[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids[1]

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RECEIVED FEBRUARY 7, 1955

The ratio a_T of all mechanical and electrical relaxation times at temperature T to their values at a reference temperature T_s can be expressed, after suitable choice of T_s, by the equation $\log a_T = -8.86\,(T - T_s)/(101.6 + T - T_s)$. Over a T range of $T_s \pm 50°$, this applies to a wide variety of polymers, polymer solutions, organic glass-forming liquids, and inorganic glasses. As chosen, T_s lies about 50° above the glass transition temperature T_g. If, alternatively, the reference temperature is chosen as T_g, then $\log a_T \cong -17.44\,(T - T_g)/(51.6 + T - T_g)$. Above $T_s + 50$ (or $T_g + 100$) the equation fails because different systems show specific properties which are no longer dominated by the non-specific behavior associated with supercooling and vitrification. The apparent activation energy for relaxation processes, unlike a_T, is not a universal function of $T - T_s$ or $T - T_g$. Our empirical equations are shown to be consistent with earlier formulations of Fox and Flory, Tobolsky, Dienes and Bueche over limited temperature ranges. Comparison with a simplified version of Doolittle's free space equation for temperature dependence of viscosity shows that our empirical constants are determined by the increase in thermal expansion coefficient at the glass transition temperature and the fractional free volume at that point. The latter quantities are calculated to be 4.8×10^{-4} deg.$^{-1}$, in rather good agreement with experimental measurements, and 0.025, a reasonable value.

Introduction

In an amorphous polymer above its glass transition temperature, a single empirical function can describe the temperature dependence of all mechanical and electrical relaxation processes.[2] The ratio a_T (or[5] κ) of any mechanical relaxation time at temperature T to its value at a reference temperature T_0, derived from transient[5] or dynamic[6] viscoelastic measurements or from steady flow viscosity,[6,7] and the corresponding ratio b_T of the values of any electrical relaxation time,[8] appear to be identical over wide ranges of time scale.[8] From the standpoint of current theories of polymer viscoelasticity,[9,10] a_T ($= b_T$) reflects primarily the temperature dependence of a segmental friction coefficient or mobility on which the rates of all configurational rearrangements depend.

The function $a_T(T)$ is thus a very important one in describing the physical properties of a polymer system. It has been customary to choose the same arbitrary reference temperature T_0 insofar as possible (often 298°K.) for comparing a_T in different systems. In this case the functions all cross at $T = T_0$ but vary widely in slope. However, if a separate reference temperature T_s is suitably chosen for each system, and a_T is expressed as a function of $T - T_s$, this function turns out to be identical for a wide variety of polymers and their solutions, as briefly reported previously.[11]

The reference temperature T_s is chosen arbitrarily for *one* system—in this case, as 243°K. for a high molecular weight polyisobutylene. Plots of $\log a_T$ or $\log b_T$ against T for other systems are matched with horizontal and vertical translations, using transparent paper, for coincidence in shape; depending on the temperature range of overlap, T_s can be determined in this manner within ±1 to ±3°.

Using a_T data from dynamic mechanical, stress relaxation and viscosity measurements in the literature, and b_T from dielectric measurements, values of T_s have been determined for 17 polymer systems, including several concentrated solutions and gels.[11] Plots of $\log a_T$, reduced to T_s, against $T - T_s$ coincide for all these systems over a temperature range of $-50° < T - T_s < +50°$.

We now examine the scope and limitations of this treatment, and its relation to previous empirical and theoretical discussions of the temperature dependence of relaxation processes, in more detail. It is found that the identical function $a_T(T - T_s)$ applies not only to polymer systems but also to a variety of organic and inorganic glass-forming liquids over a wide temperature range above the vitrification point. Moreover, it can be represented by a very simple equation whose constants can be given a reasonable physical interpretation.

Further Applications of Empirical Temperature Dependence Function

Low Molecular Weight Polymers.—The systems treated in the preceding communication[11] included high molecular weight polyisobutylene[6] and polystyrene.[12] The temperature dependence of viscosity and relaxation is not influenced by molecular weight when the latter is high[13]; but at low molecular weights the temperature dependence is modified in a manner which is correlated empirically with the effect of molecular weight on the glass transition temperature.[13] Accordingly, values of a_T have now been calculated for a number of low molecular weight fractions of both these polymers, using the viscosity measurements of Fox and Flory[13] and

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[1] Part XIX of a Series on Mechanical Properties of Substances of High Molecular Weight.

[2] Certain relaxation mechanisms[3,4] which are detected experimentally below the glass transition temperature, and therefore lie outside the scope of the present treatment, are omitted from this discussion.

[3] K. Deutsch, E. A. W. Hoff and W. Reddish, *J. Polymer Sci.*, **13**, 565 (1954).

[4] J. Heyboer, P. Dekking and A. J. Staverman, Proc. 2nd Intern. Congress Rheology, London, Butterworth's Ltd., 1954, p. 123.

[5] A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.*, **8**, 543 (1952).

[6] J. D. Ferry, THIS JOURNAL, **72**, 3746 (1950); J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.*, **24**, 911 (1953).

[7] H. Leaderman, R. G. Smith and R. W. Jones, *J. Polymer Sci.*, **14**, 47 (1954).

