Thermal Activation Relations

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A material is considered which has one or more thermally activated linear response functions that obey Boltzmann statistics to good approximation. These response functions may, for example, be mechanical or dielectric relaxation times, diffusion coefficient, viscosity, etc. Neither the entropy change, ΔS, nor the enthalpy change, ΔH, in the activation process need be temperature-independent. An expression for ΔG, the Gibbs free-energy change in the thermally activated process, is considered which applies to a system with a nonzero or zero glass transition temperature, T_g, and allows the product $c_1^g c_2^g$ of the WLF polymer equation to be interpreted and its variation with material explained by an activation energy model. Explicit expressions for the resulting temperature-dependent ΔS and ΔH are given which involve the material parameter E; this is the enthalpy and activation energy of the process only when $T_g = 0$ and thus an Arrhenius equation applies. The results pertain to mechanical and dielectric dispersion experiments on amorphous polymers and other glass-forming materials. In addition, they apply to such processes as diffusion by a vacancy mechanism, to viscous flow, and, when $T_g = 0$, to intrinsic semiconduction and many other processes. It is found that the Lawson–Keyes relation, $\Delta S/\Delta H \simeq 4\alpha$, should not be applied when $T_g \neq 0$ and may be very inaccurate even in the case where $T_g = 0$. An improved relation between ΔS and ΔH which holds for $T_g = 0$ is presented; it furnishes a possible explanation for the negative value of ΔS sometimes found experimentally. An expression for ΔG correct to first order in pressure and temperature is given which applies to all situations where an Arrhenius equation is found. On identifying the semiconductor energy gap for thermal activation as a Gibbs free energy difference, the results are illustrated by analyzing pressure and temperature data pertaining to intrinsic semiconduction in Si and Ge. Experimental dielectric dispersion results for isoamyl bromide ($T_g \neq 0$) are also analyzed and compared with results of previous work. Finally, temperature-dependent aspects of the transient and frequency response of a distributed, linear activated system with $T_g \neq 0$ are examined when either the pre-exponential factor or the activation parameter E is distributed, or when they are simultaneously distributed and are linearly related.

INTRODUCTION

THERE is a considerable and growing body of evidence which indicates that for many thermally activated mechanical[1-4] or electrical[5] processes in solids and liquids the ratio of entropy and enthalpy of activation, $\Delta S/\Delta H$, is approximately a temperature-independent material parameter, of order $10^{-3}(°K)^{-1}$. Such a result follows from the diffusion theory of Wert and Zener,[6] and Keyes[4] showed empirically that $\Delta S/\Delta H \simeq 4\alpha$, where α is the isobaric coefficient of thermal volume expansion. A considerable body of polymer mechanical relaxation results has been shown by Eby[1] to lead to excellent agreement with the above relation.

Alternatively, the author[7] showed that if ΔG, the work required for a transition from minimum to maximum Gibbs free energy in surmounting a potential barrier, is written as the following physically reasonable function of temperature:

$$\Delta G = E[1 - (T/T_0)], \qquad (1)$$

then $\Delta H = E$, $\Delta S = E/T_0$, and $\Delta S/\Delta H = T_0^{-1}$. Here, the activation energy E is temperature-independent, and

(1) is the only type of temperature dependence for ΔG which leads to the usual situation of temperature-independent ΔH and ΔS. These results were later used in a theory of the transient and temperature response of a distributed, linear, thermally activated system.[8] They may only be expected to apply within a temperature range where there is no phase change. Certain further consequences of ΔG's of the type of (1) are discussed later in the paper.

The above form of ΔG leads to an Arrhenius equation for processes such as self diffusion in solids, viscosity of liquids, and mechanical or dielectric dispersion. When there are several different dispersion processes exhibiting Arrhenius behavior within the temperature range of interest, each may involve different values of E and T_0. When, however, the process is primarily associated with the underlying pure material and not with potential barriers associated with such impurities and other defects as occur in thermal activation of electrons to the conduction band from donors in semiconductors, then T_0 may be expected to be around or above the maximum temperature of the phase, for example, the boiling point in liquids or the melting temperature, T_m, for solids.

Diffusion data for solids suggest that $T_0 > T_m$. In fact, when T_0^{-1} is set equal to 4α and the relation $\alpha T_m \simeq 0.06$, appropriate to metals and ionic compounds,[9] is used,[4]

[1] R. K. Eby, J. Chem. Phys. **37**, 2785 (1962).
[2] A. W. Lawson, J. Chem. Phys. **32**, 131 (1960).
[3] A. W. Lawson, J. Phys. Chem. Solids **3**, 250 (1957).
[4] R. W. Keyes, J. Chem. Phys. **29**, 467 (1958).
[5] K. Higasi, *Dielectric Relaxation and Molecular Structure* (Monograph No. 9, Research Institute of Applied Electricity, Hokkaido University, Sapporo, Japan, 1961), Chap. II.
[6] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).
[7] J. R. Macdonald, Physica **28**, 485 (1962). See also G. H. Vineyard and G. J. Dienes, Phys. Rev. **93**, 265 (1954).
[8] J. R. Macdonald, J. Appl. Phys. **34**, 538 (1963).
[9] C. Zwikker, *Physical Properties of Solid Materials* (Interscience Publishers, Inc., New York, 1954), p. 158.

one finds $T_0 \simeq 4.2 T_m$. Generally, smaller values than 4.2 are obtained if T_0 is related to the temperature coefficient of the shear modulus of metals, as in the theory of Wert and Zener.[6,10] Finally, Eby[1] has shown empirically that for certain polymers $T_0 \sim T_m$.

Since ΔH and ΔS are not always temperature independent, it is of interest to investigate the consequences of a more general form for ΔG which is closely related to and sheds light on the Williams–Landel–Ferry (WLF) equation,[11] which applies to a wide variety of mechanical and dielectric dispersion measurements on polymers.[11,12] The results apply, as well, to inorganic glasses[10] and to organic liquids which form glasses at low temperatures.[13,14] Methods of analyzing data for materials with glass transitions are discussed and illustrated, and a generalization is given of earlier work[8] on the response of distributed systems.

THERMODYNAMIC QUANTITIES

The specific ΔG to be investigated is

$$\Delta G = E[1 - (T/T_0)][T/(T - T_\infty)], \qquad (2)$$

where E is again taken temperature-independent and $T_\infty (\ll T_0)$ is generally 10 to 100 deg below the experimental glass transition temperature,[12,15] T_g. This equation is taken to apply over at least most of the temperature region $T_g \leq T < T_0$, provided there are no phase changes inside this span and only a single thermally activated process is of importance in the range of interest.

Let us now introduce the normalized quantities $x \equiv T_\infty/T$ and $m \equiv T_0/T_\infty$. Then (2) becomes

$$\Delta G = E[1 - (mx)^{-1}]/[1 - x]. \qquad (2')$$

The corresponding enthalpy and entropy of activation at constant pressure follow immediately from the relations

$$\Delta H = \left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P$$

and $\Delta S = T^{-1}(\Delta H - \Delta G) = -[\partial(\Delta G)/\partial T]_P$. In terms of normalized quantities the temperature-dependent results are

$$\Delta H = nE/(1 - x)^2, \qquad (3)$$

$$\Delta S = \frac{(E/T_0)(1 - 2x + mx^2)}{(1 - x)^2}, \qquad (4)$$

[10] C. Zener, *Imperfections in Nearly Perfect Crystals* edited by W. Shockley *et al.* (John Wiley & Sons, Inc., New York, 1952), p. 299.
[11] M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. **77**, 3701 (1955).
[12] J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley & Sons, Inc., New York, 1961), pp. 212–228.
[13] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).
[14] D. J. Denney, J. Chem. Phys. **27**, 259 (1957).
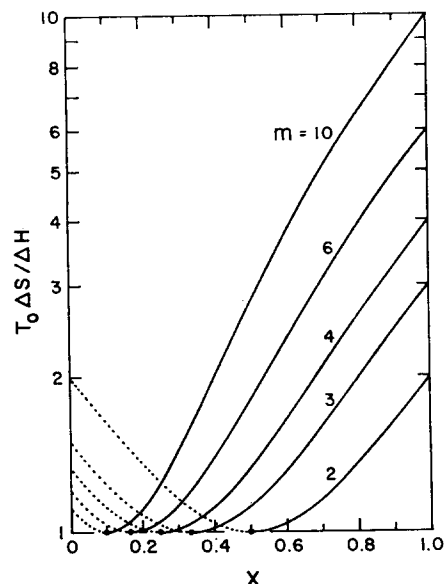[15] R. H. Cole, Ann. Rev. Phys. Chem. **11**, 149 (1960).

