

THERMAL EXPANSION, HEAT CAPACITY AND STRUCTURAL RELAXATION
MEASUREMENTS IN THE GLASS TRANSITION REGION

by

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ABSTRACT

THERMAL EXPANSION, HEAT CAPACITY AND STRUCTURAL RELAXATION MEASUREMENTS IN THE GLASS TRANSITION REGION

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Thermal expansion, density and specific heat measurements were made on the glasses and supercooled liquids of three inorganic glass forming systems to evaluate the $T_g V \Delta\alpha/\Delta C_p$ term of the Davies and Jones expression. The three glasses studied were As_2S_3 , Lillie No. 1, a soda-lime-silica glass, and Pyrex, a borosilicate glass with Corning designation number 7740. The length-temperature and enthalpy-temperature data were fitted to polynomial expressions by least square curve fitting techniques and are presented with standard deviations. Thermal expansivities and specific heats needed for the above and subsequent calculations were obtained by differentiation of these expressions.

These measurements combined with compressibility data appearing in the literature made possible the calculation of the Grüneisen constants, $\bar{\gamma}$, for these glasses. The values observed for both siliceous glasses indicate that the vibrational modes with negative γ_i 's are suppressed by additions of Na and Ca into the silica network. The value of $\bar{\gamma}$ for vitreous As_2S_3 was lower than anticipated.

A discontinuity in the thermal expansion coefficient of Pyrex which was observed at approximately 260°C was attributed to the high borate phase of the two phase glass undergoing a glass transition.

The structural relaxation resulting from sudden temperature changes in the transition region indicated that a spectrum of relaxation

times with a maximum value is needed to describe this nonlinear process. It was found that over the temperature range investigated the "equilibrium structural relaxation time" was exponentially dependent on temperature with an activation energy the same as that observed for shear relaxation times. Fictive and actual temperature have approximately the same influence on the observed effective relaxation time. The initial structural relaxation time resulting from an infinitely small change of temperature is numerically close to the shear relaxation time, though the "equilibrium structural relaxation" time is approximately thirty times the value for shear.

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TABLE OF CONTENTS

	<u>Page</u>
TITLE PAGE.	i
ABSTRACT.	ii
LIST OF FIGURES.	v
LIST OF TABLES.	vii
ACKNOWLEDGEMENTS.	viii
I. INTRODUCTION.	1
II. LITERATURE SURVEY	6
A. Thermal Properties of Solids	6
B. Thermal Properties of Liquids.	33
C. Structural Relaxation in the Transition Region	46
III. EXPERIMENTAL PROGRAM.	67
IV. APPARATUS EMPLOYED IN EXPERIMENTAL PROGRAM.	73
V. EXPERIMENTAL RESULTS.	85
VI. DISCUSSION OF RESULTS	123
VII. SUMMARY AND CONCLUSIONS	168
VIII. SUGGESTION FOR FURTHER WORK	172
IX. BIBLIOGRAPHY.	174
Appendix A-Calorimeter Operating Notes.	183
Appendix B-Drawing of Glass Vessels	188
Appendix C-Biographical Note.	189

LIST OF FIGURES

<u>Figure No.</u>	<u>Page</u>	<u>Title</u>
1	13	Linear oscillator model
2	29	Experimental and calculated values of the heat capacity of vitreous silica after Smyth ⁽⁴⁰⁾
3	44	Specific volume of B_2O_3
4	53	Schematic variation of $\tau(t)$ vs. δ when a spectrum of relaxation times is present after Goldstein ⁽⁷⁾
5	75	Sample configuration and high conductivity bed used for thermal expansion studies
6	78	Schematic diagram of furnace and ice calorimeter
7	97	Linear expansion of Lillie No. 1
8	98	Linear expansion of As_2S_3
9	99	Linear expansion of Pyrex
10	101	Linear and volumetric expansivities of Lillie No. 1
11	102	Linear and volumetric expansivities of As_2S_3
12	103	Linear and volumetric expansivities of Pyrex
13	109	Enthalpy of As_2S_3
14	110	Enthalpy of Lillie No. 1
15	111	Enthalpy of Pyrex

LIST OF FIGURES (Continued)

<u>Figure No.</u>	<u>Page</u>	<u>Title</u>
16	112	Heat capacity of As_2S_3
17	113	Heat capacity of Lillie No. 1
18	114	Heat capacity of Pyrex
19	116	Length relaxation of 500°C of a Lillie No. 1 sample initially stabilized at 475°C
20	117	Effective time constants for structural relaxation of Lillie No. 1
21	120	Equilibrium structural and shear relaxation time for Lillie No. 1
22	136	Grüneisen constants for As_2S_3 and Pyrex
23	141	$\ln(\text{free volume})$ vs. reciprocal of absolute temperature
24	143	ΔC_p as a function of T_g for Lillie No. 1
25	144	ΔC_p as a function of As_2S_3
26	145	ΔC_p as a function of Pyrex
27	154	$VT_g \Delta\alpha/\Delta C_p$ as a function of T_g
28	163	Extrapolated effective relaxation time constants for Lillie No. 1 at 500°C .

LIST OF TABLES

<u>Table No.</u>	<u>Page No.</u>	<u>Title</u>
1	93	Pyrex glass expansivity
2	104	Specific volume of glasses and supercooled liquids
3	118	Initial and final temperature for structural relaxation runs on Lillie No. 1 with extrapolated equilibrium relaxation times.
4	146	Summary of results analyzed in terms of Eyring liquid model

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I. INTRODUCTION

In the absence of crystallization a liquid will transform into a glass if it is continuously cooled below its crystalline melting point. The transformation to a glass is characterized by a decreased compressibility, heat capacity and usually, thermal expansivity, while the volume, entropy and enthalpy are continuous across the transition. To this extent, the glass transition appears to be a second order transition.

If the free energy surfaces of two phases have a common slope at the line of intersection, the phase transition is called second order. At any specified pressure there is a unique transition temperature. The expression for a second order transition, which is analogous to the Clapeyron equation for a first order transition, relating the rate of change of the transition temperature with pressure is given by

$$\frac{dT}{dP} = \frac{\Delta\beta}{\Delta\alpha} = TV \frac{\Delta\alpha}{\Delta C_p}$$

and is called the Ehrenfest equation. The Δ quantities are the differences between the values of compressibilities, volumetric expansivities and heat capacities of the two phases on either side of the transition. An interesting review of second order transitions is

given in Chapter XVIII of Slater's Introduction to Chemical Physics⁽¹⁾.

It is well recognized that the glass transition as observed experimentally is not a true second order transition, but occurs for the kinetic reason of increasing resistance of the structure to configurational change. As a consequence, the transition does not occur at a temperature, but over a narrow range of temperatures, and the range over which it occurs is a function of the cooling rate. By this argument a glass differs from its liquid only in the sense that its time constant for configurational relaxation is long compared to the time scale of the observation and thus its configuration can be considered to be fixed.

Davies and Jones⁽²⁾ have demonstrated that for a transition of this kind the differences between the supercooled liquid and glassy compressibilities, thermal expansivities and heat capacities are related by the following expression

$$\frac{\Delta\beta}{\Delta\alpha} \geq T_g V \frac{\Delta\alpha}{\Delta C_p}$$

The equality exists only under the condition that a single ordering parameter is sufficient to characterize the excess thermodynamic properties of the glass over those of the liquid. An example of a single ordering parameter description, is the Hirai-Eyring⁽³⁾ liquid model for which all excess thermodynamic properties are functions only of the number of "holes" present. This model is completely equivalent to the Tool⁽⁴⁾

fictive temperature description of the state of a glass since the number of "holes" is uniquely defined by the fictive temperature. Goldstein⁽⁵⁾ has shown that either the left or right hand term can be equal to the pressure rate of change of the glass transition temperature depending on which excess thermodynamic property is constant at the transition. The observations of O'Reilly⁽⁶⁾ and Goldstein^(5,7) for several organic glass formers and B_2O_3 indicate that the pressure dependence of the glass transition is given by

$$\frac{dT_g}{dP} = T_g V \frac{\Delta\alpha}{\Delta C_p} \leq \frac{\Delta\beta}{\Delta\alpha}$$

which suggest that the transition occurs at a fixed value of excess entropy or enthalpy but not volume as has been suggested in the past.

The rate dependence of the glass transition suggests at least three anomalies could occur with suppression of the transition temperature. The most well known is the so-called Kauzmann⁽⁸⁾ paradox. Kauzmann pointed out that in the absence of a transition the entropy of the supercooled liquid would be lower than that of the crystal on the order of 20 to 40 degrees below the normally observed transition temperature. It has been observed experimentally⁽⁷⁾ that the values of $\frac{\Delta\beta}{\Delta\alpha}$ decrease more rapidly with decreasing transition temperatures than $T_g V \frac{\Delta\alpha}{\Delta C_p}$. This suggests that if the transition temperature were suppressed sufficiently with slow cooling rates, the inequality of the Davies and Jones equation would be violated. At

temperatures slightly below the observed transition temperature the W.L.F.⁽⁹⁾ expression for shear viscosity predicts that the shear relaxation time constant will reach an infinite value. This expression, which has been empirically found to represent viscosity data over a wide temperature range, has recently been derived by Adam and Gibbs⁽¹⁰⁾ in such a way as to give it a better theoretical basis. Perhaps coincidentally, all three anomalies occur at approximately the same temperature.

It is a direct consequence of the lack of a good theoretical understanding of the liquid state that the glass transition has been primarily studied experimentally. Despite the fact that these anomalies remain unresolved in the sense that it is not known what intervenes to prevent the violations of the Third Law and the inequality of the Davies and Jones expression with a hypothetical infinitely slowly cooled liquid, there have been surprisingly few experimental studies of the transition. Reliable property measurements of the supercooled liquids of inorganic glass-forming materials are practically nonexistent. This is particularly true for the siliceous glasses which make up the bulk of the inorganic glasses.

A series of experiments were undertaken to measure the values of the glassy and supercooled liquid heat capacities and thermal expansivities of three inorganic glass-forming systems. The three materials studied were (1) arsenic trisulfide, a single component glass-former for which only the glassy expansivity has been reported,

(2) a soda-lime-silica glass whose viscosity has been studied and
 (3) a commercial borosilicate glass whose viscosity, glassy expansivity and glassy heat capacity have been reported. These property measurements, combined with room temperature density measurements, permit the evaluation of the $T_g V \frac{\Delta\alpha}{\Delta C_p}$ term of the Davies and Jones expression which apparently equals the rate of change of the glass transition temperature with pressure. Structural relaxation studies were made in the transition region in an attempt to define the transition temperature of an infinitely slowly cooled liquid by means of an appropriate extrapolation.

A great deal of insight can be gained regarding the vibrational modes and thus the structure of a solid by combining thermal expansion, specific heat and compressibility measurements from temperatures approaching absolute zero to those exceeding the characteristic temperature. Fortunately low temperature measurements have been made for glasses of composition similar to the two siliceous ones studied since the experiments reported here were not made below room temperature. Thus observations regarding the differences in their properties could be made which were consistent with the proposed operative modes of vibration which have been used to explain the anomalous properties of vitreous silica.

II. LITERATURE SURVEY

A. Thermal Properties of Solids

If an equation of state existed for solids their behavior with changes in temperature and pressure would be completely specified. Even though regular crystalline solids are the simplest form of matter to understand next to perfect gases, no simple analytic equation of state always holds and in general it is represented by a power series expressing either volume as a function of pressure and temperature or pressure as a function of volume and temperature. Experimentally the former is most conveniently determined but the latter is preferred since statistical mechanical models are made in terms of Helmholtz free energy where pressure is expressed as a function of volume and temperature. Slater⁽¹¹⁾ gives a fairly complete discussion of the experimental determination of the individual terms of the power series, their meaning, the conversion of $V = V(P, T)$ to $P = P(V, T)$ and the incorporation of the $P = P(V, T)$ equation with C_p data to write expressions for $E = E(T, V)$, $S = S(T, V)$ and $A = A(T, V)$. Even though empirical equations of state are quite useful for making thermodynamic and engineering calculations they give no direct information regarding the effect that changes of external pressure and temperature have on

atoms and their motions. A much more significant accomplishment is to arrive at an equation of state based on positions and velocities of the atoms. Clearly, if the model is correct the two approaches will give the same predicted results.

The discussion and derivations which follow were applied by Slater only to crystalline solids with rather strict assumptions as will be noted below. The resulting expressions for thermodynamic parameters are only approximate; however, they are sufficient for many purposes. In some cases it has been possible to obtain good agreement between a statistical mechanical model and the observed behavior for crystalline solids. No such results have been published for glasses, but it has been found useful to apply the models that describe crystalline solids to glasses to better understand their behavior in terms of molecular motions and interactions. It is for this reason that a simple statistical mechanical model is reviewed.

If a crystalline solid consists of N atoms it has been found that dynamically it can be treated as a set of $3N$ oscillators, each vibrating at some characteristic frequency ν_i . To the extent the restoring forces are linear functions of displacement, the oscillations will be independent of each other; thus, each behaves as a simple harmonic oscillator whose frequency is independent of its own amplitude and the amplitudes of the other oscillators.

With these assumptions expressions for E, A, S and P are readily derived (12, 13 for examples). The quantized energy of the i^{th} oscillator is

$$\epsilon_{n_i}^i = (n_i + \frac{1}{2}) h\nu_i$$

where n_i , an integer, is the quantum number associated with the i^{th} oscillator. A system quantum state is specified by the $3N$ component vector $n_1, n_2, n_3, \dots, n_{3N}$ and the system energy of this state is

$$E = \epsilon_{n_1}^1 + \epsilon_{n_2}^2 + \dots + \epsilon_{n_{3N}}^{3N}$$

The single-oscillator partition function of the i^{th} element for a Maxwell-Boltzmann distribution is

$$q_i \equiv \sum_{n_i}^{\infty} e^{-\frac{\epsilon_{n_i}^i}{kT}}$$

Thus the canonical partition function (Q)

$$Q \equiv \prod_i q_i \equiv e^{-A/kT}$$

where A is the Helmholtz free energy can be written as:

$$Q = \sum_{n_1}^{\infty} e^{-\frac{n_1 h\nu_1}{kT}} \cdot \sum_{n_2}^{\infty} e^{-\frac{n_2 h\nu_2}{kT}} \dots \cdot \sum_{n_{3N}}^{\infty} e^{-\frac{n_{3N} h\nu_{3N}}{kT}} \cdot e^{-\frac{h\nu_1}{2kT}} \cdot e^{-\frac{h\nu_2}{2kT}} \dots e^{-\frac{h\nu_{3N}}{2kT}}$$

$$Q = e^{-\frac{E_0}{kT}} \cdot \sum_{n_1}^{\infty} e^{-\frac{n_1 h\nu_1}{kT}} \cdot \sum_{n_2}^{\infty} e^{-\frac{n_2 h\nu_2}{kT}} \dots \cdot \sum_{n_{3N}}^{\infty} e^{-\frac{n_{3N} h\nu_{3N}}{kT}} .$$

$$E_0 = \sum_i^{3N} \frac{n\nu_i}{2}$$

is the energy as a function of volume at the absolute zero in temperature.

The final expression for Q can be shown to be equal to

$$Q = e^{-\frac{E_0}{kT}} \prod_{i=1}^{3N} \left(\frac{1}{1 - e^{-\frac{h\nu_i}{kT}}} \right)$$

The thermodynamic functions can be readily solved for and can be shown to be

$$A = -kT \ln(Q) = E_o + \sum_i^{3N} kT \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right)$$

$$S = \left[\frac{\partial A}{\partial T} \right]_V = k \sum_i^{3N} \left\{ \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right) + \frac{\frac{h\nu_i}{kT}}{e^{\frac{h\nu_i}{kT}} - 1} \right\}$$

$$E = \left[\frac{\partial (\ln Q)}{\partial \left(-\frac{1}{kT} \right)} \right]_V = E_o + \sum_i^{3N} e^{\frac{h\nu_i}{kT}} - 1$$

$$P = - \left[\frac{\partial A}{\partial V} \right]_T = \left[\frac{\partial E_o}{\partial V} \right]_T + \frac{1}{V} \sum_i^{3N} \gamma_i \left(e^{\frac{h\nu_i}{kT}} - 1 \right)$$

where

$$\gamma_i \equiv - \frac{V}{\nu_i} \left[\frac{\partial \nu_i}{\partial V} \right]_T$$

and $\left[\frac{\partial E_o}{\partial V} \right]_T$ is expressed as an empirical function by Slater. The derivative expressions for the specific heat at constant volume (C_v)

and volumetric expansion coefficient (α) are directly obtained from the above expressions and are

$$C_v = \left[\frac{\partial E}{\partial T} \right]_V = k \sum_{i=1}^{3N} \frac{\left(\frac{h\nu_i}{kT} \right)^2 e^{\frac{h\nu_i}{kT}}}{\left(e^{\frac{h\nu_i}{kT}} - 1 \right)^2}$$

and

$$\alpha = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_P = - \frac{1}{V} \left[\frac{\partial S}{\partial P} \right]_T = \frac{k\beta}{V} \sum_{i=1}^{3N} \frac{\gamma_i \left(\frac{h\nu_i}{kT} \right)^2 e^{\frac{h\nu_i}{kT}}}{\left(e^{\frac{h\nu_i}{kT}} - 1 \right)^2}$$

where β is the volumetric compressibility

$$\beta = - \frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_T .$$

Comparison of the expressions for α and C_v shows immediately the reason for qualitatively similar behavior of the two. Each term in the expression for α is directly proportional to an equivalent term in C_v for the same oscillator. Thus both C_v and α approach limiting values at high temperatures and approach zero as T approaches absolute zero.

Grüneisen⁽¹⁴⁾ simplified the expressions for α and C_v by assuming the quantities γ_i equal to each other and to a constant $\bar{\gamma}$

which he regarded as an empirical constant. The γ_i 's can thus be removed from the summation and

$$\alpha = \frac{\bar{\gamma} \beta C_v}{V}$$

is obtained by substitution; this is the well known Grüneisen relation. Experimentally $\bar{\gamma}$ defined this way lies between 1 and 3 for most crystalline materials indicating that the lattice frequencies vary between being inversely proportional to the volume and inversely proportional to the cube of the volume.

The expression for γ_i relates the change in frequency of an oscillator to the change in volume at constant temperature. It is interesting to note that the γ_i for a linear oscillator is zero as is shown below. If the two springs of unstretched length L_0 are attached to a mass m and compressed to a total length L as shown in Figure 1, the total force on the mass resulting from a displacement Δx from the equilibrium position is

$$F = K(L_0 - \frac{L}{2}) - K\Delta x - K(L_0 - \frac{L}{2}) - K\Delta x$$

$$F = - 2K\Delta x$$

where K is the spring constant. The restoring force F is thus independent of the compression $(L_0 - \frac{L}{2})$ of the springs; hence the

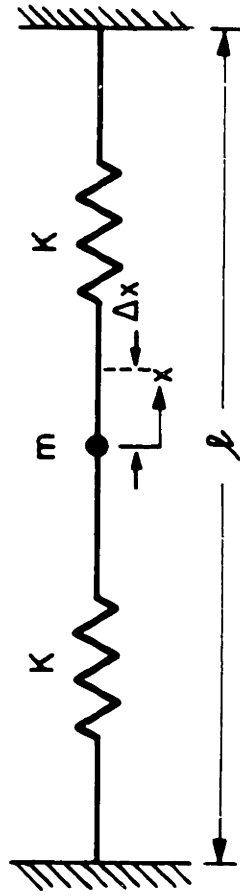


Figure 1. Linear Oscillator Model

natural frequency ν_o of this linear oscillator

$$\nu_o = \frac{1}{2} \pi \sqrt{\frac{2K}{m}}$$

is also independent of the degree of compression indicating that $\gamma = 0$. Thus it can be seen that the existence of thermal expansivity different from zero (a γ different from zero) results from the asymmetry of the potential well between two atoms and its value depends on the shape of the well and thus the type of bonding.