[8] J. D. Ferry and E. R. Fitzgerald, *J. Colloid Sci.*, **8**, 224 (1953); J. D. Ferry, M. L. Williams and E. R. Fitzgerald, *J. Phys. Chem.*, **59**, 403 (1955).

[9] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272 (1953).

[10] F. Bueche, *ibid.*, **22**, 603 (1954).

[11] M. L. Williams, *J. Phys. Chem.*, **59**, 95 (1955).

[12] L. D. Grandine, Jr., and J. D. Ferry, *J. Appl. Phys.*, **24**, 679 (1953).

[13] T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948); *J. Appl. Phys.*, **21**, 581 (1950); *J. Phys. Chem.*, **55**, 221 (1951); *J. Polymer Sci.*, **14**, 315 (1954).

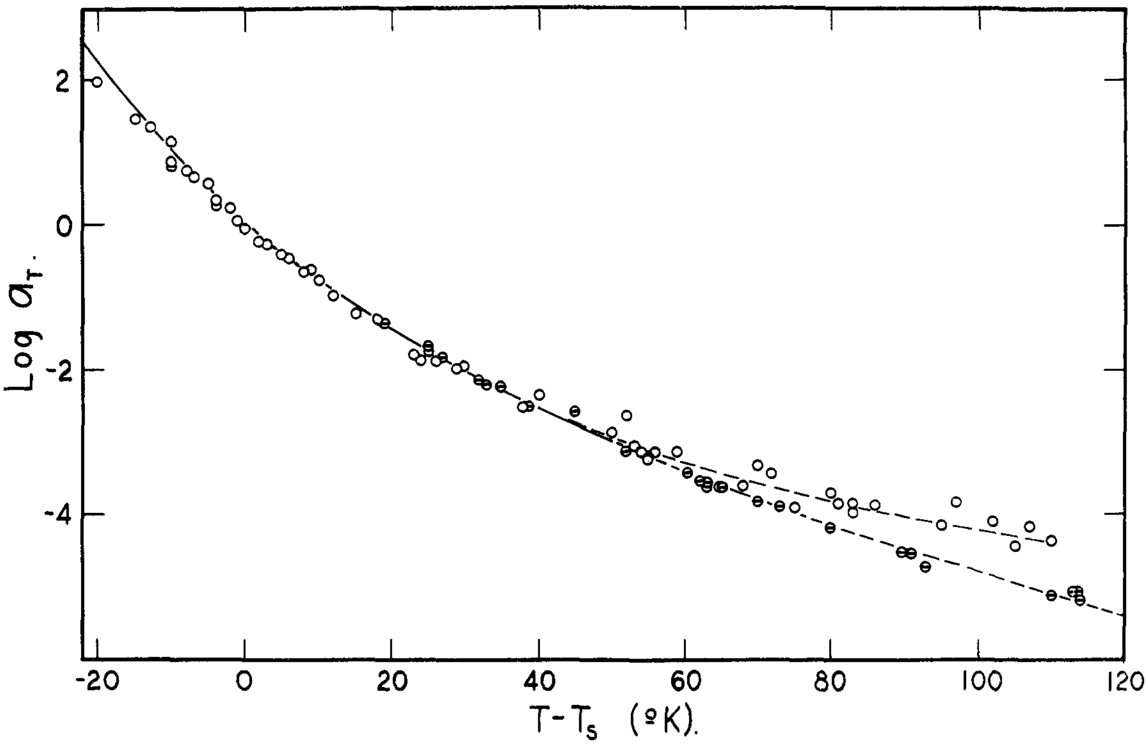

Fig. 1.—Log a_T plotted against $T - T_s$ for fractions of polystyrene (open circles) and polyisobutylene (slotted circles). Solid curve is reproduced from the composite plot of reference 11.

the formula[6] $a_T = \eta T_s \rho_s / \eta_s T \rho$. Here η and ρ are the viscosity and density at temperature T and η_s and ρ_s the corresponding quantities at T_s. The appropriate values of T_s are given in Table I, and log a_T is plotted against $T - T_s$ in Fig. 1. All fractions coincide reasonably well with the previous composite curve for $T - T_s < 50°$. At higher temperatures, however, the curves for the two polymer types diverge. This behavior is to be expected and will be further discussed below.

Table I

Reference Temperatures, °K., Polyisobutylene and Polystyrene Fractions, from Viscosity Measurements[13]

Polymer	Mol. wt.	T_s	T_g^a	$T_s - T_g$
Polyisobutylene	4170	238	194	44
	5380	241	197	44
	6610	240	200	40
	8500	240	202	38
Polystyrene	1675	358^b	313	45
	2085	371	326	45
	2600	380	335	45
	3041	383	338	45
	3590	393	348	45
	6650	395	350	45
	13300	404	359	45
	19300	407	362	45

[a] Glass transition temperatures, measured for polystyrenes[13] and calculated for polyisobutylenes from a formula given by Fox and Flory.[13] [b] The values for polystyrenes were actually taken as $T_g + 45$ instead of from curve fitting.

It is evident that a decrease in molecular weight diminishes T_s by approximately the same amount that it diminishes the glass transition temperature T_g.

