

# Linear viscoelastic creep under arbitrary temperature variations

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We discuss various temperature jump methods for the accurate determination of the activation energy  $\Delta H$  of creep for a linear viscoelastic material, and carry out a numerical computation in a discrete relaxation model to show that the effect arising from the temperature dependence of the compliances ( $\alpha\Delta T$  effect) quickly decays after the temperature jump. A general and compact expression is then derived for the creep rate of a viscoelastic solid under constant stress and subject to arbitrary temperature variations. Application of the expression to various experimental situations is discussed, and the double  $T$ -jump method is extended to cases in which a temperature pulse of arbitrary shape is imposed on the sample. A systematic analysis shows that the  $\alpha\Delta T$  effect makes a significant contribution to the expression only during a short period immediately after a  $T$ -jump and that it is otherwise totally negligible for any reasonable distribution function in relaxation time. Measurements of  $\Delta H$  for polypropylene at 40°C by single and double  $T$ -jump are in good agreement and support this theoretical prediction. The double  $T$ -jump technique is so precise that observations of variation of  $\Delta H$  with retardation time is now possible.

## INTRODUCTION

The accurate determination of the activation energy  $\Delta H$  for creep is of considerable practical interest, since it allows the prediction of long-term creep behaviour from short-term data at elevated temperatures. On the theoretical side, it would answer the questions of whether, for a particular mechanism  $\Delta H$  is constant for all elements of the distribution of retardation times, and what its stress dependence is. This in turn is crucial to an understanding of the origin of the distribution in retardation time and of creep as a rate process.

The most common and long-established method for determining  $\Delta H$  in the linear region is, of course, time-temperature superposition<sup>1</sup> derived from the equation of linear viscoelasticity. It states that the time-dependent creep  $J[T_0, t/a(T)]$  at temperature  $T_0$  is related to the compliance  $J(T, t)$  at temperature  $T$  by<sup>2,3</sup>:

$$J \left[ T_0, \frac{t}{a(T)} \right] = \frac{J(T, t)}{b(T)} + \left[ 1 - \frac{c(T)}{b(T)} \right] J_U(T_0) \quad (1)$$

where  $b(T)$  and  $c(T)$  are constants describing the temperature dependence of the relaxed and unrelaxed compliances,  $J_R$  and  $J_U$ , respectively:

$$J_R(T) - J_U(T) = b(T) [J_R(T_0) - J_U(T_0)] \quad (2)$$

$$J_U(T) = c(T) J_U(T_0) \quad (3)$$

$a(T)$  is a shift factor, which, except for  $\alpha$  relaxations of amorphous polymers, is related to the activation energy  $\Delta H$

through the Arrhenius equation<sup>3</sup>:

$$a(T) = \exp \left[ -\lambda \left( 1 - \frac{T_0}{T} \right) \right] \quad (4)$$

$\lambda$  being the dimensionless parameter  $\lambda = \Delta H/RT_0$ .

If both  $b(T)$  and  $c(T)$  are assumed equal to 1 then according to equation (1) the  $J(T, t)$  curve can be horizontally 'shifted' onto the  $J [T_0, t/a(T)]$  curve if  $J(T, t)$  is plotted against  $\log t$ . The shift distance gives  $a(T)$  whereby  $\Delta H$  can also be deduced through equation (4). This, however, is a highly inaccurate procedure: for instance,  $\Delta H$  so deduced for the  $\gamma$  relaxation of poly(methyl methacrylate) has a 50% error, which is quite typical<sup>2</sup>. The inaccuracy arises mainly from the fact that the method is susceptible to very small departures of  $b(T)$  and  $c(T)$  from unity, which would lead to an effective adjustment of the value of  $J(T, t)$  on the right of equation (1) through both the  $1/b(T)$  factor and the presence of the second term on the right. The slope of  $J(T, t)$  with respect to  $\log t$  is sufficiently low that such an adjustment even though small in magnitude, has a crucial effect on the outcome of the superposition.

Some progress has been made in case of the  $\beta$  relaxation of poly(methyl methacrylate)<sup>2</sup> and the  $\alpha$  relaxation of linear polyethylene<sup>4</sup> when one makes the less restrictive assumption  $b(T) = c(T) \neq 1$ , which still simplifies equation (1) by eliminating the second term on the right. Thus:

$$\ln J \left( T_0, \frac{t}{a(T)} \right) = \ln J(T, t) - \ln c(T) \quad (5)$$

For poly(methyl methacrylate)<sup>2</sup> high frequency modulus data were used to yield  $c(T)$ . Equation (5) was then used to obtain superposition. For linear polyethylene,  $c(T)$  and

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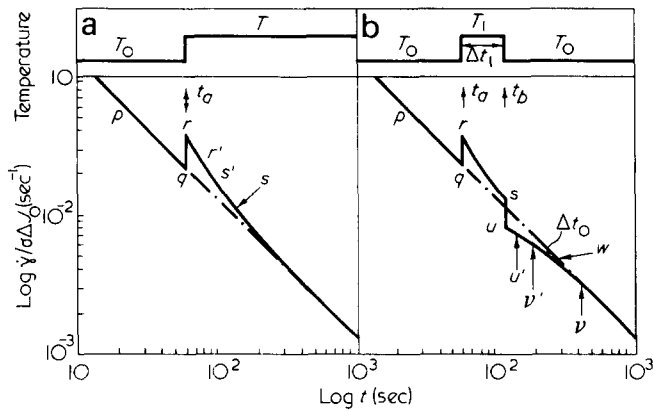


Figure 1 Dependence of  $\log \dot{\gamma}$  on  $\log t$  for discrete model calculation described in equation (11):  $\Delta J_0$  is the amplitude of each relaxation element. (a) Single  $T$ -jump experiment: positive  $T$ -jump at  $t_a = 60$  sec from  $T_0$  to  $T$ ; quantity  $qr$  yields  $\Delta H$  equation (7); (b) double  $T$ -jump experiment: positive  $T$ -jump at  $t_a = 60$  sec from  $T_0$  to  $T$  and return jump to  $T_0$  at  $t_b = 120$  sec,  $\Delta T_1 = 60$  sec; for  $t > t_b$  the rate lags behind the rate observed isothermally at  $T_0$  ( $\rho q w$ ); the time lag is  $\Delta t_0$  which yields  $\Delta H$ , equations (10) and (4)

$a(T)$  were obtained using the principle of optimum fit<sup>4</sup>: when  $\log J(T, t)$  is plotted against  $\log t$  a particular pair of values of  $\log c(T)$  (vertical shift) and  $\log a(T)$  (horizontal shift) produce optimum fit between  $\log J(T, t)$  and the master curve.

The values of  $c(T)$  were in fair agreement with high frequency data. There are polymers, however, for which the assumption  $b(T)$  is plainly not true: no combination of vertical and horizontal shifts can superimpose  $\log J(T, t)$  onto  $\log J [T_0, t/a(T)]$ .

The method of superposition is also inaccurate. For instance, the possibility of detecting a small variation in  $\Delta H$  for different elements in the distribution of retardation time is quite out of the question. Any method that involves the use of absolute values of  $b(T)$  or  $c(T)$  must, at present, be unreliable since these crucial quantities are normally not absolutely determinable.

Two methods have been developed to overcome this difficulty. It is the purpose of this paper to subject them to detailed theoretical and experimental scrutiny. The oldest and least precise is the single  $T$ -jump method, first described by Tietz and Dorn<sup>5</sup> and used to determine  $\Delta H$  for the creep of metals. The application of this technique to viscoelastic creep was developed theoretically by McCrum and Morris<sup>6</sup>, and has been applied to the creep of crystalline polymers<sup>7,8</sup>, biological tissue<sup>9</sup> and amorphous polymers<sup>10-14</sup>. A creep experiment is initiated at temperature  $T_0$  by applying a constant stress  $\sigma$  to the specimen at time  $t = 0$ . At a later time  $t_a$  the temperature is changed abruptly to temperature  $T$ . For a linear viscoelastic solid the ratio of the instantaneous creep strain rates at time  $t_a$  at the two temperatures  $T$  and  $T_0$  is<sup>2,5</sup>:

$$\ln \frac{\dot{\gamma}(t_a)}{\dot{\gamma}_0(t_a)} = \frac{\beta \kappa}{a(T)} \quad (6)$$

$\beta$  is a parameter which depends on the viscoelastic properties of the solid<sup>2</sup> and  $\kappa$  a parameter which accounts for the perturbation due to thermoelastic stresses generated by the  $T$ -jump<sup>15</sup>.  $\Delta H$  is obtained with considerable precision when both  $\beta$  and  $\kappa$  are unity. Little can be said about  $\kappa$ : if thermoelastic stresses exist ( $\kappa > 1$ ) as in linear polyethylene<sup>15</sup>, the

method fails. In polypropylene, however, it is clear that  $\kappa = 1$ <sup>16</sup>. In which case under the condition  $\beta = 1$  we have from equation (4) and (6):

$$\Delta H = \frac{RTT_0}{(T - T_0)} \ln \frac{\dot{\gamma}(t_a)}{\dot{\gamma}_0(t_a)} \quad (7)$$

The condition under which  $\beta$  is effectively equal to unity is as follows.

According to the theory of linear viscoelasticity<sup>2</sup>:

$$\beta = 1 + [b(T) - 1] A \quad (8)$$

$$A = \frac{\int_{-\infty}^{\infty} d \ln \tau \frac{\Phi_0(\ln \tau)}{\tau}}{\int_{-\infty}^{\infty} d \ln \tau \frac{\Phi_0(\ln \tau) \exp - (t_a/\tau)}{\tau}} \quad (9)$$

$\Phi_0(\ln \tau)$  is the normalized distribution of retardation times at  $T_0$  (ref 3). Now we may write:

$$b(T) = 1 + \alpha \Delta T$$

for small values of  $\Delta T$ ,  $\alpha$  being the temperature coefficient of  $[J_R(T) - J_U(T)]$ . In the absence of a precise value of  $\alpha$ , and for purposes of trial calculation in this paper, we will assume it takes the values (i) zero, (ii)  $4 \times 10^{-4} \text{C}^{-1}$  and (iii)  $40 \times 10^{-4} \text{C}^{-1}$ . The anticipated value lies within this bracket probably between zero and  $4 \times 10^{-4} \text{C}^{-1}$ . But taking the most extreme and unlikely value,  $\alpha = 40 \times 10^{-4} \text{C}^{-1}$ , we have for  $|\Delta T| < 5^\circ \text{C}$ :

$$[b(T) - 1] < 0.02.$$

It follows from equation (8) that if  $A \neq 1$ ,  $\beta$  will differ from unity by only  $\sim 2\%$ . Now it will be seen from equation (9) that  $A \neq 1$  will be, for fixed  $t_a$ , an approximation valid at temperatures low in the relaxation region: in this case numerator and denominator in equation (9) will be essentially equal. As the temperature is raised and for fixed  $t_a$  this will cease to be so because of the term  $\exp - (t_a/\tau)$  in the denominator. There will result a rapid increase in  $A$ . Thus unless the low temperature approximation holds,  $\beta \gg 1$  (see equation 8) and equation (7) fails. It is of course possible to determine  $\Delta H$  even under this condition<sup>7</sup> but the method involves considerable experimental work and analysis.