In general the frequency of an atom would be expected to increase with compression since the restoring forces are increased, resulting in a positive γ . There is no reason to expect that the potential wells for the three normal modes of vibration have the same shape, hence the γ_i 's should not be expected to have the same value even in the case of a regular lattice of like atoms.

To this point the treatment applies equally to glasses and crystals. It would be expected that even in terms of this simplified model a great many more ν_i 's and γ_i 's would have to be specified for an amorphous structure than for a regular crystalline lattice if thermodynamic variables were to be calculated from the derived expressions.

It appears that negative values of γ have to be anticipated when unlike atoms are included in the system of oscillators. This will be discussed in more detail with respect to the expansion

coefficient of vitreous silica; however, some experimental results for crystalline lattices are cited here. Barron⁽¹⁵⁾ and Blackman⁽¹⁶⁾ found a large variation of values for γ_i 's, ranging from large positive values to negative values for ionic crystals of the rock salt type. In a later publication, Blackman⁽¹⁷⁾ examined the γ_i 's to be expected from a two dimensional model lattice. The lattices that he examined were of two types: (1) an ionic lattice consisting of a square array of alternate positive and negative ions, and (2) a hexagonal lattice with a short range central interaction force. The ionic lattice had a wide variation of γ_i 's including negative ones while the hexagonal lattice had a narrow range of all positive γ_i 's.

According to Blackman⁽¹⁶⁾ the occurrence of negative γ_i 's decreases the usefulness of the Grüneisen relation, since as long as the γ_i values are positive the relation can be justified as a useful approximation, but once negative values are admitted the relation loses its general character. He further indicates that there appears to be only two conditions where the Grüneisen relation can be used. The first is where all the γ values are equal. While this condition is unlikely, one can use the expression to a good approximation when the distribution of γ_i values is sharply peaked around its average value. The second depends on finding some average value $\bar{\gamma}$ which is independent of volume. The first condition is nothing more than a

restating of Grüneisen's principle assumptions, but, the validity of the second is not clear and further even if it were valid, it is not clear that introduction of negative γ_i 's would be inconsistent with it.

This statistical mechanical derivation demonstrates the intimate relation between α and C_v . It is also obvious from this treatment that both α and C_v are properties sensitive to the atomic structure and that with polymorphic transitions, different values of α and C_v can be expected as different modes of vibration with their associated different γ_i 's and ν_i 's become possible. For the same reason it would fully be expected that the observed values for C_v and α of a glass would be different from those of a crystal of the same composition contrary to statements appearing in the literature⁽¹⁸⁾. Further, α 's would probably be more sensitive to atomic structure than C_v 's since the introduction of new modes of vibration can either add or subtract from the observed expansion coefficients, depending on the sign of γ_i 's.

A point made by Kingery⁽¹⁹⁾ should be noted here. Since the values of α and C_v are strongly dependent on temperature until the characteristic temperature is reached, it is most satisfactory to compare the values for C_v and α of different materials and of different polymorphic phases of the same material at or above their characteristic temperatures.

Even though thermal expansion and specific heat properties are closely related, most experimental studies have been confined to one or the other. This fact plus the generally poor specification of the glass systems investigated makes it logical to review the reported experimental investigation of C_v and α behavior separately.

1. Thermal Expansion

As was pointed out above, thermal expansion is extremely sensitive to atomic structure. Thus, since many substances with different atomic configurations and bonding types are found to form glasses, they should best be discussed and compared only within specific groupings. Possible groupings are those based on tetrahedral elements (SiO_2 , GeO_2 , BeF_2 , and P_2O_5) and those based on triangular elements (B_2O_3 and As_2S_3). Other groups could include hydrogen bonded and high polymer materials which form glasses. Besides the differences between the glasses noted above, the effect on thermal expansivity of additions into the host glass formers have to be accounted for. These can arise either by the intentional introduction of foreign atoms as is typical in commercial siliceous glasses or by deviations from the stoichiometric compositions. Since the thermal expansivity of even the simplest glasses is not understood completely it appears that an understanding of all the effects mentioned above is a long way off. The following discussion will primarily be limited

to silicate glasses, not because they are fundamentally more important, but because the majority of inorganic glasses are silicates. Also no attempt is made to report the voluminous papers giving "new and revised" empirical constants for the effects on expansivity for various additions to SiO_2 .

The thermal expansion coefficient of the pure SiO_2 glass is one of the lowest known in the temperature range of 100 to 1000°C . The fact that its expansivity is lower than any measured value for the many crystalline forms of SiO_2 and that it contracts on heating from 0 to 200°K have been considered to be anomalies.

This anomalous behavior in expansion as well as other apparent anomalies in low temperature specific heat, compressibility, and the temperature dependence of elastic moduli have not been completely resolved⁽²⁰⁾ to date, but an explanation for the expansion behavior has been proposed that is consistent both with a statistical mechanical model and the other apparent anomalies.

It has been suggested that in the open amorphous silica structure vibrational modes other than axial ones are possible, notably a transverse vibration of an oxygen atom between a pair of silicon atoms.^(21,22,23) This vibrational mode is apparently not strong in any of the polymorphic crystalline phases. Smyth⁽²⁴⁾ postulated that the frequency of this transverse mode decreases as volume is reduced, thus making γ_i for this mode negative. A negative γ_i

produces a negative term in the sum defining the expansion coefficient.

This effect explains both the negative expansivity at low temperatures and low expansivity at temperatures exceeding 200°K . Since the transverse vibrational mode has a lower characteristic temperature than any of the other longitudinal modes in vitreous silica, it dominates at low temperatures to an extent that the total expansivity is negative. At higher temperatures modes with positive γ_i 's raise the total expansivity. However, the large negative term in the sum keeps it low.

Experimental evidence of the existence of low characteristic temperature modes in vitreous silica with negative γ_i 's appears good. The low temperature C_v can only be explained if extremely low frequency Einstein modes are present. Some have proposed characteristic temperatures near 10, 30, and 50°K .^(25,26,27) Though it is not clear that modes of so low characteristic temperature need be present, at least one mode having a characteristic temperature near 370°K is apparently required to get good agreement.⁽²⁴⁾ The existence of negative γ_i 's is consistent both with the negative and low expansivity at low temperatures and with the increase in compressibility with increasing pressures.^(20,27) It is noteworthy that the anomalous low temperature α and C_v behavior disappears when the atomic structure is varied slightly in such a way that the low temperature modes with negative γ_i 's are suppressed. Quartz shows neither the negative

expansivity nor excess heat capacity demonstrated by vitreous silica.⁽²⁷⁾ On the other hand the low density cubic cristobalite shows an excess heat capacity, though less than the vitreous form. It has been suggested that cristobalite would also show a negative expansivity at low temperatures^(20,28) though this has not been confirmed experimentally. This is consistent with the suggestions that vitreous silica has a structure similar to that of cristobalite. Vitreous GeO_2 has an expansivity more than an order of magnitude greater than that of vitreous SiO_2 .⁽²⁹⁾ This appears consistent with the behavior observed for quartz since GeO_2 exists with either the rutile or quartz structures⁽³⁰⁾ in its crystalline forms and not in the open cristobalite form. It appears that the transverse modes are suppressed in GeO_2 even in the vitreous form and that its structure must be more similar to that of quartz than cristobalite.

Megaw⁽³¹⁾ has proposed that thermal expansion is inversely proportional to the square of the valence of the ions constituting the structure and directly proportional to the coordination number for ionic materials and has cited several examples of ionic crystals which agree with this proposal. This suggestion is only a statement that the observed expansivity is inversely proportional to the attractive force between two ions.

In most articles appearing in the literature, differences in the effects on expansivity between different substituted ions is

explained in terms of field strengths. Two of the better systematic studies showing substitutional effects on simple silicate glasses are those by Shartsis, Spinner and Capps⁽³²⁾ and another by Karkhanavala and Hummel⁽³³⁾. The details of the two experimental programs were reviewed⁽³⁴⁾ by the author previously and will not be repeated since they are relevant here only in terms of their conclusions, which can be summarized as:

- 1) When substitutions are made within a group of the periodic table, lower field strength ions will give higher expansivities.
- 2) Over a limited range the expansivity is proportional to the mole percent of the added ion.

With many components, as in commercial glasses, interactions become complex. However, it has been observed that there is a striking similarity between the magnitude of the empirical proportionality constants used in additive equations to calculate thermal expansion, and the listing of elements by bond strength.^(35,36,37) The correlation between bond strength of the substituted ion and the resulting expansivity seems to be true even between groups of the periodic table. Even though bond strength appears to explain observed behavior it has not been combined with the statistical mechanical model of the expansion of vitreous silica. The effect on expansivity of substituted

atoms into the silica network must be explained in terms of their effect on the proposed transverse vibrational mode.

If it is assumed that the effect of an addition on the observed expansivity is primarily a result of its effect on the proposed transverse vibrational mode, a qualitative understanding of the observed substitutional effects and correlations is possible. Ions which substitute directly for Si^{+4} ions in the SiO_2 network taking four fold coordination with oxygen would not be expected to influence the transverse vibrational mode as much as those entering the network at interstices or substituting for Si^{+4} with different coordination numbers. Formation of non-bridging oxygens completely eliminates an oscillator capable of vibrating in this mode. Any interference with this mode should lead to an increase in the observed expansivity, with substitutions which eliminate it being most influential. Thus the effect of substitutions on expansivity can be qualitatively understood in terms of the position they take in the network and network defects created. If this concept is combined with Sun's⁽³⁵⁾ model relating the position a substituting atom takes in the network as a function of its bond strength, the observed correlation between bond strength and expansivity is consistent with this explanation of substitutional effects.

Since this model is highly qualitative and the structure of glasses is not understood it is of questionable value to speculate as

to the exact interactions of specific ions. It follows from the Zachariasen and Warren model of silicate glasses that the introduction of monovalent or divalent ions such as sodium, potassium or calcium will go into the interspaces in the network while forming a non-bridging oxygen. Thus the introduction of these ions would be expected to be very effective in reducing the transverse vibrational mode by both eliminating one bond which vibrates in this manner for every non-bridging oxygen that is formed and by blocking the free transverse vibration of others by taking up a modifier position at the interspaces of the network.

Introduction of B^{+3} into the SiO_2 network has little effect on the observed expansivity of vitreous silica. Vycor brand glass contains approximately 4% B_2O_3 yet its expansivity is only 7.5×10^{-7} (cm/cm⁰C) compared with 5.5×10^{-7} (cm/cm⁰C) for pure SiO_2 . In terms of this model the B^{+3} ions have substituted directly for the Si^{+4} ions of the SiO_2 network without interfering with the transverse mode of vibration.

It is interesting to note that Al^{+3} ions can be added to an alkali-silicate glass with a reduction in the observed expansivity even though introduction of Al^{+3} ions directly into vitreous silica will increase the thermal expansion, though not so much as ions like Na^{+1} , K^{+1} , or Ca^{+2} . This might be explained in terms of the network defects, as proposed by Stevels.⁽³⁸⁾ According to him an alkali ion

is bound to the electronic defect created by substituting an Al^{+3} ion for a Si^{+4} ion. With the so-called $\text{Al}_{\text{Na}}^{\text{P}}$ center the Si-O-Si bond is reformed. While the exact influence on the transverse mode of vibration is speculative, however, it seems plausible that with the bonding of the alkali ion to the substituted Al^{+3} ion and the elimination of a broken Si-O-Si bond, that it is more likely to be operative.

This interpretation of substitutional effects on glassy expansivity is clearly only qualitative and applies only to gross effects. In contrast to the bond strength and/or field strength explanations of substitutional effects, it is based on an accepted statistical mechanical treatment and further is based on effects which are apparently responsible for the anomalous properties of vitreous silica at low temperatures. It is clear that any vibrational modes which are active at low temperatures will also be present at high temperatures, and also that they will be influenced by changes in the network structure due to substitutions.

2. Heat Capacity

The derived expression for specific heat at constant volume based on the harmonic oscillator model can be evaluated only if the distribution of frequencies (or harmonics) is known. Two well-known solutions are the Einstein and Debye models.

The Einstein solution assumes that all the quantized oscillators vibrate at the same frequency which is independent of temperature, giving

$$C_v = k \sum_{i=1}^{3N} \frac{\left(\frac{h\nu_i}{kT} \right)^2}{\left(e^{\frac{h\nu_i}{kT}} - 1 \right)^2} = 3Nk \frac{\left(\frac{h\nu_i}{kT} \right)^2}{\left(e^{\frac{h\nu_i}{kT}} - 1 \right)^2}$$

This expression gives values for specific heat rising from zero to the classical value of $3R$ at high temperatures in agreement with the Third Law and the experimental law of Dulong and Petit. For elemental crystals values of ν (or θ , the characteristic temperature) can be found such that the Einstein formula gives a fairly good approximation to the observed specific heats except at very low temperatures. Close to the absolute zero, the Einstein formula predicts a specific heat falling too sharply to zero. It is observed that specific heat falls more slowly and is approximately proportional to T^3 at low temperatures.

The Debye model allows all frequencies (harmonics) of vibration up to a maximum cutoff frequency whose wavelength corresponds roughly to the lattice spacing of a crystal. A distribution of frequencies is used which is approximately wedge shaped and weighted to high frequencies. Each quantized harmonic has a characteristic temperature. The expression resulting from these approximations is

$$C_v = 9Nk \frac{1}{x_0^3} \int_0^{x_0} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where

$$x = \frac{h\nu}{kT} \quad , \quad \text{and} \quad x_0 = \frac{h\nu_{\max}}{kT}$$

It cannot be integrated analytically. However, numerous tabulations of the integral exist. This expression predicts that the specific heats of all substances will be the same at the same fraction of the corresponding Debye temperatures (θ_D), where

$$\theta_D = \frac{h\nu_{\max}}{k}$$

Similar to the Einstein formula, the predicted value of specific heat is zero at the absolute zero and rises to $3R$ at high temperatures. At low temperatures it predicts that C_V is proportional to T^3 which is observed to be true for a variety of substances. For crystalline compounds the general expression for specific heat has to be interpreted as being summed over all harmonics of all the atoms making up the crystal. An analytical solution is extremely complex, and has only been done successfully for a few cases. In molecular crystals it is usually possible to separate the vibrations according to inter- and intra-molecular vibrations to good approximations⁽³⁹⁾ even though the different modes are coupled together to some extent. In CaCO_3 , for instance, it is possible to separate the vibrations into a low frequency vibration of the Ca^{+2} and CO_3^{-2} ions as a whole and the high frequency vibrations within the carbonate ion. With this spectrum the specific heat of the crystal can be

represented by using a Debye expression for the acoustical frequencies and a number of Einstein terms to account for the intramolecular vibrations. The alkali halides can be represented fairly accurately in a manner similar to elemental crystals. No distinction between the ions need be made, and thus the specific heat can be treated as being a Debye function where N is the number of ions.

In glasses, solving of the general expression for specific heats is made even more complex than for crystalline compounds because of the random structure with resulting coupling of vibrations and scattering of displacement waves. It would also be expected that each type of ion would find itself in a variety of local environments due to the randomness of the structure, hence the mathematical treatments used in the Debye model could not be applied directly. It appears therefore that the most promising treatment for calculation of specific heats of glasses is to use the Einstein method⁽⁴⁰⁾ where each type of ion is assumed to vibrate in a number of modes with fixed quantized frequencies.

Smyth has used this model to represent the specific heat of vitreous silica⁽⁴⁰⁾ and obtained good agreement except at very low temperatures. The deviation at low temperatures is not surprising since this deviation for the Einstein expression has been observed and pointed out for elemental crystals. It has been proposed that the low temperature behavior can be explained by the presence of Einstein modes lying near 10, 30, and 50°K^(25,26,27) though it is not clear that the difference in calculated and observed specific heats is not due entirely to failure of the Einstein model to fit at low temperatures.

The model used by Smyth to calculate the specific heat per mole of SiO_2 is three independent oscillators with a silicon frequency (ν_{Si}), two independent oscillators with a longitudinal oxygen frequency (ν_{L}) and four independent oscillators with a transverse oxygen frequency (ν_{T}). The molar heat capacity is then given by

$$C_v = R \left\{ 3 \frac{\left(\frac{h\nu_{\text{Si}}}{kT} \right)^2 \frac{h\nu_{\text{Si}}}{kT}}{\left(e^{\frac{h\nu_{\text{Si}}}{kT}} - 1 \right)^2} + 4 \frac{\left(\frac{h\nu_{\text{T}}}{kT} \right)^2 \frac{h\nu_{\text{T}}}{kT}}{\left(e^{\frac{h\nu_{\text{T}}}{kT}} - 1 \right)^2} + 2 \frac{\left(\frac{h\nu_{\text{L}}}{kT} \right)^2 \frac{h\nu_{\text{L}}}{kT}}{\left(e^{\frac{h\nu_{\text{L}}}{kT}} - 1 \right)^2} \right\}$$

It was found that the "best" characteristic temperatures ($\theta_i = \frac{h\nu_i}{k}$) for the silicon, oxygen transverse and oxygen longitudinal modes respectively were $\theta_{\text{Si}} = 1100^\circ\text{K}$, $\theta_{\text{T}} = 370^\circ\text{K}$, and $\theta_{\text{L}} = 1220^\circ\text{K}$. The calculated values for this equation are compared with experimentally observed values in Figure 2. It is suggested by Smyth that because of the coupling between neighbors a much greater number of frequencies would be encountered than the three used and that their proper inclusion would allow a much better fit.

Sharp and Ginther⁽⁴¹⁾ report both attempting to fit the low temperature specific heat of vitreous silica to the usually observed T^3 law and the high temperature behavior to the Debye function with little success. It would seem that if a number of different modes were vibrating, each with a different maximum frequency, ν_{max} , and hence different Debye temperature each contributing to the total specific heat

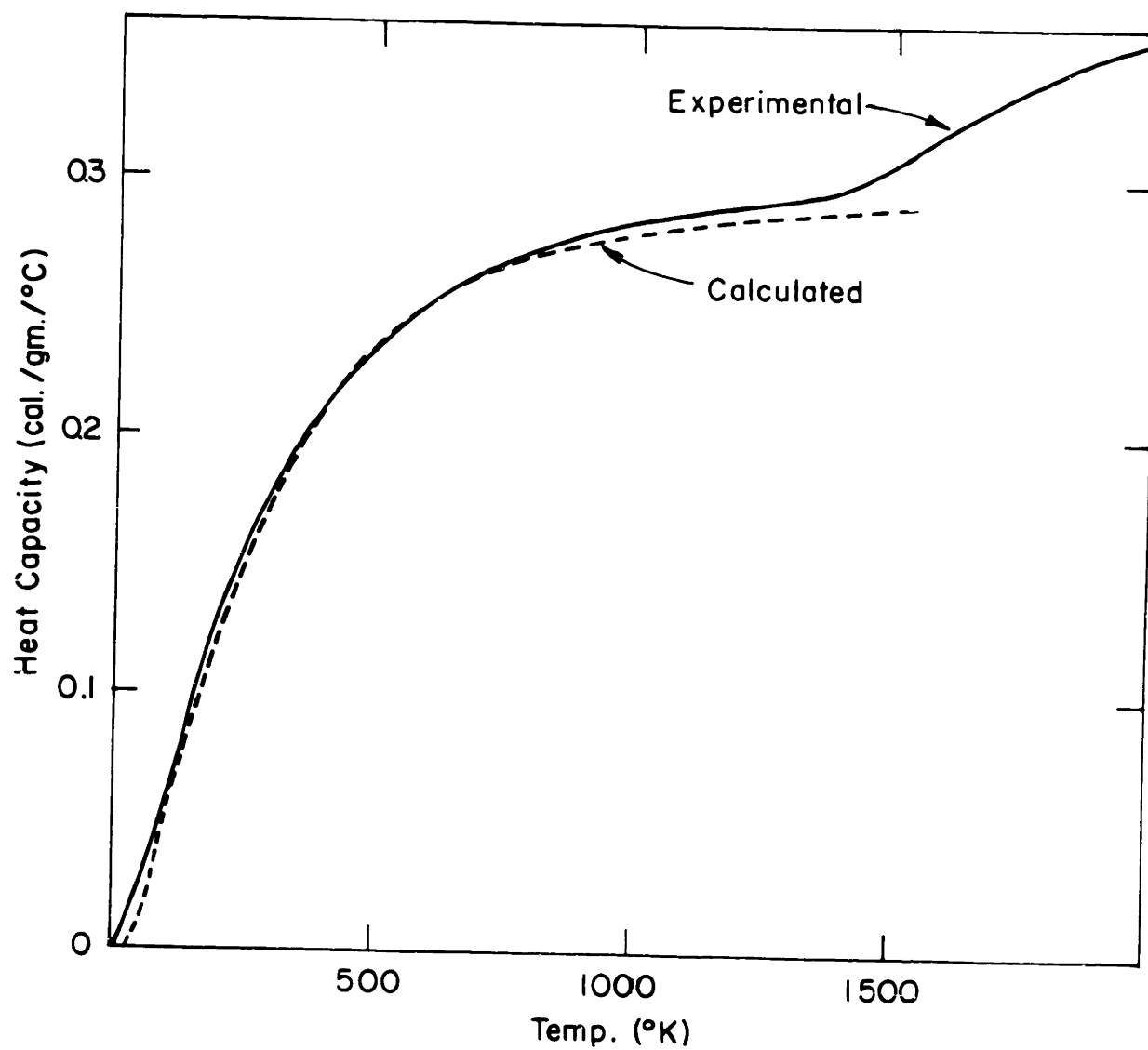


Fig. 2 Experimental and Calculated Values of the Heat Capacity of Vitreous Silica after Smyth⁽⁴⁰⁾

that the Debye relationship derived for elemental crystalline solids would not apply.

