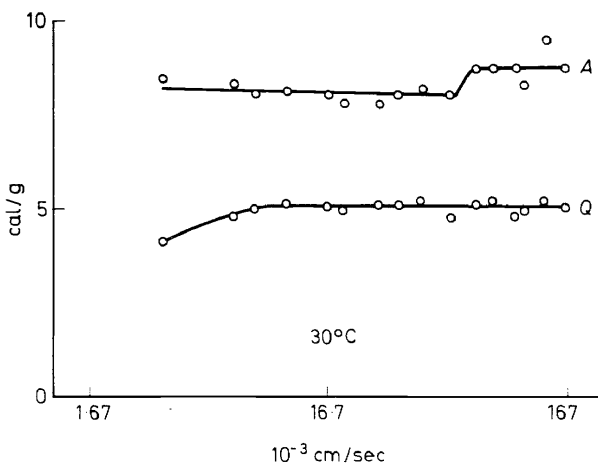

Figure 8. Results of heat and work as function of drawing rate (two decades variation) for polycarbonate. Every point is the mean value of at least five measurements in accordance with *Figure* 7.

We have discussed this matter in detail[8]. Even if the total balance of energy is known for a series of different deformation temperatures it is impossible to obtain information on the entropies. The reason is that for evaluation of entropy changes the second law of thermodynamics must be used. However, this is only permitted if the initial and final states are in a state of equilibrium in a thermodynamical sense. And this does not apply in the least to the state of the sample after deformation. What therefore happens depends on the 'way of processing'. The important consequence is that measured heat cannot properly be divided into a part Q_{diss} (friction heat) and a part Q_E (entropy change).

Certainly we can speak of entropy in a nonequilibrium state too[16]. We are convinced that entropy also varies with partial plastic deformation. And we are sure that there are differences in various kinds of deformations, e.g. for different stretching rates (as seen in *Figure 8*). But we have *no direct* possibilities of finding out the values of ΔS.

Occasionally there are indirect methods of obtaining information concerning the change of entropy. One case is the drawing of polycarbonate[17]. Because of the well defined geometrical shape of the necking zone the Stefan–Trouton formula for an estimate of the viscosity η of the material during drawing in the necking zone can be applied.

$$\eta = \frac{2}{3} \cdot \frac{\sigma_B \cdot B^3 \cdot 2\pi(\lambda - 1)}{q_F(\lambda + 1)} \cdot \frac{1}{v} \tag{3}$$

A second estimate is obtained by assuming that all of the measured heat is caused by friction.

$$\left(\dot{Q} = \eta \left[\frac{dv}{dy}\right]^2\right) \qquad \eta = \frac{2}{3} \cdot \frac{Q \cdot B}{\Delta l(\lambda + 1)^2} \cdot \frac{1}{v} \tag{4}$$

The latter values of η are three times larger than those of the Trouton Formula, (*Table 1*), so that it is safe to state that one third of the measured heat is enough to explain the friction heat. Two thirds of the measured heat, therefore, has to be attributed to changes of entropy by cold stretching.

Table 1. Calculated values of viscosity η within the necking zone

by	formula 3	formula 4
$v = 8 \times 10^{-3}$ cm/sec	0.9×10^7 poise	2.8×10^7 poise
$v = 1.7 \times 10^{-3}$ cm/sec	0.46×10^7 poise	1.4×10^7 poise

In all these examples the main point is to discover the accuracy of these results. Quite a few assumptions and approximations are made when using both formulas as well as an estimation of the shear gradient from the geometry of the neck when using equation 3. The estimates would be even more difficult to get at—as observed in the case of polymide and PC—if the form of the neck varies with the drawing rate[18].

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6. DEFORMATION OF RUBBER

Classical examples for thermodynamic questions of polymer deformations are the heat effects on rubberlike samples. In case of ideal rubber the entire work of deformation should be reversibly transformed to heat: during deformation the same spreads the elastic stored energy as heat to the environment. When the full mechanical work is taken off during unloading the sample should absorb the same amount of heat from the environment.
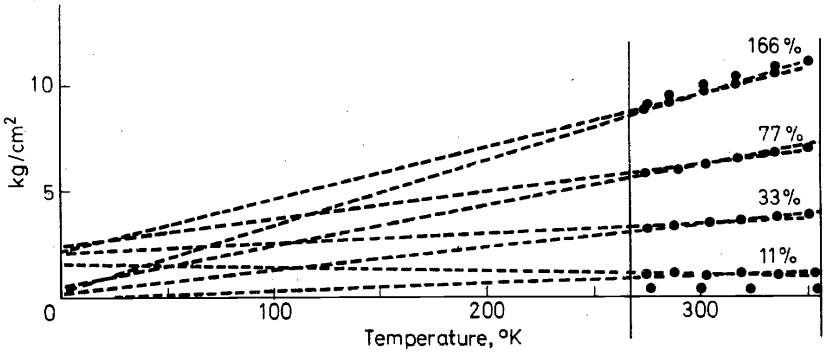