FIG. 1. Semilogarithmic plot of the ratio $T_0 \Delta S/\Delta H$ vs $x \equiv T_\infty/T$ for various values of the parameter $m \equiv T_0/T_\infty$.

where $n \equiv (T_0 - T_\infty)/T_0 = (1 - m^{-1})$. Note that when $T = T_0$, $\Delta H = E/n$ and $\Delta S = E/nT_0$. Since m may be expected to range from perhaps 2 to 8 or 10, n will correspondingly vary with material from about 0.5 to 0.9. Finally, Eq. (2) leads to

$$\Delta S/\Delta H = (nT_0)^{-1}(1 - 2x + mx^2), \qquad (5)$$

which reduces to the $T_\infty = 0$ value of T_0^{-1} at $T = T_0$. Figure 1 shows how $T_0 \Delta S/\Delta H$ varies with x for several values of m. The possibly nonphysical region $x < m^{-1}$ (i.e., $T > T_0$) is shown dotted for each curve. It is clear that for reasonable values of m there is no appreciable temperature region where the ratio is temperature independent.

It should be pointed out that ΔH and ΔS obtained as above from ΔG are good thermodynamic variables. Davidson and Cole[13] have mentioned in a similar situation that the entropy and activation energy could not be deduced. Further, Williams, Landel, and Ferry[11] have given an equation, equivalent in form to (3), for what they term the apparent activation energy. ΔH is here actually the real enthalpy or heat of activation. When ΔG and ΔH are temperature dependent, the term "activation energy," if used, should be precisely defined; it is not employed in the present work except when $\Delta H = E$ and it is thus temperature-independent.

THERMAL ACTIVATION

For a thermally activated system obeying Boltzmann statistics we may write quite generally,[6,7,10]

$$\tau(T) = \tau_d(T) \exp(\Delta G/kT), \qquad (6)$$

where $\tau(T)$ is the relaxation time for the process. When there is a distribution of relaxation times, τ is taken as the most probable value. Although the present treat-

ment is carried through in terms of mechanical or dielectric dispersion relaxation times, it applies as well, for example, if τ^{-1} and τ_d^{-1} are replaced by appropriate diffusion coefficients.[5]

The quantity $\tau_d(T)$ is an inverse vibrational frequency or an attack or dwell time. There is considerable controversy whether it is a function of temperature or not.[6,10,16] Rate theory [6,17] yields $\tau_d(T) \cong ph/kT$, where p is the number of equivalent paths by which a transition may occur. Wert and Zener[6] and Zener,[10] on the other hand, have advanced a cogent argument to show that when $\tau(T)$ is written in the form (6), involving the actual change in Gibbs free energy, $\tau_d(T)$ does not contain the T^{-1} factor. For generality, we use $\tau_d(T)$ to include both possibilities and write τ_d for $\tau_d(T)$ when no temperature dependence is to be understood.

From mechanical and dielectric dispersion measurements one may obtain $\tau(T)$. The problem then remains of obtaining important material parameters from results for $\tau(T)$. In the present situation, the temperature-independent parameters to be obtained are E, T_0, T_∞, and possibly τ_d. An example of their derivation from pertinent experimental data is presented later.

In the present instance of a relatively complicated ΔG, there are a number of seemingly different but equivalent ways $\tau(T)$ may be written. When Eq. (2) is substituted in (6) and various rearrangements are carried out, we find

$$\tau(T) = \tau_d(T) \exp\left(\frac{E}{kT_0}\frac{T_0 - T}{T - T_\infty}\right) \tag{7}$$

$$= \left\{\tau_d(T) \exp\left[\frac{-E}{kT_0}\frac{T^2 - 2T_\infty T + T_0 T_\infty}{(T - T_\infty)^2}\right]\right\}$$

$$\times \left\{\exp\left[\frac{nET/k}{(T - T_\infty)^2}\right]\right\} \tag{7'}$$

$$= \left[\tau_d(T) \exp\left(\frac{-E}{kT_0}\right)\right]\left[\exp\left(\frac{nE/k}{T - T_\infty}\right)\right]. \tag{7''}$$

In Eq. (7'), the first term in parentheses includes the contribution from the temperature-dependent ΔS, while the second exponential term contains the heat of activation, ΔH. It is clear that this form of $\tau(T)$ is not very practical for deriving parameters.

Equation (7'') is of the form

$$\tau = A_1 \exp[B/(T - T_\infty)], \tag{8}$$

first apparently suggested by Vogel[18] for temperature dependence of viscosity and frequently used in analysis of dielectric measurements on glass-forming mate-

rials.[13–15,19,20] Here B is temperature-independent, as is A_1 if $\tau_d(T)$ is taken as τ_d. There is considerable temptation when $\tau(T)$ is written in the form (7'') to identify $\Delta S = E/T_0$ and $\Delta H = nE$. This is incorrect; although

$$nE = \frac{kd\ln(\tau/\tau_n)}{d(T - T_\infty)^{-1}},$$

this procedure does not give the real, temperature-dependent enthalpy, ΔH. In this derivative τ_n is an arbitrary, temperature-independent normalization relaxation time, and $\tau_d(T)$ is again taken temperature-independent.

RELATION TO THE WLF EQUATION

Let us introduce the new normalized variable

$$Z(T) \equiv Z = \ln\left[\frac{\tau(T)/\tau_d(T)}{\tau(T_n)/\tau_d(T_n)}\right]$$

$$= \frac{\Delta G(T)}{kT} - \frac{\Delta G(T_n)}{kT_n}, \tag{9}$$

when T_n is a normalization temperature conveniently selected within the experimental range. $[\tau_d(T_n)/\tau_d(T)]$ will either be unity when $\tau_d(T) = \tau_d$ or (T/T_n) when the ordinary rate-theory pre-exponential form is used.

From (2) and (9) we obtain

$$Z = \left(\frac{E}{kT_0}\right)\left(\frac{T_0 - T_\infty}{T_n - T_\infty}\right)\left[\frac{T_n - T}{T - T_\infty}\right], \tag{10}$$

which reduces to

$$Z \equiv Z_0 = \left(\frac{\Delta G}{kT}\right) = \left(\frac{E}{kT_0}\right)\left[\frac{T_0 - T}{T - T_\infty}\right]$$

$$= \left(\frac{E}{kT_0}\right)\left[\frac{mx - 1}{1 - x}\right], \tag{11}$$

where $T_n = T_0$. The quantity

$$\frac{Z_0}{(E/kT_0)}$$

is plotted vs x in Fig. 2 for several m values. The curves in Fig. 2 are similar to those one might obtain directly from $\tau(T)$ measurements and show the appreciable curvature often found experimentally when $T_\infty > 0$.

Let us now take $T_n = T_g$ and $T_g \equiv T_\infty + c_2{}^g$, where $c_2{}^g$ is a temperature-independent parameter appearing in the WLF equation. We may now write from (10), since $Z = Z_g$,

$$\log_{10}[\exp(Z_g)]$$

$$= \left(\frac{0.4343E}{kT_0}\right)\left(\frac{T_0 - T_g + c_2{}^g}{c_2{}^g}\right)\left[\frac{T_g - T}{T - T_g + c_2{}^g}\right]. \tag{12}$$

[16] R. H. Doremus, J. Chem. Phys. 34, 2186 (1961).
[17] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), Chap. IX.
[18] H. Vogel, Physik. Z. 22, 645 (1921).

[19] A. Matsumoto and K. Higasi, J. Chem. Phys. 36, 1776 (1962).
[20] D. W. Davidson, Can. J. Chem. 39, 2139 (1961).

The WLF equation written for $T_n = T_g$ involves the parameter c_1^g and is[21]

$$\log_{10}[\tau(T)/\tau(T_g)] \equiv \log_{10} a_{T_g}$$

$$= c_1^g[(T_g - T)/(T - T_g + c_2^g)]. \quad (13)$$

Equations (12) and (13) are of the same form provided $\tau_d(T) \equiv \tau_d$. In this case, we may compare the equations directly and obtain

$$c_1^g = \frac{0.4343(E/kT_0)(T_0 - T_g + c_2^g)}{c_2^g}$$

$$= 0.4343 nE/kc_2^g. \quad (14)$$

This result provides a new and interesting connection between the activation energy parameter, nE, and the temperature-independent WLF product $c_1^g c_2^g$.