It appears from the success of Smyth's simple model to predict the heat capacity behavior of SiO_2 that at least simple glasses can be treated to a first approximation in a manner similar to crystals. As can be seen in Figure 2 the experimentally observed specific heat approaches the classical $3R$ value of $0.297 \text{ (cal/gr } ^\circ\text{C)}$ for SiO_2 . It should be pointed out that the approximation that the specific heats at constant pressure and volume are equal is particularly good for vitreous SiO_2 since it has such a low expansivity. A calculation using expression

$$C_p - C_v = \frac{TV\alpha^2}{\beta}$$

indicates that the difference is only approximately $10^{-5} \text{ (cal/gr } ^\circ\text{C)}$.

Contrary to the statement by Stevels⁽³⁷⁾ that the sharp rise in the experimental value of C_v at temperatures above 1300°C cannot be explained it seems obvious that this is nothing other than the characteristic behavior observed at the glass transition. The fact that the C_v does not reach the approximately constant value of the supercooled liquid is probably a manifestation of the employed experimental technique and the heat treatments given the sample. Similarly shaped curves were obtained for B_2O_3 in its transition region by Thomas and Parks,⁽⁴²⁾ but it could be altered considerably depending on heat treatment.

There are numerous studies reporting the effects on heat capacity from additions to silica. See references 37, 41, and 43 for summaries. However, they will not be reviewed here. Morey⁽⁴³⁾ indicates that the empirically derived relationships for C_p are additive and further that the additive relations for specific heat hold over a wider composition range than for other properties. Sharp and Ginther⁽⁴¹⁾ derive expressions which reportedly fit experimental heat data with an accuracy generally better than 1% in the range from 0 to 1300°C. The fact that such good agreement between empirical additive equations and experimental results is possible appears related more to the fact that the variation in specific heats between different substances is small compared to thermal expansion, for instance, than to the idea that heat capacity of a mixture is characterized by the bond strengths and masses of the component atoms. As was pointed out in the discussion of molecular compounds, the component ions can oscillate as molecules and hence introduce completely different frequency distributions.

The empirical relations and terms which might be interpreted as partial molar specific heats do not lend themselves to theoretical interpretation. The constants are generally not based on the pure components but rather on the effect they have on the siliceous glass. The relations derived by Sharp and Ginther are indicated to be employable to temperatures on the order of 1300°C which clearly includes the transition region of all siliceous glasses where a discontinuity in the specific heat occurs. Since they represent both the glassy and

supercooled liquid specific heats by one equation it is impossible even to use them to isolate the oscillatory component and the configurational components of specific heat.

In general the heat capacity studies of glasses are carried out on an empirical basis, but it appears from Smyth's results for SiO_2 that reasonable calculations can be made based on the harmonic oscillator model for single component glasses. It would seem that if sufficient information of the details of the glass structure were available, there would be nothing to prevent similar calculations for multicomponent glasses, though it would be anticipated that they would be considerably more complex. It is seen in Figure 2 that the heat capacity of vitreous SiO_2 approaches the classical $3R$ per gram atom value. However, there is no general requirement that the heat capacity of a glass reach it prior to the intervention of the glass transition. Indeed, in the case of B_2O_3 which has a bond strength similar to SiO_2 in magnitude,⁽³⁵⁾ the heat capacity is only approximately 6/10 the classical value at the glass transition.⁽³⁷⁾ Detailed studies of heat capacity are useful for constitutional studies of glass as is demonstrated by combination of property measurements of vitreous SiO_2 at low temperatures to explain what appeared to be anomalous properties.⁽²⁰⁾ Tarasov⁽⁴⁴⁾ claims to have developed a quantum theory of heat capacity which enables him to distinguish chain, layer, and three-dimensional network structures from one another. Application of this theory has lead to interesting though not unquestioned⁽⁴⁵⁾ conclusions regarding glass structure.

B. Thermal Properties of Liquids

The liquid phase is the least well understood of the three phases (crystalline solid, liquid and gas) matter is found in. Historically, studies of liquids have been approached either by way of dense gas models or by extensions of the lattice theory of solids to liquids. Both approaches have reason, since at conditions near the critical point there is very little or no distinction between a liquid and a gas; on the other hand, it is well known from X-ray studies that at conditions near the melting point considerable short-range order exists which appears to be similar to the corresponding crystalline state. It is not surprising that imperfect gas theories of liquids are suitable near the critical point, that disordered-crystal theories work near the melting point and that both fail badly at points in between.⁽⁴⁶⁾

At present attempts to arrive at a correct equation of state of liquids are being made from two directions. The first is the formal mathematical approach combining the intermolecular forces and statistical mechanics. Though it is possible to write a formal and exact theory, the solution by this approach has not been achieved.⁽⁴⁷⁾ The second approach is from a physical model which is as faithful to reality as can be devised and yet be soluble. Impressive results have been achieved by both approaches, though at present there is no completely satisfactory equation of state for liquids.

The statistical mechanical approach will not be reviewed other than to give briefly a partial solution that has been attained, because it applies only to simple liquids. At present it can not be extended to give useful information about the complex, multicomponent liquids with directional bonding typically found as glass formers. It is mentioned because it is probable that an understanding of the liquid state will be achieved only within the framework of the statistical mechanical approach with the implementation of suitable approximations.

It can be shown with certain important assumptions that the equation of state for N molecules or atoms in a "simple" liquid phase is

$$\frac{PV}{NkT} = 1 - \frac{N}{6VkT} \int_0^{\infty} g(r) \frac{dU(r)}{dr} 4\pi r^3 dr$$

where $U(r)$ is the potential energy of interaction between molecules and $g(r)$ is a pair correlation function, i.e., a radial distribution function.^(47,48,49) The pair correlation function, $g(r)$, can be measured experimentally and the potential energy of interaction can presumably be calculated on the basis of molecular bonding forces. Direct calculation of either $g(r)$ or the configurational integral represents an impossible task and currently many approximate techniques are being employed in an attempt to obtain useful solutions (see references 47 and 48 for discussion and other references). A solution for

the equation of state for liquids in terms of the formal statistical mechanical treatment is the so-called "significant structures theory" proposed by Eyring and coworkers.^(50,51) The liquid is viewed as a mixture of crystal-like and gas-like regions, which are represented by crystal and ideal gas partition functions. The agreement of this solution with experimental results is surprisingly good in view of the unrealistic model that has been assumed. Even though this solution is obtained within the framework of a statistical mechanical solution based on a molecular model, it should be regarded as empirical. A derivation for the heat capacity at constant pressure and volumetric thermal expansion coefficient of a liquid which follows from this model will be given later.

There are a number of molecular descriptions of liquids appearing in the literature, among which are those described by Bernal,^(52,53) Tilton,⁽⁵⁴⁾ Cohen-Turnbull,^(55,56,57) Frenkel,⁽⁵⁸⁾ and the above-mentioned model of Eyring and colleagues.^(50,51,3,59) A very important model is one developed by Gibbs and DiMarzio⁽⁶⁰⁾ for linear polymer-melts, or rubbers. This theory is based on the kinetic theory of rubber elasticity⁽⁶¹⁾ and thus can only be extended to inorganic glass forming melts qualitatively. Recently the Gibbs-DiMarzio model was extended by Gibbs and Adam⁽¹⁰⁾ to explain the empirically derived and semi-theoretically justified W.L.F. equation⁽⁹⁾ which relates shear viscosity to temperature.

Of the models mentioned above, only the Frenkel and Eyring models have been developed to a point where quantitative calculations can be made for complex melts. The two models are quite similar in concept and mathematically are distinguished only by the Eyring model's taking into consideration the difference in size between a "hole" and a molecule. The Eyring solution has had successes, but fails to agree with some experimental results. The Eyring model is described in detail because it has led to some significant results even though it is difficult to accept it as realistic.

According to the Hirai-Eyring hole model of liquids an equilibrium exists between "holes" and phonons associated with the liquid "lattice." Each hole is characterized by a molar volume v_h and the molar excess energy over the no hole situation, E_h . The molecules are in rapid motion, jumping into vacancies and smearing out the empty space. This loosening leads to the disappearance of long range order and to the appearance of mobile structures of less symmetry than crystals show. Since liquids both supercool and superheat, it is presumed that there are no regions of order large enough to act as nuclei for crystal growth and no holes large enough to act as nuclei for bubble formation.

The free energy increase* due to introducing N_h holes of free energy F_h into a liquid of N_o molecules is

*This derivation is a corrected version of the one appearing in the Hirai-Eyring reference 3. It has been submitted to Eyring and accepted as correct.

$$\Delta F = kT \left[N_h \ln \left(\frac{N_h}{nN_o + N_h} \right) + nN_o \ln \left(\frac{nN_o}{nN_o + N_h} \right) \right] + N_h (\epsilon_h + Pv_h - Ts_h)$$

where n is the volume ratio of molecules to holes ($n = v_o/v_h$). The number of holes, N_h , at equilibrium can be determined by the condition where ΔF is minimized, i.e.,

$$\left. \frac{\partial \frac{\Delta F}{kT}}{\partial N_h} \right]_{n, N_o, T, P, \epsilon_h} \equiv 0 = \ln \left(\frac{N_h}{nN_o + N_h} \right) + \frac{\epsilon_h + Pv_h - Ts_h}{kT}$$

when $nN_o \gg N_h$.

Rewritten, the number of holes is

$$N_h = \frac{n}{\sigma} N_o e^{-\frac{\epsilon_h + Pv_h}{kT}}$$

where $\ln(\sigma) = -s_h/k$. If the molar volume of the liquid V is the sum of the molecular (solid) and hole volumes, i.e.,

$$V = V_s + V_h$$

the volumetric expansion coefficient can be written as

$$\alpha \equiv \left. \frac{1}{V} \frac{\partial V}{\partial T} \right]_P = \frac{1}{V} \frac{\partial V_s}{\partial T} + \frac{1}{V} \frac{\partial V_h}{\partial T} \Big]_P = \alpha_s + \alpha_h$$

where

$$\alpha_s = \left[\frac{1}{V} \frac{\partial V_s}{\partial T} \right]_P$$

and

$$\alpha_h = \left[\frac{1}{V} \frac{\partial V_h}{\partial T} \right]_P \quad .$$

Clearly the hole expansivity (α_h) is what is referred to as the configurational expansion coefficient in the glass literature and is the difference between the supercooled liquid and glass expansivities.

$$\alpha_h \equiv \Delta\alpha = (\alpha_{\text{liquid}} - \alpha_{\text{glass}})_{@T_g}$$

The configurational thermal expansivity can be solved for in the following way. The total hole volume is

$$V_h = N_h v_h$$

and

$$dV_h = v_h dN_h$$

so that

$$\alpha_h = \left[\frac{1}{V} \frac{dV_h}{dT} \right]_P = \left[\frac{v_h}{V} \frac{\partial N_h}{\partial T} \right]_P = \frac{v_h}{V} \frac{n}{\sigma} N_o \frac{\epsilon_h}{RT^2} e^{-\frac{\epsilon_h + Pv_h}{kT}}$$

When

$$n = V_o/V_h$$

is substituted and the approximation made that

$$v_o N_o \hat{=} V$$

then

$$\alpha_h = \frac{1}{\sigma} \cdot \frac{\epsilon_h}{kT^2} e^{-\frac{\epsilon_h + Pv_h}{kT}} .$$

The heat capacity at constant pressure can be solved for in a similar manner by saying

$$C_p = C_{ps} + C_{ph}$$

where C_{ps} and C_{ph} are the heat capacities due to the molecules and holes respectively. The C_{ph} is not the heat capacity of the holes, but rather represents the thermal energy that must be added to the liquid to change the number of holes, N_h , as temperature is increased consistent with the expression for $N_h(T)$. The meaning of C_{ph} is analogous to α_h in that it is the difference between the supercooled liquid and glassy specific heats at the glass transition, or the

configurational specific heat. If C_{ph} is written as

$$C_{ph} = \epsilon_n \left[\frac{\partial N_h}{\partial T} \right]_p = \epsilon_h \frac{n}{\sigma} N_o \frac{\epsilon_h}{RT^2} e^{-\frac{\epsilon_h + Pv_h}{kT}}$$

$$C_{ph} = \frac{n}{\sigma} k N_o \left(\frac{\epsilon_h}{RT} \right)^2 e^{-\frac{\epsilon_h + Pv_h}{kT}}$$

In both the expressions for α_h and C_{ph} the term prior to the exponent should contain the enthalpy of hole formation, $\epsilon_h + Pv_h$, and not just the energy of hole formation, ϵ_h . The expressions were written to agree with those derived by Eyring^(3,59) which presumably result from the approximation that $\epsilon_h \gg Pv_h$, though no comment was made in the noted references.

In a manner similar to that employed above, an expression for liquid compressibility (β) can be derived. With correct expressions for C_p , α , and β an equation of state can be derived giving $V = f(P, T)$ for liquids. In terms of the Eyring hole model discussed above, all thermodynamic⁽⁵⁹⁾ properties of a liquid are functions of the number of so-called holes present. In other words, this is a single ordering parameter model of the liquid state.

The most significant failure of the Eyring hole model to agree with experiments results from its glass being described by a single ordering parameter. It has been shown that the behavior in the vicinity of the glass transition is described by the expression^(62,2,5)

$$VT_g \frac{\Delta\alpha}{\Delta C_p} \leq \frac{\Delta\beta}{\Delta\alpha}$$

where T_g is the glass transition temperature and the Δ quantities are the quantities attributed to holes by Eyring. The inequality persists whenever more than one ordering parameter is needed to describe the excess thermodynamic properties of the glass. It appears from the experimental data that exists^(5,6) that one ordering parameter is not sufficient to describe a glass and indicates that while the Eyring model may agree with some experimental results, it is clearly an oversimplification.

A second significant failure of the hole model of liquids is in its prediction of the liquid entropy^(47,63) which apparently results because hole or quasi-crystalline models inherently overestimate the molecular order. This error is greater for simple monatomic liquids than for liquids where the correlation between molecules is very strong because of orientation dependent forces such as hydrogen or covalent bonds. Typical glass forming liquids are characterized by a high degree of directional bonding. It appears to be impossible to explain negative expansion coefficients of liquids in a manner which is consistent with the Eyring hole model. Such behavior is known to exist for water from 0 to 4°C and has been observed indirectly for vitreous silica from 1100°C to 1500°C.^(64,65) This behavior is probably caused by bond rearrangements and thus can not be accounted for by a model which does not include directional bonding.

Despite these inadequacies, the model does remarkably well

in generating thermodynamic properties of liquids compared with other models.⁽⁶³⁾ One of the earliest successes of the hole model was to explain the law of rectilinear diameters.⁽⁴⁷⁾ It has also been applied with good agreement to the dynamic properties of liquids which include shear and bulk viscosity^(3,59) as well as structural relaxation.⁽⁶⁶⁾

When the Eyring model is used to calculate the volume of B_2O_3 melts, the agreement from the glass transition region to $200^\circ C$ above the melting point is within 5%. If a constant energy of hole formation (ϵ_h) is assumed, the predicted volume exceeds the observed value by approximately a factor of two at temperatures near the boiling point. Despite the poor quantitative agreement, the V-T prediction in the high temperature region is qualitatively correct. Since the total liquid expansivity can be expressed as

$$\alpha_l = \alpha_g + \Delta\alpha$$

where α_g is the glassy expansivity and $\Delta\alpha$ is the configurational expansivity, the temperature where it attains a maximum can be solved for by setting

$$\left. \frac{\partial \alpha_l}{\partial T} \right]_{P, \epsilon_h} = 0 = \left. \frac{\partial \alpha_g}{\partial T} \right]_{P, \epsilon_h} + \left. \frac{\partial \Delta\alpha}{\partial T} \right]_{P, \epsilon_h}$$

If it is assumed that α_g is constant with temperature then

$$0 = \frac{\epsilon_h}{\sigma R} \left[\frac{1}{T^2} e^{-\frac{\epsilon_h}{RT}} - \frac{E_h}{RT^2} - \frac{2}{T^3} e^{-\frac{\epsilon_h}{RT}} \right]$$

and

$$\frac{\epsilon_h}{RT} = 2$$

at the point where α_l attains its maximum value. For temperatures above that defined by the above relation the V-T curve should be concave downward, and at very high temperatures the liquid expansivity should be equal to α_g . Since the value of $\frac{\epsilon_h}{RT_g}$ for B_2O_3 is 1.9⁽⁶⁷⁾ the V-T curve should be concave downward for temperatures above the glass point. It can be observed from Figure 3 (compiled from sources^(68,69,70)) that the predicted behavior agrees qualitatively both with respect to the negative curvature and the high temperature value of expansivity. However, the high temperature values of volume are in poor quantitative agreement with the observed values when a constant value for ϵ_h is assumed.