There is a Catch-22 paradox implicit in the above statements, which was not appreciated formerly. It may be stated thus with slight exaggeration. Equation (7) fails unless the low temperature approximation holds: the low temperature approximation holds only at temperatures low enough for creep rates to be negligible. The detailed resolution of this paradox, which is one of the major purposes of this paper, is sketched in the next paragraph.

The course of a single  $T$ -jump experiment is illustrated in Figure 1a which shows calculations for the discrete single-relaxation time model described below. For  $\alpha \Delta T = 0$ , the  $T$ -jump at  $t_a = 60$  sec causes  $\log \dot{\gamma}$  to follow the course  $pqr$ . The quantity  $qr$  yields  $\Delta H$ , equation (7):  $q$  is easily obtained since measurements of  $\dot{\gamma}$  are taken right up to time

$t_a$ . But after the  $T$ -jump, even with the fastest equipment, it takes a number of seconds for the new temperature  $T$  to be established. Data can therefore only be observed reliably in the region  $s's$  and it is necessary therefore to extrapolate  $\log \dot{\gamma}$  back to the point  $r$ . But in addition to rejecting data in the region  $rs'$  for experimental reasons we will show that the perturbation introduced by  $\alpha\Delta T \neq 0$  is effective only in a region immediately after the  $T$ -jump, symbolized by  $rr'$  in *Figure 1a*. Thus the low temperature approximation holds if data in the region  $rr'$  is excluded. For then, extrapolation of the valid data back to  $t_a$  will generate the point  $r$ .

The relative positions of  $r'$  and  $s'$  may be reversed. The position of  $r'$  is a detailed theoretical problem elucidated below: the position of  $s'$  depends on the efficiency of the  $T$ -jump equipment. It is determined by monitoring the temperature. Under the conditions of the single  $T$ -jump experiments described in this paper, the evidence is that  $r'$  precedes  $s'$ , as indicated in *Figure 1a*: the data excluded for experimental reasons include all the data which should be excluded for theoretical reasons. The evidence for this statement is derived largely from measurements of  $\Delta H$  using the new double  $T$ -jump technique, which is not subject to comparable uncertainty.

The determination of  $\Delta H$  by double jump<sup>17</sup> requires two experiments, one with  $T$ -jump and one without, both at the same stress. This is illustrated by calculation using the discrete relaxation time model given below. In the experiment without  $T$ -jump  $\log \dot{\gamma}$  follows the line  $pqw$ , *Figure 1b*, at temperature  $T_0$ . The specimen is then permitted to recover under zero stress. The second experiment is then performed with a  $T$ -jump from  $T_0$  to  $T_1$  at  $t_a = 60$  sec and the reverse jump from  $T_1$  back to  $T_0$  at  $t_b = 120$  sec. As illustrated in *Figure 1b* for  $(T_1 - T_0) = \Delta T_1 = +3^\circ\text{C}$ ,  $\log \dot{\gamma}$  follows the line  $pqrstuv$ . For  $\alpha\Delta T = 0$  theory shows that the time shift  $\Delta t_0$ , between the lines  $uv$  and  $qw$  is related to  $a(T)$  by<sup>17</sup>:

$$\frac{1}{a(T)} = 1 - \frac{\Delta t_0}{\Delta t_1} \quad (10)$$

in which  $\Delta t_1 = (t_b - t_a)$ , the time for which the specimen was at  $T_1$ :  $\Delta t_0$  is independent of  $t$ . Thus measurement of  $\Delta t_0$  yields  $\Delta H$ . After the second  $T$ -jump, there is a period of time of the order of seconds, indicated by  $uv'$  in *Figure 1b*, in which the data will be unreliable due to time taken for the temperature to come into equilibrium at  $T_0$ . In practice, therefore, the time shift is measured between the lines  $v'v$  and  $qw$ : data in the region  $uv'$  is rejected. It will be shown below that equation (10) fails at times immediately after the  $T$ -jump, symbolized by  $uu'$  in *Figure 1b*. This failure is due to the assumption  $\alpha\Delta T = 0$ . In the perturbed region  $uu'$  the separation in time between the lines  $uv$  and  $qw$  is no longer constant. This can be recognized from the data and the position of  $u'$  established unambiguously.

The two major experimental problems are: (i) the rise time of temperature from  $T_0$  to  $T$  (and in the double  $T$ -jump experiment also from  $T$  back to  $T_0$ ); (ii) the maintenance of precise temperature control particularly when the creep rate becomes low. Hooley, Caruthers and Cohen<sup>11</sup> have investigated theoretically the influence of a non-instantaneous  $T$ -jump and have shown how effects due to long rise times may be corrected. Their analysis included a study of creep rates following an arbitrary temperature history. This problem we approach below following the discrete model calculation (equation 11). We then describe experimental factors with particular attention to the rise time.

In the Results section we describe the experimental observation of  $\Delta H$  by single and double  $T$ -jump in polypropylene at  $40^\circ\text{C}$ . The results and applications of the techniques are then discussed.

## THEORY

### Discrete retardation time model

Before a full treatment of creep under arbitrary temperature variations and with a general distribution function of the retardation time, it is helpful to extract some of the results by the use of a simple model to avoid mathematical complications.

In this model it is assumed that creep at temperature  $T$  proceeds by a number of discrete time constants  $\tau^i$  ( $i = 1, 2, \dots, N$ ), which are related to the corresponding time constant  $\tau_0^i$  for reference temperature  $T_0$  by:

$$\tau^i = a(T)\tau_0^i$$

It will be assumed that the amplitudes associated with each  $\tau_0^i$  are all equal,  $\Delta J_0$ , and that the temperature dependence of each  $\Delta J_0$  is:

$$\Delta J = b(T)\Delta J_0$$

For the purpose of this calculation the effect of  $\Delta J_0$  varying with  $\tau_0^i$  has been shown to be negligible by trial calculation.

In the single  $T$ -jump experiment, a shear stress  $\sigma$  is applied at  $t = 0$  with the specimen at temperature  $T_0$ . The creep rate at time  $t$  is:

$$\frac{\dot{\gamma}(t)}{\sigma\Delta J_0} = \sum_i \frac{\exp(-t/\tau_0^i)}{\tau_0^i} \quad (11)$$

If a  $T$ -jump is imposed at time  $t_a$  then for  $t > t_a$ :

$$\frac{\dot{\gamma}(t)}{\sigma\Delta J_0} = \sum_i \left(\frac{1}{\tau^i}\right) \exp\left(-\frac{t-t_a}{\tau^i}\right) \left[ \exp\left(-\frac{t_a}{\tau_0^i}\right) + \alpha\Delta T \right] \quad (12)$$

These curves are shown in *Figure 2* for  $\Delta T = +3.0^\circ\text{C}$ . To make the calculation as relevant as possible the parameters are chosen to be as typical as possible for polypropylene under the conditions imposed in our experiments:  $T_0 = 40^\circ\text{C}$ ;  $t_a = 60$  sec;  $\Delta H = 34.5$  kcal/mol;  $\tau_0^i = 0.12 \times 10^n$  sec,  $0.3 \times 10^n$  sec,  $0.6 \times 10^n$  sec, for  $n = 0, 1, 2, \dots, 6$ . Values of  $\tau_0^i$  outside the band quoted above have negligible effects on the result. It will be seen from *Figure 2* that the  $\alpha\Delta T$  term in equation (12) causes the three curves to fan out at times just after the  $T$ -jump. The  $\alpha = 0$  and  $\alpha = 4 \times 10^{-4}$  curves fall into coincidence to within 1%, 5 sec after the  $T$  jump; the  $\alpha = 0$  and  $\alpha = 40 \times 10^{-4}$  curves coincide to within 1%, 250 sec after the  $T$ -jump.

*Figure 3* shows curves calculated from equations (1) and (2) for  $\Delta T = -3.0^\circ\text{C}$ . Coincidence to within 1% of the  $\alpha = 0$  line occurs 20 sec after the  $T$ -jump ( $\alpha = 4 \times 10^{-4}$ ) and 400 sec after the  $T$ -jump ( $\alpha = 40 \times 10^{-4}$ ). The perturbation introduced by finite  $\alpha$  occurs over a longer interval than for

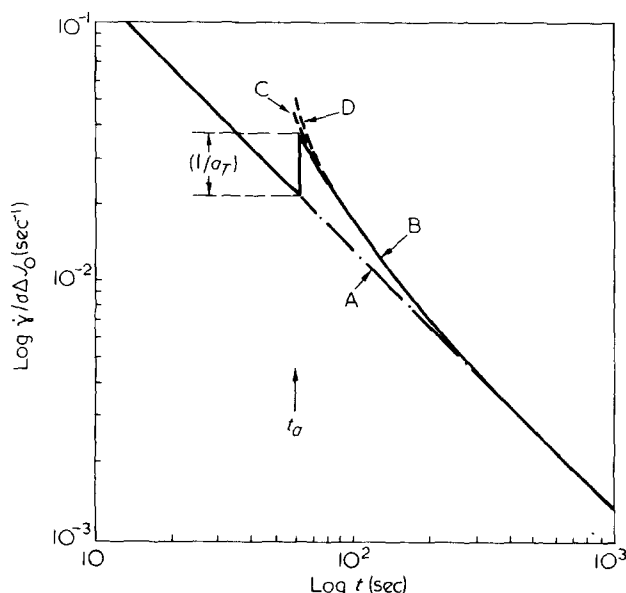


Figure 2 Single  $T$ -jump experiment, positive  $\Delta T$ : dependence of  $\log \dot{\gamma}$  on  $\log t$  for discrete retardation time model: A, isothermal,  $T_0 = 40.0^\circ\text{C}$ ; B, C and D,  $T_0 = 40.0^\circ\text{C}$  with  $T$ -jump of  $+3.0^\circ\text{C}$  at  $t_a = 60$  sec; B,  $\alpha = 0$ ; C,  $\alpha = 4.0 \times 10^{-4}$ ; D,  $\alpha = 40.0 \times 10^{-4}$

a positive  $T$ -jump. Nevertheless, if the data is excluded in the appropriate region of time after the  $T$ -jump, extrapolation of  $\log \dot{\gamma}$  back to time  $t_a$  will yield a value of  $\log \dot{\gamma}(t)$  representative of the  $\alpha = 0$  curve and which may be inserted therefore in equation (7) to yield  $\Delta H$ . The determination of the appropriate region of time in which to exclude data is clearly of central significance, a point to which we return later.

In the double  $T$ -jump experiment the creep rate after the second jump ( $t > t_b$ ) is:

$$\frac{\dot{\gamma}(t)}{\sigma \Delta J_0} = \sum_i \frac{\exp\left(-\frac{t-t_a}{\tau_0^i}\right)}{\tau_0^i} \exp\left(-\frac{1}{\tau_0^i}\right) \left[ t_a + \frac{\Delta t_1}{a(T)} \right] + \alpha \Delta T \left[ -1 + \exp\left(-\frac{\Delta t_1}{\tau^i}\right) \right] \quad (13)$$

Figure 4a shows this curve plotted for the model ( $\log \dot{\gamma}$  versus linear  $t$ ) with  $\Delta T = \pm 3^\circ\text{C}$ ,  $t_a = 60$  sec,  $t_b = 120$  sec for  $\alpha = 0, 4 \times 10^{-4}$  and  $40 \times 10^{-4} \text{C}^{-1}$ . Also plotted in Figure 4 is equation (11) which gives  $\dot{\gamma}(t)$  at  $T_0$  for the experiment with no  $T$ -jump (full line). It will be seen from Figure 4a that the  $\alpha \Delta T$  term in equation (13) causes the curves to diverge immediately after  $t_b$  but to come into coincidence with increasing time. For  $\Delta T = -3.0^\circ\text{C}$  the  $\alpha = 0$  curve coincides to within 1% of the  $\alpha = 4 \times 10^{-4}$  curve for  $(t - t_b) = 10$  sec. and the  $\alpha = 40 \times 10^{-4}$  curve for  $(t - t_b) = 60$  sec. For  $\Delta T = +3.0^\circ\text{C}$ , coincidence to within 1% of the  $\alpha = 0$  line occurs for  $(t - t_b) = 20$  sec ( $\alpha = 4 \times 10^{-4}$ ) and  $(t - t_b) = 120$  sec ( $\alpha = 40 \times 10^{-4}$ ).