Organic Glass-forming Liquids.—As a supercooled liquid of low molecular weight approaches its glass transition temperature, there is an enormous increase in viscosity and slowing of dielectric relaxation processes. The distribution of electrical relaxation times in such systems[14] is quite different from (and considerably sharper than) those in polymers, and the wide distribution of mechanical relaxation times which characterizes polymers seems to be absent entirely.[15] Nevertheless, the *temperature dependence* of the relaxation processes has in several cases[14,16,17] been found to be the same for both viscosity and dielectric relaxation in supercooled organic liquids as it is in polymers, and now this temperature dependence turns out to follow the same function which we have used for polymers.

Values of a_T have been calculated from viscosity data of Parks on glucose[18] and abietic acid[19] and of Fitzgerald and Miller on dimethylthianthrene.[17] The data for glucose are especially valuable because of the wide range of temperatures covered. Values of b_T have been calculated from dielectric dispersion data of Cole[14] on *n*-propanol, propylene glycol and glycerol. With a suitable choice of T_s, plots of log a_T against $T - T_s$ coincide for all six liquids and

(14) D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951).

(15) J. J. Benbow, *Proc. Phys. Soc.* (*London*), **B67**, 120 (1954).

(16) W. Kauzmann, *Rev. Modern Phys.*, **14**, 12 (1942).

(17) E. R. Fitzgerald and R. F. Miller, *J. Colloid Sci.*, **8**, 148 (1953).

(18) G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, *Physics*, **5**, 193 (1934).

(19) G. S. Parks, M. E. Spaght and L. E. Barton, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 115 (1935).

moreover coincide with the previous composite curve obtained for polymer systems, as shown in Fig. 2. The appropriate values of T_s are given in Table II.

Inorganic Glasses.—In the same manner, viscosity data on inorganic glasses can be used to calculate a_T as a function of temperature and the latter can be fitted to the empirical composite curve. The appropriate values of T_s for boron trioxide[20] and three optical glasses[21-23] are given in Table III, and the plot against $T - T_s$ is shown in Fig. 3. It does not extend below T_s, but in the range covered the coincidence with the previous composite curve for polymers and organic glasses is remarkable, considering the great difference in chemical composition and actual location on the absolute temperature scale. It is expected, therefore, that the empirical function $a_T(T - T_s)$ will have widespread applicability.

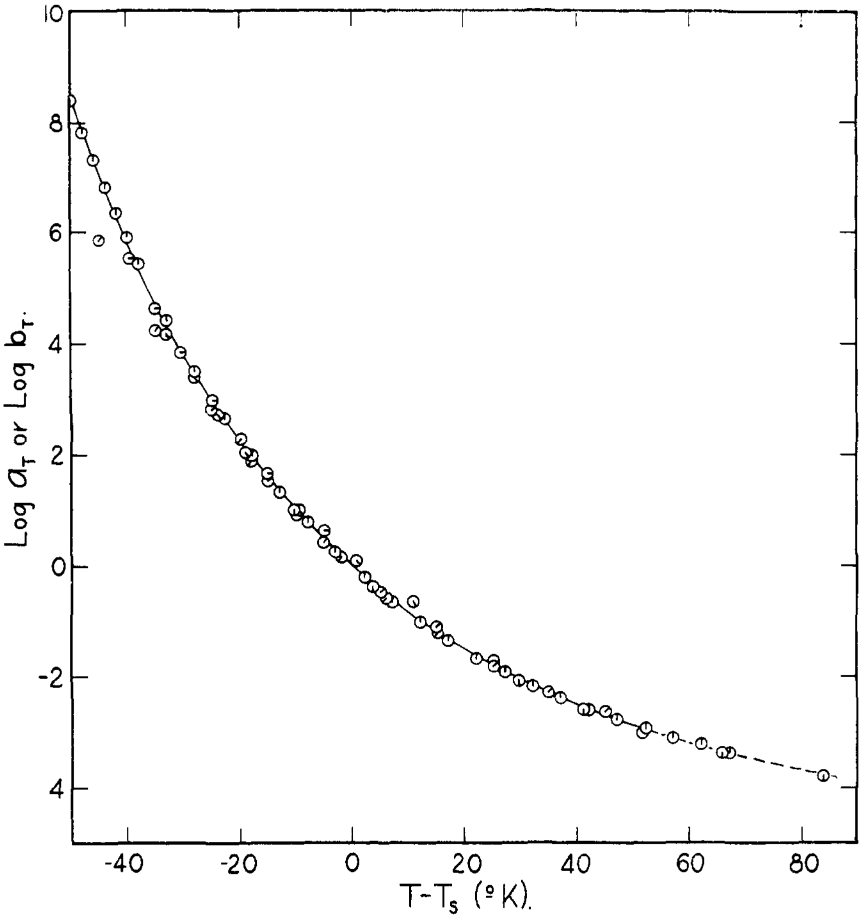

Fig. 2.—Log a_T and log b_T plotted against $T - T_s$ for organic glasses: pip up, glucose; successive 45° rotations clockwise, abietic acid, glycerol, propylene glycol, *n*-propanol and dimethylthianthrene. Solid curve is reproduced from the composite plot of reference 11. Dashed curve is reproduced from that for the polystyrene fractions in Fig. 1.