In the first discussion of the WLF equation, c_2 and c_1 were taken as approximately $100°K$ and 9, respectively, independent of material and temperature, and curve fitting for different materials was accomplished by variation of the normalization temperature. The resulting "universal" value for the product $c_1 c_2$ corresponds to a value of nE of 0.18 eV or 4.1 kcal/mole. Frenkel[22] has given reasons for the small value and relatively small variation with material of the activation energies for diffusion and viscosity in liquids. Since these quantities are usually closely related to the activation energy (or energies) for mechanical or dielectric dispersion, the same conclusions should apply to nE in the dispersion case and explain why only fairly small variation should be found in $c_1 c_2$. In a listing presented by Ferry,[23] the quantity $c_1^g c_2^g$ varies from $449°$ to $2305°K$, but the average value is about $1300°K$. In this later work, the quantities are referred to the glass temperature, and c_1^g and c_2^g are allowed to vary with material in order to fit data for the various materials. For example, in Ferry's listing c_2^g lies between $20.2°$ and $129.4°K$.[21]

Ferry[12] has pointed out that the WLF equivalent of Eq. (3) yields a ΔH which reduces to $2.303kc_1^g c_2^g$ at high temperatures. This quantity is equal to nE in the present analysis. A more cogent limit to consider is that at $T = T_0$, near or above the highest experimentally available temperature possible without phase change. As already mentioned, the value of ΔH at this temperature is $E/n = ET_0/(T_0 - T_\infty)$. This quantity may certainly be expected to vary somewhat from material to material since E, T_0, and T_∞ are all specific material parameters. Note that the quantity B of Eq. (8) is equal to $(nE/k) = 2.303 c_1^g c_2^g$ when comparison is made with (7″) or (10). It is not proportional to T_∞, as stated by Cole,[15] but to $(T_0 - T_\infty)/T_0$. Matsumoto and Higasi[19] have written E/R for B, where R is the gas constant and E is the same quantity appearing in their
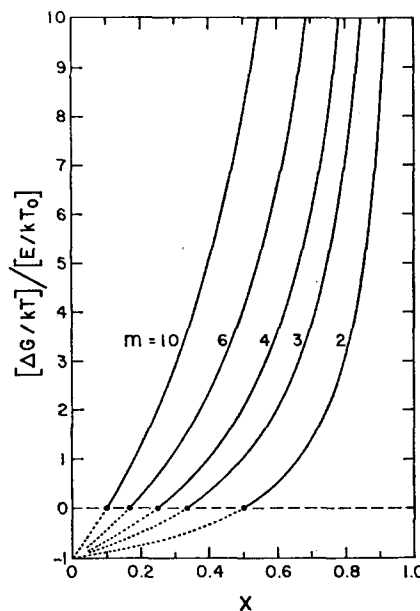

FIG. 2. The ratio $[\Delta G/kT]/[E/kT_0]$ vs x for various m values.

Arrhenius equation. The more precise value for B of nE/k (or nE/R in different units) has the virtues that at $T = T_0$, $B/(T - T_\infty)$ becomes just (E/kT_0), and a necessary distinction is made between the case where the activation energy is E and that where the heat of activation varies with temperature. The value of nE obtained from applying an equation of the form of (8) to viscosity data for water has been incorrectly identified by Miller[24] as the true temperature-independent activation energy for viscous flow. In cases where $T_\infty \neq 0$, the only meaningful activation energy is ΔG, the temperature-dependent Gibbs free energy of activation.

Equation (13) has been derived by Williams, Landel, and Ferry[11] by modification of a free-volume viscosity equation of Doolittle.[25,26] An equation of the same form has also been obtained by Bueche,[27] who analyzed the motion of a group of n polymeric segments. Doolittle's equation is in agreement with a wide variety of liquids over a wide range of temperatures. Therefore, and because the results will be useful later, the implications of the unmodified form will be investigated.

Doolittle[25] wrote $\ln\eta = A + D(v_0/v_f)$, where η is the viscosity, A and D are constants, and we have written D in place of Doolittle's original B to avoid confusion with the B already defined herein. Let v be the specific volume; then the free volume $v_f \equiv v - v_0$, where v_0 is[26] "the limiting specific volume to which a real liquid would contract if it were to continue to be unassociated and

[21] Reference 12, p. 216.
[22] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), pp. 202–204.
[23] Reference 12, p. 219.

[24] A. A. Miller, J. Chem. Phys. **38**, 1568 (1963).
[25] A. K. Doolittle, J. Appl. Phys. **22**, 1471 (1951).
[26] A. K. Doolittle and D. B. Doolittle, J. Appl. Phys. **28**, 901 (1957). See also M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).
[27] F. Bueche, J. Chem. Phys. **24**, 418 (1956).

undergo no phase change down to $T=0$." The quantity v_0 is at least approximately equal to the limiting van der Waals molecular volume. At least to first order, we may write for $T \geq T_g$,

$$(v_f/v_0) \cong (v_{fg}/v_0) + \alpha_f(T - T_g), \qquad (15)$$

where v_{fg} is the value of v_f at $T = T_g$ and α_f is the isobaric thermal expansion coefficient for the relative free volume. On making the assumption that viscosity and diffusion or mechanical dispersion in liquids or noncrosslinked polymers involve the same activation processes, we may write

$$D\left(\frac{v_0}{v_f}\right) = D\left[\frac{v_{fg}}{v_0} + \alpha_f(T - T_g)\right]^{-1} \cong \frac{nE/k}{T - T_\infty}. \qquad (16)$$

This leads, with no further approximations or assumptions, to the relations

$$D \cong \alpha_f(nE/k), \qquad (17)$$

$$c_1{}^g \cong 0.4343D(v_0/v_{fg}), \qquad (18)$$

$$c_2{}^g \cong \alpha_f^{-1}(v_{fg}/v_0). \qquad (19)$$

The expressions for $c_1{}^g$ and $c_2{}^g$ differ somewhat from those derived by Ferry.[12] Note that the use of (15) in Doolittle's equation together with (19) makes it completely equivalent to Vogel's[18] original viscosity equation. Doolittle's equation is, however, more general since the temperature dependence of v_0/v_f is still unspecified. D has been taken as unity by Ferry for simple liquids. Note that through (17) this then leads to a simple relation between α_f and E. Doolittle's values range, however, from 0.04 for Hg to 1.0 for CCl$_4$.

Note added in proof: M. Goldstein, J. Chem. Phys. **39**, 3369 (1963), has recently given an interesting discussion of free volume, the WLF equation, and the Doolittle equation.

The free volume approach has been questioned by Gilchrist, Early, and Cole[28] who find that $\Delta G(T)$ increases as the temperature decreases for 1-propanol and glycerol held at constant volume. Thus, ΔG cannot be a pure volume function, independent of temperature at constant volume. It may be shown thermodynamically that

$$(\partial \Delta G/\partial T)_V = -\Delta S + (\alpha/\beta)\Delta V$$
$$= (\alpha_{\Delta G}/\beta)\Delta V, \qquad (20)$$

where β is the isothermal compressibility,

$$\Delta V \equiv (\partial \Delta G/\partial P)_T$$

is the activation volume, and $\alpha_{\Delta G} \equiv V^{-1}(\partial V/\partial T)_{\Delta G}$. The above experimental results are not inconsistent with the present form for ΔG when $T_\infty \neq 0$ provided $\alpha_{\Delta G}$ is nonzero. It must be negative when $\Delta V > 0$ to accord with the above results. Physically, the $(\partial \Delta G/\partial T)_V$

[28] A. Gilchrist, J. E. Earley, and R. H. Cole, J. Chem. Phys. **26**, 196 (1957).

term arises from the direct interaction of the activated unit with its surroundings in the absence of dilation. The dilation term which contributes to ΔS is that involving $(\alpha/\beta)\Delta V$. Since ΔS may exceed $(\alpha/\beta)\Delta V$, $(\partial \Delta G/\partial T)_V$ may be negative.

EMPIRICAL RELATIONS $(T_g = 0)$

In this section we are concerned with some exact thermodynamic, approximate thermodynamic, and empirical relations between the thermodynamic activation variables ΔH, ΔS, and ΔV. Lawson[3] first investigated the approximate equation,

$$\Delta V \cong (\beta/\alpha)\Delta S, \qquad (21)$$

and tested its applicability for diffusion data. This equation is an approximation to the well-known exact thermodynamic relation

$$\Delta S = \beta^{-1}(\alpha - \alpha_{\Delta G})\Delta V$$
$$= (\chi\alpha/\beta)\Delta V, \qquad (22)$$

a version of (20). Here

$$\chi \equiv 1 - (\alpha_{\Delta G}/\alpha). \qquad (23)$$

Lawson felt that $\alpha_{\Delta G}$ could be neglected, to good approximation, compared to α. This is equivalent to assuming that the dilation contribution to ΔS is much larger than that arising from the direct interaction of the activated unit with its surroundings at constant volume. The data of Gilchrist *et al.*[28] cited in the last section show this assumption is invalid for the $T_g \neq 0$ case; in the present section we cite instances where it is also very inaccurate when $T_g = 0$.