Figure 9. Force as a function of temperature T for different degrees of stretching for a rubber sample according to

$$F = \frac{\partial U}{\partial \Delta l} - T \frac{\partial \Delta S}{\partial \Delta l}$$

o = measured points. This illustrates the difficulties of ensuring an extrapolation to $T \to 0$, to find out the energyelastic part of force $F_e = \partial U/\partial l$.
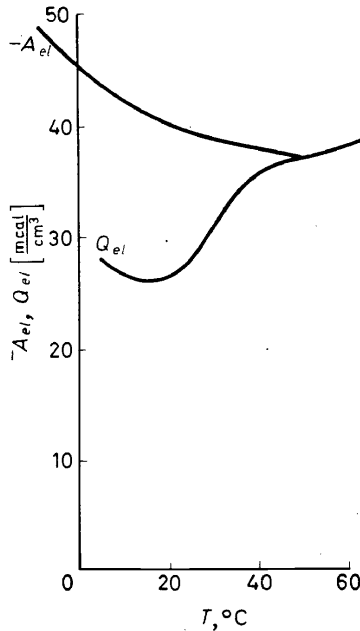

Figure 10. Measured values of work and heat for polyacryethylester as function of temperature. Deviation of ideal rubber behaviour below 40–50°.

The validity of this relation can be proven indirectly by means of the temperature dependency of the force for constant elongation, i.e. pure mechanical investigations are sufficient, though they are difficult to perform (see *Figure 9*)[19]:

$$Z = \frac{\partial \Delta F}{\partial l} = \frac{\partial \Delta U}{\partial l} - T \frac{\partial \Delta S}{\partial l} \tag{5}$$

These properties of rubber could also be tested with the stretching calorimeter. The main features of various rubbers reflected in the literature could be confirmed by us, i.e. generally ideal rubberlike behaviour, $Q = A$ being the exception That means, in normal cases, there are contributions to the elastic force, which result from changes of energy, whereas ideal rubber should only show elastic forces by change of entropy[20].

An example of such a rare ideal rubber is polyacrylacidethylester, cross-linked by 0·5 per cent glycoldimethacrylate, for temperatures above 40°. By the way, this material has no difference in energy level of *gauche* and *trans*configurations of the chain. The glass transition temperature of this material is about −18°. At temperatures between 0° to 30° it is a *slow* rubber, that means after deformation it only creeps back slowly to its original form because of high inner friction.
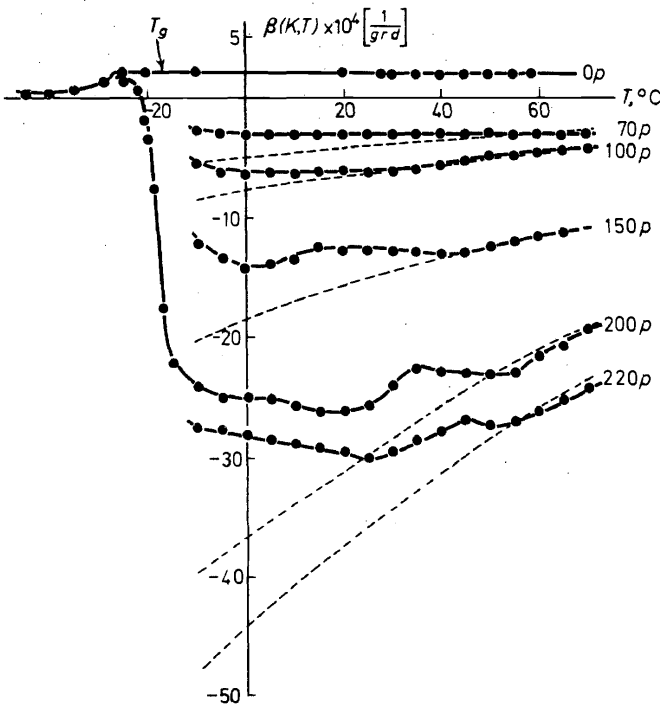

Figure 11. Measured values of the linear thermal elongation coefficient of the same material as *Figure 10* as a function of temperature and parameter: load. To the left below −20° glassy state, to the right β negative for higher loads (elongations).