Wunderlich⁽⁷¹⁾ has used the Eyring hole model of liquids to arrive at what he calls the "rule of constant heat capacity increment." In terms of this model, heat capacities of different substances should be compared on the basis of one mole of fundamental units. According to him the fundamental unit in the hole model is the molecular unit which corresponds to a hole, which he has dubbed a "bead". With organic

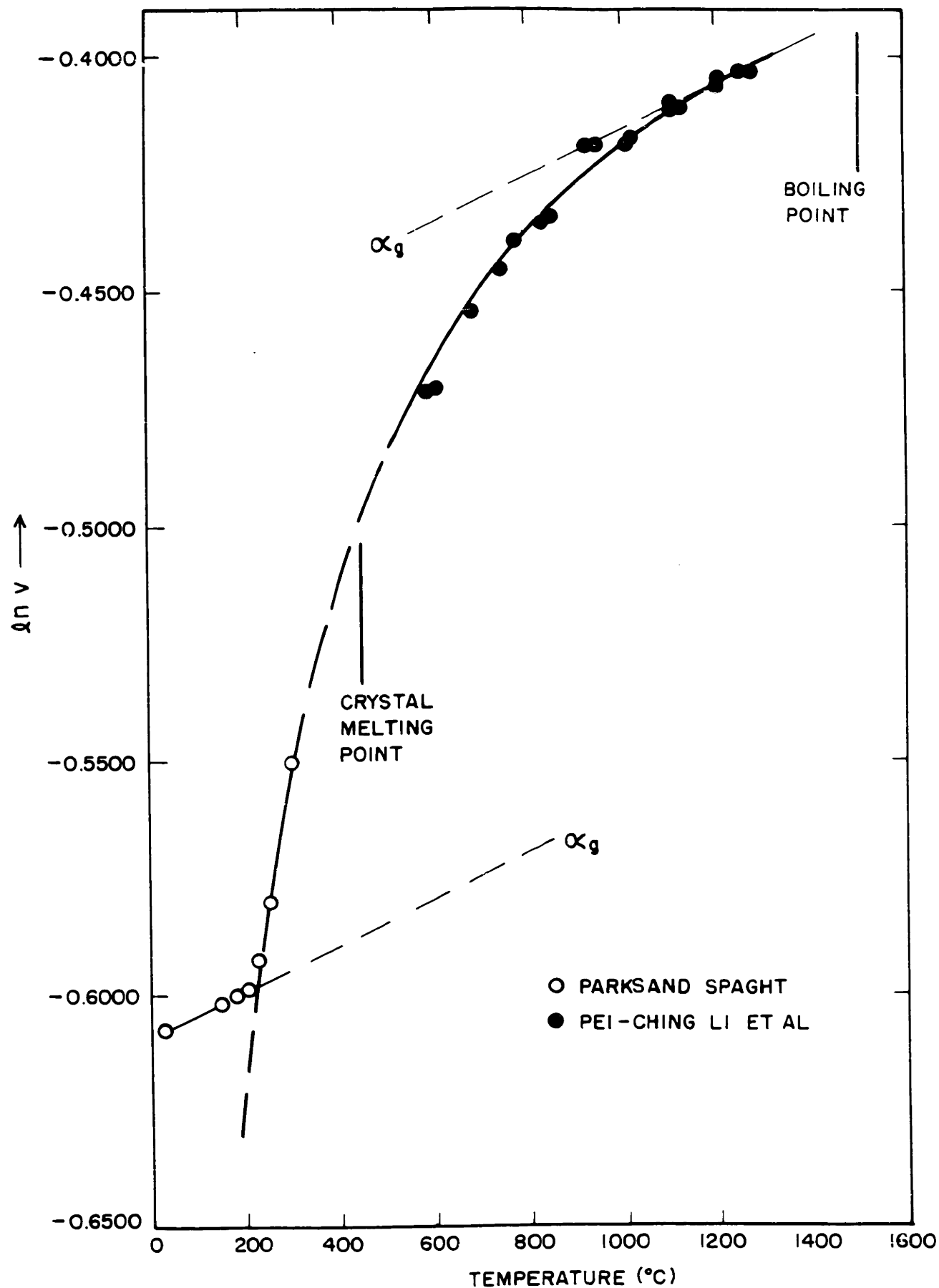


Fig. 3 Specific Volume of B_2O_3

glass formers he found a relatively constant value for 39 substances of

$$\Delta C_p = 2.7 \pm 0.5 \left[\frac{\text{cal}}{^\circ\text{C mole beads}} \right]$$

when the bead molecular weight was assumed to be that of 1 mer of the polymer chain. Poor agreement was observed for inorganic glasses when each oxygen was assumed to act as a bead, though he apparently made at least one computational error in the case of B_2O_3 which when corrected brings it into agreement with the value observed for organic materials. He further demonstrated that a value for ΔC_p of

$$\Delta C_p \Big|_{\text{cal}} = 2.9 \left[\frac{\text{cal}}{^\circ\text{C mole beads}} \right]$$

could be calculated on the basis of the observations that $n = \frac{V_o}{V_h} \approx 5$ (3,59) and that the free volume at the glass transition is approximately 2 percent.

It is difficult to assess the significance of Wunderlich's observation. However it is true that he has arrived at the constant for a wide variety of materials by assuming a reasonable molecular group to participate in the formation of a hole, and also he has calculated an approximately equal value for ΔC_p directly from the Eyring equations with the use of observed values for n and free volume at the glass point. Thus, the result appears to be consistent both with the model and with

independently observed results. Combination of ΔC_p and $\Delta \alpha$ data at T_g permits the calculation of the volume ratio of atoms to holes (n) and the energy of hole formation (ϵ_h) without any assumptions other than $\ln(\sigma) \cong 1$ which experimentally appears to be justified.^(3,59,72)

In conclusion, the Eyring relations resulting from the model of liquids should be regarded as empirical even though they are derived from a molecular model, both because the model is unrealistic and it does not conform to certain important experimental results. However, it is quite accurate in its predictions of thermodynamic variables and also has been extended with some success to explain liquid viscosities (shear and bulk). Even though it cannot be regarded as a general solution for the equation of state of liquids, the Eyring model does work fairly well, and in particular for supercooled liquids and melts near the melting temperature.

C. Structural Relaxation in the Transition Region

It is recognized that there are two classes of relaxation processes in the transformation region. The first is that treated by visco-elasticity and is associated with stress relaxation and creep phenomena where the structure is considered as fixed. The second is structural relaxation of a glass toward the equilibrium supercooled liquid structure after a sudden change in pressure or temperature. In commercial applications the former class is associated with stress relief and tempering and the latter with stabilization. The two classes

can be compared two ways, phenomenologically and mechanistically.

Mechanistically the processes of shear and structural (thermally) and pressure induced) relaxation are similar. If it is considered that at any temperature and pressure some equilibrium distribution of molecular states will be established and the probability of occupancy of any state $P(i)$ is proportional to

$$P(i) \propto e^{-\frac{E_i + PV_i}{kT}}$$

where E_i and V_i are the energy and volume associated with the molecule existing in state (i). The overall distribution is one where the free energy is minimized. When the temperature is changed or when the energies of the states are altered by the application of a shear or hydrostatic pressure, a new distribution of molecules is required to minimize the free energy. In general it can be said that the number of molecules leaving state (i) will be equal to the product of the number in state (i) and the molecular jump frequency. The system relaxes to the new equilibrium distribution by these molecular jumps and equilibrium is established when the net rate of jumps into all molecular states is equal to zero. It can also be said that increases in temperature will tend to shift the distribution to higher energy states, where increases in pressure will tend to shift it toward reduced volume states. It is not necessarily true that higher energy states are equivalent to smaller volume states, thus it would not be expected that

In the treatment of these equations it is assumed that all the E_i 's are equal and only the η_i 's vary between elements giving distributions of τ_i 's. The expressions for $\epsilon(t)$ and $\sigma(t)$ can also be written in the integral form where the distribution of τ_i 's is treated as a continuous function. Experimentally it is generally found that a single relaxation time is not adequate to describe the observed viscoelastic behavior. In principle an infinite number of τ_i 's extending to infinite relaxation times might be needed; however, most results can usually be described by either a finite number of τ_i 's or a continuous distribution of relaxation times with a finite maximum value.

It is found from stress relaxation or creep experiments that curves produced at different temperatures lie parallel to one another and can be shifted along the time axis to coincide, making a master curve.⁽⁷³⁾ The activation energy calculated from the shift factor is equal to the activation energy of shear viscosity. The so called "time-temperature superposition principle" is based on the premise that the activation energies of the viscosities of the elements are equal. This phenomena was first observed for organic materials in the transition and rubbery regions, but has recently been found to apply to siliceous glasses by Kurkjian.⁽⁷⁴⁾

The viscoelastic behavior of siliceous glasses has been summarized⁽⁷³⁾ as "these facts seem to establish very nicely indeed that the relaxation and creep functions of stabilized glass are more

complicated than the single exponential, but if they are expressed as a series of exponentials then each exponential has the same activation energy, and also that stabilized glass is a thermo-rheologically simple linear viscoelastic substance."

It is important to note here that the existence of a distribution of relaxation times does not necessarily imply a multiplicity of independent molecular mechanisms. Goldstein⁽⁷⁾ cites several examples where a distribution of relaxation times is needed to fit observed results originating from one or at most two molecular processes. On the other hand, if it was known that a variety of molecular motions existed then a spectrum of relaxation times would be expected. Thus the existence of a spectrum provides little insight as to the molecular motions of a relaxation process.

In contrast to the relatively simple solution that was found for the rheological behavior of glasses, structural relaxation of glasses in their transformation region is found to be non-linear. In the present state of the study of nonlinear behavior, there is no precise experimental procedure for determining a response function which will adequately describe the behavior phenomenologically.⁽⁷⁾ It is possible, however, to write expressions for volumetric relaxation occurring because of sudden pressure and temperature changes, and from there to gain some insight into the sources of the nonlinearity.

The differential equations for the structural relaxation resulting from sudden changes in pressure (ΔP) and temperature (ΔT) are

$$\Delta P = \frac{1}{\Delta\beta} \delta - \eta_B \frac{d\delta}{dt}$$

and

$$\Delta T = \frac{1}{\Delta\alpha} \delta + \eta_\alpha \frac{d\delta}{dt}$$

where δ is equal by definition to $\frac{V-V_\infty}{V_\infty}$, η_B is defined as bulk viscosity in terms of the above expression and has the units of poise similar to shear viscosity, and η_α is a viscous resistance to thermal change and has the units (degree/time). If $\Delta\beta$, $\Delta\alpha$, η_B and η_α are constant during the relaxation process and no distribution of relaxation times exists, the differential equations can readily be solved. For the volume relaxation due to change of pressure

$$\delta(t) = -\Delta\beta \Delta P \left(1 - e^{-\frac{t}{\tau_B}} \right)$$

where

$$\tau_B = \Delta\beta\eta_B.$$

A similar expression for $\delta(t)$ can be written for sudden temperature changes. If a spectrum of relaxation times exists, then the volume response to a sudden pressure change is

$$\delta(t) = -\Delta P \int_0^{\infty} \Delta\beta(\tau) (1 - e^{-\frac{t}{\tau}}) d\tau.$$

However, this expression assumes that $\Delta\beta$ and η_B are not functions of δ . An instantaneous "effective" relaxation time $\tau(t)$ can be defined by

$$\frac{1}{\tau(t)} \equiv -\frac{1}{\delta} \frac{d\delta(t)}{dt} = \frac{\int_0^{\infty} \frac{\beta(\tau)}{\tau} (1 - e^{-\frac{t}{\tau}}) d\tau}{\int_0^{\infty} \beta(\tau) (1 - e^{-\frac{t}{\tau}}) d\tau}.$$

The extent of variation of $\tau(t)$ during a relaxation process is a qualitative measure of the breadth of the spectrum; however there is no simple quantitative interpretation. It can be shown⁽⁷⁾ that if the spectrum has a unique maximum relaxation time τ_{\max} , then $\tau(\infty)$ equals τ_{\max} , but if the spectrum is continuous $\tau(\infty)$ increases without limit. Some other results of a spectrum and the non-linearity will be discussed later in conjunction with Figure 4.

Three origins of nonlinearity have been considered⁽⁷⁾. The first, clearly the most important, is the dependence of the viscosity on

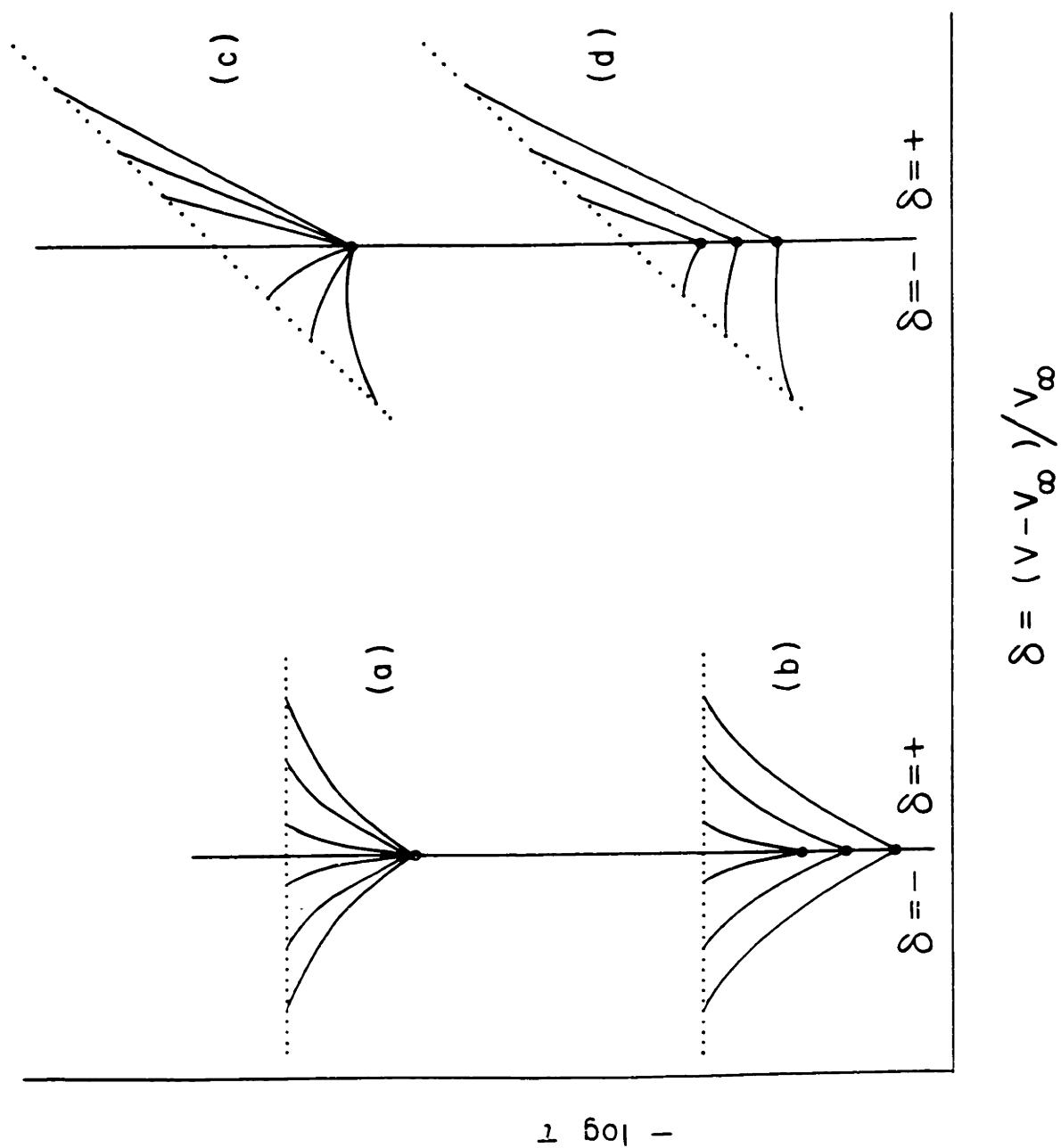


Fig. 4 Schematic Variation of $\tau(t)$ vs. δ when a Spectrum of Relaxation Times is Present after Goldstein⁽⁷⁾

the instantaneous thermodynamic state of the relaxing glass as well as the external pressure and temperature. In its simplest form, this effect is treated in terms of the volume alone and the equations derived on this premise are equivalent to those obtained on the basis of fictive temperature⁽⁴⁾ or free volume theories⁽⁷⁵⁾. The second possible source of non-linearity could arise from variations in α , β or C_p of the liquid with temperature and pressure. Experimentally it appears that α and C_p show very little variation in the transformation region; however, there is some evidence of a relatively rapid variation in β in this region⁽⁷⁶⁾. A third possible origin for non-linearity is a breakdown of the linear relation between the driving force and flow. Of the three, the first is evidently the most important, and a few attempts have been made to incorporate it into quantitative models.

It is interesting to point out that in a non-linear relaxation process, the observed behavior will necessarily be non-simple exponential whether or not a distribution of relaxation times exists. However, like linear viscoelastic materials, the presence of a spectrum of τ 's is indicated for non-linear materials if memory effects are observed. Thus although there is no direct way to handle a spectrum in a non-linear process in a quantitative manner, a clear cut experimental criterion exists for telling whether a spectrum is present or not.

Figure 4 is reproduced from Figure 1, page 101, of Goldstein's article⁽⁷⁾ and schematically shows what might be expected in a system behaving non-linearly due to the dependence of the relaxation times on the thermodynamic state in which there is also a spectrum of relaxation times. The dotted lines denote the dependence of the initial mean relaxation time (at δ_{\max}) on the volume, measured here by δ . In the non-linear case, c and d, τ_i is clearly a function of δ_i (where the subscript i denotes initial value after the change in temperature or pressure) while in the linear case, a and b, τ_i is constant. In the idealized free volume models, where no distribution of relaxation times is considered and τ is a function of V , and hence δ , only, the mean relaxation time during the relaxation process would be represented by the dotted lines. The solid curves represent the relaxation of the volumes at the temperature and pressure of measurement. The behavior depicted in a and c is that for a spectrum with a maximum time τ_{\max} . That shown in b and d depicts what would be expected if the spectrum were continuous. These curves do not extrapolate to the same τ , but rather the limiting τ as δ goes to zero is larger the larger the initial amplitude $|\delta_i|$. It would seem that contrary to the way the relaxation curves were drawn in b and d that the τ must approach infinity as $\delta \rightarrow 0$ and the apparent existence of a τ_{\max} must in fact be due to a presumed limit in experimental precision.

There have been a number of stabilization experiments on organic and inorganic glasses. Generally a spectrum of relaxation times was not included in the equations used to describe the results and the range of initial conditions was not wide. Empirical or semi-empirical equations have been found to fit the observed data satisfactorily.

As was mentioned above, the most plausible explanation for the non-linearity in the transition region is the sensitivity of viscous resistance to the thermodynamic state of the substance. Commonly it is assumed that the volume alone is determining. The Williams-Landel-Ferry⁽⁹⁾ equation is derived on this assumption, and has been found to give excellent representation of the shear and dielectric relaxation processes above the transition region for organic and some inorganic systems.

Even though the W.L.F. equation was originally proposed as an empirical expression it can be derived directly on the basis of Doolittle's⁽⁷⁷⁾ free space equation for shear viscosity. The Doolittle and W.L.F. equations are:

$$\eta = A e^{\frac{B}{f}}$$

and

$$\log \frac{\eta_T}{\eta_{T_2}} = \frac{-C_1 (T - T_2)}{(C_2 + T - T_2)}$$

respectively where f is the free volume fraction, B , C_1 and C_2 are constants and η_{T_2} is a viscosity corresponding to the reference temperature T_2 . Commonly the reference T_2 that is used is the experimental glass temperature T_g , then the constants C_1 and C_2 can be shown to be

$$C_1 = \frac{1}{2.303 f_g}$$

$$C_2 = \frac{f_g}{\Delta\alpha}$$

where f_g is the free volume fraction at the glass transition and $\Delta\alpha$ is the difference between the supercooled liquid and glass volumetric expansivities at the glass transition. The W.L.F. equation predicts an infinite viscosity at a temperature where the denominator goes to zero, at $T = T_2 - C_2$. For most materials this anomaly occurs 20 to 40°C below the kinematic glass transition and if it is assumed that the bulk viscosity behaves in a similar manner, it corresponds to a temperature where complete structural relaxation cannot occur.