Keyes[4] later suggested the nonthermodynamic expression

$$\Delta V = c\beta\Delta H, \qquad (24)$$

where c (termed k by Keyes) was empirically determined from diffusion data to be 4. Lawson, Rice, Corneliussen, and Nachtrieb[29] on the basis of a continuum model of the solid state later gave the explicit relation $c \cong 2(\gamma - \frac{1}{3})$, where γ is the Grüneisen number. ΔV may thus be negative[30] when this expression applies and $\gamma < \frac{1}{3}$. Keyes[4] also combined (21) and (24) to obtain

$$\Delta S/\Delta H \cong c\alpha. \qquad (25)$$

The combination of (22) and (24) yields

$$\Delta S/\Delta H = \chi c\alpha, \qquad (26)$$

which we may take as an alternative definition of c. Let us further define from such c the quantity $\gamma_c \equiv (c/2) + \frac{1}{3}$ to compare with γ values obtained from other kinds of measurements than those leading to ΔS and

[29] A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960).
[30] R. T. Payne and A. W. Lawson, J. Chem. Phys. **34**, 2201 (1961).

ΔH. Note that such an equation as (26) should not be applied in the limiting low-temperature region where other processes, such as tunneling through a potential barrier, dominate thermal activation.

Next, let us consider the applicability of such equations as (25) and (26) when ΔS and ΔH are temperature dependent. When $T_g \neq 0$ Eqs. (5) and (26) and Fig. 1 show that $\chi c \alpha$ must vary strongly with temperature. Only when $T = T_0$ is $\chi c \alpha$ equal to T_0^{-1}, a temperature-independent parameter. Now since $\chi \alpha \equiv \alpha - \alpha_{\Delta G}$, a quantity which should not vary strongly with temperature, the majority of the strong variation of $\chi c \alpha$ for temperatures near T_g when $T_g \neq 0$ must be associated with c. But c loses much of its utility if it is not at least quasiconstant, relatively independent of material and measurement temperature. Therefore, we believe that (25) and (26) should not be applied at all when $T_g \neq 0$ unless an Arrhenius equation still applies.

In previous applications of such equations as (21), (24), and (25), no explicit mention of temperature dependence of α, β, and c has been made, and it has not always been made clear whether ΔS, ΔH, and ΔV had to be temperature independent also. Lawson[2] has partly tested Eq. (25) (with $c = 4$) using data obtained from diffusion of various impurities into polyvinyl acetate. He found that $\Delta S/\Delta H$ was nearly constant (but the constant was not quantitatively compared with 4α) when ΔS and ΔH were determined from data taken just above T_g. The above considerations show that if all ΔS and ΔH values were calculated from data taken at the same temperature, say T_1, then $\Delta S/\Delta H$ would be found constant but not, in general, equal to 4α. Instead, $\Delta S/\Delta H$ would equal the value of $\chi c \alpha$ pertinent at $T = T_1$.

Lawson also tested (25) for impurity diffusion at temperatures just below T_g. If the measuring temperature used was sufficiently below T_g, an Arrhenius equation should apply,[31] and ΔS and ΔH should then be temperature-independent. Even then, comparison of $\Delta S/\Delta H$ should be made with $\chi c \alpha$, not $c \alpha$. When ΔS and ΔH are indeed temperature-independent over the temperature range of interest, (26) requires that $\chi c \alpha$ also be. Then we may write

$$T_0 \equiv (\chi c \alpha)^{-1}. \qquad (27)$$

Note, however, that the T_0 applicable in the Arrhenius temperature region below T_g will in general be entirely different from the T_0 which enters into (2) and is applicable for $T > T_g$. We shall use the designation $T_g = 0$ to indicate a temperature region of a material where Arrhenius behavior is found. Thus, $T_g = 0$ does not necessarily mean that a material has no glass transition but rather that a temperature region where its influence is negligible is being considered.

Finally, the question arises whether (26) can hold

with $\chi c \alpha \equiv T_0^{-1}$ temperature-independent but ΔS and ΔH similarly dependent on temperature. Differentiation of $\Delta H = T_0 \Delta S$ yields $(\partial \Delta H/\partial T)_P = T_0(\partial \Delta S/\partial T)_P$. But thermodynamics requires that $(\partial \Delta H/\partial T)_P = -T(\partial^2 \Delta G/\partial T^2)_P$ and $(\partial \Delta S/\partial T)_P = -(\partial^2 \Delta G/\partial T^2)_P$. These results show that $\Delta S/\Delta H$ can only equal a temperature-independent constant when $(\partial^2 \Delta G/\partial T^2)_P = 0$. When this is the case, ΔG must be of the form (1) as far as temperature dependence is concerned, and ΔS and ΔH are then themselves temperature-independent and $T_g = T_\infty = 0$.

Lawson $et\ al.$[29] have derived a form of (24) for $T = 0$ where $\Delta G = \Delta H$, a condition satisfied by Eq. (1) but not by (2). If we force (24) and (26) to apply for $T_g \neq 0$ as well as $T_g = 0$, we may expect that the c which applies in the Arrhenius temperature range will be different from that for $T \gtrsim T_g$. Only the former can be approximately identified with $2(\gamma - \frac{1}{3})$. Keyes[32] later wrote (24) with ΔH replaced by ΔG, a slightly different definition of c. When ΔH and c are temperature-independent, the definitions are only equivalent for low temperatures where $\Delta G \cong \Delta H$. As far as pressure dependence is concerned, however, the situation considered by Keyes, we shall later see that the replacement of ΔH by ΔG is permissible, at least to first order in pressure, when ΔH is temperature-independent.

We now explicitly consider only the situation where ΔS and ΔH are temperature-independent, and an Arrhenius equation holds over the temperature range of interest. We further restrict consideration to a temperature range where there are no phase changes and a single type of thermal activation mechanism is dominant. The pertinent $\Delta G(P, T)$ may then be written as

$$\Delta G = E[1 + \beta_E(P - P_n)] - \alpha_E T, \qquad (28)$$

a form of (1), where E is the activation energy at $T = 0$ and at the standard pressure P_n. The quantity α_E, the experimentally measurable isobaric temperature coefficient of ΔG, is taken temperature and pressure-independent in the ranges of interest. Let us initially take β_E, the measurable isothermal compressibility coeficient of ΔG, only temperature-independent. It follows immediately from (28) that $\Delta S = \alpha_E$, $\Delta H = E[1 + \beta_E(P - P_n)]$, and $\Delta V = E\beta_E + E(P - P_n)(\partial \beta_E/\partial P)_T$. These expressions for ΔH and ΔV, together with (24), lead to a differential equation for β_E which involves the pressure dependence of $c\beta$.

It has been found[33] that almost all of Bridgman's data on compression of liquids and solids can be represented very accurately over a wide pressure range by an expression of the form[34] $\beta = \beta_n/[1 + q\beta_n(P - P_n)]$, where q is a positive constant greater than unity. Let us generalize this result by replacing β by $c\beta$ and β_n by

[31] Reference 12, p. 235.

[32] R. W. Keyes, J. Chem. Phys. **32**, 1066 (1960).
[33] Unpublished work of the author.
[34] J. R. Macdonald and C. A. Barlow, Jr., J. Chem. Phys. **36**, 3062 (1962).

TABLE I. Data for Ge and Si.

Quantity	Ge	Si
α $(°K)^{-1}$	2×10^{-5}	$1.3 \times 10^{-5c,d}$
β (cm^2/dyn)	$1.3 \times 10^{-12a,b}$	1×10^{-12a}
$\alpha_E{}^e$ $(eV/°K)$	3.9×10^{-4f}	2.83×10^{-4f}
$\beta_E{}^g$ (cm^2/dyn)	$\sim 6.4 \times 10^{-12h}$	$(A) \sim -1.3 \times 10^{-12h}$ $(B) \sim 4.1 \times 10^{-12i}$
E^g (eV)	0.782^f	1.205^f
$T_m (°K)$	1210^f	1693^f
γ	1.86^j	1.96^k

[a] E. M. Conwell, Proc. Inst. Rad. Engrs. **40**, 1327 (1952).

[b] M. E. Fine, J. Appl. Phys. **24**, 338 (1953).

[c] M. E. Straumanis and E. J. Aka, J. Appl. Phys. **23**, 330 (1952).

[d] R. O. A. Hall, Acta Cryst. **14**, 1004 (1961).