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For these reasons, this material appeared to be an excellent model for a study of the transition from the glassy state to the ideal rubber state[21] The question was at what temperature could contributions of energy elasticity in addition to the pure entropy elasticity be seen *Figure 10* shows that the energy elastic mechanism begins to play a certain role already below 40°, that is to say at a temperature about 60° above the glass-transition In order to get these results a careful separation of the irreversible parts of the heat originating from the dissipation effects was necessary

We were also interested in how far the previously mentioned formula 1 could be used instead of direct calorific measurements For this purpose this formula must be written in an integral form:

$$Q = \int_0^z dQ = \int \beta(l, T) \, l(Z) \, dZ \tag{6}$$

The linear thermal elongation coefficient of the material was investigated over a sufficiently broad range of temperature and with different loads as a parameter (*Figure 11*) Using this data it was possible to compute the heats by the above formula, the results being a near enough approximation
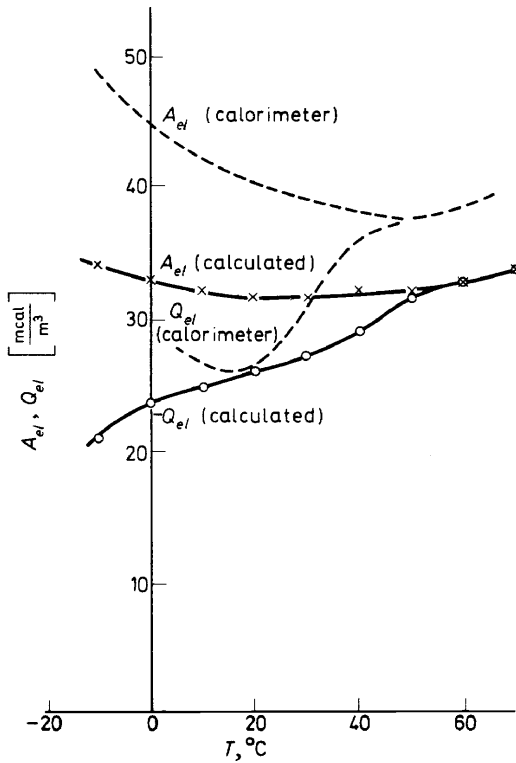

Figure 12. Comparison of curves calculated from the values of *Figure 11* with the measured values (dotted lines, taken from *Figure 10*).

For example β should be given as function of elongation. In *Figure 11* β is measured with different constant loads for experimental reasons.

The result is shown in *Figure 12*. The difference between calculated values and measured values are understandable because of the precision of the different experiments compared with the others.

7. CRYSTALLIZATION OF RUBBER BY STRAIN

Let me conclude this lecture by giving an outlook on investigations now under way. They too deal with rubber, natural rubber and polyisobutylene. Both are known to show crystallization when stretched. By investigating the density as a function of time it was already possible to learn something about the kinetics of crystallization[22]. The current measuring of the degree of crystallization as function of time by X-ray analysis, however, is rather difficult[23, 24]. In this case, too, the calorimetric method seems very appropriate.

An early measurement on a technical rubber sample could only be explained if a further continuous production of heat was assumed after termination of stretching as by crystallization (*Figure 13*). The asymmetry of the $\dot{Q}$ record for loading and unloading also indicates that crystallization plays
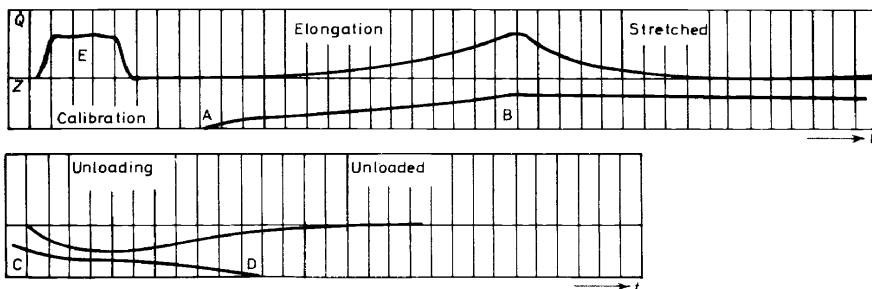
Figure 13. Recording of heat and work of a technical rubber sample (an early measurement)[11].
[See text for explanations.]

a role. Crystallization of the rubber needs time, but melting also needs time. There heat uptake during unloading is retarded too[25].

Quantitative conclusions in detail from such calorific measurements demand, however, the demodulation of the heat production as a function of time. Indeed, this is one case which shows that time-demodulation of the $\dot{Q}$ record is important. The experiments proved to be successful. *Figure 14* depicts a demodulated curve for polyisoprene. Heat production by stretching must stop immediately the elongation process is finished. As long as there is still further heat production, as to be seen in *Figure 14*, crystallization takes place.