In an analogous though not mathematically identical manner, Tool^(4,78) proposed that the resistance to the approach of a glass to its equilibrium volume was a function both of temperature and of the instantaneous configuration. This formulation assumed a single ordering parameter description of the instantaneous configuration and that a

single relaxation time was uniquely determined by the configuration. He used "fictive temperature," T_f , as a measure of instantaneous configuration. A set of equivalent equations for length, volume, density or refractive index relaxation can be derived from the Tool expression; however the fictive temperature is in some ways a more convenient parameter.⁽⁷⁾ Tool's original equation for the relaxation of the fictive temperature is

$$\frac{dT_f}{dt} = A e^{\frac{T}{g}} e^{\frac{T_f}{h}} (T - T_f) \quad .$$

An infinite time it can be seen that $T_f \equiv T$. It is not clear why he expressed the exponential dependence on temperature and structure in the $e^{\frac{T}{g}}$ and $e^{\frac{T_f}{h}}$ form rather than the more familiar $e^{-\frac{A}{T}}$ and $e^{-\frac{B}{T_f}}$ form which results from rate theory; however, the two functional forms behave similarly over a narrow temperature range, and the form used by Tool is often more readily integrable. The Tool expression has been found to represent refractive index relaxation reasonably well when $T_f > T$ by Collyer,⁽⁷⁹⁾ but the agreement for $T_f < T$ is generally poor.⁽⁸⁰⁾

Ritland⁽⁸⁰⁾ found it necessary to modify the Tool expression to fit his results for isothermal volumetric stabilization of a borosilicate crown glass. The following expression fit his data for

volume dependent relaxation time. The derived equation is complex and in general the agreement with observed results is poor. Kovacs attributes the discrepancies in main to the existence of a spectrum of relaxation times. The presence of a spectrum is clearly indicated in Kovacs' plot of observed $\ln \left(\frac{1}{\tau_{\text{eff}}} \right)$ vs. δ values for polyvinyl acetate which is reproduced by Goldstein in⁽⁷⁾. For $T_f > T$ the effective relaxation time varies by as much as one order of magnitude for the same δ , indicating memory effects, and hence the presence of a spectrum of τ 's. For volumetric stabilization runs where $T_f > T$ or $\delta > 0$, the τ_{eff} vs. δ curves extrapolate to the same point at $\delta = 0$, indicating a maximum value in the distribution of relaxation times. The behavior for $\delta < 0$ is strikingly different from that observed for $\delta > 0$. For volumetric stabilization runs where $T_f < T$ the extrapolated τ_{eff} 's to $\delta = 0$ do not coincide, but increase with increasing initial amplitude δ_i . It is clear from these results that a spectrum needs to be taken into account to adequately describe the behavior of polyvinyl acetate, though at present it appears impossible to do.

Goldstein⁽⁸¹⁾ studied the volumetric relaxation of zinc chloride glass to ascertain if "single relaxation time" behavior found with acoustic means above its melting point⁽⁷⁶⁾ remains in the transformation region. Structural relaxation was observed at 100, 95, and 88°C. Runs with $T_f > T$ and $T_f < T$ were made at 95°C; however, at 100°C only runs with $T_f < T$ and at 88°C only runs with $T_f > T$ were made. His investigation led to the following conclusions.

The $\ln \left(\frac{1}{\tau_{\text{eff}}} \right)$ vs δ curves observed for various T_f 's at any one of the three stabilization temperatures fail to coincide. It follows from this that a distribution of relaxation times is necessary to describe volumetric relaxation. In contrast to Kovacs' polyvinyl acetate results, where τ_{eff} 's were observed to vary by a factor of 30 to 40 at any given δ , the maximum variation in τ_{eff} observed by Goldstein for ZnCl_2 was approximately a factor of two. This would suggest, that though present, the spectrum of relaxation times is narrow. Similar to Ritland's results, as recalculated by Goldstein, the values of τ_{eff} at any stabilization temperature extrapolate to the same point, independent of the initial δ_i . This indicates that there is apparently a finite maximum τ_i in the distribution of relaxation times.

Eyring and Hirai^(3,59) have derived expressions to describe volumetric relaxation resulting both from hydrostatic pressure and temperature changes requiring configurational changes of the liquid to reach equilibrium as well as that associated with delayed elasticity. The derivation is based on the hole model of liquids and consequently is a single relaxation time - single ordering parameter model which experimentally has been shown to be inadequate. The Tool equation for volumetric relaxation in the transition region follows directly from this treatment, and as a result, the Eyring solutions have the same inadequacies as the Tool expression. This treatment does lead to the prediction of the relaxation times for delayed elasticity, τ_B , shear

viscosity, $\tau_S \equiv \frac{\eta_S}{B}$, and thermally induced volumetric configurational relaxation $\tau_{B,T}$. It follows from their treatment that

$$\tau_S > \tau_B > \tau_{B,T} .$$

Clearly, the derivation predicts finite constants τ_{eff} 's at $\delta = 0$ and τ_{eff} should be a function of δ , T and P only.

At approximately the same time that Eyring and Hirai published references 3 and 59, Eyring was coauthor to a paper which reportedly explained non-Newtonian relaxation in amorphous solids⁽⁶⁶⁾. By using the Eyring rate theory, and an assumed biasing of the jump barrier due to an imaginary stress caused by a deviation of a system from equilibrium, it was possible to derive equations for relaxation of a system to equilibrium. The expression obtained was

$$-\frac{d \ln \Phi}{dt} = 2k_f \sinh (\alpha' \Phi)$$

where Φ equals $\frac{V - V_\infty}{V_0 - V_\infty}$, k_f is the specific rate constant of the reaction, and α' is a factor which is inversely proportional to the absolute temperature. Since it can be shown that $d \ln(\Phi) = d \ln(\delta)$ it follows that

$$\frac{1}{\tau_{\text{eff}}} = 2 k_f \sinh (\alpha' \Phi) .$$

Thus in terms of this model, $\tau_{\text{eff}} \rightarrow \infty$ as $V \rightarrow V_{\infty}$. T. Ree, who presented the paper, indicated that their expression fitted the Ritland relaxation data better than either the Tool or the Ritland expressions. However, it is obvious that the τ_{eff} behavior predicted by this model is not even qualitatively similar to that calculated by Goldstein from the Ritland data. If Ritland's values for $\Delta\alpha$ are employed in conjunction with the values for k_f and α' that Ree claimed fitted Ritland's data, a value of τ_{eff} equal to 1,250 hours is calculated for $(T_f - T)$ equal to 2°C at T equal to 520°C . Goldstein observed a value of τ_{eff} of approximately four hours for the same $(T_f - T)$ at 533°C . For an order of magnitude check it can be assumed that

$$\tau_{\text{eff}} = \tau_o e^{\frac{Q}{RT}}$$

where τ_o is a constant and Q is the activation energy and is set equal to that observed by Ritland, i.e., 125 kcal/mole. On this basis, the τ_{eff} to be expected at 520°C should be approximately 14.5 hours. Thus it can be seen that this model gives extremely poor agreement with the observed derivative quantity τ_{eff} , though it apparently fits the volume vs. time data reasonably well. This inconsistency may result because the integrated function is insensitive to errors at small ϕ 's.

Two other comments regarding this model are pertinent. The first is that the value of α' , though empirically determined to fit

data, is made up of molecular parameters and thus should be constant at constant temperatures. Ree indicates, however, that it was necessary to use a value of $\alpha' = 0.5$ for $T_f < T$ and $\alpha' = 3.0$ for $T_f > T$ at $T = 520^\circ\text{C}$ to fit Ritland's data. It appears to be inconsistent with the derivation that α' should depend on whether $T_f < T$ or $T_f > T$. The authors showed that the Tool equation could be derived as a special case of their expression. However, the approximation that $\sinh x = \frac{1}{2} e^x$ was used. This approximation is good only for large positive values of x , and thus the Tool expression is consistent with their expression only for large values of Φ . Experimentally it appears that the Tool expression is a better approximation for small Φ 's than large.

Phenomenonologically the rheological properties of siliceous glasses appear to be described by linear viscoelastic treatments; however, the structural relaxation behavior due either to rapid pressure or temperature changes cannot be described yet. The well known Tool expression can only be considered as a first rough approximation to structural relaxation, but it attempts to contain what appears to be an essential feature, which is the dependence of the resistance to structural change on the instantaneous thermodynamic state of the system. Its failure to agree with observed relaxation behavior can be attributed to the assumption that a single ordering parameter T_f is adequate to describe the state of the system and the neglecting of a distribution of relaxation times. The

consequences of both assumptions were realized by Tool, and various experiments appear to indicate that they were wrong. As was indicated above, attempts to verify the Davies and Jones equation have indicated the need of more than a single ordering parameter, and the presence of a spectrum of relaxation times is clearly indicated by memory effects.

Goldstein indicates⁽⁷⁾ that at present there appears to be no adequate phenomenological description of non-linear relaxation with a distribution of τ 's. He indicates that even if a relaxation spectrum could be determined for such small "stresses" that the response was linear, it is not clear that the spectrum could be applied to the non-linear case with modification of the introduction of a dependence of the relaxation time spectrum on the instantaneous state. Ritland's modification of the Tool expression appears to be an attempt to represent the effects of a distribution of τ 's.

There is no direct mathematical relationship between the distribution of τ 's observed for stress relaxation and creep measurements and that observed for the non-linear volumetric relaxation. It does appear, however, that similar to the distribution of τ 's observed by Kurkjian, that for inorganic glasses there is a finite maximum τ in the distribution for volumetric relaxation. Goldstein⁽⁸⁴⁾ suggests that this extrapolated τ_{eff} , representing a relaxation time when the glass has relaxed to its equilibrium volume, and the "fictive" and true

temperature are equal, may be thought of as a "equilibrium" relaxation time.

When the logarithms of the extrapolated τ_{eff} 's observed by Goldstein for ZnCl_2 are plotted against the reciprocal of the absolute temperature, within the experimental accuracy, the points lie on a straight line, indicating a simple exponential dependence of τ_{eff} on temperature. Ritland reports a similar result, and further finds that the activation energy calculated from the temperature dependence of τ_{eff} is equal to that observed for shear viscosity at the same temperature. The equality of the activation energies for the two processes is consistent with the Eyring-Hirai derivations.

It is not possible to compare the relative magnitude of the relaxation times for the two processes with the Eyring-Hirai prediction for the glass used by Ritland. Goldstein⁽⁸³⁾ has suggested that the time constant for structural relaxation must be much larger than that for shear flow since Lillie⁽⁸⁴⁾ was able to observe the change in viscosity with changing structure while shear deformation was occurring. This contradicts the predictions of the Eyring-Hirai derivation. To date there have been no systematic studies of configurational volume relaxation due to rapid pressure changes with the exception of one made by Mackenzie⁽⁸⁵⁾ which does not lend itself readily to interpretation, so it appears impossible to indicate the magnitude of the pressure induced structural relaxation times relative to the temperature induced structural relaxation times.

III. EXPERIMENTAL PROGRAM

To examine the relations and paradoxes discussed in the Introduction, a number of physical properties would have to be studied. Examination of the Davies-Jones relation requires measurement of the volumetric expansivity, compressibility and specific heat of the glass and supercooled liquid as well as the rate of change of the glass point with changing pressure. Further, it appeared from limited experimental data from the literature⁽⁷⁶⁾ that the inequality expressed in this equation could be violated due to the rapid variation of $\Delta\beta$ with T_g compared with that observed for $\Delta\alpha$ and ΔC_p , so the dependence of $\Delta\beta$, $\Delta\alpha$ and ΔC_p on T_g should be experimentally determined. To compare the observed time constants for structural relaxation with those for shear viscosity, both with respect to their relative magnitude and to the anomalous infinite time constant predicted by the W.L.F. equation, the kinetics of the approach to the equilibrium structure after sudden changes in pressure and temperature must be studied. Finally, if the temperature at which the entropy of the supercooled liquid becomes equal to that of the crystal, at the so-called Kauzmann paradox⁽⁸⁾ point, both the heat of fusion and the specific heat of the crystalline material must be determined.

It is evident that the experimental program implied above is very extensive and would require four or five specialized pieces of equipment to make the required measurements. The study undertaken was limited to the following areas. It was believed that the $\Delta\beta$ and $\Delta\beta(T_g)$ measurements were to be made in another laboratory. However, these measurements have apparently not been made. The first area of investigation was that of structural relaxation behavior. According to Goldstein⁽⁷⁾ relaxation behavior is the outstanding experimental characteristic of the glass transition, and any molecular theory must explain it. It appeared from the literature that there was a good chance that a maximum value in the distribution of relaxation times might be expected and hence a τ_{eff} at $\delta = 0$ could be defined which was independent of δ initial. Goldstein referred to it as an equilibrium relaxation time of the structure⁽⁸¹⁾. According to the Eyring-Hirai^(3,59) models, the equilibrium relaxation time is related to the shear viscosity relaxation time, but, there appeared to be some question as to whether the models predicted correct relative magnitudes. It was also important to see whether the equilibrium relaxation time behaved in a manner similar to that predicted by the W.L.F. equation for the shear viscosity relaxation time, in that an infinite relaxation time would be predicted at temperatures slightly below the kinetic glass transition point. The terminal volume of a structural relaxation experiment is by definition the equilibrium

volume at that temperature; thus, experiments of this type at several temperatures determined the specific volume of the supercooled liquid as a function of temperature and hence its thermal expansivity.

Without the $\Delta\beta$ and dT_g/dP measurements, it is not possible to examine the Davies and Jones relations and to make any judgement regarding the excess thermodynamic variable which determines the glass transition; however, measurements of $\Delta\alpha$, ΔC_p and v_{T_g} do allow the calculation of the minimum values of $\Delta\beta$ and dT_g/dP that are consistent with the equations. If the O'Reilly⁽⁶⁾ and Goldstein⁽⁵⁾ observations can be extended to the investigated glasses, these parameters allow the calculation of dT_g/dP .

To complete the areas of investigation indicated above, linear thermal expansion and enthalpy measurements were made on the glasses and supercooled liquids for three systems. Structural relaxation measurements which extended over a time scale of several minutes to over three months were carried out on one of the glass systems. The other two were investigated only over time scales which readily allowed the determination of supercooled liquid expansivities.

It can be shown that if both linear expansivity (a) and volumetric expansivity (α) are based on the actual length or volume respectively rather than some low temperature reference length or volume

$$\alpha = 3a$$

for an isotropic material. It follows directly that

$$\ln \left(\frac{V_2}{V_1} \right) = \int_{T_1}^{T_2} \alpha(T) dT = 3 \int_{T_1}^{T_2} a(T) dT$$

or

$$V_2 = V_1 e^{\int_{T_1}^{T_2} \alpha(T) dT} = V_1 e^{3 \int_{T_1}^{T_2} a(T) dT}$$

so that the specific volume of the supercooled liquid needed for the evaluation of the $T V \frac{\Delta \alpha}{\Delta C_p}$ term can be calculated directly from linear expansivities and low temperature density measurements if the fictive temperature is known.

Implicit in the use of a drop calorimeter for the measurement of specific heats of a supercooled liquid is the assumption that for drops sufficiently above the formation range, the excess enthalpy of the glass sample will be independent of the drop temperature. This can be shown to be true to the extent that the fictive temperature is a function only of the cooling rate. Solutions for transient heat flow exist for various geometrical shapes (see 86 for example) which have the form

$$\ln \left(\frac{T_\infty - T(x, t)}{T_\infty - T_0} \right) = k_1 t + k_2$$

after a short time, where T_∞ , T_0 and $T(x, t)$ are the environment, initial and instantaneous temperature at time t and position x respectively

and the constants k_1 and k_2 are functions of the thermal conductivity, the surface coefficient, specific heat, geometry of the sample and the position (x) of the point in question. It follows that

$$\frac{dT_{(x,t)}}{dt} = -k_1(T_{\infty} - T_{(x,t)})$$

or that the instantaneous rate of cooling of every point is dependent on its instantaneous temperature and independent of the initial drop temperature T_0 . From this it follows that each point in the sample has the same cooling rate history, after the above relation for $T(t)$ applies, and thus all points in the sample would be expected to have the same fictive temperature, independent of the initial drop temperature. An experimental indication of the validity of this argument would be demonstrated by the equality of the densities of samples dropped from different temperatures, however as a proof, it is restricted to the applicability of a single ordering parameter description of a glass. A more legitimate, though experimentally less precise, proof would be by the demonstration of the equality of the heats of solution of samples dropped from different temperatures.

The three glass systems that were studied are (1) Lillie No. 1, a soda-lime-silica glass which was mixed and melted in platinum crucibles to duplicate a glass made by Lillie⁽⁸⁴⁾ (nominal composition in weight %: Na_2O , 20.96; CaO , 9.05; R_2O_3 (Fe_2O_3 and Al_2O_3), 0.18; and

SiO_2 , 69.73); (2) Arsenic Trisulfide (As_2S_3) manufactured and contributed by the American Optical Company, Southbridge, Massachusetts; and (3) Pyrex Brand glass manufactured by the Corning Glass Company of Corning, New York, with code number 7740.

The Lillie composition was selected primarily because it is a siliceous glass typical of the soda-lime class. Also, it has been studied in the past with respect to viscosity⁽⁸⁴⁾ and thermal expansivity.⁽⁸⁷⁾ Pyrex was selected as a representative borosilicate glass, and As_2S_3 because it is a single component glass former which might be thought of as a "simple glass", and its properties have not been reported.

IV. APPARATUS EMPLOYED IN EXPERIMENTAL PROGRAM

To complete the experimental program outlined in the previous section, two apparatuses were assembled. The first was constructed to measure linear thermal expansion of glasses and their supercooled liquids. This device was also used to study the relaxation behavior in the transition region. The second was a calorimeter used to measure specific heats at constant pressure of glass formers in their glassy and supercooled liquid states.

A. Thermal Expansion and Relaxation Apparatus

The measurements of length as a function of time and temperature were made by sighting on wires located at both ends of a sample with telescopes mounted on cathetometers. An error analysis had indicated that this technique was as accurate as the more precise interferometer technique provided a 23.5 cm long sample was measured with cathetometers capable of recording changes in length of one μ and provided the temperature was maintained constant along the length of the sample. A study of the input power configuration needed to produce a uniform temperature distribution was conducted and the furnace described in the S.M. thesis submitted by the author⁽⁸⁸⁾ was constructed. The furnace, sample configuration, and cathetometers used in this study were essentially the same as those described in the

mentioned thesis except for an improved sample support which is described below.

The samples were supported by a high thermal conductivity bed (nickel plated copper) to reduce temperature gradients along its length as shown schematically in Figure 5. Flame polished sapphire rollers were placed between the ground surfaces of the bed and the sample to allow changes in length to occur with a minimum of resistance due to friction. If the sighting wires were located exactly between adjacent rollers, ideally viscous deformation would not influence the observed length of the sample. In practice it was found that this condition could not be achieved and viscous deformation had a small influence on the observed length. However this support scheme minimized the effect of viscous deformations and allowed length measurements to be made well above the glass transition temperature.

The furnace temperature was regulated by a Honeywell Electro-Volt proportional controller system. It was found that these controllers would hold a set temperature to $\pm 0.25^{\circ}\text{C}$ for periods of months when properly tuned. Occasional temperature variations in excess of this spread would occur with wide fluctuations of line voltage to the furnace. These fluctuations of temperature were of short duration (less than two minutes) and rarely exceeded 1°C from the set point.