The analytical procedure for the double  $T$ -jump experiment is illustrated with this data in Figures 4b and 4c. The  $\Delta T = +3.0^\circ\text{C}$  data shown in Figure 4a is plotted in Figure 4b with a time shift of  $+41.5$  sec. The  $\Delta T = -3.0^\circ\text{C}$  data of Figure 4a is plotted in Figure 4c with a time shift of  $-24.9$  sec. These are the time shifts computed for the model ac-

ording to equation (10). As anticipated, the  $\alpha = 0$  data fall on the no  $T$ -jump curve. The  $\alpha = 4 \times 10^{-4}$  and  $40 \times 10^{-4}$  points diverge as expected at short times after the second  $T$ -jump.

The strength of the double  $T$ -jump technique is illustrated particularly well in Figure 4b. The experimental procedure is to plot the no  $T$ -jump and  $T$ -jump data on separate sheets of transparent graph paper. The  $T$ -jump graph is placed above the no  $T$ -jump graph and translated along the  $t$ -axis. Coincidence of the two sets of data yields the time shift  $\Delta t_0$ . Data in the early time region perturbed by the  $\alpha \Delta T$  can be recognized as not falling on the no-jump line and can be rejected from the analysis. The time shift measured from the unperturbed data at longer times can then be used in equation (10) to obtain  $a(T)$  and hence  $\Delta H$ .

We performed a considerable number of double  $T$ -jump experiments and did not once observe in polypropylene graphical evidence of the  $\alpha \Delta T$  perturbation. Data in the region 30 sec after  $t_b$  were excluded for experimental reasons. The perturbed points fall within this region and will doubtless be observed with faster  $T$ -jump equipment now being brought into use.

The origin of the perturbation introduced by the  $\alpha \Delta T$  term is easily understood from the discrete single retardation time model. Consider a single  $T$ -jump at  $t_a = 60$  sec from  $T_0$  to  $T$ . At  $T_0$  at 60 sec, relaxation time 6 sec and shorter no longer contribute significantly to  $\dot{\gamma}$ : they are completely relaxed having each contributed their full relaxed component  $\sigma \Delta J_0$  to the total strain. Consider one of these relaxation times,  $\tau_0^j$  ( $\tau_0^j < 6$  sec). Immediately after the  $T$ -jump the instantaneous strain in the  $j$ th element at  $T$  is  $\sigma \Delta J_0$  but the equilibrium strain is now  $\sigma \Delta J$ . The element will therefore immediately creep from the instantaneous value to the equilibrium, the resulting additional strain being  $\sigma(\Delta J - \Delta J_0)$ . This quantity is indeed small compared to  $\sigma \Delta J_0$ :

$$\frac{\sigma(\Delta J - \Delta J_0)}{\sigma \Delta J_0} = \alpha \Delta T = 0.004 \Delta T \quad (14)$$

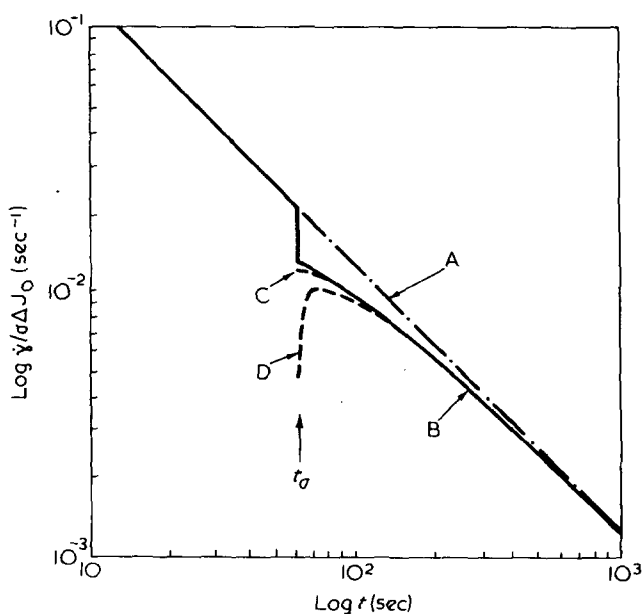


Figure 3 Single  $T$ -jump experiment, negative  $\Delta T$ : dependence of  $\log \dot{\gamma}$  on  $\log t$  for discrete relaxation time model: A, isothermal,  $T_0 = 40.0^\circ\text{C}$ ; B, C and D,  $T_0 = 40.0^\circ\text{C}$  with  $T$ -jump of  $-3.0^\circ\text{C}$  at  $t_a = 60$  sec; B,  $\alpha = 0$ ; C,  $\alpha = 4.0 \times 10^{-4}$ ; D,  $\alpha = 40 \times 10^{-4}$

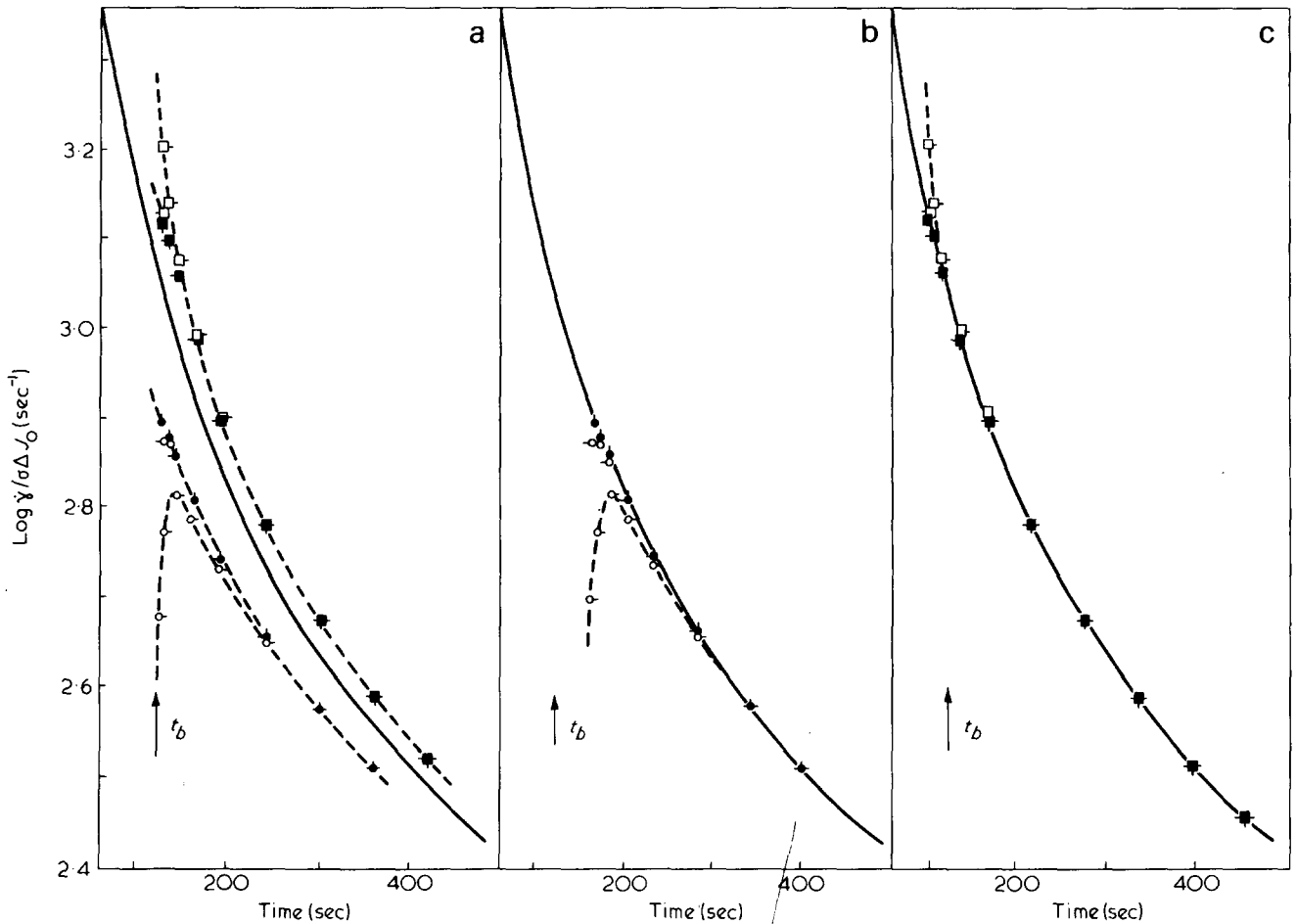


Figure 4 (a) Dependence on  $\log \dot{\gamma}$  on  $t$  for discrete retardation time model,  $T_0 = 40.0^\circ$  at times  $t > t_b$ : —, isothermal  $T_0 = 40.0^\circ$  C.  $\square$  are a result of square temperature pulse of  $\Delta T = -3.0^\circ$  C of duration 60 sec applied at  $t = 60$  sec and removed at  $t_b = 120$  sec;  $\blacksquare$ ,  $\alpha = 0$ ;  $\square$ ,  $\alpha = 4.0 \times 10^{-4}$ ;  $\square$ ,  $\alpha = 40.0 \times 10^{-4}$ . Circled points are a result of square temperature pulse of  $\Delta T = +3.0^\circ$  C of duration 60 sec applied at  $t_a = 60$  sec and removed at  $t_b = 120$  sec;  $\bullet$ ,  $\alpha = 0$ ;  $\circ$ ,  $\alpha = 4.0 \times 10^{-4}$ ;  $\circ$ ,  $\alpha = 40.0 \times 10^{-4}$ . (b) Temperature pulse data of (a) ( $\Delta T = +3.0^\circ$  C) plotted with time shift  $+41.5$  sec; (c) Temperature pulse data of (a) ( $\Delta T = -3.0^\circ$  C) plotted with time shift of  $-24.9$  sec

assuming the most extreme value of  $\alpha = 40 \times 10^{-4} \text{C}^{-1}$ . Thus a  $\Delta T = -2.5^\circ \text{C}$  will cause a 1% lowering in equilibrium strain. The significant point is that the rate at which the  $j$ th element relaxes from  $\sigma \Delta J_0$  to  $\sigma \Delta J$  will be extremely rapid immediately after the  $T$ -jump, since we are considering only short relaxation times,  $\tau_0^j < 6$  sec. The instantaneous rate at  $t_a$  at  $T$  is:

$$\dot{\gamma}_j(t_a) = \frac{\alpha \Delta T \Delta J_0}{a(T) \tau_0^j}$$

Clearly for any finite  $\alpha \Delta T$  (no matter how small)  $\dot{\gamma}_j(t_a) \rightarrow \infty$  as  $\tau_0^j \rightarrow 0$ . Thus, it is the short relaxation times which are the origin of the  $\alpha \Delta T$  perturbation and it is this fact that causes the perturbation to decay rapidly after  $t_a$ .