[e] From optical data.

[f] R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, England, 1959), pp. 351–368.

[g] β_E has been obtained using the value of E given. Although the difference is small, we have used the value of E obtained by linear extrapolation to $T=0$ rather than the actual value at $T=0$.

[h] W. Paul, J. Phys. Chem. Solids **8**, 196 (1959).

[i] H. Y. Fan, M. L. Shepherd, and W. Spitzer, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, Inc., New York, 1956), p. 184.

[j] D. S. Beers, C. D. Cody, and B. Abeles, Proc. Intern. Conf. Phys. Semiconductors, Exeter, England, 1962, p. 41.

[k] H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, Phys. Rev. **130**, 1743 (1963).

$(c\beta)_n$. Then the differential equation may be integrated for rational q, and, for $q>0$, the result is

$$\beta_E = \{[1+q(c\beta)_n(P-P_n)]^{1/q}-1\}/(P-P_n)$$
$$\cong (c\beta)_n[1-\tfrac{1}{2}(q-1)(c\beta)_n(P-P_n)+\cdots], \quad (29)$$

which, for real materials $(q>1)$, will decrease with increasing $(P-P_n)$. Using this result for β_E, the resulting expressions for ΔG, ΔH, and ΔV are consistent and correct to first order in $(P-P_n)$. A direct relation between β_E, $c\beta$, and $(P-P_n)$ may now be written, but unfortunately no accurate data to test it seem available. Note that consistency with a pressure-independent $\Delta S = \alpha_E$ requires, according to (26) that T_0 be proportional to $[1+\beta_E(P-P_n)]$. Any direct dependence of α_E on pressure would introduce a second-order pressure-dependent term in ΔG and is beyond the scope of the present first-order treatment. The pressure dependence of $T_0 \equiv (\alpha \chi c)^{-1}$ inferred above is reasonable, however, since α at least should decrease with increasing $(P-P_n)$.

In the present $T_g=0$ case, we may take $v_{fg}=0$ in Eq. (17), $n=1$, and $\alpha_f \equiv \alpha$. We then obtain

$$D=\alpha E/k. \quad (30)$$

The D in (30) is related to viscosity in the liquid or viscoelastic case, and (30) is, for this situation, based on the validity of Doolittle's equation and the equality of the activation energy for viscosity and that for mechanical or dielectric dispersion. In view of these uncertainties and because D has no direct physical interpretation for thermal activation in nonviscoelastic solids, we shall take (30) as directly defining D, a parameter which may be at least approximately related to viscosity for liquids. The analysis of the rest of this section will then apply generally to thermal activation in either liquids or solids. It will not apply to polymers, viscoelastic materials with $T_g \neq 0$, except for activation processes for which the pertinent ΔH and ΔS are temperature-independent in the temperature range of interest.

Keeping first-order pressure terms in ΔG but dropping them in expressions for ΔV and ΔH leads to the relations

$$\Delta S = \alpha_E \cong \chi c\alpha E = (D\chi)ck, \quad (31)$$

$$\beta_E \cong \Delta V/E \cong c\beta, \quad (32)$$

$$(\partial \Delta G/\partial T)_V \cong E(\beta_E/\beta)\alpha_{\Delta G} \cong -\alpha_E + E(\beta_E/\beta)\alpha$$
$$\cong cE\alpha_{\Delta G} \cong -\alpha_E + cE\alpha, \quad (33)$$

where for convenience $(c\beta)_n$ has been written as $c\beta$. These results show that even when an Arrhenius equation is satisfied which arises from a ΔG correct to first order in pressure, $(\partial \Delta G/\partial T)_V$ and $\alpha_{\Delta G}$ will be zero only when

$$\alpha_E \cong E(\beta_E/\beta)\alpha \cong cE\alpha \cong ckD, \quad (34)$$

a relation which will certainly not be satisfied in general.

Note that in the present formulation of the situation, there is really no question of comparing $\Delta S/\Delta H$ and $\chi c\alpha$. Rather, the constant c must be obtained from β_E and β values, then χ obtained from α_E and E values. The pertinent comparisons will then be between χ and c and their expected values.

In order to investigate the application and implications of the foregoing equations, we need materials for which as many of the above parameters are known as possible. Among the very few substances for which sufficient parameters are reasonably well known are the semiconductors Ge and Si. The thermally activated process considered should be one associated with bulk properties of the material, and intrinsic activation of holes and electrons across the forbidden energy gap E_g is suitable in the nondegenerate temperature range where the Boltzmann distribution applies. Application of the present results to intrinsic semiconductors require that the (free) energy gap be identified with the Gibbs free energy change of the thermal activation process, ΔG. Such identification has been made by Brooks.[35] When hole–electron thermal activation is written in the form of Eq. (6), it is of interest to note that the analogue of $\tau_d(T)$ is proportional to T^{-3}.

[35] H. Brooks, Advan. Electron. Electron Phys. **7**, 85 (1955).

TABLE II. Derived quantities for intrinsic Ge and Si.

Quantity	Equation	Ge	A	Si	B
D	(30)	0.181		0.182	
c	(32)	4.9	−1.3		4.1
χ	(31)	5.1	−13.9		4.4
$c\chi$	...	25		18	
T_0/T_m	(27)	1.66		2.51	
$E/kT_0 = \alpha_E/k$	(27)	4.5		3.3	
$\alpha_{\Delta G}(°K)^{-1}$	(23)	-8.1×10^{-5}	1.94×10^{-4}		-4.42×10^{-5}
$(\alpha_{\Delta G}/\beta)\Delta V = (\partial \Delta G/\partial T)_V$ (eV/°K)	(33)	-3.1×10^{-4}	-3.04×10^{-4}		-2.19×10^{-4}
$-(\alpha/\beta)\Delta V$ (eV/°K)	(32)	-7.7×10^{-5}	2×10^{-5}		-6.4×10^{-5}
$D\chi$	...	0.92	−2.53		0.80
γ_c/γ	...	1.50	−0.162		1.21

To use the present equations in analyzing experimental data it is only necessary to establish that in fact in the temperature range of interest an Arrhenius type of equation is satisfied and so ΔS and ΔH are temperature-independent. When the Boltzmann distribution is a good approximation, this is the case for intrinsic conduction in semiconductors, and such behavior is indeed found[36] over wide temperature ranges for Ge and Si. Keyes[37] has given a treatment of energy-band behavior under pressure in semiconductors which depends on a detailed model of the solid; alternatively, much can be learned from the present approach which depends on no more model than is specified by the general form of ΔG given in (28), itself necessarily consistent with Arrhenius behavior.

The starting data for calculations on Ge and Si are shown in Table I; many of the values are imperfectly known and may be in error by 10% or more. Since there is some temperature dependence of α and β, their values have been selected as much as possible to be appropriate to the relatively high-temperature range where intrinsic charge carrier activation is usually observed in Ge and Si. It will be noted that two quite different values for β_E for Si have been given. The best evidence seems to indicate that (A) is the more accurate; however, we carry through the calculations with both values for illustrative purposes.

The results of the calculations for Ge and Si are shown in Table II. Many of these results are not good to more than one or two significant figures; thus, the near equality in the values of D must be a coincidence. It is of interest to note, however, that Doolittle's[26] experimentally determined value for liquid Na is 0.179. Further, the values of D calculated from (30) for GaSb and InP are about 0.195 and 0.22; other compound semiconductors yield appreciably different results, however. The

values of χ are surprisingly large and show that its replacement by unity, as in Eq. (21), is not at all justified for these materials. In fact, it should never be approximated by unity without direct experimental evidence.

The value of c for Ge and that for Si following from the much less likely value of β_E are rather close to the value of 4 frequently assumed or empirically determined. On the other hand, the most likely value of c for Si is far different from 4, and this value and that for Ge lead to values of γ_c/γ which suggest that the relation $c \simeq 2(\gamma - \frac{1}{3})$ is a poor approximation for thermal activation across semiconductor energy gaps. This is not surprising since the above expression for c was derived from a continuum model of a solid and involves Grüneisen's law, which depends on molar volume and specific heat. The values of γ given in Table I are derived, on the other hand, from thermal conductivity measurements. Much lower values (giving worse agreement between γ_c and γ) are found from thermal expansion measurements.[38] Although these measurements do, in fact, yield a negative value of γ for Si, this applies only below 120°K. At room temperature and above where the actual determinations of β_E were carried out, the thermal expansion value of γ is about 0.4 according to Gibbons.[38] Thus, it appears that $c \simeq 2(\gamma - \frac{1}{3})$ should not be applied in the semiconductor energy gap thermal activation case even as a first approximation. Instead, where possible both c and χ should be calculated directly from the data as in Table II.