Discussion

Relation between T_s and T_g.—In Tables I and II, values of the glass transition temperature are also given, and this evidently lies about 50° below T_s. Further comparisons for some of the polymers whose T_s values already have been reported[11] are given in Table IV. The average value of $T_s - T_g$ with its standard deviation for all these systems is 50 ± 5°.

TABLE II

REFERENCE TEMPERATURES, °K., ORGANIC GLASS-FORMING LIQUIDS

Liquid	T_s	T_g	$T_s - T_g$
Glucose	351	305[a]	46
Abietic acid	358	..	..
Dimethylthianthrene	288	..	..
n-Propanol	143	98[b]	45
Propylene glycol	217	160[b]	57
Glycerol	238	187[b]	51

[a] From thermal expansion measurements by G. S. Parks and S. B. Thomas, THIS JOURNAL, **56**, 1423 (1934). [b] From heat capacity measurements by G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **31**, 1842 (1927).

In principle T_g would be a better reference temperature than T_s, since it can be specified by an

TABLE III

REFERENCE TEMPERATURES, °K., INORGANIC GLASSES

Glass	Reference	T_s
Boron trioxide	20	521
Sodium-lead-silicate, no. 6	21	689
Sodium-calcium-silicate	22	743
Sodium-calcium-silicate, no. 10	23	795

TABLE IV

COMPARISON OF T_s AND T_g FOR POLYMERS

	T_s	T_g	Ref.	$T_s - T_g$
Polyisobutylene	243	202	25	41
Butadiene-styrene, 75/25	268	212	26	57
Polymethyl acrylate	324	276	27	48
Polyvinyl chloroacetate	346	296	26	50
Polyvinyl acetate	349	301	28	48
Polystyrene	408	354	29	54
Polymethyl methacrylate	433	378	30	55

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[20] G. S. Parks and M. E. Spaght, *Physics*, **6**, 69 (1935).

[21] J. Boow and W. E. S. Turner, *J. Soc. Glass Tech.*, **26**, 215 (1942).

[22] N. W. Taylor, E. P. McNamara and J. Sherman, *ibid.*, **21**, 61 (1937).

[23] H. A. Robinson and C. A. Peterson, *J. Amer. Ceram. Soc.*, **27**, 129 (1944).

[24] R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).

[25] R. N. Work, private communication.

[26] R. H. Wiley and G. M. Brauer, *J. Polymer Sci.*, **3**, 455 (1948); **5**, 609 (1950).

[27] E. Jenckel, *Z. physik. Chem.*, **A190**, 24 (1941).

[28] E. Jenckel, *Kolloid-Z.*, **100**, 163 (1942).

[29] W. Patnode and W. J. Scheiber, THIS JOURNAL, **61**, 3449 (1939). Somewhat higher values for T_g have been reported.

[30] T. G. Fox and S. Loshaek, *J. Polymer Sci.*, **15**, 371 (1955).

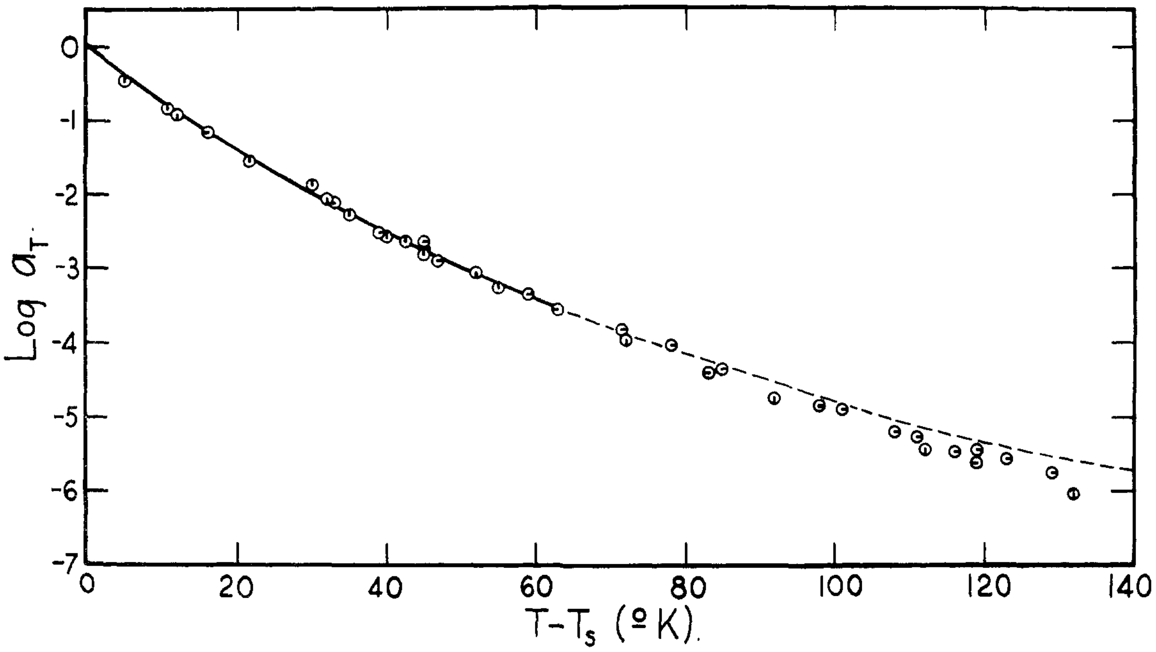

Fig. 3.—Log a_T plotted against $T - T_s$ for inorganic glasses: pip up, Taylor, *et al.*; right, silicate no. 6; down, boron trioxide; left, silicate no. 10. Solid curve is reproduced from the composite plot of reference 11. Dashed curve is reproduced from that for polyisobutylene fractions in Fig. 1.