It will be seen then that an absolute determination of  $b_T$  is not necessary: we require merely to exclude perturbed data points and since we deal with strain rates  $\dot{\gamma}(t)$ , the additional parameter  $c(T)$  (equation 1) which is an additional complication in time-temperature superposition is of no significance.

#### General theory

Having seen the sort of result that one can expect from a model of discrete retardation time, we now proceed to the general case. Suppose starting at  $t = 0$  a specimen of a viscoelastic material is put under constant shear stress,  $\sigma$ , and it is

subsequently subject to a prescribed but completely arbitrary variation in temperature,  $T(t)$  (Figure 5). Its distribution function  $\phi[\ln \tau, T(t)]$  is then a function of time, with a time-dependent shift factor  $a(t) = a[T(t)]$ , which is related to  $\Delta H$  through equation (4) where the reference temperature  $T_0$  is conveniently chosen to be  $T(0)$ .  $\phi$  is related to the reference distribution function  $\phi_0(\ln \tau) [\equiv \phi(\ln \tau, T_0)]$  by  $\phi[\ln \tau, T(t)] = \phi_0[\ln \tau - \ln a(t)]$ . The unrelaxed and relaxed limiting compliances  $J_U$  and  $J_R$  would be constantly changing, thus making the difference compliance factor  $b(T)$  also a function of time:  $b(t) = b[T(t)]$ .

The shear strain  $\gamma(t)$  of the specimen at time  $t$  is, according to the principle of superposition, an integral over the strain in all the preceding time intervals, with the appropriate exponential decay of each contribution taken into account. Consider the strain arising at time  $t$  from the stress pulse applied between time  $v$  and  $(v + dv)$ , Figure 5. In the first instance we assume a single retardation time  $\tau$  which is subject to the continuously varying relative shift factor  $a(u)/a(v)$ ,  $u$  being the time variable changing from  $v$  to  $t$  (Figure 5). According to the principle of superposition, this contribution is:

$$\Delta \gamma(v \rightarrow t) = \sigma \Delta J(v) \frac{\Delta v}{\tau} \exp - \int_v^t \frac{du}{a(u)\tau/a(v)}$$

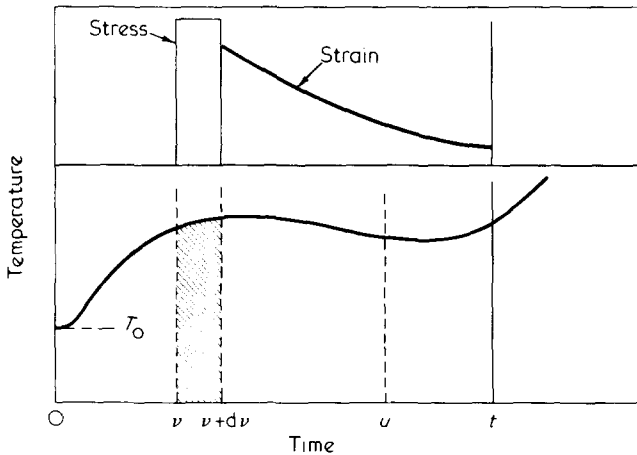


Figure 5 A stress pulse is applied between times  $\nu$  and  $\nu + d\nu$ . The temperature has a known but quite arbitrary time dependence. The time dependence of the strain  $\Delta\gamma(\nu \rightarrow t)$  is given by equation (17)

where the integral in the exponential factor takes into account the effect of temperature variation on the relative shift factor. We now further take into account the distribution in relaxation time by introducing the distribution function  $\phi[\ln\tau, T(\nu)]$  appropriate for the temperature at time  $\nu$ , and integrate over  $\ln\tau$ . Thus:

$$\Delta\gamma(\nu \rightarrow t) = \sigma \Delta J(\nu) \Delta\nu \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau/a(\nu)} \right] \quad (15)$$

Shifting  $\phi$  to  $\phi_0$  through  $a(\nu)$  and  $\Delta J(\nu)$  to  $\Delta J_0$  through  $b(\nu)$ , we obtain:

$$\frac{\Delta\gamma(\nu \rightarrow t)}{\sigma \Delta J_0} = b(\nu) \Delta\nu \int d(\ln\tau) \phi_0(\ln\tau) \frac{1}{a(\nu)\tau} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau} \right] \quad (16)$$

The total strain  $\gamma(t)$  is obtainable by integrating  $\Delta\gamma(\nu \rightarrow t)$  over  $\nu$  from 0 to  $t$  and added onto it the instantaneous response to stress, i.e.  $\sigma J_u(t)$ :

$$\frac{\gamma(t)}{\sigma \Delta J_0} = c(t) \frac{J_u(0)}{\Delta J_0} + \int_0^t d\nu b(\nu) \int d(\ln\tau) \phi_0(\ln\tau) \frac{1}{a(\nu)\tau} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau} \right] \quad (17)$$

The strain rate  $\dot{\gamma}(t) = d\gamma(t)/dt$  is:

$$\frac{\dot{\gamma}(t)}{\sigma \Delta J_0} = \dot{c}(t) \frac{J_u(0)}{\Delta J_0} + \frac{b(t)}{a(t)} \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} -$$

$$\int_0^t d\nu b(\nu) \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \frac{1}{a(\nu)} \frac{1}{a(t)\tau} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau} \right] \\ = \dot{c}(t) \frac{J_u(0)}{\Delta J_0} + \frac{1}{a(t)} \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \left\{ b(t) - \int_0^t d\nu b(\nu) \frac{d}{d\nu} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau} \right] \right\} \quad (18)$$

If we assume  $b(t) = c(t) = 1$  then the first term on the right disappears and the integration over  $\nu$  could be immediately carried out, yielding:

$$\frac{\dot{\gamma}(t)}{\sigma \Delta J_0} = \frac{1}{a(t)} \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \exp \left[ - \frac{t}{\tau A(t)} \right] \quad (19)$$

where  $A(t)^{-1}$  is the time-averaged inverse shift factor defined as:

$$\frac{1}{A(t)} \equiv \frac{1}{t} \int_0^t \frac{du}{a(u)} \quad (20)$$

The fact that  $b(t)$  and  $c(t) \neq 1$  means the following remainder term  $R_0$  should be added onto the right-hand side of (19):

$$R_0 = \dot{c}(t) \frac{J_u(0)}{\Delta J_0} + \frac{1}{a(t)} \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \left\{ b(t) - 1 - \int_0^t d\nu [b(\nu) - 1] \frac{d}{d\nu} \exp \left[ - \int_{\nu}^t \frac{du}{a(u)\tau} \right] \right\} \quad (21)$$

Equations (19)–(21) are our main results.

In the rest of this section we ignore  $R_0$ . The effect of  $R_0$  perturbation is described in the Discussion.

To see the significance of equation (19) consider  $T(t) = T_0$ , i.e. the sample temperature is held constant for all time, so  $a(t) = b(t) = c(t) = A(t) = 1$ . Denoting  $\dot{\gamma}$  by  $\dot{\gamma}_0$  for this case, we recover the familiar formula:

$$f_0(t) = \frac{\dot{\gamma}_0(t)}{\sigma \Delta J_0} = \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \exp \left( - \frac{t}{\tau} \right) \quad (22)$$

where the notation  $f_0(t)$  has been introduced for future convenience. By the change of variable of integration  $k = 1/\tau$ , equation (22) shows that  $f_0(t)$  is but the Laplace transform of  $\phi_0$ , the latter being regarded as a function of  $k$ :

$$f_0(t) = \int_0^{\infty} dk e^{-kt} \phi_0(k) \quad (23)$$

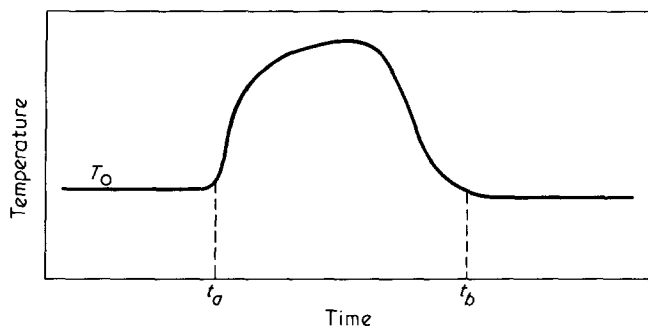


Figure 6 Time dependence of temperature in the arbitrary temperature pulse experiment

As discussed in detail in Appendix 1, this allows an explicit calculation in close analytic form of the distribution function  $\phi_0$  from the experimental values of  $\gamma_0$  by inverse Laplace transform.

From equations (19) and (22) it is apparent that so long as the  $R_0$  term is negligible then all creep rate curves  $\dot{\gamma}(t)$  produced by arbitrary temperature variations are reducible to the basic functional form  $f_0(t)$  by means of the parameter  $a(t)^{-1}$ , the instantaneous inverse shift factor and  $A(t)^{-1}$ , the time-averaged inverse shift factor<sup>18</sup>. Thus:

$$\frac{\dot{\gamma}(t)}{\sigma \Delta J_0} = \frac{1}{a(t)} f_0 \left[ \frac{t}{A(t)} \right] \quad (24)$$

and equation which may also be derived following Hopkins<sup>18</sup> procedure.

### Applications

It is quite simple to apply the general result equations (19) or (24) to any particular thermal history, since one need only evaluate the time-averaged inverse shift factor in each case according to equation (20).

For instance, in case of the single  $T$ -jump experiment  $T(t) = T_0 + \Delta T \theta(t - t_a)$ , where  $\Delta T$  and  $t_a$  are the magnitude and time of the temperature jump, respectively, and  $\theta(t)$  is the usual step function defined to be 0 for  $t < 0$  and 1 for  $t > 0$ . Consequently  $a(t) = 1 + (a_1 - 1)\theta(t - t_a)$ , where  $a_1 = a(T_0 + \Delta T)$ , and substitution into equation (20) gives  $A(t)^{-1} = [1 + (a_1 - 1)t_a/t]/a_1$  for  $t \geq t_a$ . Denoting the creep rate in this case by  $\dot{\gamma}_{SJ}$ , equation (24) shows that:

$$\frac{\dot{\gamma}_{SJ}(t)}{\sigma \Delta J_0} = \frac{1}{a_1} f_0 \left[ \frac{t}{a_1} + \left(1 - \frac{1}{a_1}\right) t_a \right] \quad (t \geq t_a) \quad (25)$$

Setting  $t = t_a$  we immediately recover the previous result  $\dot{\gamma}_{SJ}(t_a)/\dot{\gamma}_0(t_a) = 1/a_1$ .