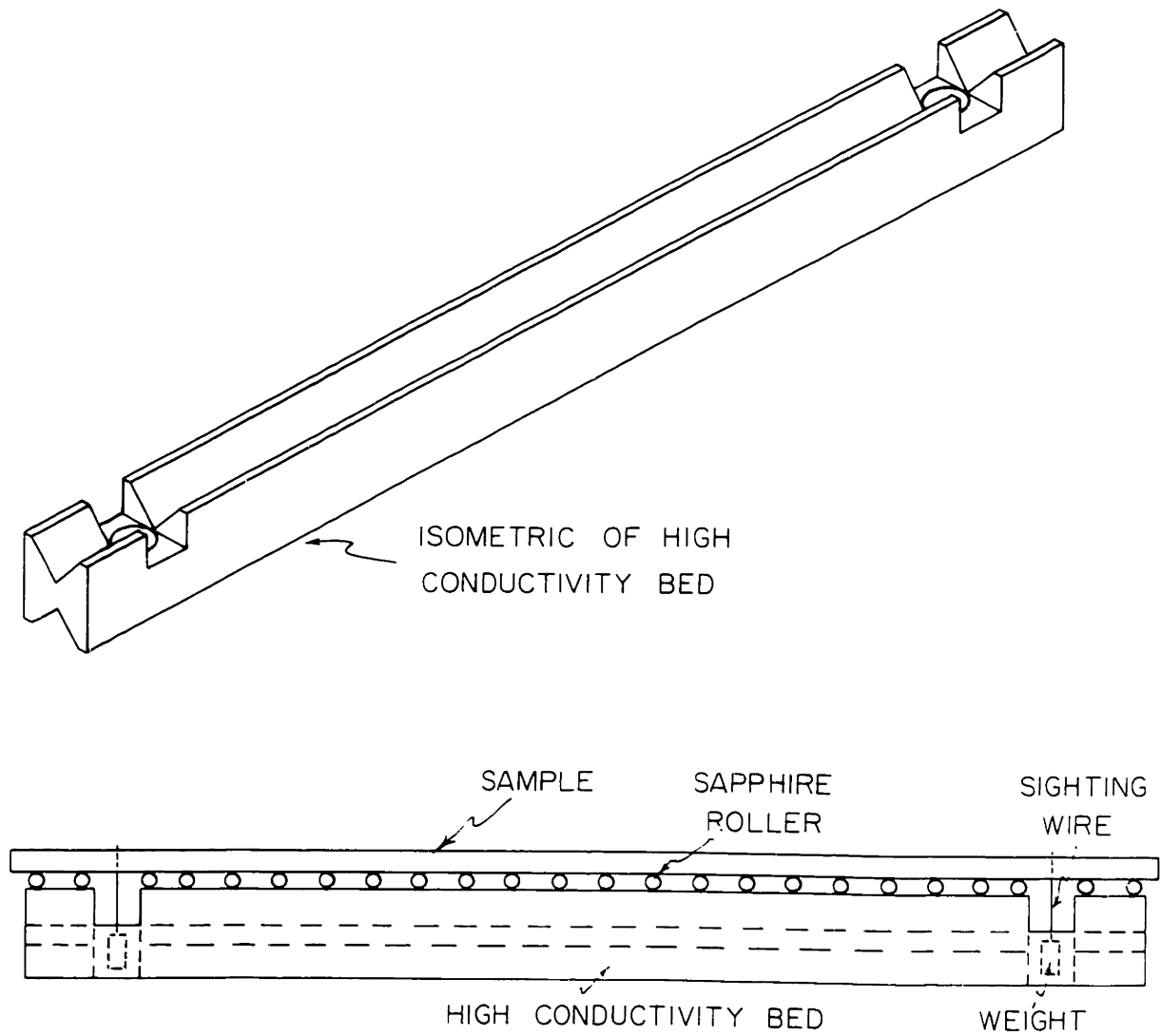


Fig. 5 Sample Configuration and High Conductivity Bed Used for Thermal Expansion Studies

Thermal expansion measurements in the glassy region were made by setting the controller to a set point and recording the length of the sample after the temperature and thermal equilibrium had been achieved. In the supercooled liquid region both thermal equilibrium and structural equilibrium had to be achieved before an equilibrium length could be measured. Hence the equilibrium length at any temperature was taken as the terminal length (L_{∞}) of the corresponding relaxation experiment.

The errors encountered in the measured expansion coefficients are discussed in the presentation of results.

B. Calorimeter

A Bunsen ice calorimeter was constructed which followed closely the details of one in use at the National Bureau of Standards^(89,90,91,92 etc.). It was felt that this particular transformation calorimeter combined a number of desirable features, namely, an inherent high precision over a wide range of temperatures, relative ease of achieving this accuracy in operation and rather simple construction. A drop calorimeter has the disadvantage for use with glass forming systems that high cooling rates are encountered when the sample enters the calorimeter. This means that it is not possible to make specific heat measurements of the supercooled liquid in the transformation range due to the sluggishness of the structure there.

The principle of operation of this type of calorimeter is as follows. Ice, water and mercury are maintained in a closed fixed volume which is in thermal contact with the sample receiving well of the calorimeter. The mercury is connected to a mercury reservoir outside the fixed volume chamber. As heat is introduced into the receiving well, ice melts and mercury is drawn in from the outside reservoir to maintain the constant occupied volume. Calculation of the amount of heat introduced is done by careful accounting of the mercury drawn into the calorimeter from the reservoir.

The calorimeter, furnace and ice bath are shown schematically in Figure 6. The discussion of the unit is limited here to pointing out operating procedures and minor alterations of the apparatus which has been described very thoroughly in the above noted references.

Similar units have been built which have substituted metal vessels for the Pyrex vessels (P); however, it became obvious during use that the recommendation of T. B. Douglas as to the absolute necessity of being able to see the ice mantle was correct. This pertains both to achieving the correct mantle profile during freezing and to its inspection after a number of drops.

Stainless steel was substituted for Inconel in the calorimeter well, mercury tempering coil and vessel caps. It was felt that this metal provided adequate resistance to corrosion with

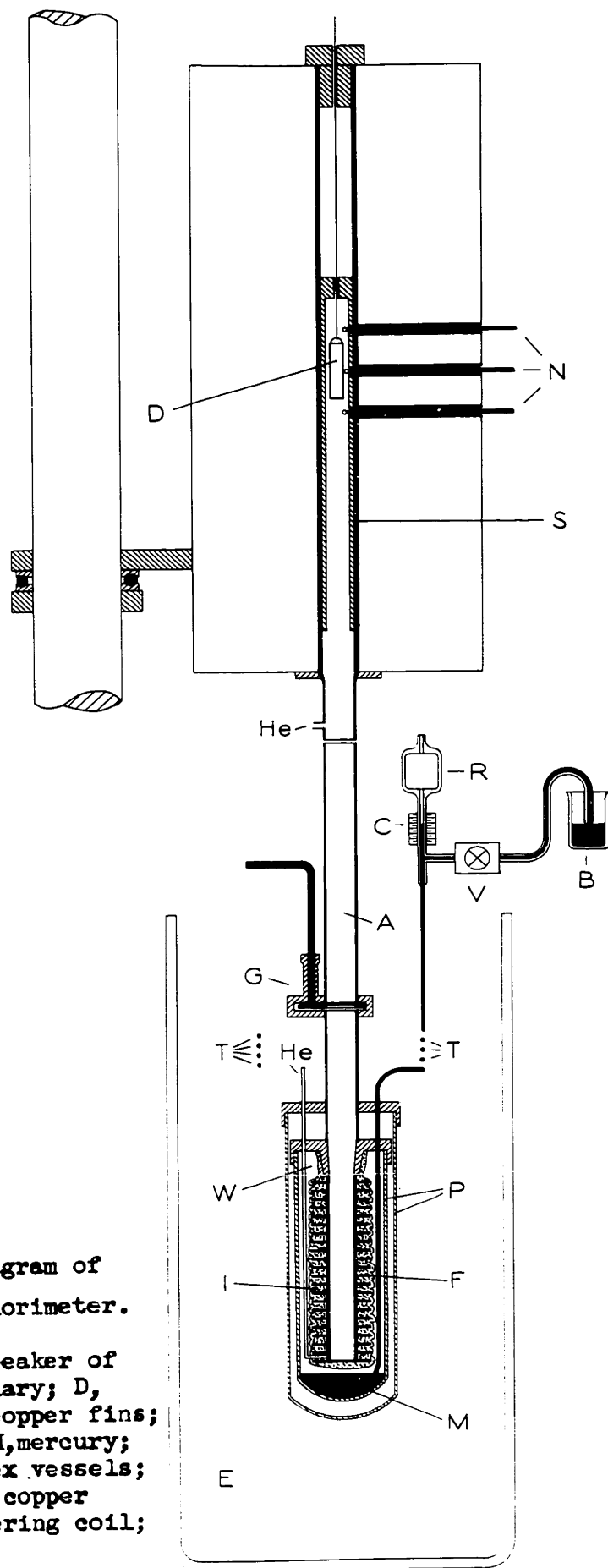


FIGURE 6. Schematic Diagram of the Furnace and Ice Calorimeter.

A, calorimeter well; B, beaker of mercury; C, glass capillary; D, sample; E, ice bath; F, copper fins; G, gate; I, ice mantle; M, mercury; N, thermocouples; P, Pyrex vessels; R, mercury reservoir; S, copper sleeve; T, mercury tempering coil; V, valve; W, water.

considerably reduced cost and improved fabrication properties.

The vessel caps were Helie arc welded to the calorimeter well and the copper fins and spacers were silver soldered in place. The well and fin assembly was electroless nickel plated to prevent galvanic action between the stainless steel and copper.

House distilled water which had been passed through an ion exchange column was used to fill the vessel. Its conductivity was less than $2 \times 10^{-7} \left(\frac{1}{\text{ohm cm}} \right)$. Dissolved gases were removed by a vacuum distillation process. The water was stored under a vacuum equal to its vapor pressure until it was introduced into the calorimeter.

The calorimeter was filled by first evacuating the vessel by means of a vacuum pump attached to the reservoir (R). After the pressure had reached 20μ of mercury, a predetermined amount of water was allowed to enter the vessel through the tube connecting the valve (V) and beaker (B), followed by enough mercury to fill the remaining volume. The water was maintained under partial vacuum during the filling operation to prevent the resolution of gases. A detailed description of the filling procedure and machine drawings of the glass vessels are given in appendices A and B.

It was necessary to stir the ice bath to maintain a uniform temperature of 0°C with advanced melting of the ice in the bath. This was done with three air lift pumps. These pumps provided

considerable circulation without the vibration and hazards to the glass calorimeter vessels encountered with mechanical paddles. The air used for these pumps was passed through another ice bath so it entered at 0°C, thus eliminating it as a source of heat.

Under operating conditions the heat leak was found to be approximately 1.2 calories per hour, corresponding to a drift rate in the weight of the mercury reservoir of 0.02 grams of mercury per hour. This value is approximately four times that reported by Ginnings and Corruccini⁽⁹²⁾. Since the drift rate seemed to be fairly sensitive both to the amount of crushed ice that was packed around the valve (G) and calorimeter well, as well as to changes in room temperature, it is probable that the path of the heat leak was one of conduction along the tube of the calorimeter well. It was felt that because the amount of heat lost due to the leak was usually on the order of two parts in ten thousand in a typical drop, and that it was quite reproducible and hence could be subtracted out, any attempt to reduce the conductance of the calorimeter well either by lengthening it or using thinner wall tubing was unnecessary.

The furnace is a wire wound Marshall Furnace with an internal diameter of 1.0 inches and a hot zone 18.0 inches in length. The windings are 40% rhodium- 60% platinum, which allow continuous operation to temperatures of 1550°C. The winding is divided into 12 zones which may be shunted to produce a uniform temperature

distribution. For temperatures up to 650°C a nickel plated copper sleeve (S) one inch in outside diameter and 0.80 inches in inside diameter and 12 inches long was inserted into the furnace to facilitate maintaining a uniform temperature. Helium was introduced to the furnace at all drop temperatures to improve thermal conductivity and hence reduce temperature gradients as well as reduce the time needed by samples to attain thermal equilibrium.

The temperature of the furnace was controlled by a Honeywell proportional controller like the one used on the thermal expansion apparatus. Temperatures were measured by means of three 90% platinum-10% rhodium thermocouples (N). The potentiometer and galvanometer that were used allowed readings of thermocouple voltages to two microvolts corresponding to approximately 0.1°C .

The operating procedure for a drop was as follows. A sample (D) was lifted into the furnace by means of a wire and held till it had achieved thermal equilibrium. If Newtonian heating is assumed the sample configuration that was used should reach 99.99% of the environment temperature in approximately 20 minutes at 450°C . A minimum of one hour was always allowed to insure that equilibrium was achieved. Just prior to the drop the mercury column was adjusted to a reference mark in the capillary (C), the valve (V) closed and the beaker weighed. The beaker was then replaced and the valve opened so that mercury could flow into the vessel as ice melted. After the

temperature of the sample had been measured the furnace was rotated into place over the calorimeter, the gate valve (G) opened and the can was released. Immediately after the drop the gate valve was closed and the support wire detached so that the furnace could be rotated away from the calorimeter to minimize the heat introduced into the calorimeter from the furnace. The beaker was weighed periodically with the mercury column adjusted to the reference mark until a constant drift rate of approximately 0.02 grams per hour occurred. With a good mantle the system achieved equilibrium in 1/2 to 3/4 hour after the drop.

Both siliceous glasses were contained in open stainless steel cans which had been electrolytically plated approximately 0.001 inches thickness with gold. Gold was used to reduce the corrosion of the stainless steel by the atmosphere and the glass. Neither glass wets gold. In addition, gold has a low emissivity, which was considered to be an advantage since it results in a reduced initial cooling rate. The arsenic trisulfide samples were contained in stainless steel cans which had been sealed under vacuum by welding with an electron beam. It was necessary to seal the As_2S_3 because of its high vapor pressure and the toxicity of various arsenic oxides formed at temperatures in excess of 200-225°C.

A discussion of the probable errors in the determined values of specific heats is made in a later section; however, a few remarks

regarding precision of this calorimeter are made here.

The number of grams of mercury existing between the mercury tempering coil and the beaker (B) is ideally constant. Any change in room temperature caused some slight change in the number of grams contained in this region due to differences in expansion coefficients. Hence if the mercury column was reset to the same reference point in the capillary (C) the mass of the mercury in the beaker (B) varied with changing temperature. When a gas fired furnace that was in the vicinity of the calorimeter was put into operation, changes in room temperature on the order of 30°F in one hour occurred. This difference in temperature caused a change in the mass of the mercury in the beaker of approximately 0.1 grams, corresponding to an error of six to eight calories. Even though operation of the calorimeter was not attempted during conditions as severe as those mentioned, the effect of room temperature variations was noted and it is felt that it was a major source of error.

Recently Rossing⁽⁹³⁾ measured the enthalpy of CaF_2 from $0\text{-}1200^{\circ}\text{C}$ on this calorimeter. Comparison of his results with those of Naylor⁽⁹⁴⁾ and Krestovnikov and Karetnikov⁽⁹⁵⁾ indicate an approximate error of ± 3 calories per drop in his measurements. It is felt that this is a reasonable measure of the accuracy of the calorimeter under operating conditions.

The data obtained from the enthalpy and thermal expansion measurements is recorded in Research Note-books Nos. 361, 386 and 398 which are filed with the Division of Ceramics, Department of Metallurgy, Massachusetts Institute of Technology.

V. EXPERIMENTAL RESULTS

Enthalpy as a function of temperature and length as a function of temperature as well as time in the transition region have been experimentally measured for the glass systems as As_2S_3 , Lillie No. 1, and Pyrex, Corning No. 7740. These properties were measured both in the glassy and supercooled liquid states. The resulting $\Delta H(T)$ and $L(T)$ data for both states have been represented by equations derived by least square curve fitting techniques and the derivative properties, $C_p(T)$ and $\alpha(T)$, were obtained by differentiation of the resulting expressions. The effective time constants for volumetric relaxation were calculated by graphically differentiating the length-time curves with the use of a front surfaced mirror as described by Goldstein.⁽⁸¹⁾

It is well-known that values of the constants z_1, z_2, \dots, z_m which give the best fit to a set of n points represented by the general expression

$$g(x) = z_1 f_1(x) + z_2 f_2(x) \dots + z_m f_m(x)$$

are those which minimize the total variance between the observed and calculated values for $g(x)$, where the variance is defined by

$$V = \sigma_{g(x)}^2 = \frac{\sum (g(x)_{\text{obs}} - g(x)_{\text{cal}})^2}{n - 2},$$

and $\sigma_{g(x)}$ is the standard deviation of $g(x)$. Physical significance can be attached to the values of the constants z_i only if 1) the errors are random; 2) the correct functional form for $g(x)$ is known; and, 3) a large number of points are used. Even when the above conditions are met, significant variation in the constants (or error if they are known from some a priori physical theory) is expected with each series of experiments or sampling of points.

Generally the more terms used in the $g(x)$ expressions the smaller the variance. An n term polynomial will fit exactly n experimental points, that is, a set of constants z_1 to z_n can be found such that $g(x)$ calculated will equal every $g(x)$ observed and the variance will be zero. Similarly, two straight lines can usually be found to fit a set of data points with a smaller variance than either a single straight line or a parabola since four constants can be selected freely to fit the points rather than two or three. The same holds true for higher orders of polynomials. It was in fact the use of the variance as a numerical criteria for the goodness of fit that led Booth and Dixon⁽⁹⁶⁾ to the erroneous conclusion that a discontinuity existed in thermoelectric power of rhodium. They found that two intersecting parabolas fit their data "better" than a simple parabola. In the light of the above remarks it should be expected that two equations with a total of six terms would have a smaller variance than one with three terms. The erroneous application of the variance as a measure of closeness

of fit by the above authors was pointed out by Wensel and Tuckerman⁽⁹⁷⁾ and the more useful Gauss⁽⁹⁸⁾ criterion for closeness of fit was reviewed.

A numerical criterion for the relative closeness of fit of two formulae fitted to the same n data points is given by the expression

$$\Omega = \frac{\sum (g(x)_{\text{obs}} - g(x)_{\text{cal}})^2}{n - m}$$

where m is the total number of freely adjustable constants. The expression(s) giving the better fit has the smaller Ω . In principle, the best representation of a set of data may be found by fitting various $g(x)$'s to it until a minimized Ω is found. It is important to note that even for this condition of minimum Ω , no physical significance can be attached to the form of the resulting expression. It can only be said that this expression for $g(x)$ is the best representation of that particular set of data and that probably a different expression would result with a minimized Ω for a second set of data subject to random errors from a similar series of experiments.

In the above discussion it was assumed that the mathematics of calculating the constants to minimize the variance could be carried out exactly. In the case of three term polynomial curve fitting, terms of the order of x^6 are found. In this series of experiments

where temperatures approached 1000°C ($x = 10^3$) numbers of the order of 10^{18} were encountered in the calculation of constants z_1 , z_2 , and z_3 . With single precision arithmetic, computers carry only eight or nine significant figures, which leads to computational errors from rounding off which can exceed experimental errors.

It is for the above reason that a poorer fit in terms of the Ω criterion can be obtained with a correct functional form of $g(x)$ for a set of data than with an incorrect lower order one. Even if the derived expression gives a reasonable fit with the correct functional form, in that the variance is low, the individual constants can be greatly in error when rounding occurs during calculations. Error in the individual constants can be particularly serious if the least square expressions are differentiated which is equivalent to making calculations from the derived values of the constants.

If the correct functional form is used for $g(x)$ and no computational errors are encountered, it is possible to compute the probable error in the derivative quantity $g'(x)$, ($C_p(T)$ or $a(T)$). For instance if ΔH was correctly represented by

$$\Delta H = A + C_p T \quad ,$$

the probable error in C_p can be shown to be⁽⁹⁹⁾

$$P_{C_p} = P_{\Delta H} \sqrt{\frac{n}{n \left(\sum_n T_n^2 \right) - \left(\sum_n T_n \right)^2}}$$

where $P_{\Delta H}$ is the probable error in ΔH and is related simply to the standard deviation by⁽⁹⁹⁾

$$P_{\Delta H} = 0.6745 \sigma_{\Delta H}$$

For higher order representations of ΔH or $\ln(L)$, the expression for the probable error in C_p , or a , is given by

$$P_{C_p} = \left[\sum_i \left(\frac{\partial C_p}{\partial x_i} \right)^2 P_{x_i}^2 \right]^{1/2}$$

where the x_i 's are all the kinds of terms appearing in the expression for C_p and would thus be all the remaining constants after differentiation of $g(x)$ and the temperature. The values of P_{x_i} can be predicted from the standard deviation of the least square expression $g(x)$ if no machine errors are encountered. However, with rounding errors in the least square curve fitting procedure, it is impossible to estimate the P_{x_i} 's and thus it is impossible to set accuracy limits on C_p 's or a 's obtained in this way.