Note that the addition of the second ΔV term in Table II to the first yields just $-\alpha_E = -\Delta S = (\partial \Delta G/\partial T)_P$. For both Ge and Si, the first term arising from electron–lattice interaction is much larger in magnitude than the dilation term.

The two values of $D\chi$ near unity suggest that for some materials the approximation $D\chi = 1$ may be valid.

[36] F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954); *ibid.* **96**, 28 (1954).

[37] R. W. Keyes, Solid State Phys. **11**, 149 (1960).

[38] D. F. Gibbons, Phys. Rev. **112**, 136 (1958).

When this is the case, one obtains $\Delta S = ck = 8(c/4)$ cal·mole/°K, $E/kT_0 = c$, and $\alpha_E \beta = k\beta_E$. Many values of ΔS do, in fact, cluster around 8 cal·mole/°K, but much smaller and larger values are frequently found. Note that when $D = 1$ as well as $D\chi = 1$, $\alpha_{\Delta G} = 0$. This conclusion does not necessarily apply in the $T_g \neq 0$ case where the situation is complicated by the strong temperature dependence of ΔS and ΔH.

Next, let us write, in analogy to (9),

$$Z(P) \equiv \ln\left[\frac{\tau(P)/\tau_d(P)}{\tau(P_n)/\tau_d(P_n)}\right]$$
$$= [\Delta G(P) - \Delta G(P_n)]/kT. \qquad (35)$$

It is probable that $\tau_d(P_n)/\tau_d(P)$ may be reasonably well approximated by unity in most cases of interest. Now using (28) in (35), we obtain

$$Z(P) = E\beta_E(P - P_n)/kT. \qquad (36)$$

Since this result only holds to first order in $(P - P_n)$, β_E may be replaced by $(c\beta)_n \simeq c\beta$. If Eq. (2) is modified as was (28) so it is correct to first order in $(P - P_n)$ and the product of first-order pressure and first and higher-order temperature terms neglected, again all pressure dependence will appear in ΔH and none in ΔS. Then (36) will apply in the $T_g \neq 0$ case as well, but $\chi c\alpha$ will be pressure-dependent and T_0 and T_∞ will not be, to this order of approximation. Ferry and Stratton[39] have slightly modified an earlier expression of Cohen and Turnbull[26] and arrived at a result for the $T_g \neq 0$ case similar to (36) but involving higher-order $(P - P_n)$ terms as well.

There have been a number of instances where ΔS has been found negative for a thermally activated system apparently obeying an Arrhenius equation.[40,41] Undoubtedly, such results have sometimes arisen from experimental inaccuracy or the use of too simple formulas for ΔG or $\tau_d(T)$. The assumption of $\tau_d(T) = h/kT$ when this value is inappropriate is perhaps the most frequent cause of apparently negative ΔS. In addition, errors in obtaining $\tau(T)$ may arise if a distributed system is not recognized as such in the analysis.

The present results suggest another explanation for $\Delta S < 0$. Equations (23), (31), and (33) may be used to show that when $c \gtrless 0$, ΔS will be negative if $\alpha \lessgtr \alpha_{\Delta G}$, where the upper inequalities go together as do the lower ones. Payne and Lawson[30] have considered Eqs. (21), (24), and (25) with $c = 2(\gamma - \frac{1}{3})$ for a situation where α and ΔV are negative. They calculate γ from Grüneisen's relation and obtain a value yielding $c \sim -4.5$, whereas the AgI data they used yields a value of c from β_E/β which is very much larger in magnitude but still negative. They then conclude from (25) that ΔS, a quantity for which no experimental value was given,

will be positive. The more appropriate Eq. (22) or (31) shows that ΔS may, in fact, be negative if $\alpha > \alpha_{\Delta G}$. Since $\alpha_{\Delta G}$ cannot be calculated without a value of $\Delta S = \alpha_E$, whose availability would obviate the need for the test, it cannot be concluded from the available data in the AgI situation whether ΔS is positive or negative. A conclusion that it is positive, is, however, unwarranted.

There have been three main inputs to the analysis of of the present section. One involves the ΔG of Eq. (28), the most general form possible to first order in temperature and pressure. The next is the assumption of a thermally activated process which obeys Boltzmann statistics so that (6) applies. The final input is Eq. (24), [or (32)], which defines the material parameter c. A question of great interest is to what degree c is universal. This question must finally be answered by comparison with experiment but a few comments are in order.

Although c values obtained from diffusion data and those obtained herein from intrinsic semiconduction are reasonably close except for the value $c = -1.3$ for Si, and although the first two input assumptions discussed above hold in both situations, nevertheless, the situations are considerably different. Processes such as diffusion, viscous flow, and mechanical and dielectric dispersion involve activation over a potential barrier and ΔG measures the difference between an initial and an intermediate or virtual state. On the other hand, intrinsic or extrinsic semiconduction involves thermal activation across forbidden band gaps and ΔG measures the difference between initial and final states (in the Boltzmann approximation). If we consider a single material, one might expect that the c's derived from all processes of the first type might be at least roughly the same but that they would be likely to differ appreciably from those obtained on the same material from processes of the second type. Also, although the latter values of c may be expected to vary appreciably with different energy gaps, the resulting values should still show some connection with the underlying material. Finally, considering the two classes separately, one would expect that the c values, especially of the first type, obtained from different but similar materials would vary relatively little, or at most in a regular way, from material to material. In the above comparison, we have neglected possible temperature dependence of c, a possibility which might somewhat complicate comparisons of the above types. Since c should not depend strongly on temperature, however, comparison should still be significant and should afford considerable insight into thermally activated processes in solids and liquids.

COMPARISON WITH EXPERIMENT ($T_g \geq 0$)

Here, we shall primarily discuss how $\tau(T)$ results may be analyzed to obtain pertinent temperature-independent parameters when $\tau(T)$, or a physical analog, is expected to be of the form (7).

[39] J. D. Ferry and R. A. Stratton, Kolloid Z. 171, 107 (1960).
[40] Reference 5, pp. 12–13 and references cited therein.
[41] G. J. Dienes, Phys. Rev. 89, 185 (1953).

Eby[1] has investigated the applicability of Eq. (25) with $c=4$ to mechanical-dispersion internal friction measurements of a variety of polymers. ΔH and ΔS were obtained from analysis of the simple rate theory equivalent of Eq. (6) with $p=1$. Since it was recognized that ΔH and ΔS are temperature-dependent for polymers when $T>T_g$, an effort was made to avoid temperatures near T_g, and it is stated that the derived ΔH and ΔS values are averages characteristic of the temperature midway between high- and low-frequency relaxation temperatures. Figure 1 shows, however, that even when m is as small as 2, there is still an appreciable difference for $x>m^{-1}$ between the actual value of $\Delta S/\Delta H$ and T_0^{-1}, its limiting value when $x=m^{-1}$, or $T=T_0$. Now m will usually exceed 2, and it will frequently be impossible to make measurements near $T=T_0$. Unless Eby was able to derive all his results for $\Delta S/\Delta H$ from data taken at $T\simeq T_0$ for each of his different materials, his values of $\Delta S/\Delta H$ should not equal $(\chi c\alpha)_{T=T_0}\equiv T_0^{-1}$, much less 4α. The fact that he did find good agreement with 4α for many materials suggests either that $(\chi c)_{T=T_0}\simeq 4$ for these materials or that the data or analysis were in error.

In order to obtain pertinent physical parameters from $\tau(P,T)$ data in the $T_g\geq 0$ case, the following procedure may be used. First, values of E, T_∞, and T_0 are derived, when possible, from $\tau(T)$ data as discussed below. These results, together with (5) and (26) allow the temperature dependence of $\chi c\alpha$ to be obtained. Let it be assumed that the temperature dependences of α and β are known from other experiments. Then that of χc may be calculated and finally that of χ if c is assumed temperature-independent. A more accurate procedure is to obtain $\beta_E(T)$ at $P=P_n$ using (36) and measurements such as those of Gilchrist et al.[28] at different temperatures. Since (32) will still apply if ΔS is sufficiently pressure-independent, one may derive $c(T)$ from these results. Finally, $\chi(T)$ may then be calculated.