In the double  $T$ -jump experiment with temperature increment  $\Delta T$  imposed between  $t_a$  and  $t_b$  one has:

$$T(t) = T_0 + \Delta T \theta(t - t_a) \theta(t_b - t) \quad (26)$$

with a similar expression for  $a(t)$ . Direct integration yields  $A(t)^{-1} = 1 - (1 - 1/a_1)\Delta t/t$  for  $t \geq t_b$ , that is, denoting the creep rate by  $\dot{\gamma}_{DJ}$ , we have:

$$\frac{\dot{\gamma}_{DJ}(t)}{\sigma \Delta J_0} = f_0 \left[ t - \left(1 - \frac{1}{a_1}\right) \Delta t \right] \quad (t \geq t_b) \quad (27)$$

The shift factor is again  $a_1 = a(T_0 + T)$ . It is therefore immediately clear that  $\dot{\gamma}_{DJ}(t) = \dot{\gamma}_0(t - \Delta t_{DJ})$ , where  $\Delta t_{DJ} = (1 - 1/a_1)\Delta t$  is the constant time interval separating the  $\dot{\gamma}_{DJ}$  and  $\dot{\gamma}_0$  curves, and that  $a_1$  and hence  $\Delta H$  can be accurately determined from these two curves.

There is now a natural extension of the double  $T$ -jump method. In experimental situations where abrupt changes of temperature as characterized by  $\theta$  functions are not practical one need only impose a temperature pulse of known (but nevertheless quite arbitrary) profile  $T(t)$  on top of  $T_0$  between  $t = t_a$  and  $t = t_b$  (Figure 6). In that case equation (26) still holds, even though  $\Delta T$  is now a known function of time. Similarly it is straightforward to show that the expressions for  $A(t)^{-1}$  and for the creep rate  $\dot{\gamma}_P$  (i.e. equation 27) remain valid, so that one can again experimentally determine a time interval  $\Delta t_P$  which separates  $\dot{\gamma}_P$  from  $\dot{\gamma}_0$  at all levels of creep rates. The shift factor  $a_1$  so deduced,  $a_1 = 1 - \Delta t_P/\Delta t$ , is however related to the activation energy in a more complicated manner:

$$\frac{1}{a_1} = \frac{1}{\Delta t} \int_{t_a}^{t_b} dt' \exp \left\{ \lambda \left[ 1 - \frac{T_0}{T_0 + T(t')} \right] \right\} \quad (28)$$

Changing the variable of integration to  $u' = t' - t_a$  and denoting  $T(u')/T_0$  by  $y(u')$ , this can be rewritten as:

$$\frac{1}{a_1} = \frac{1}{\Delta t} \int_0^{\Delta t} du' e^{\lambda h(u')} \quad (29)$$

where  $h(u') = 1 - 1/[1 + y(u')]$ . Given  $y(u')$ , this equation allows a determination of  $\lambda$  (or  $\Delta H$ ) from  $a_1$  in principle.

In practice  $\lambda$  can best be found by iteration. Suppose  $\lambda_0$  is a trial value and its difference from the true value  $\lambda$  is relatively small, so that  $\exp[\Delta \lambda h(u')]$  can be approximated by the first order expansion  $1 + \Delta \lambda h(u')$ , where  $\Delta \lambda = \lambda - \lambda_0$ . It then follows from equation (29) that, in this approximation:

$$\lambda = \lambda_0 + \frac{1}{\langle h(u') e^{\lambda_0 h(u')} \rangle} \quad (30)$$

where  $\langle \rangle$  indicates time-averaging over  $u'$  from 0 to  $\Delta t_1$  and generally requires numerical integration. One can therefore obtain an improved value  $\lambda_1$  for  $\lambda$  from  $\lambda_0$ , substitute the former into the right-hand side of equation (30), and repeat the process. When the resultant value  $\lambda'$  becomes highly accurate the second term on the right vanishes (as is expected from equation 29), and the equation reduces to the self-consistency condition  $\lambda = \lambda'$ . In an actual example in which this is carried out the iteration converges very quickly to a final value of  $\lambda$ .

### EXPERIMENTAL

The specimen of isotactic polypropylene (Propathene PXC 8830) was received from Imperial Chemical Industries Ltd in the form of a rod which had been extruded by a process designed to keep voiding to a minimum. Its density at 23°C

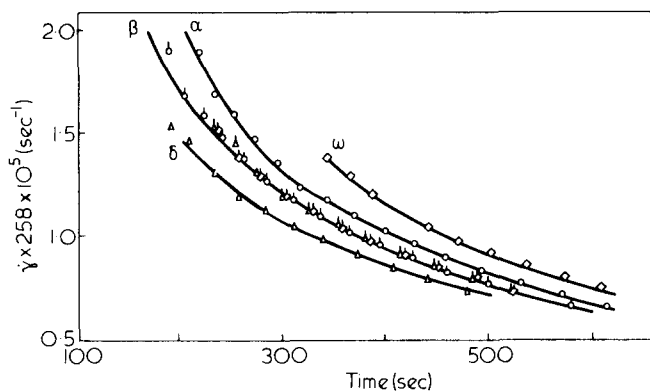


Figure 7 Result of group of double  $T$ -jump experiments: time dependence of  $\dot{\gamma}$  for  $t > t_0$  at 40.0°C for three runs, with temperature pulse ( $\delta$ ,  $\alpha$  and  $\omega$ ) and one without ( $\beta$ ). Solid lines are obtained by method B: the points without vertical pointer give data computed according to method A; the points with vertical pointers give the same data plotted with horizontal shifts along the time axis so as to coincide with the  $\beta$  curve:  $\delta$  shifted by +41.0 sec;  $\alpha$  shifted by -32.2 sec;  $\omega$  shifted by -84.0 sec. The imposed experimental conditions (values of  $\Delta T$ ,  $\Delta t_1$ ) and the derived results ( $\Delta t_0$ ,  $\Delta H$ ) are given in Table 1

was 0.905 g/cm<sup>3</sup>. It was machined into a thin walled tube of dimensions: length 60 mm, internal radius 3.94 mm, wall thickness 0.23 mm.

The tube was thermostatically controlled by a flow of water which passed rapidly both outside and inside the tube. The facility for a fast  $T$ -jump was obtained with equipment similar to that described by Matthews and McCrum<sup>19</sup>. Two baths of deionized water are maintained at  $T_0$  and  $T$ . At the start of the experiment the water in the  $T$  bath is pumped through the cavity surrounding the specimen, and up into a small surge tank from which it falls by gravity into the  $T_0$  bath. At the time of the  $T$ -jump, valves are switched so that the water in the  $T$  bath is pumped into the cavity instead of water from the  $T_0$  bath. The pumps are of high capacity and the water flows at a fast rate through the cavity in plug flow at the time of the  $T$ -jump. Because of the thin wall thickness the specimen comes into thermal equilibrium with the flowing water within one second.

The value of  $\Delta T$  was obtained using three copper-constantan thermocouples in series placed in the cavity close to the specimen. The EMF was displayed on a chart recorder so that the sharpness of the  $T$ -jump was monitored. The thermocouples were calibrated against an accurate mercury and glass thermometer.

There are two time constants controlling the onset of thermal stability after the  $T$ -jump. The first is of order 3 sec and controls 90% of the  $T$ -jump. The second time constant is of far smaller amplitude and about 10 times longer. As an example in one experiment with a final  $\Delta T$  of 2.29°C the recorded values were at times after  $T$ -jump:

$$4 \text{ sec: } \Delta T = 2.16^\circ\text{C}; 30 \text{ sec: } \Delta T = 2.30^\circ\text{C}$$

$$1 \text{ min: } \Delta T = 2.29^\circ\text{C}; 2 \text{ min: } \Delta T = 2.28^\circ\text{C}$$

$$4 \text{ min: } \Delta T = 2.28^\circ\text{C}; 6 \text{ min: } \Delta T = 2.29^\circ\text{C}$$

The first time constant depends on the rate of flow of water, thermal capacity of the pipes and cavity, etc. The main experimental problem is the second and longer time constant. It is caused by the fact that after the  $T$ -jump the return line from the surge tank has to be switched from the  $T_0$  to the  $T$ -bath. A small amount of water enters the  $T$ -bath immediately after the switch at a temperature close to  $T$ . This

slightly perturbs the equilibrium of the  $T$ -bath which takes several tens of seconds to equilibrate. This perturbation was reduced by the following steps:

- (1) retarding the switch of the return flow from the surge tank by a few seconds;
- (2) enlarging the baths to 25 l;
- (3) by pre-heating (or pre-cooling) the  $T$ -bath.

This latter step when performed with finesse, produces an extremely sharp and clean  $T$ -jump. The amount of pre-heating (or pre-cooling) is well below 0.1°C for  $T$ -jumps of the usual size ( $|\Delta T| < 3^\circ\text{C}$ ). The normal temperature fluctuation of the bath at 40° when in equilibrium is  $\pm 0.01^\circ\text{C}$ .

The specimen was mounted in a torsional creep machine<sup>2</sup>. The rotation of the specimen was observed with an optical lever with a throw of 9 m. The time dependence of the deflection of the light spot was observed with a graphisplot. The shear strains were between 0.0015 and 0.0025, within the range of linear viscoelasticity.

## RESULTS

### Double $T$ -jump experiment

The measurements of  $\Delta H$  by both single and double  $T$ -jump were all obtained at 40°C. The specimen was maintained at this temperature for over 100 h before measurements commenced. Apart from the period of the  $T$ -jump, the specimen was kept continuously at 40°C for the duration of the experimental period. Each experiment was complete within 700 sec. The specimen was then left for at least 3 h to recover under zero stress before the next experiment.

If  $x$  is the deflection of the light spot as recorded on the graphisplot chart paper, then it follows that  $\dot{\gamma}(t) \propto \dot{x}(t)$ . Values of  $x(t)$  were obtained from the chart paper and the differentiation performed by two independent methods.

*Method 'A'.*  $\dot{\gamma}(t)$  obtained by local differentiation:

$$\dot{\gamma}(t) \propto \frac{\dot{\gamma}(t + \delta t) - \dot{\gamma}(t - \delta t)}{2\delta t}$$

$\delta t$  being chosen to keep  $\delta\gamma$  approximately constant. The time lag  $\Delta t_0$  is then obtained graphically as described above.

*Method 'B'.* The time dependence of  $\dot{\gamma}$  is fitted by polynomials in  $\ln t$ . The time derivatives are then obtained by analytic differentiation and  $\Delta t_0$  obtained point-by-point. This is done over a range of creep rates. A final value of  $\Delta t_0$  is then obtained by taking a weighted average over the entire range of creep rate. The weight used is the inverse square of the error in  $\Delta t_0$ , as computed from the errors in the coefficients of the polynomials.

Method 'A' is simple in conception and application, and can be easily applied to the entire creep curve with equal certainty, even though it lacks sensitivity. In applying Method 'B' it was found that the creep curves (recorder pen displacement  $\sim 8$ –15 cm, read to 0.01 cm) could be fitted extremely well (usually better than 0.06%) by either third or fourth order polynomials. However, as expected, the fit is less reliable near the ends of the curves. The method can therefore only give values of  $\Delta t_0$  corresponding to the central portion of the creep curves.

Twelve measurements of  $\Delta H$  were obtained, six with positive  $\Delta T$  and six negative. The experiments fell into groups, each group containing one isothermal reference experiment. Results from one group are shown in Figure 7.