independent physical measurement, whereas the group of T_s values is based on one original arbitrary choice. However, T_g is markedly influenced by small amounts of residual solvent or other diluent[24] as well as thermal history, and values determined in different laboratories vary; in fact, the scatter in $T_s - T_g$ is attributed partly to this cause. Moreover, viscosity and other mechanical measurements are more difficult near T_g, and data in this region are often lacking. We prefer, therefore, to retain T_s as a reference temperature; it can always be estimated approximately as $T_g + 50$ if detailed data for fitting the composite a_T curve are not available.

Analytical Expression for a_T.—An empirical formula for a_T can be inferred by modifying an expression which has previously been applied[31,32] to the viscosity (η) and dielectric dispersion[14] of supercooled liquids, as well as to creep[33] of polymers: $\log \eta = A + B/(T - T_\infty)$. Here A, B and T_∞ are constants, T_∞ falling well below the glass transition temperature. This equation would imply the following form for a_T

$$\log a_T = -c_1(T - T_s)/(c_2 + T - T_s) \qquad (1)$$

and from certain published values[14] of B and T_∞ it would appear that c_1 and c_2 should be about 9 and 100, respectively. Actually, a test plot of $(T - T_s)/\log a_T$ against $T - T_s$, using the composite curves of Figs. 1–3 and reference 11, gives a good straight line from which c_1 and c_2 are found to be 8.86 and 101.6. Values of a_T read from the composite curve and calculated from eq. 1 are compared in Table V. The agreement is highly satisfactory except for $T - T_s < -50$, *i.e.*, $T < T_g$. Equation 1 could not be expected to hold very far below T_g, since it predicts a monotonic increase of $\log a_T$ with decreasing temperature instead of the inflection point which is generally agreed to exist[13,34] near T_g; moreover, $\log a_T$ would become infinite at $T = T_s - c_2$. However, between T_g and $T_g + 100$, at least, this very simple formula should serve to predict temperature dependence of mechanical and dielectric properties. Here eq. 1 describes the composite function $\log a_T$ within a standard deviation of about 0.03. Any individual system may deviate somewhat more, judging from the scatter of points on the composite curve of reference 11, but it is not certain how much of this is due to experimental error and how much to specific differences in polymer systems.

Table V

Empirical Temperature Dependence Function

$T - T_s$	$\log a_T$ Composite curves	Eq. 1	$T - T_s$	$\log a_T$ Composite curves	Eq. 1
−60	12.00	12.78	10	−0.75	−0.79
−50	8.95	8.58	20	−1.43	−1.46
−40	5.75	5.75	30	−2.02	−2.02
−30	3.72	3.71	40	−2.50	−2.50
−20	2.25	2.17	50	−2.93	−2.92
−10	0.99	0.97	60	−3.29	−3.29
0	0	0			

Since T_s is based on an arbitrary choice, the form of eq. 1 should be independent of this original selection. In fact, if T_s is replaced by $T_s' = T_s + \delta$, the only change in eq. 1 is the replacement of c_1 by $c_1' =$

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[31] H. Vogel, *Physik Z.*, **22**, 645 (1921).

[32] G. Tammann and W. Hesse, *Z. anorg. allgem. Chem.*, **156**, 245 (1926).

[33] F. S. Conant, G. L. Hall and W. J. Lyons, *J. Appl. Phys.*, **21**, 499 (1950).

[34] J. R. McLoughlin and A. V. Tobolsky, *J. Colloid Sci.*, **7**, 555 (1952); E. Catsiff and A. V. Tobolsky, *J. App. Phys.*, **26**, 1092 (1954).

$c_1c_2/(c_2 + \delta)$ and of c_2 by $c_2' = c_2 + \delta$. Thus a formula can be written in terms of T_g, taking $\delta = -50°$.

$$\log a_T = -17.44(T - T_g)/(51.6 + T - T_g) \quad (2)$$

However, this is less accurate than eq. 1 because of uncertainty in specifying T_g and difficulty of experimental measurements near T_g; moreover, the form of the equation forces coincidence at the reference temperature, and if the latter is near the limit of the range of applicability (as T_g is) a deviation of eq. 1 from the data at this point can produce a deviation of eq. 2 over the entire temperature range.