An expression of the form

$$H = A + BT + CT^2 + D/T$$

was used to represent the enthalpy data in the glassy region. This conforms in form to much data presented in the literature⁽¹⁰⁰⁾ for solids. Whenever the four term expression was used, a double precision

least square analysis was employed. To represent enthalpy in the supercooled liquid state and $\ln(\text{length})$ both in the glassy and supercooled liquid states, two and three term polynomial expressions were fitted, and the one selected which gave the best fit in terms of the Ω test.

A. Thermal Expansion and Specific Volume

If the linear thermal expansion coefficient is calculated on the basis of the actual length rather than a low temperature reference length, the volumetric expansivity (α) is exactly equal to three times the linear expansivity (a) for an isotropic material. For a non-isotropic material, $\alpha = a_1 + a_2 + a_3$ where the a_i 's are the three orthogonal linear expansivities.

The length-temperature data were fit to the functional forms

$$\ln L = A + BT$$

and

$$\ln L = A + BT + CT^2 .$$

The linear expansion coefficient is thus

$$a \equiv \frac{dL}{LdT} = \frac{d \ln L}{dT} = B + 2CT$$

and is equal to B when a linear expression was found to fit best ($C \equiv 0$). In the actual least square curve fitting calculations, the function $\ln L(T)' = \ln L(T) - K$ was used since variations in the values of $\ln L(T)$ took place in the third place after the decimal point over the entire range of temperatures. It was felt that this shift in coordinates was necessary to produce a sufficiently rapidly varying function over the temperature range so that a meaningful curve fit might be obtained. It is thus necessary to add the value K to the derived A values if the actual lengths of the samples are to be calculated. A value of 5.459 was used for K for all calculations except for Pyrex (1) and Pyrex (4) where a value of 5.460 was used. It should be noted that this shift in coordinates has no effect on the values of the calculated expansivities, since both A and K disappear when the derivative is taken, the standard deviations of $\ln L$, A and B, or the value of Ω . All equations representing expansion data are fitted in degrees Centigrade.

The best expressions for $\ln L = \ln L(T)$ are given below for As_2S_3 glass and supercooled liquid, Lillie No. 1 glass and supercooled liquid and Pyrex supercooled liquid together with the standard deviations for $\ln L(T)$ and B when linear expressions for $\ln L(T)$ are given. The results of three attempted fits to Pyrex glass are given in more detail in Table 1 to demonstrate that its glassy expansivity was best represented by two intersecting straight lines.

1. As_2S_3 - Glass

$$\ln L' = 5.4273 \times 10^{-3} + 2.3394 \times 10^{-5}T \quad 25 \leq T \leq 105^\circ\text{C}$$

$$\sigma_{\ln L'} = 2.499 \times 10^{-5}$$

$$\sigma_B = 4.0169 \times 10^{-7}$$

2. As_2S_3 - Supercooled Liquid

$$\ln L' = -1.403 \times 10^{-3} + 12.966 \times 10^{-5}T \quad 162 \leq T \leq 233^\circ\text{C}$$

$$\sigma_{\ln L'} = 89.81 \times 10^{-5}$$

$$\sigma_B = 134.52 \times 10^{-7}$$

3. Lillie No. 1 - Glass

$$\ln L' = -32.276 \times 10^{-5} + 0.93914 \times 10^{-5}T + 38.558 \times 10^{-10}T^2$$

$$61 \leq T \leq 422^\circ\text{C}$$

$$\sigma_{\ln L'} = 0.9196 \times 10^{-5}$$

4. Lillie No. 1 - Supercooled Liquid

$$\ln L' = -13.189 \times 10^{-3} + 3.7089 \times 10^{-5}T \quad 470 \leq T \leq 540^\circ\text{C}$$

$$\sigma_{\ln L'} = 12.002 \times 10^{-5}$$

$$\sigma_B = 14.183 \times 10^{-7}$$

5. Pyrex - supercooled Liquid

$$\ln L' = -2.3857 \times 10^{-3} + 0.85472 \times 10^{-5}T \quad 486 \leq T \leq 565^\circ\text{C}$$

$$\sigma_{\ln L'} = 0.1787 \times 10^{-5}$$

$$\sigma_B = 0.243 \times 10^{-7}$$

6. Pyrex

TABLE 1 - PYREX GLASS EXPANSIVITY

a) Linear fit for all data points

Run	1	4	17
temperature range °C	24 to 403	147 to 413	34 to 443
number experimental points	17	21	21
$A \times 10^5$	26.34	-18.90	14.16
$B \times 10^5$	0.3421	0.3366	0.3241
$\sigma_{\ln L} \times 10^5$	1.535	0.7182	0.5134
$\Omega_2 \times 10^{10}$	2.359	0.5158	0.2636

b) Parabolic fit for all data points

Run	1	4	17
temperature range °C	24 to 403	147 to 413	34 to 443
number experimental points	17	21	21
$A \times 10^5$	23.62	-22.73	13.06
$B \times 10^5$	0.3790	0.3670	0.3349
$C \times 10^{10}$	-8.799	-5.520	-2.136
$\sigma_{\ln L} \times 10^5$	1.05	0.6396	0.4229
$\Omega_3 \times 10^{10}$	1.186	0.432	0.1887

c) Data points divided into two temperature regions

$$\text{Low region } \ln L' = A_1 + B_1 T$$

$$\text{high region } \ln L' = A_2 + B_2 T$$

Run	1	4	17
Low temperature range, °C	24 to 250	147 to 271	34 to 279
High temperature range, °C	275 to 403	284 to 413	300 to 443
number experimental points	11/6	11/10	13/8
$A_1 \times 10^5$	24.83	-21.68	13.44
$B_1 \times 10^5$	0.3538	0.3507	0.3283
$A_2 \times 10^5$	38.55	-18.37	16.87
$B_2 \times 10^5$	0.3050	0.3346	0.3166
$\sigma_{B_1} \times 10^7$	0.4535	0.4642	0.2022
$\sigma_{B_2} \times 10^7$	0.3995	0.4183	0.0519
intersection temperature T_i , °C	281.5	204.5	293.0
probable error in T_i , °C	31.5	91.0	43.5
$\sigma_{\ln L'} \times 10^5$	0.8772	0.5468	0.3831
$\Omega_4 \times 10^{10}$	0.8879	0.3342	0.1641

It can be seen that as was expected, the standard deviation of $\ln L$ decreased as more terms were added in the expression for $g(x)$ to represent the experimental data. It is evident though, from these results, that

better fits were obtained as the number of terms increased since

$$\Omega_4 < \Omega_3 < \Omega_2$$

for all three runs. The best fit was given by dividing the data into two regions and fitting both with linear functions which intersect at a temperature $T_i = 259.7 \pm 35.2^\circ\text{C}$. A single four term polynomial was not fitted to the Pyrex data for purposes of comparing its Ω_4 with the Ω_4 's calculated from the four freely chosen constants of the two linear functions, since large rounding errors were encountered even with the double precision arithmetic with four term fitting relative to that encountered with two term fitting and thus it was not felt that a comparison of the Ω_4 's would be meaningful.

The probable errors in T_i are calculated from the standard deviations in A_1 , B_1 , A_2 and B_2 . The large probable errors result from the small difference in the slopes of intersecting lines, and thus the T_i 's are very sensitive to the values of the A's and B's. The probable error of the average T_i ($\pm 35.2^\circ\text{C}$) was calculated by substituting the probable errors of the individual T_i 's into equation 40 reference 99. The values of the three observed T_i 's are consistent with their probable errors.

The variation observed between the linear expansion coefficients (B's) for the three runs in both the high and low temperature regions is

not consistent with their observed standard deviations. It is not clear whether the variation is real and if not whether it results from systematic errors or from an insufficiently large sample of points. The average values for B_1 and B_2 are 0.3442×10^{-5} and 0.3287×10^{-5} (cm/cm^oC) respectively. The probable errors in the average values B_1 and B_2 cannot be calculated from the probable errors of the individual B_i 's since they are not large enough to cover the observed range of B_i 's. The probable errors were calculated by considering each as a separate measurement, finding the standard deviation from the mean and calculating the probable error of the mean by dividing P_{B_i} by the square root of the number of measurements to give \bar{P}_{B_i} .⁽⁹⁹⁾ Thus the linear expansivities of the low and high temperature regions are

$$a_1 \equiv \bar{B}_1 = 0.3442 \pm 0.0087 \times 10^{-5} \left(\frac{\text{cm}}{\text{cm}^{\circ}\text{C}} \right)$$

$$\text{for } T \leq 260^{\circ}\text{C}$$

and

$$a_2 \equiv \bar{B}_2 = 0.3187 \pm 0.0087 \times 10^{-5} \left(\frac{\text{cm}}{\text{cm}^{\circ}\text{C}} \right)$$

$$\text{for } T \geq 260^{\circ}\text{C}$$

respectively.

The graphical representation of the thermal expansion measurements for Lillie No. 1, As₂S₃ and Pyrex, run one, are given in Figures 7, 8, and 9 respectively. The lines are drawn from the

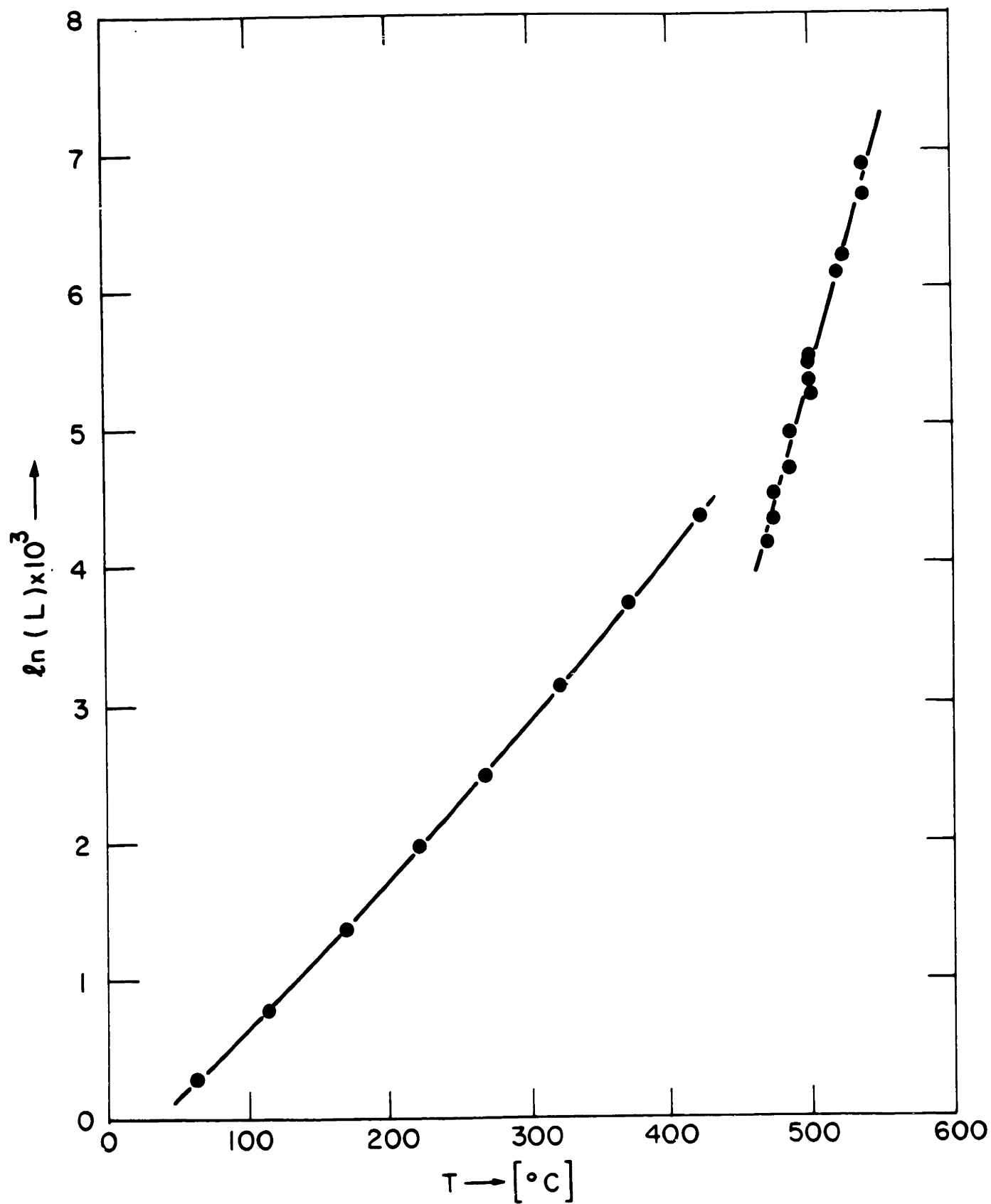


Fig. 7 Linear Expansion of Lillie No. 1

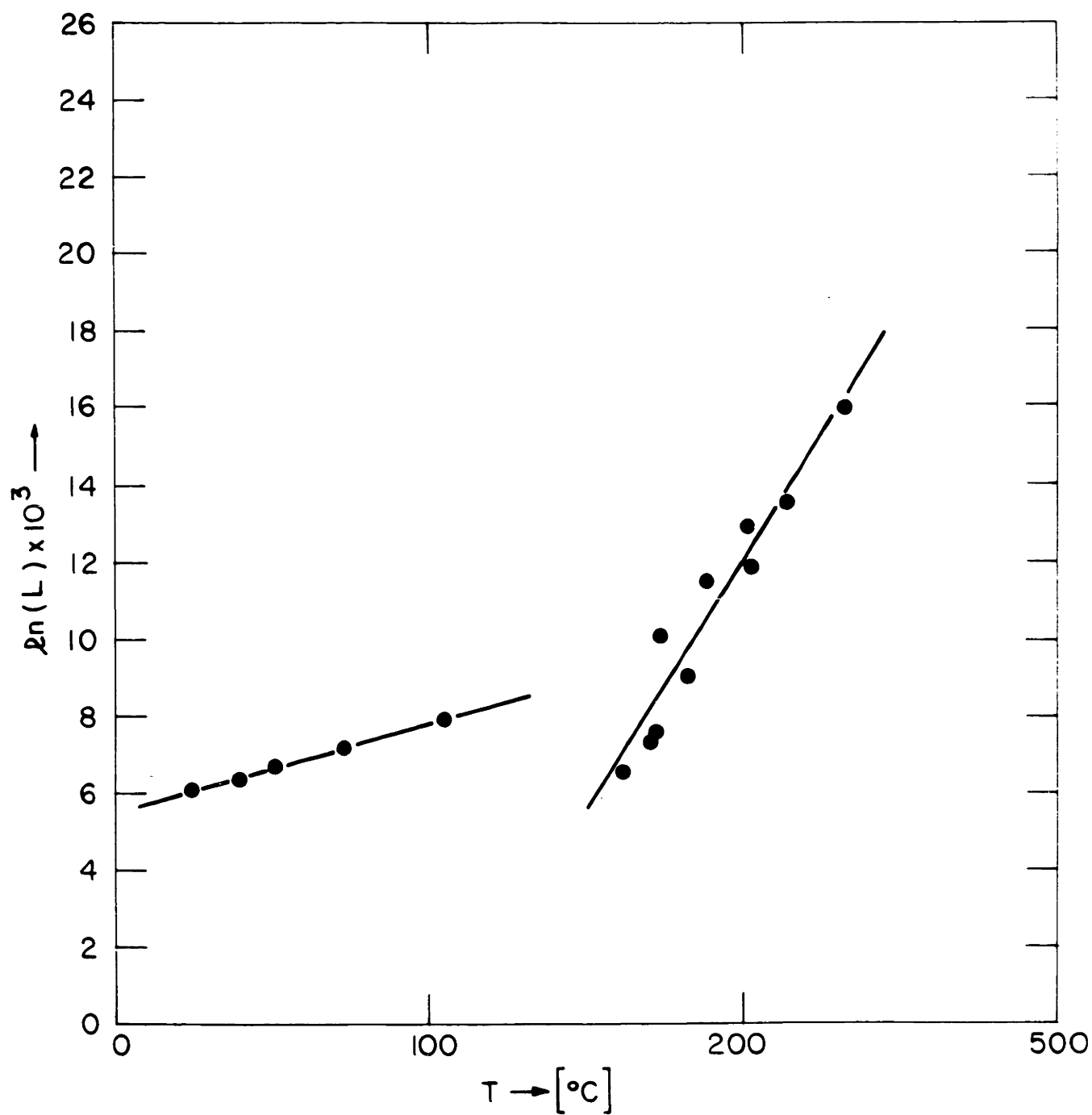


Fig. 8 Linear Expansion of As_2S_3

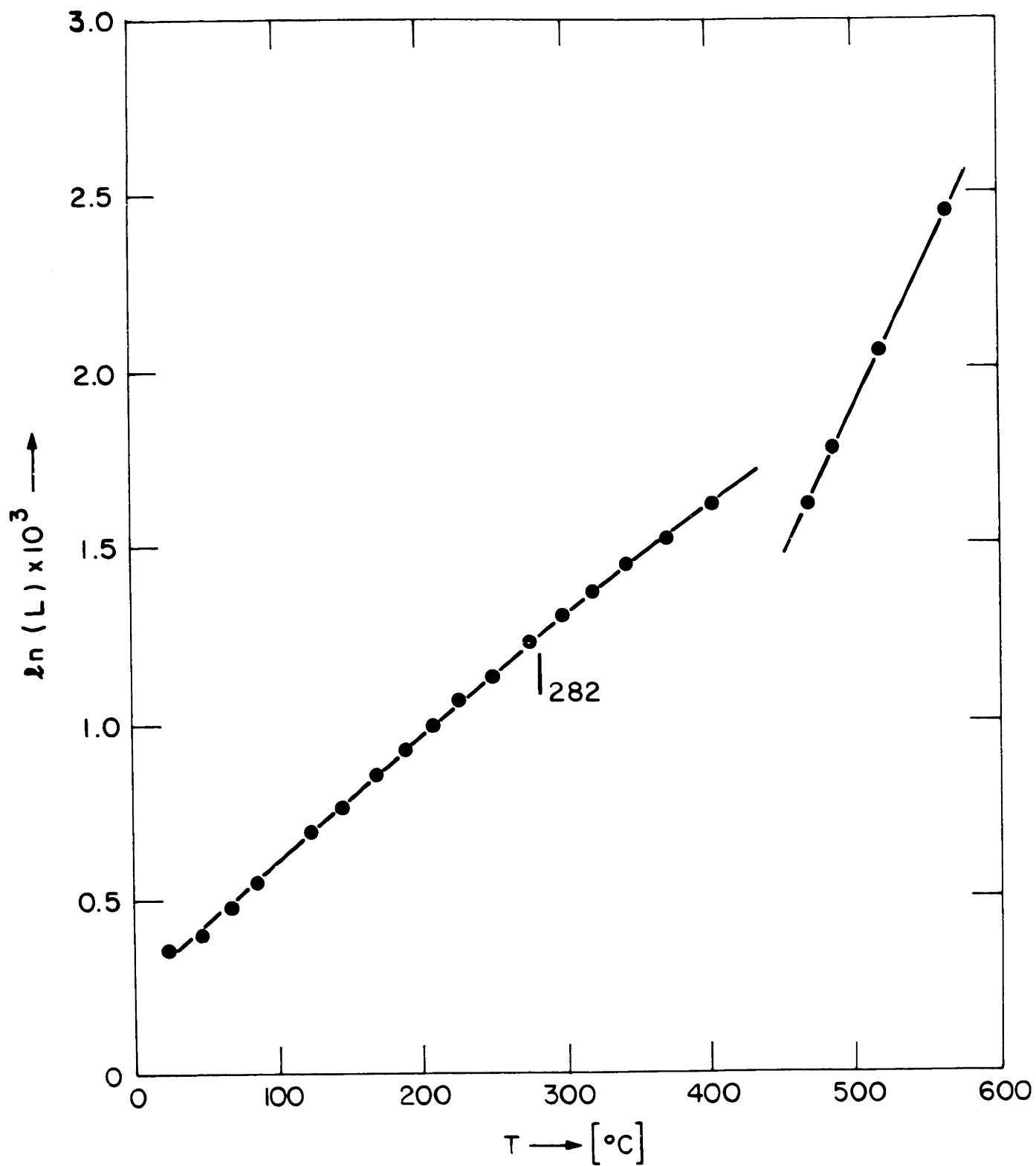


Fig. 9 Linear Expansion of Pyrex

equations given above which fit the observed data points best. The linear and volumetric thermal expansion coefficients derived by differentiation of the best fit equations are given in Figures 10, 11, and 12 for the three glass systems. The values shown for the glassy expansivity of Pyrex in Figure 12 are the average values B_1 and B_2 given above.