**Table 1** Experimental details of a group of double  $T$ -jump experiments at  $T_0 = 40.0^\circ\text{C}$ .  $T$ -jump from  $T_0$  to  $T_1$  ( $\Delta T = T_1 - T_0$ ) for time  $\Delta t_1$ , produces time shift  $\Delta t_0$ . The elapsed time  $t_e$  is the time specimen has been maintained at  $T_0$  (apart from  $T$ -jumps of short duration) prior to the experiment.  $\beta$  is the isothermal reference experiment

Run	$t_e$ (h)	$\Delta T$ ( $^\circ\text{C}$ )	$\Delta T_1$ (sec)	Method 'A'		Method 'B'	
				$\Delta t_0$ (sec)	$\Delta H$ (kcal/mol)	$\Delta t_0$ (sec)	$\Delta H$ (kcal/mol)
$\alpha$	312	-2.62	87.0	32.2	34.1	33.7	36.1
$\beta$	326	0	—	—	—	—	—
$\delta$	333	2.83	61.0	-41.0	35.7	-42.5	36.7
$\omega$	356	-2.93	201.5	84.0	35.5	84.3	35.7

The experimental details for this group are recorded in *Table 1*.

It was found that the data points computed by methods 'A' and 'B' were in excellent agreement; see *Figure 7*. It will be seen also from *Figure 7* that there is no sign of an  $\alpha\Delta T$  perturbation at short times after  $t_b$  of the type illustrated in *Figure 4*. No systematic departures at short times of the type shown in *Figure 4* were observed in any of the experiments. We conclude that under the conditions of our experiment the data excluded for experimental reasons (region  $uv'$ , *Figure 1b*) include the data perturbed by the  $\alpha\Delta T$  term.

The mean value of  $\Delta H$  for both positive and negative values of  $\Delta T$  computed by methods 'A' and 'B' from the twelve experiments is:

$$\Delta H = 34.7 \pm 0.3 \text{ kcal/mol}$$

There were small systematic differences observed between values computed for positive and negative values of  $\Delta T$ .

The mean values of  $\Delta H$  for positive  $\Delta T$  were:

$$\Delta H(+,A) = 35.4 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H(+,B) = 35.3 \pm 0.3 \text{ kcal/mol}$$

and for negative  $\Delta T$ :

$$\Delta H(-,A) = 33.4 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H(-,B) = 34.8 \pm 0.4 \text{ kcal/mol}$$

A 'Students'  $-t$  analysis of the data shows that the differences:

$$\Delta H(+,A) - \Delta H(-,A) = 2.0 \pm 0.6 \text{ kcal/mol}$$

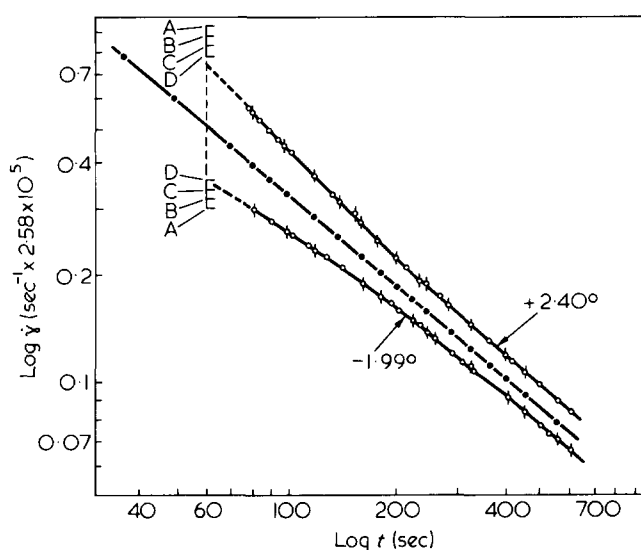
$$\Delta H(+,B) - \Delta H(-,B) = 0.5 \pm 0.5 \text{ kcal/mol}$$

are statistically significant. The mean of the  $+\Delta T$  values from methods 'A' and 'B' differ by 0.1 kcal/mol, a difference which is not statistically significant. This is not so for  $-\Delta T$ :

$$\Delta H(-,B) - \Delta H(-,A) = 1.4 \pm 0.7 \text{ kcal/mol}$$

'Students'  $-t$  analysis shows this difference to be statistically significant. The likely origin of this small difference is described in the Discussion.

It will be noticed that the errors (standard deviation over square root of number of observations) are greater for negative  $\Delta T$  than positive. This is due to the fact, as may be seen from equation (10), that positive values of  $\Delta T$  lead to



**Figure 8** Result of group of single  $T$ -jump experiments showing dependence of  $\log \dot{\gamma}$  on  $\log t$ :  $\bullet$ —, isothermal at  $T_0 = 40.0^\circ\text{C}$ ; the other two curves are for  $\Delta T = +2.40$  and  $\Delta T = -1.99^\circ\text{C}$  applied at  $t_a = 60$  sec:  $\circ$ , data computed according to method A;  $\circ$ , data computed according to method B. Values of  $\log \dot{\gamma}$  for  $t < 60$  sec for the two  $T$ -jump experiments are not plotted since they coincide with the isothermal data. The derived values of  $\Delta H$  are 30.4 kcal/mol ( $+2.40^\circ\text{C}$ ) and 35.6 kcal/mol ( $-1.99^\circ\text{C}$ ).  $\Delta H$  (kcal/mol): A, 50; B, 45; C, 40; D, 35

larger time shifts than negative values of  $\Delta T$  (note *Figure 4*). For negative  $\Delta T$  the time shift  $\Delta t_0$  can at most equal  $\Delta t_1$ . For positive  $\Delta T$  the time shift can exceed  $\Delta t_1$  for values of  $\Delta T > 4^\circ\text{C}$ .

#### Single $T$ -jump experiment

In order to compare the double  $T$ -jump with the single  $T$ -jump experiments, two groups of single  $T$ -jump experiments were performed at  $T_0 = 40.0^\circ\text{C}$ . Three experiments were performed in each group: a creep curve at  $40.0^\circ\text{C}$  without  $T$ -jump and two  $T$ -jump experiments, one with positive and the other negative  $\Delta T$ .

Values of  $\dot{\gamma}_0(t)$  and  $\dot{\gamma}(t)$  were computed according to methods 'A' and 'B'. *Figure 8* shows the isothermal data for  $T_0 = 40.0^\circ\text{C}$  and data for  $t > 60$  sec for values of  $\Delta T = 2.40^\circ\text{C}$  and  $\Delta T = -1.99^\circ\text{C}$ . The data computed according to methods 'A' and 'B' were in good agreement. The best extrapolation of  $\dot{\gamma}(t)$  back to  $t_a = 60$  sec came from method 'B' and yielded values of  $\Delta H = 30.4$  kcal/mol ( $+2.40^\circ\text{C}$ ) and  $\Delta H = 35.6$  kcal/mol ( $-1.99^\circ\text{C}$ ). The second group of single  $T$ -jump experiments yielded  $\Delta H = 29.7$  kcal/mol ( $+2.01^\circ\text{C}$ ) and  $\Delta H = 32.4$  kcal/mol ( $-2.13^\circ\text{C}$ ). The mean value of all four experiments is 32.0 kcal/mol. A discussion of these

values with those from the double  $T$ -jump experiment will be found below.

## DISCUSSION

There are three topics which will be examined. In greatest detail, the effect of the  $\alpha\Delta T$  perturbation on the observed values of  $\Delta H$  by both double and single  $T$ -jump. This is the primary purpose of the paper. In less detail we discuss the classical hypothesis that  $\Delta H$  is constant for all elements in the retardation spectrum. The experiments were not designed to test this hypothesis. However, the small but statistically significant discrepancies between the positive and negative double  $T$ -jump experiments bring it into question. Finally we discuss a hypothesis basic to the theory of thermo-viscoelasticity<sup>18,6,3</sup> which may be stated thus: after a  $T$ -jump  $J_U(T)$ ,  $J_R(T)$  and  $\phi(\ln\tau)$  take up values which are functions of  $T$  alone and independent of  $t_e$ , the elapsed time at  $T$ .

### The $\Delta H$ hypothesis

The hypothesis that  $\Delta H$  is constant for all elements in the distribution of retardation times, is not necessarily particularly restrictive. For example consider a temperature of 40°C and assume the observed  $\Delta H = 34.5$  kcal/mol. Consideration of the measurements of the imaginary part of the dynamic compliance at  $\sim 1$  Hz for polypropylene due to Passaglia and Martin<sup>20</sup>, shows that the retardation spectrum is distributed approximately as follows at 40°C: shortest retardation time  $10^{-1}$  sec: retardation time of the maximum at the centre of the relaxation,  $10^5$  sec. The low frequency half of the relaxation is thus six decades wide. Now at a temperature of 40°C and at a creep time of  $t = 100$  sec retardation times in the region of 10 to  $10^3$  sec alone contribute significantly to  $\dot{\gamma}$ . Thus the hypothesis  $\Delta H$  constant for data taken at 40°C at  $t = 100$  sec, implies that  $\Delta H$  is effectively constant (i.e. to within the error of the experiment to be interpreted) for the retardation times of interest: for those between 10 and  $10^3$  sec and not for the whole spectrum.

In general it is correct to accept a widely used hypothesis over an alternative, other things being equal. The reason is that being widely used it might be thought to be widely tested. This is not so in the case of the hypothesis  $\Delta H$  a constant for all elements of the retardation spectrum. The precision of measurement in the past has been so poor that its validity is essentially untested.

What of the alternative, that  $\Delta H$  varies and  $\tau_\infty$  (value of  $\tau$  at  $T^{-1} = 0$ ) is constant? (We leave for the present the most physically realistic but more complicated hypothesis of Zener<sup>21</sup>, that both  $\Delta H$  and  $\tau_\infty$  differ for each element.) Consider the retardation time  $\tau = 10^2$  sec at 40°C and let its value of  $\Delta H = 34.5$  kcal/mol: if the value of  $\tau_\infty$  holds for all elements in the distribution of retardation times, it then follows from simple graphical analysis that for the retardation time  $\tau = 10$  sec at 40°C,  $\Delta H = 32.9$  kcal/mol and for  $\tau = 10^3$  sec at 40°C,  $\Delta H = 35.8$  kcal/mol. It will be seen that at 40°C in the region of  $\tau = 10^2$  sec the predicted change in  $\Delta H$  is of the order 1.5 kcal/mol per decade.

For imprecise experimentation this change is without significance and would not noticeably perturb the result. However, our experiments and in particular the double  $T$ -jump experiment, are on the verge of a precision sufficient to observe such small changes. Because of this it is necessary to consider the possibility that  $\Delta H$  is not, in fact, constant. This follows because the positive and negative  $T$ -jumps

sample the retardation times in a slightly different manner. For instance for  $(t - t_b) = 40$  sec the  $\Delta T = +3^\circ$  experiment samples retardation times centred in the region of 300 sec whereas for the same value of  $(t - t_b)$  the sampling of the  $\Delta T = -3^\circ$  experiment is near 100 sec, approximately half a decade apart. According to the above estimate, this could result in a difference in  $\Delta H \sim 3/4$  kcal/mol. The  $\Delta H$  from the  $-\Delta T$  experiment would be the lower by a quantity of this order. The evidence from the double  $T$ -jump experiment supports to some extent this result. The values of  $\Delta H$  obtained from negative temperature jumps are lower than the values obtained from positive jumps. This conclusion will be rigorously tested in further experimentation using the double  $T$ -jump technique in which  $\Delta H$  will be determined at temperatures in the region 30° to 80°C.

### The $\alpha\Delta T$ perturbation: theoretical aspects

The main theoretical result [equation (19) or equivalently equation (24)] and its applications to the determination of  $\Delta H$  have been obtained on the assumption that the remainder term  $R_0$  is negligible. This has been shown to be true for the simple model discussed above. We would now examine this assumption more systematically and in greater detail.