Now let us assume that $\tau_d(T)=a_1T^{-s}$, where a_1 is temperature-independent and s is a constant which is either known or can be determined from the analysis. Next, introduce a fixed normalization relaxation time τ_n, a known value, and define for $T_\infty\geq 0$,

$$Z_n\equiv\ln[T^s\tau(T)/\tau_n]=\ln(a_1/\tau_n)+g[(T_0-T)/(T-T_\infty)]$$

$$\equiv A+BW, \tag{37}$$

where we have used (7) and defined $g\equiv E/kT_0$. Note that E is here an activation energy parameter but not *the* activation energy unless $T_g=0$. In (37),

$$A\equiv\ln(a_1/\tau_n)-g, \qquad B\equiv nE/k=(T_0-T_\infty)g,$$

and $W\equiv (T-T_\infty)^{-1}$. Although there are four unknown constants in the first form of (37), the second form shows that only A, B, and T_∞ may be independently obtained from $\tau(T)$ data. The situation is similar to that when $T_\infty=0$ and an Arrhenius equation applies.

TABLE III. Least-squares parameters (Eq. 37) for isoamyl bromide.

Quantity	$s=0$	$s=1$
A	-2.89	-1.60
$B(°K)$	588	522
$T_\infty(°K)$	94.3	96.1
r	0.9990	0.9985
S.D.	0.287	0.329

Without independent knowledge of $\tau_d(T)$, ΔS then cannot be calculated, or *vice versa*.

Equation (37) may be analyzed by least squares by assuming a series of values for T_∞, carrying out least-squares fitting, and picking that value of T_∞ which minimizes the sum of squares. The resulting final values of A, B, and T_∞ are then best in a least-squares sense. If there is doubt about the proper value of s to use in the analysis, the above procedure may be repeated with several s values and that which yields the minimum sum of squares accepted.

Unless ΔS can be directly measured, as in the intrinsic semiconduction case, independent knowledge of $\tau_d(T)$ or E is required to allow ΔS, or its principal parameter T_0, to be obtained from $\tau(T)$ data. When the rate-theory approach is used with $T_g\geq 0$, there will still be doubt about its applicability[5] and about what value of p to use. It is apparently worth emphasizing that when (1) holds and an Arrhenius type of equation applies, a plot of Z_n vs T^{-1} does not yield ΔG (unless $T_0=\infty$) as Bhanumathi[42] has apparently assumed, but instead the slope of the resulting straight line is E, the temperature-independent heat or energy of activation, not the free energy of activation. This error of interpretation leads to the conclusion that the experimentally determined pre-exponential factor should be identified with h/k when the simple rate-theory approach applies. Actually the temperature-independent part of $T\tau(T)$ involves ΔS as well, explaining both the deviations from h/k found by Bhanumathi and the variation found from material to material.

In order to illustrate the analysis procedure, we have analyzed dielectric dispersion data of Denny[14] and Glarum[43] on isoamyl bromide. In the temperature range considered, 120°–300°K, there is some distribution of relaxation times, and $\tau(T)$ values were obtained by the above authors by fitting to a Davidson–Cole distribution. The 15 data-point values used are slightly uncertain because of small uncertainties in the relaxation distribution parameter but are sufficiently good for illustrative purposes.

The direct least-squares results for $s=0$ and 1 are shown in Table III; here r is the correlation coefficient and S.D. the standard deviation. The very small value of $(1-r)$ indicates that (37) is a good fit to the data;

[42] A. Bhanumathi, Indian J. Pure Appl. Phys. 1, 79, 148 (1963).
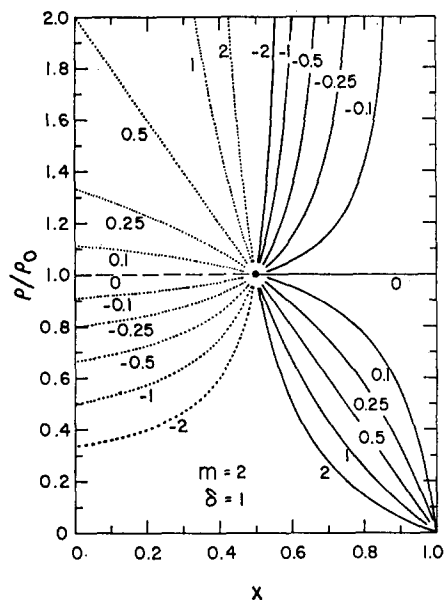[43] S. H. Glarum, J. Chem. Phys. 33, 639 (1960).

FIG. 3. ρ/ρ_0 vs $x \equiv T_\infty/T$ for $m=2$, $\delta=1$, and various values of χ. Negative branches omitted.

further, T_∞ could be determined quite accurately by the above trial and error procedure. The distribution of errors for both $s=0$ and $s=1$ indicated, however, that there are present principally systematic, rather than random, deviations from (37). Such deviations may arise from errors in the data or from progressive failure of (37) to represent the data well.

Since $B=2.303c_1{}^g c_2{}^g$ according to (14), the value of 588°K corresponds to $c_1{}^g c_2{}^g=255$°K, quite a bit lower than the value of about 900°K originally used in the WLF equation. Davidson[20] has suggested that a value of $c_1{}^g c_2{}^g$ of 985°K is characteristic of many liquids at low temperatures. It does not seem characteristic of isoamyl bromide. The values of r and S.D. in Table III suggest that the choice $s=0$ is slightly preferable to $s=1$. The differences are not statistically significant at the 0.05 level of significance, however.

Glarum[43] analyzed his high-temperature $\tau(T)$ values for isoamyl bromide on the basis of an Arrhenius equation and obtained a value of 0.095 eV for the activation energy. For a material with $T_g \neq 0$ the Z_n vs T^{-1} curve will only be approximately a straight line when $T \gg T_\infty$. When also $T_\infty/T_0 \ll 1$, the resulting apparent activation energy is $nE \cong E$, but E is still not *the* activation energy. On combining the above value of E with the values of B and T_∞ in the table, one finds that it leads to $T_0=202$°K when $s=0$ and 183°K for $s=1$. These values are not sufficiently high that $T_\infty/T_0 \ll 1$. The curvature in Glarum's $Z_n(T)$ values was apparently largely obscured by experimental error in the high-temperature part of the temperature range; obviously, for a material with $T_g \neq 0$, a wide temperature range extending as close to T_g as possible should be used. Direct calculation of nE from the B values in the table leads to 0.051 and 0.045

eV for $s=0$ and 1, respectively. If $T_0=\infty$, these are also the values of E, not the activation energy but the value of ΔH in the high-temperature limit.

Now if it is assumed that simple rate theory may be applied to isoamyl bromide at least to determine $\tau_d(T)$, then on taking $p=1$, one obtains $a_1=h/k=4.8 \times 10^{-11}$ °K·sec. Together with the $s=1$ values in the table, this value leads to $g=-1.44$, to $T_0=-266$°K, and finally to $E=0.033$ eV. The ratio m is thus negative and the entropy will be negative from $T > T_\infty$ up to the temperature

$$\frac{|T_0|}{\{1+|T_0/T_\infty|\}^{\frac{1}{3}}-1}.$$

A much larger value of p than is physically plausible would be required in order to make T_0 positive when a_1 is taken as ph/k. Although a negative entropy change is by no means impossible, its appearance here casts some doubt on the applicability of the above expression for a_1. It should be noted, however, that in the diffusion case, where the pre-exponential factor can probably be determined theoretically to higher accuracy than that represented by the assumption $a_1=h/k$, negative ΔS values still sometimes appear.[41,44]

TIME, FREQUENCY, AND TEMPERATURE RESPONSE, $T_g \neq 0$

The transient, frequency, and temperature responses of a linear, distributed, thermally activated system obeying Eq. (1) have been considered in some detail in earlier treatments.[7,8,45] A distribution function of relaxation times proportional to $\tau^{-(1+\rho)}$ with a finite
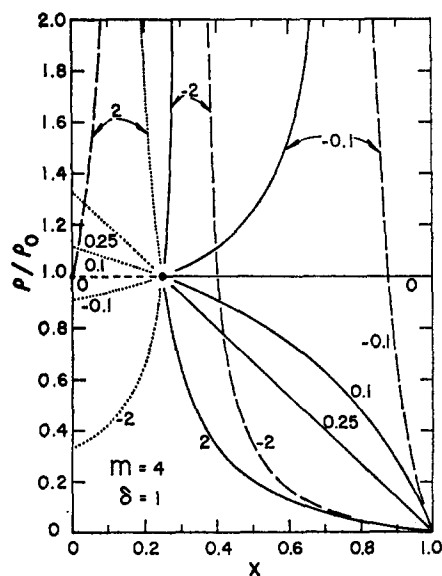

FIG. 4. ρ/ρ_0 vs x for $m=4$, $\delta=1$, and various values of χ. Negative branches shown dashed and reversed in sign.