Apparent Activation Energy.—Often temperature dependence of relaxation processes has been expressed in terms of an apparent activation energy, $\Delta H_a = R\,d \ln a_T/d(1/T)$. Differentiation of eq. 1 yields

$$\Delta H_a = 2.303Rc_1c_2T^2/(c_2 + T - T_s)^2 \quad (3)$$

This is *not* a function of $T - T_s$ alone. Thus, although there is a universal a_T function, there is no universal ΔH_a function; at constant $T - T_s$, ΔH_a is proportional to T^2. Examples are shown in Fig. 4, where ΔH_a is plotted against $T - T_s$ for polystyrene and polyisobutylene. This feature seriously limits the usefulness of ΔH_a in comparing the properties of different polymer systems.

Fox and Flory[13] have shown that ΔH_a is closely proportional to $1/T^5$ and $1/T$, respectively, for the two polymers depicted in Fig. 4. Though this appears at first inconsistent with the preceding paragraph, the alternative empirical expressions of Fox and Flory, shown by dashed curves in Fig. 4, are actually fairly close to the predictions of eq. 3 within the range where both treatments are considered to be applicable.

Limitations of Treatment.—Outside the range of 100° above T_g, eq. 1–3 cannot be expected to hold. Below T_g, $\log a_T$ actually increases less rapidly with decreasing temperature as previously pointed out. At high temperatures, on the other hand, experimental curves for different systems diverge as illustrated in Fig. 1. This must be expected, since for ordinary liquids far above their glass transition temperatures (or freezing points) the temperature dependence of viscosity varies widely and is related to specific details of molecular structure.[35] It is only in supercooled liquids, within 100° above the point of vitrification, that an abnormally high temperature dependence—independent of molecular structure—overwhelms such specific differences and makes possible our universal function.

Comparison with Previous Expressions for Temperature Dependence.—Besides the empirical equations of Fox and Flory[13] for polyisobutylene and polystyrene, several other expressions have been given previously for the temperature dependence of viscosity and relaxation processes in polymers.

Tobolsky's reduced equation for viscoelastic properties,[36] based on a reference temperature T_d which is close to or identical with T_g, corresponds to $\log a_T = (1/h)f(T/T_d)$, where h is a characteristic constant. Within a range of $0.95 < T/T_d < 1.05$, the function f can be approximated by $-36(T/T_d - 1)$; also it is found empirically that $h = 100/T_d$ for several polymers. With these modifications, Tobolsky's equation becomes $\log a_T = -0.36(T - T_d)$. To compare with eq. 2, we note that when T/T_g is near 1 the latter reduces to $\log a_T = -0.34 \cdot (T - T_g)$. Thus, very near the glass transition the two treatments are identical. Moreover, Tobolsky's also predicts proportionality of ΔH_a to T_d^2 at T_d. Below the glass transition the treatments differ, and Tobolsky's appears to be preferable in that it predicts a maximum for ΔH_a at T_d. Above the glass transition, however, where the predictions also differ, no attempt has been made to apply Tobolsky's equation above about $T_g + 20$, whereas ours is applicable up to $T_g + 100$.

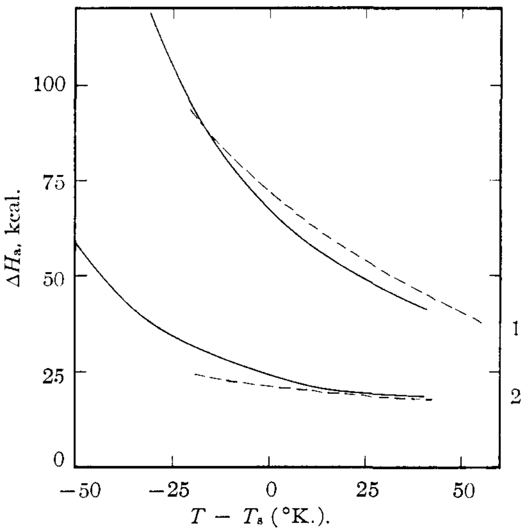

Fig. 4.—Apparent activation energy for polystyrene (1) and polyisobutylene (2), plotted against temperature: solid curves, calculated from eq. 3; dashed curves, from empirical equations of Fox and Flory.

Dienes[37] has proposed an equation for the temperature dependence of viscosity which corresponds to

$$\log a_T = -\frac{T - T_s}{2.303R}\left\{\frac{E}{TT_s} + \frac{U}{(T - T_0)(T_s - T_0)}\right\} \quad (4)$$

Here U is an activation energy for structural changes associated with local ordering, E an activation energy for viscous flow of the disordered liquid, and T_0 a temperature below which short-range order is complete. At sufficiently low temperatures, the term in E can be neglected; in this case, eq. 4 reduces to the same form as eq. 1 with $c_1 = U/2.303R(T_s - T_0)$ and $c_2 = T_s - T_0$. According to our numerical values of c_1 and c_2, $T_s - T_0$ should be 102° and U should be 4.2 kcal. However, in Dienes' application of eq. 4 to experimental data, the values of U chosen by empirical fit vary widely and $T_s - T_0$ is not a constant for all systems. These apparent inconsistencies are undoubtedly due to the fact that his constants are derived from data in temperature ranges extending well above $T_g + 100$, where specific effects of chemical structure outweigh the non-specific vitrification phenomenon.

Bueche's theory of segmental mobility in polymers near their glass transition temperatures[38]

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(35) A. Bondi, *Ann. N. Y. Acad. Sci.*, **53**, 870 (1951).