Let us start with a feature common to all three applications of the theory. That is,  $\dot{\gamma}(t)$  is of interest at time  $t$  later than a certain moment  $t_f$ , when the temperature is held at a constant value  $T_f$  (which may or may not equal  $T_0$ ), such that  $\dot{T}(t) = 0$ ,  $\dot{c}(t) = 0$ ,  $b(t) = b_f$ ,  $a(t) = a_f$  for  $t \geq t_f$ . Part of the integration over  $v$  in equation (21) can then be carried out, and  $R_0$  becomes:

$$R_0 = \frac{1}{a_f} \int d(\ln\tau) \frac{\phi_0(\ln\tau)}{\tau} \left\{ (b_f - 1) \exp\left(-\frac{t'}{a_f\tau}\right) - \int_0^{t_f} dv [b(v) - 1] \frac{d}{dv} \exp\left[-\frac{1}{\tau} \left[ \frac{t'}{a_f} + \int_v^{t_f} \frac{du}{a(u)} \right] \right] \right\} \quad (31)$$

where  $t' = t - t_f$ .

In case of the single  $T$ -jump experiment  $b(v) = 1$  for  $v \leq t_f$  such that the second term on the right of 31 vanishes and so from 24 and 25 we obtain the following fractional error  $\delta_{SJ}$  for neglecting the remainder term  $R_0$  (here denoted as  $R_{SJ}$ ):

$$\delta_{SJ} \equiv \left| \frac{R_{SJ}}{\dot{\gamma}_{SJ}/\sigma\Delta J_0} \right| = (b_f - 1) \frac{f_0\left(\frac{t'}{a_f}\right)}{f_0\left(t_a + \frac{t'}{a_f}\right)} \quad (32)$$

Similarly, for the double  $T$ -jump experiment  $b_f = a_f = 1$ , and  $b(v) = b_1$ ,  $a(v) = a_1$  for the period  $t_a < v < t_a + \Delta t$ . The integrals in equation (31) over  $u$  and  $v$  can be easily carried out, resulting in the following fractional error  $\delta_{DJ}$  for neglecting  $R_0$ :

$$\delta_{DJ} \equiv \left| \frac{R_{DJ}}{\dot{\gamma}_{DJ}/\sigma\Delta J_0} \right| = (b_1 - 1) \frac{f_0(t') - f_0\left(t' + \frac{\Delta t}{a_1}\right)}{f_0\left(t' + t_a + \frac{\Delta t}{a_1}\right)} \quad (33)$$

In case the temperature increase  $\Delta T$  imposed in the interval  $(t_a, t_a + \Delta t)$  is not constant in time, it can be shown that equation (33) still applies, except that  $b_1 \rightarrow \max b(v)$  for  $t_a \leq v \leq t_a + t$ , and

$$a_1^{-1} \rightarrow \int_a^{t_a + \Delta t} [\Delta t a(u)]^{-1} du$$

Since  $f_0$  is a superposition of exponential decay functions the ratio  $f_0(q)/f_0(q + q_1)$  appearing in equations (32) and (33) would tend to 1 as  $q \rightarrow \infty$ , and so from these equations it is seen that for large  $t' = t - t_f$  the error in neglecting  $R_0$  is mainly of the order  $b - 1$ , i.e. less than 1% for  $\Delta T$  equal to a few degrees. As a matter of fact, in case  $T_f = T_0$  ( $\Delta T$  may or may not be time dependent) equation (33) shows that  $\delta_{DJ} \rightarrow 0$  as  $t' \rightarrow \infty$ , when  $f_0(t') \rightarrow f_0(t' + \Delta t/a_1)$ . In other words, the effect of the  $R_0$  term eventually disappears completely in case of the double  $T$ -jump experiment and also the arbitrary temperature pulse experiment. This does not detract from the fact that immediately after the termination of temperature variation, i.e. at  $t' \simeq 0$  the  $R_0$  term has a very large effect, because  $\phi_0(\ln \tau)$  has a great deal of short decay time components and  $f_0(0) = \int d(\ln \tau) \phi_0(\ln \tau) / \tau$  is very large when compared to  $f_0(t_a)$ . It is therefore of much practical interest to make an estimate of the time interval it takes for  $R_0$  to become negligible. As shown in Appendix 2 this in general happens at  $t'_c \simeq 0.3 a_f t_a$  and  $0.3 [t_a + (\Delta t/a_1)]$  for the single- and double- $T$  (as well as pulse) jump experiments, respectively. If previous parameters are used, then numerical values for  $t'_c$  are of the order 20–40 sec, in agreement with the estimates made in the Theory above. In more general terms, it is seen that the use of equations (19) or (24) is valid when  $t'$  is of the same order of magnitude as  $t_f$ , the precise value depending on the accuracy desired.

Finally, the  $R_0$  term can also be estimated in the most general case. Transforming the integral over  $v$  in equation (21) by integration by parts, interchanging the order of integration in  $\ln \tau$  and  $v$ , making use of the defining equations (20) and (22), one can rewrite  $R_0$  as follows:

$$R_0 = \frac{J_U(0)}{\Delta J_0} \dot{c}(t) + \frac{1}{a(t)} \int_0^t dv b(v) f_0 \left[ \frac{t}{A(t)} - \frac{v}{A(v)} \right] \quad (34)$$

The first term does not need much comment: it clearly depends on the rate of temperature change at  $t$ . Upon application of the mean-value theorem for integrals, the second term can be written as:

$$[b(t) - 1] f_0 \left[ \frac{t}{A(t)} - \frac{v_a}{A(v_a)} \right] / a(t)$$

where  $v_a$  is a certain average value of  $v$  satisfying  $0 < v_a < t$ . Using our previous notation, the ratio of this term to  $\dot{\gamma}(t) / \sigma \Delta J_0$  is:

$$\delta = [b(t) - 1] \frac{f_0 \left[ \frac{t}{A(t)} - \frac{v_a}{A(v_a)} \right]}{f_0 \left[ \frac{t}{A(t)} \right]} \quad (35)$$

$\delta$  would be of the same order as  $b(t) - 1$  unless  $v_a$  is very close to  $t$ , resulting in a very large factor  $f_0(0)/f_0[t/A(At)]$  on the right. But that would happen only if  $b(v)$  is very large (that is, there is an extremely large temperature change) at a time close to  $t$ . Thus, in conclusion, the  $R_0$  term is negligible and our expression 24 for  $\dot{\gamma}(t)$  is valid in general except immediately after extreme temperature variations, which can be regarded as a natural extension to the results on  $\delta_{SJ}$  and  $\delta_{DJ}$ .

#### The $\alpha \Delta T$ perturbation: experimental aspects

It was anticipated that any  $\alpha \Delta T$  perturbation would: (1) increase the observed  $\Delta H$  above the true value; (2) be more troublesome in the positive  $\Delta T$  experiment than in the negative (see Figure 4). It might then be argued that a small  $\alpha \Delta T$  perturbation exists, that it is not detected by eye during the graphical analysis of method 'A' and that it perturbs the positive  $\Delta T$  values making them slightly larger than the negative.

This argument is difficult to reject entirely, but we find it less persuasive than the alternatives. These are: (1) that a small difference in  $\Delta H$  exists (as argued in the discussion above); (2) that when the time shift  $\Delta t_0$  is measured in methods 'A' and 'B' the eye and computer weight the data differently and in a systematic way. In experiment  $\alpha$  (Table 1) a misreading of  $\Delta t_0$  by only 1 sec causes an error in  $\Delta H$  of 1.3 kcal/mol. The extent of the systematic difference in the time shift observation between methods 'A' and 'B' required to explain the low value of  $\Delta H(-, A)$  is thus quite small. It could conceivably be due to the eye giving slightly more weight to the data from the shorter retardation times which are dominant at small values of  $(t - t_b)$  and which by the arguments of the previous section could have slightly lower  $\Delta H$ . This is a matter which will be decided by further experiment.

That no  $\alpha \Delta T$  perturbation was ever observed in double  $T$ -jump is fairly certain: we cannot be so sure this is so for single  $T$ -jump. In single  $T$ -jump the effect of  $\alpha \Delta T$  perturbation is to enhance a curvature in the  $\log \dot{\gamma}$  versus  $\log t$  plot, a curvature that already exists for the curve  $\alpha \Delta T = 0$  (see Figures 2 and 3). Nevertheless the fact that the measured values in single  $T$ -jump,  $\Delta H = 32.0$  kcal/mol were slightly lower than the double jump values, is strong evidence that the single jump data is unperturbed.

The small systematic difference between the  $\Delta H$  values from double jump and single jump experiments, is probably due mainly to errors arising in the extrapolation procedure in the single jump analysis. In our experience the computer extrapolation is to be preferred to a graphical extrapolation. Nevertheless, the computer fit to the data is least satisfactory at the two ends of the recorded set of data points. The reliability of the extrapolation is particularly sensitive to the fit to the data points at the shortest times after the  $T$ -jump.

There is also the possibility that the difference could be due to a variation of  $\Delta H$  with retardation time. The imposed conditions of the single jump experiments placed the dominant retardation times lower than in the double jump experiments.

#### The elapsed time effect

The effect is well-known in amorphous<sup>22-24</sup> and semi-crystalline polymers and has been observed in measurements of specific volume and mechanical properties. Most study has been centred in the region of the glass transition by dilatometry where the effects are greatest. The usual ex-

perimental procedure is to quench from above  $T_g$  to  $T$  below  $T_g$  and to follow the isothermal volume contraction at  $T$ . Large elapsed time effects are observed which give rise to changes in both volume and viscoelastic properties. In the glass transition region of a semicrystalline polymer analogous volumetric effects are anticipated and have been observed by Davis and Eby<sup>28</sup>. But at temperatures well removed from  $T_g$  in polypropylene, Struik has observed that quenching from 120°C produces large changes in compliance at 20°C as a function of  $t_e$  at 20°C: (the  $T_g$  of polypropylene is -15°C). Now it is possible that this effect is due in some degree to a minute amount of recrystallization, considering the proximity of 120°C to the annealing temperature of the specimen 135°C and the melting point. The effect has been confirmed at temperatures where recrystallization is unlikely<sup>30</sup> (for instance quenching from 60° to 40°C). In linear polyethylene large elapsed time effects are observed at temperatures down to -190°C being particularly intense in the viscoelastic relaxation regions<sup>26,27</sup>.

In the design of our experiments we have sought to minimize and detect any possible elapsed time effect in the following way. First, the specimen of polypropylene was annealed at 130°C, slow-cooled, thermally cycled between 20° and 80°C and then maintained at 40°C for 100 h before measurements commenced. Second, the  $T$ -jumps were of small magnitude, less than 5°C, and mostly in the region of 3°C. Third, elapsed time effects are likely to be entirely different in single and double  $T$ -jump. The double  $T$ -jump in particular is particularly well designed to be exempt. Fourth, the effects of both positive and negative values of  $\Delta T$  were observed. It will be seen from the Experimental that in the double  $T$ -jump experiments the systematic differences between the positive and negative  $\Delta T$  values of  $\Delta H$  were of order 4%. Now if an elapsed time effect seriously perturbed the experiment it is most unlikely that the perturbation would have the same sign for positive and negative  $\Delta T$ . If it were argued that this systematic difference of 4% were due to elapsed time effect then it would in any case be a small effect. In our view it is more likely that the difference is due to a small variation of  $\Delta H$  with  $\tau$ , as argued in this section. The conclusion therefore is that the dominant effect of the  $T$ -jump is the temperature induced Arrhenius shift and that the analysis used in deriving the theory is not vitiated by elapsed time effects on  $J_U(T)$ ,  $J_R(T)$  or  $\phi(\ln\tau)$ .