[44] J. B. Wachtman, Jr., Phys. Rev. 131, 517 (1963).
[45] J. R. Macdonald, Annual Meeting, Society of Rheology, Baltimore, Maryland, October 1962.

range was considered and led to the possibility of time dependence of dielectric discharge current, or rate of strain, of the frequently observed form $t^{-(1+\rho)}$ (or of this form but with different values of ρ for different time intervals) for times greater than the minimum (τ_1) and less than the maximum (τ_2) relaxation time of the system. Also, the sign and magnitude of ρ affected the skew of a Cole–Cole frequency dispersion plot.[7,19,45,46] The temperature dependence of ρ and of τ_1 and τ_2 was examined when the original distribution of relaxation times arose from a distribution of pre-exponential factors only $(\beta_2=0)$, a distribution of activation energies only $(\beta_1=0)$, or a simultaneously present distribution of activation energies and a distribution of $\ln\tau_d(\beta_1\neq0, \beta_2\neq0)$ with E and $\ln\tau_d$ linearly related. It was implicitly assumed in this work that T_0 was not distributed (or, more precisely, it was taken constant and so had a delta function distribution).

Here, we present the generalization of some of the above work appropriate when $T_g\neq0$ and Eq. (2) applies. Combining the earlier and present work, one readily finds

$$\rho=\lambda/M, \tag{38}$$

$$(\tau_2/\tau_1)=r^{2|M|}, \tag{39}$$

where

$$M\equiv\beta_1+\beta_2[(T_0-T)/(T-T_\infty)]. \tag{40}$$

In these equations λ, β_1, and β_2 are temperature-independent, positive or negative constants. Here, r^2 is also a constant, the value of τ_2/τ_1 when $|M|=1$.

Let us define $\delta\equiv1$ when $\beta_1\neq0$ and $\delta\equiv0$ when $\beta_1=0$. Further, let $\chi\equiv\beta_2/\beta_1$ or 1 and $\rho_0\equiv\lambda/\beta_1$ or λ/β_2 when $\beta_1\neq0$ or $\beta_1=0$, respectively. When $\beta_2=0$ there is no temperature dependence of ρ and (τ_2/τ_1), and this case
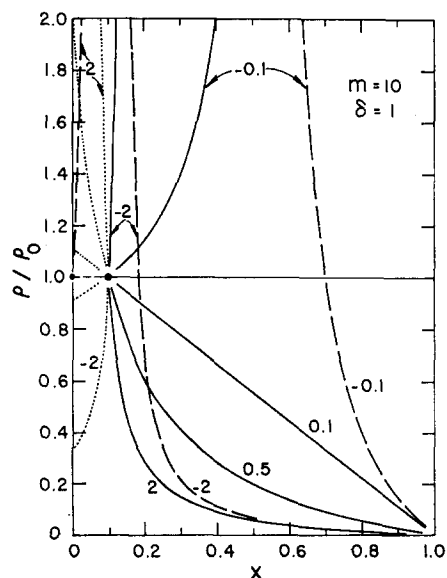

FIG. 5. ρ/ρ_0 vs x for $m=10$, $\delta=1$, and various values of χ. Negative branches shown dashed and reversed in sign.
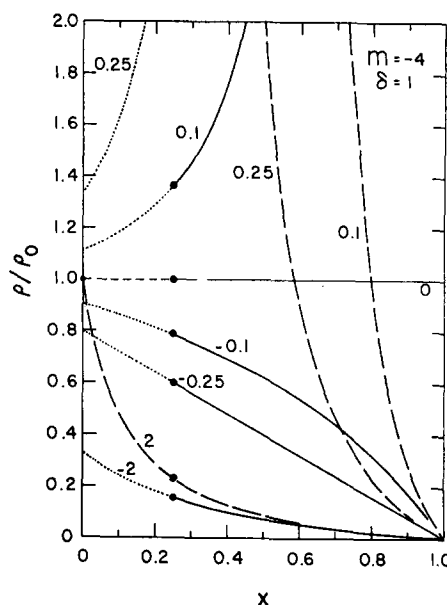
[46] J. R. Macdonald, J. Chem. Phys. **36**, 345 (1962).

FIG. 6. ρ/ρ_0 vs x for $m=-4$, $\delta=1$, and various values of χ. Negative branches shown dashed and reversed in sign.

need not be further considered. We may now write

$$\rho=\frac{\rho_0}{\delta+\chi[(T_0-T)/(T-T_\infty)]}$$

$$=\frac{\rho_0}{\delta+\chi[(mx-1)/(1-x)]}, \tag{41}$$

where we have again introduced the variable $x\equiv T_\infty/T$. Note that $mx\equiv T_0/T$ and when $T_\infty\rightarrow0$, $(mx-1)/(1-x)\rightarrow(T_0/T)-1$. Again, we have made the simplifying assumption that T_0 is not distributed and we shall also take T_∞ as undistributed. The present χ should not be confused with that used earlier in the paper.

Equation (41) shows that when $\beta_1=0$ so that only the activation energy parameter E is distributed, ρ is inversely proportional to the $\Delta G/kT$ given by (11); thus the curves of Fig. 2 are then proportional to ρ^{-1}, and we shall not present additional curves showing how ρ depends on temperature in this case. Since both ρ_0 and χ may be positive or negative, temperature dependence is more complicated when $\beta_1\neq0$, $\beta_2\neq0$ and thus $\delta=1$. When β_1 and β_2 have the same sign, the distributions of E and $\ln\tau_d$ are simply related.[7,8] When the signs are opposite, the relation is between E and $\ln(\tau_d)^{-1}$ and χ is negative. In the absence of specific, detailed material information either possibility is equally likely.

Figures 3–6 show some of the curve shapes which follow from (41) for $\delta=1$ and various values of the remaining parameters. The parameter value given for each curve is that of χ. The dashed lines shown on Figs. 4–6 are negative values which have been inverted to save space. For clarity, no negative branches have been included in Fig. 3, although they exist in the case $m=2$ for all curves with $\chi<0$ and for $\chi=1$ and 2. As before, curves for $T>T_0(x<m^{-1})$ are shown dotted except

when they must be dashed. The point at $x = m^{-1}$ is shown by a heavy solid circle. Note that since ρ_0 may be either positive or negative, the positive and negative curves shown in the figures may individually lead to either positive or negative values of ρ.

The pole where ρ/ρ_0 changes sign occurs at a value of x given by $(1-\chi)/(1-m\chi)$. At points where $|\rho| \to \infty$, previous work shows that the distribution of relaxation times reduces to a delta function.[7,8] At the same time, (39) indicates that when $|\rho| \to \infty$ because $M \to 0$, then $\tau_2/\tau_1 \to 1$, and there is only a single effective relaxation time. Then simple Debye dispersion is found, and transient response involves a single exponential decay.

Data are lacking for a full, detailed comparison of experimental ρ vs x curves with the theoretical curves of Figs. 3–6. The theoretical curves are included here to give some idea of the varieties of dependence possible when the present model applies. In previous work,[7,46] $\rho(T)$ data for the case $T_g = 0$ have been discussed which seem to be in reasonable agreement with the predictions of theory when E alone is distributed and when E and $\ln\tau_d$ are distributed and linearly related.

Williams[47] has recently presented data on polyoxymethylene from which $\rho(T)$ values may be derived. For this material, $T_g \sim 186°K$, and Williams found dielectric discharge currents which were approximately of the

form $t^{-(1+\rho)}$ for a variety of temperatures. The data show that ρ is zero near T_∞, increases to a maximum of 0.43 at 203°K, then decreases somewhat irregularly to -0.54 at 293°K, the highest temperature of measurement. Williams explains the results qualitatively by means of two different relaxation mechanisms. Since the curve of frequency of maximum dielectric loss vs T^{-1} presented seems smooth and of the form required by Eq. (11), it appears that the model of the earlier sections should apply over most, if not all, of the measured temperature range. The $\rho(T)$ results are then in approximate agreement with the predictions of (41) provided there is "damping" which causes the pole at $x = (1-\chi)/(1-m\chi)$ to be replaced by a finite doublet. Then when ρ_0, χ, and m have the proper combination of signs and magnitudes, ρ will be zero at T_∞, will reach a positive maximum, will decrease to a negative maximum, and will finally then decrease in magnitude as the temperature increases. The necessary damping may arise from the presence of a distribution of T_0 and/or T_∞ wider than a single delta function and from other causes of inexact correspondence between the ideal model and the experimental material including even an inhomogeneous temperature distribution in the sample. A more precise treatment would require the calculation of the standard deviation of the distribution of Z_n when E, $\ln\tau_d$, T_0, T_∞, and possibly T itself all were distributed with separate but perhaps related distributions.

[47] G. Williams, Polymer 4, 27 (1963).