(36) J. Bischoff, E. Catsiff and A. V. Tobolsky, THIS JOURNAL, **74**, 3378 (1952); A. V. Tobolsky and E. Catsiff, *ibid.*, **76**, 4204 (1954).

(37) G. J. Dienes, *J. Appl. Phys.*, **24**, 779 (1953).

(38) F. Bueche, *J. Chem. Phys.*, **21**, 1850 (1953).

provides the following temperature dependence of segmental jumping frequency P

$$P = (P_0/2)\{1 - \mathrm{erf}[A/BT^{1/2} - BT^{1/2}]\}$$

where $B = \alpha_2(V_{00}/2\beta R)^{1/2}$ and $A = \alpha_2(Q_{00} - V_{00})/2\beta R$; β is the compressibility, α_2 the increase in thermal expansion coefficient at the glass transition temperature, V_{00} the critical volume within which expansion must occur to permit configurational changes, and Q_{00} the corresponding expanded volume (both extrapolated to absolute zero). Near T_g, the argument of erf is small and the latter can be expanded into a simple exponential. Since $\log a_T$ referred to T_g is $\log P_g - \log P$, we obtain

$$\log a_T = -B^2(T - T_g) + A^2(T - T_g)/B^2TT_g \quad (5)$$

This can be a universal function near T_g only if $(V_{00}/\beta)/[(Q_{00} - V_{00})^2/V_{00}{}^2T_g{}^2 - \alpha_2{}^2]$ is a constant for all systems. For the parameters derived by Bueche for polystyrene and polyisobutylene, this is approximately the case, and substitution of those numerical values in eq. 5 gives (near T_g) $\log a_T = -0.34(T - T_g)$, in agreement with eq. 3. The significance of the above condition is not entirely clear, but it agrees qualitatively with Bueche's conclusions that Q_{00}/V_{00} is the same for both polymers and that a high T_g is associated with a high V_{00}.

Relation of a_T to Free Volume.—A much simpler theoretical relation than those of Dienes or Bueche, which is identical in form with eq. 2 and relates the empirical constants to simple physical quantities, can be derived from a modification of Doolittle's free-space equation for viscosity.[39]

The view has been emphasized that the temperature dependence of viscosity arises largely from its dependence on free volume.[39,13] Doolittle's remarkably accurate equation, in which temperature does not appear explicitly at all, applies to simple liquids at high enough temperatures so that the proportion of free volume is relatively high

$$\ln \eta = \ln A + Bv_0/v_f \quad (6)$$

Here A and B depend on the nature of the liquid, and v_0 and v_f are the occupied and free volume, respectively, per g. Our treatment does not include this temperature range, where specific differences among liquids are obvious. However, as pointed out by Fox and Flory,[13] when the glass transition is approached the relative free volume diminishes sharply, and this, again, is believed to be primarily responsible for the accompanying large viscosity increase. The existence of a universal function such as eq. 1 or eq. 2 implies that the nature of this volume change and its effect on the rates of molecular rearrangements are essentially the same for all supercooled systems, polymeric, non-polymeric and mixtures, independent of molecular structure.

For supercooled systems, eq. 6 can be modified by noting that v_f is small and v_0 is practically equal to the specific volume $(v_0 + v_f)$, so v_f/v_0 can be replaced by the fractional free volume, $v_f/(v_0 + v_f) = f$. (For the purposes of this treatment, it is not necessary to specify exactly which of the possible definitions of free volume[40] applies here.) The constant B is found by Doolittle to be of the order of unity; for supercooled liquids, the existence of a universal a_T function implies that it must be the same for all, and we simply make it unity. Then, since a_T reduced to T_g is approximately η/η_g (the T and ρ factors varying relatively slightly with temperature), we have

$$\log a_T = (1/2.303)(1/f - 1/f_g) \quad (7)$$

where f_g is the fractional free volume at T_g.

The dependence of free volume on temperature is taken by several authors[13,38] to be the difference between the thermal expansion coefficients above and below the glass transition temperature, α_2. Thus $f = f_g + \alpha_2(T - T_g)$. Substitution in eq. 7 yields

$$\log a_T = -(1/2.303\, f_g)(T - T_g)/(f_g/\alpha_2 + T - T_g) \quad (8)$$

This is identical in form with eq. 2, and by equating the constants we find $\alpha_2 = 4.8 \times 10^{-4}$ deg.$^{-1}$ and $f_g = 0.025$.

The above value of α_2 is in reasonable agreement with measured values for amorphous polymers, such as the following ($\times 10^{-4}$): polyisobutylene[41] 4.5, polystyrene[13] 4.4, polyvinyl acetate[42] 4.6, polyvinyl butyral[42] 4.6. Values for non-polymeric systems vary somewhat more widely: boron trioxide[43] 5.5, propylene glycol[44] 5.0, glycerol[45] 4.4, glucose[46] 2.8 (all $\times 10^{-4}$), but are similar in magnitude. The value of f_g seems to be reasonable, but any comparison with other data would require a more specific interpretation of f. In the case of glycerol, it agrees rather closely with the relative excess volume of the glass over the crystalline state at T_g ($= 0.022$).[45] The existence of a universal value of f_g is, of course, consistent with the view of Fox and Flory[13] that the glass transition point is an iso-free-volume state.