The degree of crystallinity can be calculated from the measured heat, the weight of the sample and the molar melting heat of the monomer unit. *Figure 15* shows the crystalline part as a function of time with maximum
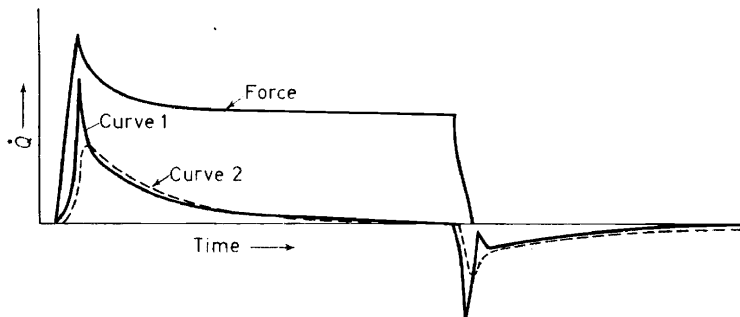
Figure 14. A recent record of stretching and unloading of a polyisoprene sample. Strong relaxation, large after-effect for the heat by crystallization, perceptible by the exponential decrease of $\dot{Q}$ instead of momentary reduction to zero at the end of the stretching process. Curve 1: demodulated curve for $\dot{Q}$; Curve 2: recorded curve.
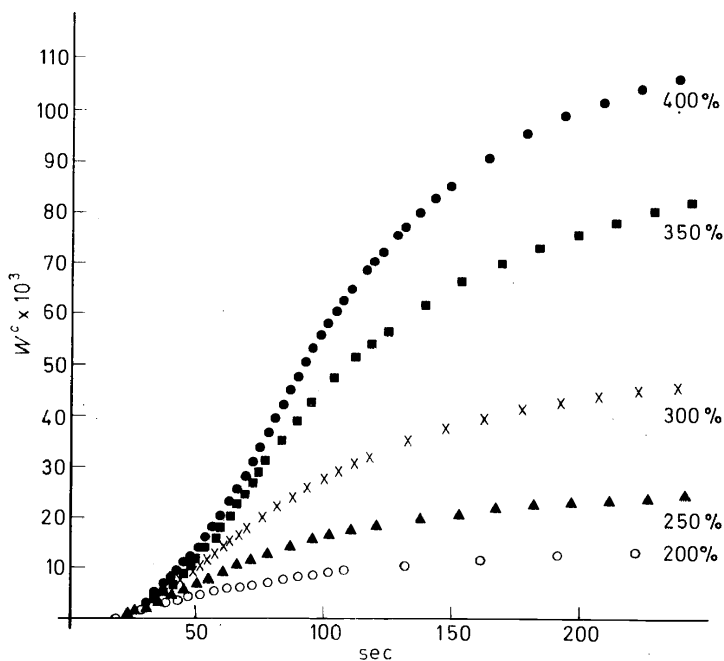

Figure 15. Measured values of crystalline part of polyisoprene (natural rubber) as a function of time from the first moment of stretching; parameter: the final degree of stretching.

elongation as a parameter. The sensitiveness of the calorific method seems to be excellent. The crystallized part varies from 1 to 11 per cent.