## CONCLUSIONS

The single and double  $T$ -jump techniques have been shown to be unperturbed by systematic errors which arise in other techniques due to the temperature dependence of the limiting compliances. The values of  $\Delta H$  obtained by the two techniques are in good agreement. The precision of the double  $T$ -jump technique is such that small variations in  $\Delta H$  with retardation time may be detected.

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## APPENDIX 1

### Distribution function of relaxation times

The curve of creep  $\gamma(t)$  at constant temperature could be fitted by a polynomial in  $\ln t$  to very high accuracy:

$$\frac{\gamma(t)}{\sigma\Delta J} = \sum_{n=1}^N a_n (\ln t)^{n-1} \quad (\text{A1})$$

For a time span of  $10^2 - 3 \times 10^4$  sec the order of fit  $N - 1$  is usually chosen to be between 2 and 4 for best results, for which the deviation of data from fit would be well within 0.1% except near the ends of the curve, where the deviation rises to 0.1 to 0.3%. Differentiating equation (A1) we obtain  $\dot{\gamma}_0/\sigma\Delta J_0$ , or  $f_0$ :

$$f_0(t) = \sum_{n=2}^N (n-1)a_n \frac{(\ln t)^{n-2}}{t} \quad (\text{A2})$$

Comparing this with equation (23) we see that the distribution function  $\phi_0(k)$  is simply the inverse Laplace transform of the series on the right of equation (A2). This could be carried out very easily, since it is known<sup>†</sup> that the Laplace transform of  $(\ln k)^m$  is precisely a series of the form equation (A2), with its own characteristic coefficients. Simple algebra leads to the following general formulae, where  $L^{-1}$  indicates inverse Laplace transform:

$$\begin{aligned} L^{-1} \frac{1}{t} &= 1 \\ L^{-1} \left( \frac{\ln t}{t} \right) &= -(C + \ln k) \\ L^{-1} \left[ \frac{(\ln t)^2}{t} \right] &= C^2 - \frac{\pi^2}{6} + 2C \ln k + (\ln k)^2 \\ L^{-1} \left[ \frac{(\ln t)^3}{t} \right] &= \psi_2 + C \left( \frac{\pi^2}{2} - C^2 \right) + \left( \frac{\pi^2}{2} - 3C^2 \right) \ln k \\ &\quad - 3C(\ln k)^2 - (\ln k)^3 \end{aligned} \quad (\text{A3})$$

where  $C$  is the Euler number and  $\psi_2$  the second derivative of the Euler function evaluated at 1, i.e.  $\psi''(1)$ :

$$\begin{aligned} C &\equiv \lim_{s \rightarrow \infty} s \cdot \left( \sum_{m=1}^s \frac{1}{m} - \ln s \right) \sim 0.577215 \\ \psi_2 &\equiv -2 \sum_{n=1}^{\infty} \frac{1}{n^3} \sim -2.402 \end{aligned}$$

Thus equations (23), (A2) and (A3) combine to give the following result for the distribution function, where we have reintroduced  $\tau = 1/k$  as the variable:

<sup>†</sup> I. S. Gradshteyn and I. M. Ryzlik: *Tables of Integrals, Series and Products* (Academic Press, London, 1965), p 573-576 and p 943

$$\phi_0(\ln\tau) = \sum_{n=1}^{N-1} c_n(\ln\tau)^{n-1} \quad (\text{A4})$$

The coefficients  $c_n$  of the first few terms are related to  $a_n$  in the original series, equation (A1), (for  $N$  up to 5) as follows:

$$\begin{aligned} c_1 &= a_2 - 2Ca_3 + 3\left(C^2 - \frac{\pi^2}{6}\right)a_4 + 4\left[\psi_2 + C\left(\frac{\pi^2}{2} - C^2\right)\right]a_5 \\ c_2 &= 2a_3 - 6Ca_4 - 4\left(\frac{\pi^2}{2} - 3C^2\right)a_5 \\ c_3 &= 3a_4 - 12Ca_5 \\ c_4 &= 4a_5 \end{aligned} \quad (\text{A5})$$

It should be emphasized that equation (A1) is only valid over the specific time interval, say  $(t_1, t_2)$ , in which it has been fitted to data. Similarly, we expect the distribution function  $\phi_0(\ln\tau)$  derived from the fit (i.e. equations (A4) and (A5)) to be correct only in approximately the same interval, i.e. for  $\tau$  in  $(t_1, t_2)$ . An actual example for creep data fitted over the interval  $t = 5$  to 3000 sec shows that  $\phi_0(\ln\tau)$  for PP at 42.5°C is extremely flat over this region, implying an almost equal distribution of relaxation, but with a slight monotonic increase towards the long time region.

## APPENDIX 2

### The decay time for the $b-1$ effect

To obtain an estimate for the time it takes for the  $b-1$  effect to become negligible, we first look at the monotonically decreasing ratio  $f_0(w)/f_0(w+w_0)$  and confine ourselves to the time interval for which the parametrization, equation (A1), is valid. From equation (A2) we have:

$$\begin{aligned} \frac{f_0(w)}{f_0(w+w_0)} &= \left(1 + \frac{w_0}{w}\right) \frac{F(w)}{F(w+w_0)} \\ &\leq \left(1 + \frac{w_0}{w}\right) \eta \end{aligned} \quad (\text{B1})$$

where  $F(w)$  is the polynomial:

$$\sum_{n=2}^{N-1} (n-1)a_n(\ln w)^{n-2}$$

and  $\eta = \max F/\min F$  over the time-interval concerned. For the example quoted in Appendix 1 the coefficients  $a_n$  are all positive, such that  $F(w+w_0) > F(w)$  and one can simply set  $\eta = 1$ . In general we expect  $\phi_0$  to be a rather flat distribution and  $\eta$  to be of order 1.

Combining equations (32) and (B1) (with  $w_0 = t_a$ ,  $w = t'/a_f$ ) we see that  $\delta_{DJ}$  would be approximately  $1.3(b_f - 1)$  or less than 1% for  $t' > 0.3a_f t_a$ . In case of the double  $T$ -jump experiment there are two terms in the numerator of equation (33), but since  $f_0(t')$  always  $> f_0[t' + \Delta t/a_1]$

clearly  $\delta_{DJ} < (b_1 - 1)f_0(t')/f_0(t' + t_a + \Delta t/a_1)$ , and we can again apply equation (B1) to it, with  $w = t'$  and  $w_0 = t_a + \Delta t/a_1$ , leading to the condition that the  $R_0$  term is negligible, i.e.  $\delta_{DJ} \leq 1.3(b_1 - 1)$ , if  $t' > 0.3(t_a + \Delta t/a_1)$ . The case of the arbitrary temperature pulse experiment yields the same result, except that  $a_1^{-1}$  must be interpreted as the time-averaged inverse shift factor given by 29 and  $b_1 - 1$  as the maximum value of  $b(t) - 1$  within the duration of the temperature pulse. When typical experimental values are substituted into these conditions, it is found that in practice they present no additional experimental problem at all, since one usually would have to wait a certain period after a sharp temperature change before temperature stabilizes and creep data become useful, and this already imposes the same (if not more stringent) conditions on  $t'$ .

It is also possible to obtain a condition analogous to equation (B1) for a more general distribution function  $\phi_0(\ln\tau)$ , without the need of explicitly using an experimental parametrization, but since this leads to essentially the same result while involving a great deal more mathematical manipulation, we do not feel it worthwhile to go into details.

## REFERENCES

- 1 Leaderman, H. in 'Elastic and creep properties of filamentous materials and other high polymers', Washington, D. C., Textile Foundation, 1943
- 2 McCrum, N. G. and Morris, E. L. *Proc. Roy. Soc. (A)* 1964, **281**, 258
- 3 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967
- 4 McCrum, N. G. and Morris, E. L. *Proc. Roy. Soc. (A)* 1966, **292**, 506
- 5 Tietz, T. E. and Dorn, T. E. *Trans. Am. Inst. Min. Met. Eng.* 1956, **206**, 156
- 6 McCrum, N. G. and Morris, E. L. *Phil. Mag.* 1962, **7**, 2115
- 7 McCrum, N. G. and Pearce, D. L. *Nature (Phys. Sci.)* 1973, **243**, 52
- 8 Hutchinson, J. M., McCrum, N. G. and Pearce, D. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1974, **12**, 1255
- 9 Cohen, R. E., Hooley, C. J. and McCrum, N. G. *Biomechanics* 1976, **9**, 175
- 10 Sherby, O. and Dorn, J. J. *Mech. Phys. Solids* 1958, **6**, 145
- 11 Hooley, C. J., Caruthers, J. M. and Cohen, R. E. *Rheol. Acta* 1977, **16**, 69
- 12 Caruthers, J. M. and Cohen, R. E. *J. Polym. Sci.* 1976, **14**, 1891
- 13 Caruthers, J. M. and Cohen, R. E. *Polym. Eng. Sci.* 1976, **16**, 41
- 14 Caruthers, J. M. and Cohen, R. E. *Rubber Chem. Technol.* 1978, **51**, 335
- 15 Hutchinson, J. M. and McCrum, N. G. *Nature (Phys. Sci.)* 1972, **236**, 115
- 16 Hutchinson, J. M., McCrum, N. G., Pearce, D. L. and Matthews, J. F. *Plast. Polym.* April 1974, p 76
- 17 McCrum, N. G. and Pizzoli, M. *J. Mater. Sci.* 1977, **12**, 1920
- 18 Hopkins, I. L. *J. Polym. Sci.* 1958, **28**, 633
- 19 Matthews, J. F. and McCrum, N. G. *J. Phys. (E)* 1973, **6**, 583
- 20 Passaglia, E. and Martin, G. M. *J. Res. Nat. Bur. Stand.* 1964, **68**, 519
- 21 Zener, C. in 'Imperfections in Nearly Perfect Crystals', (Ed. W. Shockley) Wiley, New York, 1952, p 289
- 22 Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* 1964, **3**, 394
- 23 Struik, L. C. E. *Rheol. Acta.* 1966, **5**, 303
- 24 Struik, L. C. E. TNO Centraal Laboratorium Communication No 565, Delft, 1977
- 25 McCrum, N. G. *J. Polym. Sci.* 1961, **54**, 561
- 26 Cooper, J. W. and McCrum, N. G. *J. Mater. Sci.* 1972, **7**, 1221
- 27 Cooper, J. W. and McCrum, N. G. 'Advances in Polymer Science and Engineering' (Eds K. D. Pae et al.), Plenum Press, New York, 1972
- 28 Davis, G. T. and Eby, R. K. *J. Appl. Phys.* 1973, **44**, 4274
- 29 Bucknall, C. B. and Hutchinson, J. M. in press
- 30 Chai, C. K. and McCrum, N. G. to be published

NOTE ADDED IN PROOF

See also the recent paper of C. J. Hooley and R. E. Cohen (*Rheol. Acta* 1979, **17**, 538) who reach similar conclusions to those found here regarding the  $\delta_{DJ}$  effect in single  $T$ -jump.