Conclusions

The universal function for temperature dependence of viscosity and mechanical and electrical relaxations in amorphous polymers and other supercooled, glass-forming liquids arises from the fact that the rates of all such processes depend on temperature primarily through their dependence on free volume. The theoretical implications are more evident when the reference temperature is chosen as T_g; then it is apparent that three quantities—T_g, α_2 and f_g—determine the temperature dependence of a_T over a range of 100° above T_g. For practical purposes, however, it is more accurate to choose a higher reference temperature T_s, and use the empirical constants of eq. 1 in predicting the temperature dependence of mechanical and electrical properties. This treatment is quite independent of the nature of the relaxation spectrum and the *time* dependence of mechanical and electrical properties; it appears to be equally applicable to narrow and broad relaxation distributions.

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Acknowledgment.—This work was supported in part by Picatinny Arsenal, Ordnance Corps, Department of the Army. It was also part of a program of research on the physical structure and properties of cellulose derivatives and other polymers supported by the Allegany Ballistics Laboratory, an establishment owned by the United States Navy and operated by the Hercules Powder Company under Contract NOrd 10431.

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The Iodine Bromide Catalyzed Reaction of Bromine with Mesitylene in Carbon Tetrachloride Solution

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RECEIVED FEBRUARY 14, 1955

The reaction between mesitylene and bromine in carbon tetrachloride solution is catalyzed by iodine bromide. At low concentrations of mesitylene the rate of disappearance of bromine is second order in iodine bromide, first order in bromine and first order in mesitylene. At concentrations of mesitylene above 1 *M* the effect of increasing mesitylene concentration on the rate of reaction may be explained on the basis that both free and complexed iodine bromide act as a catalyst for the conversion of a 1–1 mesitylene–bromine complex to ring substituted bromomesitylene.

Bruner's[1] data on the iodine-catalyzed bromination of benzene have been reinterpreted by several different workers.[2] Robertson[2b] and co-workers state that the data may be explained by two simultaneous reactions both of which are fourth order in halogen. In addition they present data for the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride solution which they treat in terms of two simultaneous reactions that are third order in halogen. Tsuruta[2c] and co-workers interpret Bruner's data in terms of a single reaction which is third order in iodine bromide and first order in bromine. This is in agreement with calculations carried out in this Laboratory. In a later publication Tsuruta[3] and co-workers have shown that the rate of bromination of toluene in carbon tetrachloride is third order in iodine bromide, first order in bromine and first order in toluene. However, the reactions which they investigated were subject to an induction period. This fact suggests that an appreciable fraction of the bromination proceeded by a hydrogen bromide catalyzed reaction of the type reported for mesitylene.[4] Thus their conclusions as to the order of the reaction with respect to iodine bromide may not be valid. Therefore an investigation of the iodine bromide catalyzed reaction of bromine with mesitylene was undertaken.

The Effects of Changes in Reaction Conditions.—In carbon tetrachloride solutions containing excess bromine, iodine is almost completely converted to iodine bromide.[5] On adding excess mesitylene to such solutions bromination of the mesitylene takes place until the excess bromine is used up and the reaction then practically stops. Thus the rate of reaction of iodine bromide with mesitylene in carbon tetrachloride solution is negligible compared to the iodine bromide catalyzed bromination reaction.

In a previous communication[4] it was shown that carbon tetrachloride solutions of mesitylene could be brominated using hydrogen bromide as a catalyst only when water also was present.

To minimize the amount of the reaction proceeding by hydrogen bromide catalysis all solutions used in the rate runs were stored over freshly regenerated "Drierite" and all glassware was coated with Desicote. Even after these precautions were taken there was a noticeable autocatalytic effect when the iodine bromide concentration was less than 0.5×10^{-3} *M*, however, there was no evidence of an induction period. The solutions of bromine and mesitylene in the presence of iodine bromide were much less photosensitive than corresponding solutions without the iodine bromide. The brominated mesitylene from several of the rate runs was found to have 99% of the bromine attached to the ring thus indicating a negligible amount of side chain bromination.

Kinetic Studies.—Carbon tetrachloride solutions of iodine, bromine and mesitylene were mixed and the bromine concentration of the reaction mixture was determined spectrophotometrically at 520 mμ at various times. In these runs the mesitylene concentration was at least ten times that of bromine so that the mesitylene concentration remained nearly constant throughout the reaction. Under these conditions the individual runs were found to be first order in bromine

$$-\frac{d(\mathrm{Br}_2)_\mathrm{T}}{dt} = k_1(\mathrm{Br}_2)_\mathrm{T} \qquad (1)$$

The first-order rate constants, k_1, reported in the upper part of Table I were calculated from the slopes of the straight lines obtained by plotting log $(\mathrm{Br}_2)_\mathrm{T}$ *versus* time in minutes. The term $(\mathrm{Br}_2)_\mathrm{T}$ refers to the bromine in excess of the amount required to form iodine bromide. The first-order dependence of the rate of reaction on the bromine concentration is demonstrated by the constancy of the calculated k_1 values over a tenfold variation in initial bromine concentration (first four runs).

The order of the reaction with respect to mesityl-

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