The maximal value of the crystallized part as function of elongation is shown in *Figure 16*. This figure reflects one curve for the total degree of crystallization and two other curves showing the crystallized part during stretching and after termination of the stretching process. We have chosen
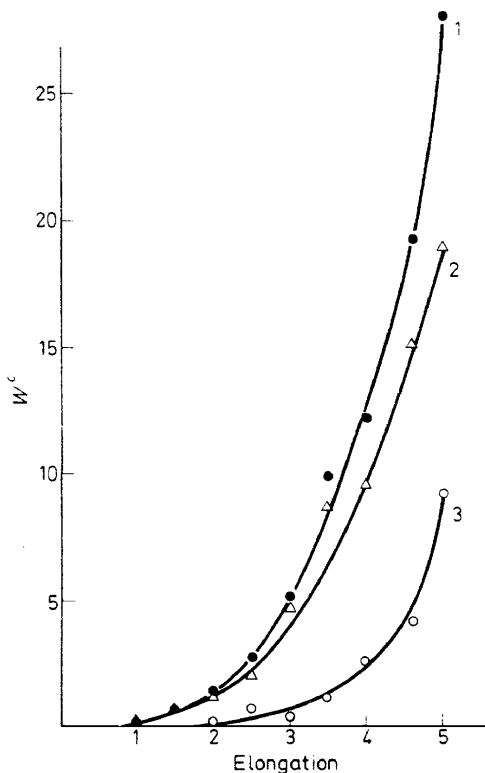
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Figure 16 Degree of crystallinity, of rubber as a function of elongation: 1 = total. 2 = after the end of drawing, 3 = already crystallized during the elongation of the sample
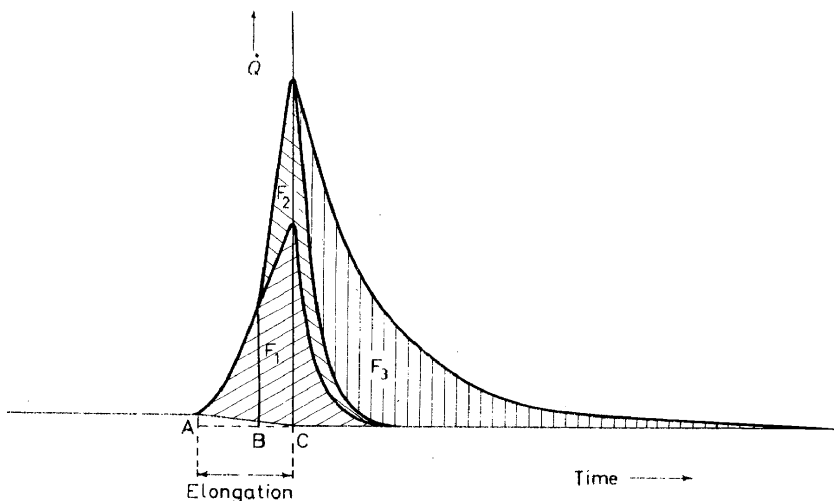

Figure 17 Separation of total amount ($\sim F_1 = F_2 + F_3$) of crystallized polyisoprene, separated into one part ($\sim F_2$) occuring still during the stretching process, and a second part (F_3) which crystallizes after termination of elongation

a rather high stretching rate of 25 cm/min. In spite of a high drawing rate for high elongation part of the crystallization still takes place during deformation. We tried to separate this portion by segregation into heat production by orientation (entropy heat) and into heat production by crystallization. The latter starts as soon as the $\dot{Q}$ record shows a distinct turn of slope (*Figure 17*). This segregation is of course somewhat arbitrary.
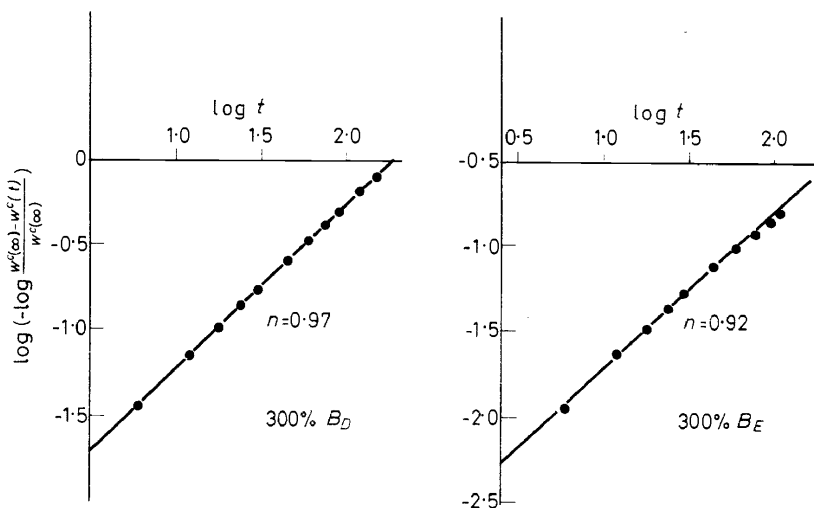

Figure 18. Avrami plot: left side for drawing (crystallization), right side for unloading (melting of crystalline part).

It may be of interest that the stretching velocity of 25 cm/sec is enough to yield a remarkable development of friction heat. Therefore, it is easily understood that high values of heat were found by Votinow[26] for extreme high deformation rates of rubber samples.

Finally an Avrami plot of the degree of crystallization (*Figure 18*) shows that the exponent is one. This was also found for density measurements. The same plot applied to melting results also in a straight line with exponent one. This simply means that melting (as well as crystallization) are exponential functions of time.

These cursory remarks on the present investigations by D. Göritz which were started only a few months ago, indicate that a number of interesting conclusions may be drawn from calorimetric investigations of stretching crystallization by applying the redistorted (demodulated) heat stream curves.

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