The specific volume of the supercooled liquid can be calculated directly by combining the integrated volumetric expansivity functions with room temperature densities of glasses of known fictive temperature. In terms of the true expansivity these equations take the following form,

$$\frac{d \ln V(T)}{dT} = \alpha(T) = 3\alpha(T)$$

$$\ln V(T) - \ln V(T_1) = 3 \int_{T_1}^T \alpha(T) dT$$

$$V(T) = V(T_1) \exp \left[3 \int_{T_1}^T \alpha(T) dT \right]$$

where $V(T_1)$ and T_1 are specific volume of the glass measured at the temperature T_1 . It is of course possible to calculate the specific volume of the supercooled liquid over a temperature range by extending the integration beyond the fictive temperature; however, only the values at the fictive temperature (T_f) are given since the calculation is so easily done by anyone interested in the values.

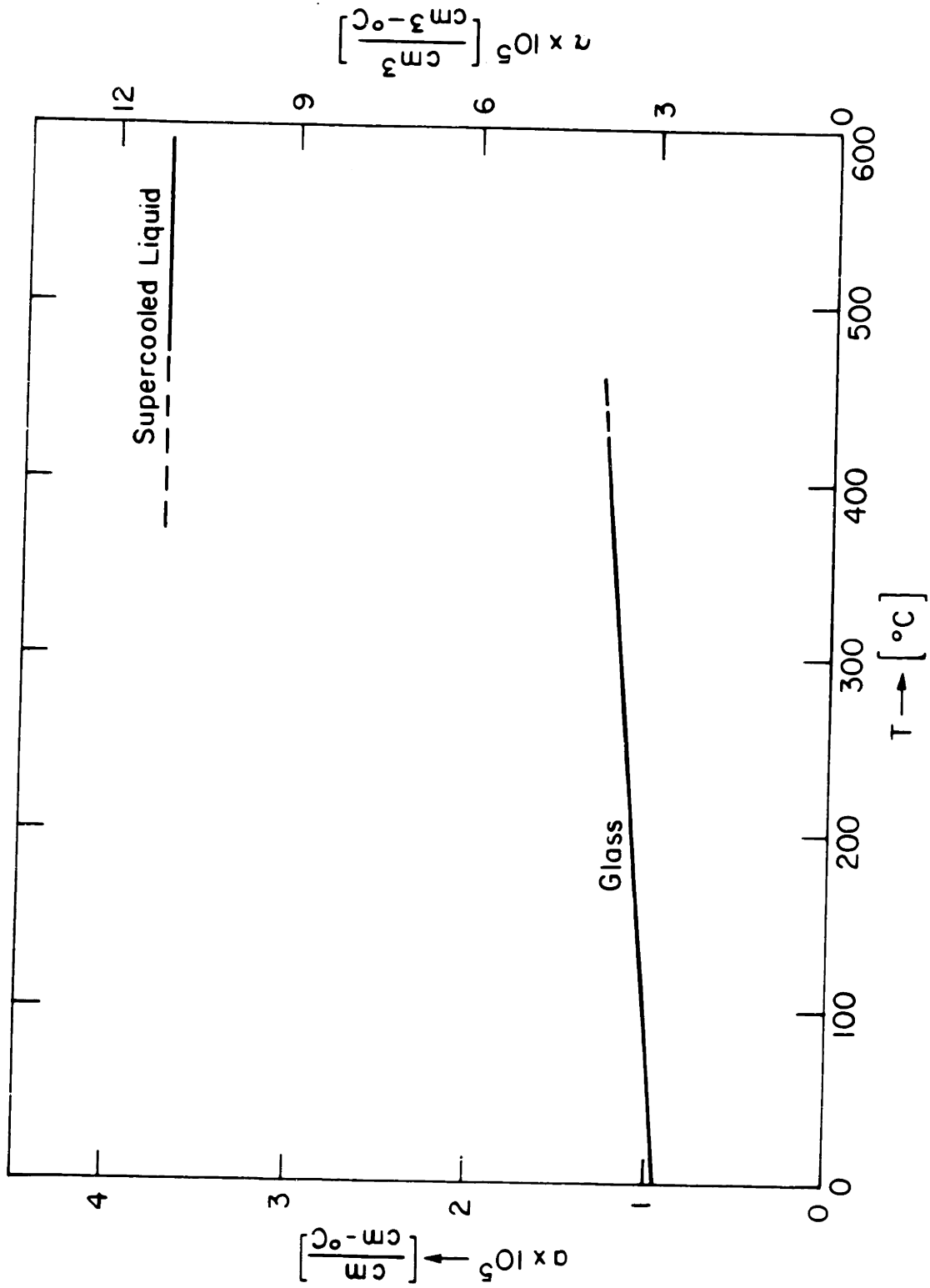
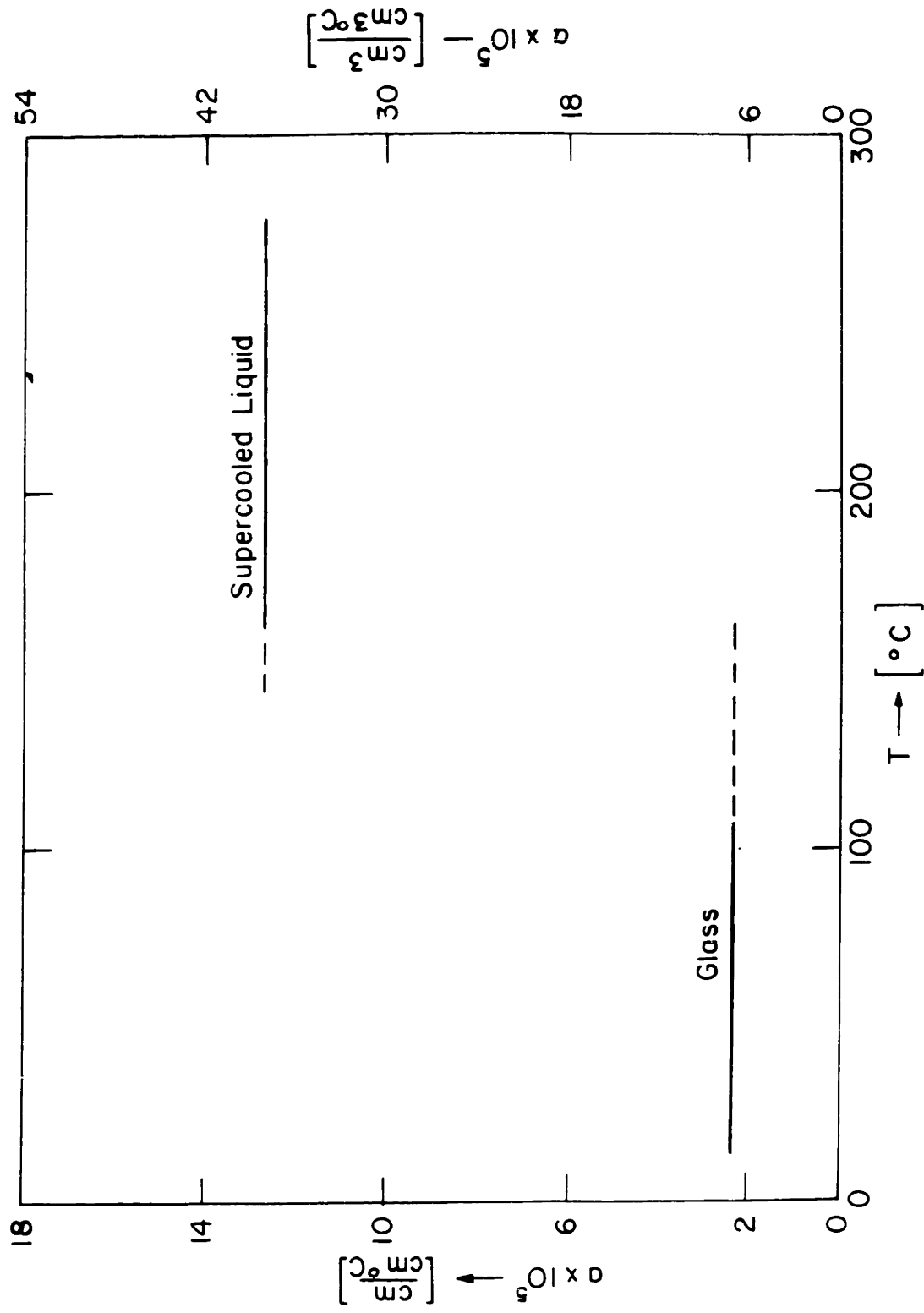


Fig. 10 Linear & Volumetric Expansivities of Lillie No. 1

Fig. 11 Linear & Volumetric Expansivities of As_2S_3

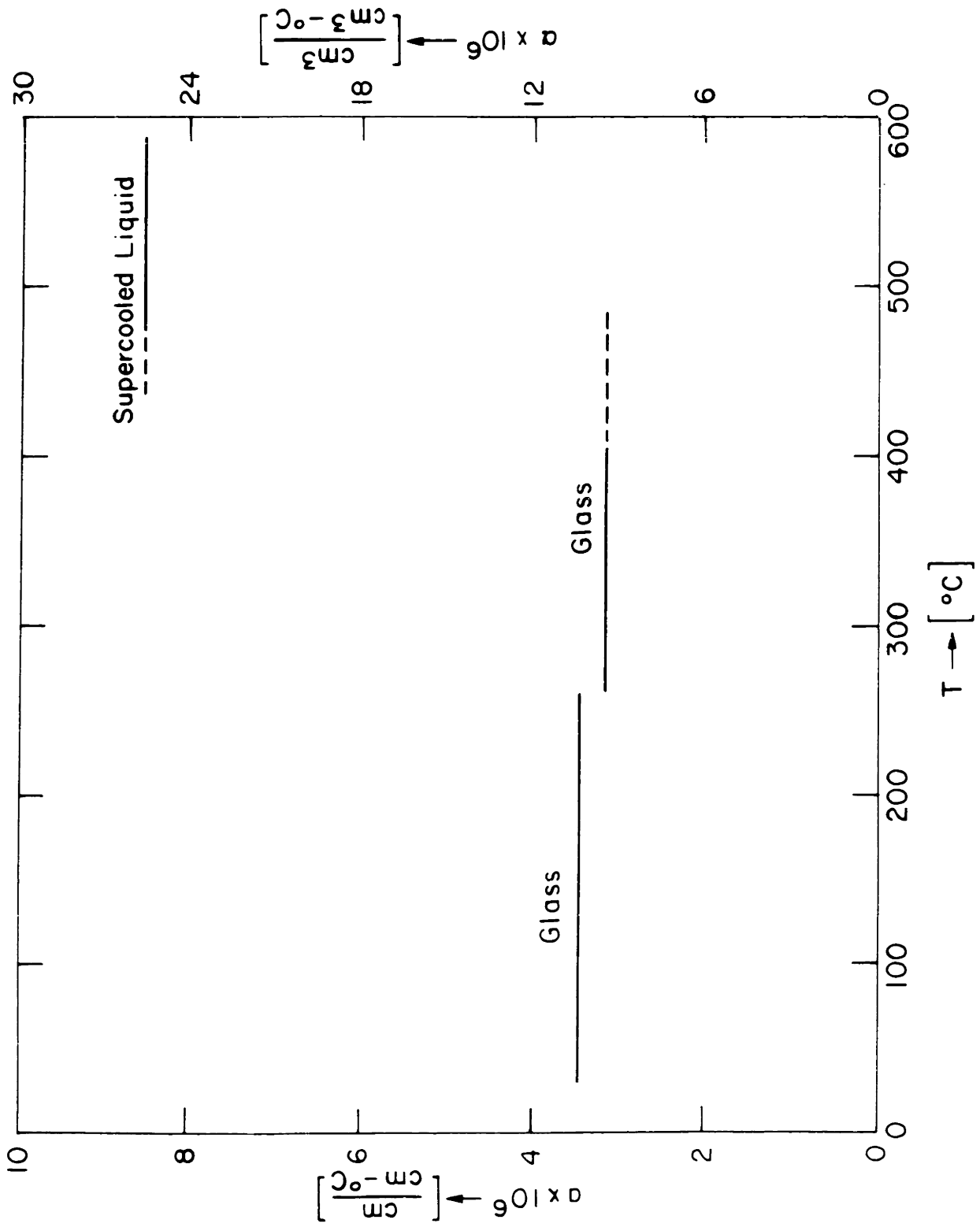


Fig. 12 Linear & Volumetric Expansivities of Pyrex

The densities of the glasses were determined by measuring the difference between the weights of glass samples weighed in air and in toluene. The specific volumes of the glasses are given at T_1 and T_f in Table 2. The values at T_f were calculated by substituting the expressions for $a(T)$ derived from the best fits of the observed data points into the above expressions. The results of two measurements of the specific volume of the same Pyrex sample are given to demonstrate the reproducibility of the measurements.

TABLE 2
SPECIFIC VOLUMES OF GLASSES AND SUPERCOOLED LIQUIDS

	Pyrex (a)	Pyrex (b)	As_2S_3	Lillie No. 1
$T_1 (^{\circ}\text{C})$	25.8	24.6	25.8	24.5
$V_1 (\text{cm}^3/\text{gr})$	0.448503	0.448849	0.313105	0.401198
$T_f (^{\circ}\text{C})$	490		162	473
$V_{T_f} (\text{cm}^3/\text{gr})$	0.450580		0.316112	0.407349

Since the expected change in V due to a temperature change of 1.2°C is only $5.55 \times 10^{-6} \text{ cm}^3/\text{gr}$, the observed differences between specific volumes of Pyrex is due to experimental error and is 0.077 percent. The specific volumes of the glasses calculated at T_f are equal by definition to the specific volumes of the supercooled liquids at $T = T_f$.

B. Enthalpy

The enthalpy data for all three systems was fit to an equation of the form $\Delta H = A + BT + CT^2 + D/T$ in the glassy region. It was found that due to rounding errors made by the computer, the fit of the four term expression for As_2S_3 glass was so poor that the derived equation passed well below every data point. The presence of large rounding errors was indicated by the fact that the standard deviation of the derived four term expression was considerably larger than either of those computed with the derived two and three term polynomials. The occurrence of the excessively large rounding errors with As_2S_3 only results from the relatively narrow temperature range over which the equation was fit to experimental data. All of the enthalpy data is represented by equations in which the temperature is in degrees Kelvin. The ΔH is the difference in heat content between T and 273.18° Kelvin, or if $(T + 273.18)$ is substituted for T in the derived expressions, it is the difference in heat content between T and 0°C . The graphical representations of the equations and experimental data are plotted in degrees centigrade vs. $\Delta H_{T-0^\circ\text{C}}$ so that the temperature scale would be the same as that used to represent the thermal expansion behavior.

The units that ΔH is reported in are (calories/gram) where the calorie is defined as 4.1840 absolute joules by the National Bureau of Standards. There are at least three other calories, the 20°C ,

the 15°C and the mean calorie which are 4.181, 4.185 and 4.186 absolute joules respectively. (101)

The best representations of the enthalpy data observed for the three glass systems in both the glassy and supercooled liquid states are given by the following equations.

1. As_2S_3 - Glass

$$\Delta H_{T-273.18} = -33.4670 + 0.10769T + 1.33 \times 10^{-5} T^2$$

$$273.18 \leq T \leq 470^\circ\text{K}$$

$$\sigma_{\Delta H} = 0.0524 \frac{\text{cal}}{\text{gr}^\circ\text{C}}$$

2. As_2S_3 - Supercooled liquid

$$\Delta H_{T-273.18} = -60.2322 + 0.17285T + 0.82 \times 10^{-5} T^2 \left(\frac{\text{cal}}{\text{gr}}\right)$$

$$375 \leq T \leq 875^\circ\text{K}$$

$$\sigma_{\Delta H} = 0.0910 \left(\frac{\text{cal}}{\text{gr}}\right)$$

3. Lillie No. 1 - Glass

$$\Delta H_{T-273.18} = -36.3766 + 0.134679T + 9.658 \times 10^{-5} T^2 - \frac{2.423518 \times 10^3}{T} \left(\frac{\text{cal}}{\text{gr}}\right)$$

$$273 \leq T \leq 850^\circ\text{K}$$

$$\sigma_{\Delta H} = 0.3108 \left(\frac{\text{cal}}{\text{gr}}\right)$$

4. Lillie No. 1 - Supercooled liquid

$$\Delta H_{T-273.18} = -158.8158 + 0.356962T \left(\frac{\text{cal}}{\text{gr}} \right)$$

$$850 \leq T \leq 1200^{\circ}\text{K}$$

$$\sigma_{\Delta H} = 1.297 \left(\frac{\text{cal}}{\text{gr}} \right)$$

$$\sigma_{C_p} = 0.516 \times 10^{-2} \left(\frac{\text{cal}}{\text{gr}^{\circ}\text{C}} \right)$$

5. Pyrex - Glass

$$\Delta H_{T-273.18} = -94.8852 + 0.232481T + 4.3953 \times 10^{-5} T^2 + \frac{8.08317 \times 10^3}{T} \left(\frac{\text{cal}}{\text{gr}} \right)$$

$$373 \leq T \leq 850^{\circ}\text{K}$$

$$\sigma_{\Delta H} = 0.4977 \left(\frac{\text{cal}}{\text{gr}} \right)$$

6. Pyrex - Supercooled liquid

$$\Delta H_{T-273.18} = -152.2888 + 0.347142T \left(\frac{\text{cal}}{\text{gr}} \right)$$

$$850 \leq T \leq 1200^{\circ}\text{K}$$

$$\sigma_{\Delta H} = 0.9548 \left(\frac{\text{cal}}{\text{gr}} \right)$$

$$\sigma_{C_p} = 0.2955 \times 10^{-2} \left(\frac{\text{cal}}{\text{gr}^{\circ}\text{C}} \right)$$

The graphical representation of the enthalpy data and equations which fit best are given in Figures 13, 14 and 15 for the As_2S_3 , Lillie No. 1 and Pyrex systems respectively. The lines drawn are calculated from the equations given above. The heat capacities derived by differentiation of the above expressions are represented in Figures 16, 17 and 18 for the three glass systems.

C. Structural Relaxation

The structural relaxation following sudden changes in temperature was followed by measuring length as a function of time at the soak temperature. It can be shown that the effective time constant calculated on a volume basis is the same as that calculated on a length basis. Thus

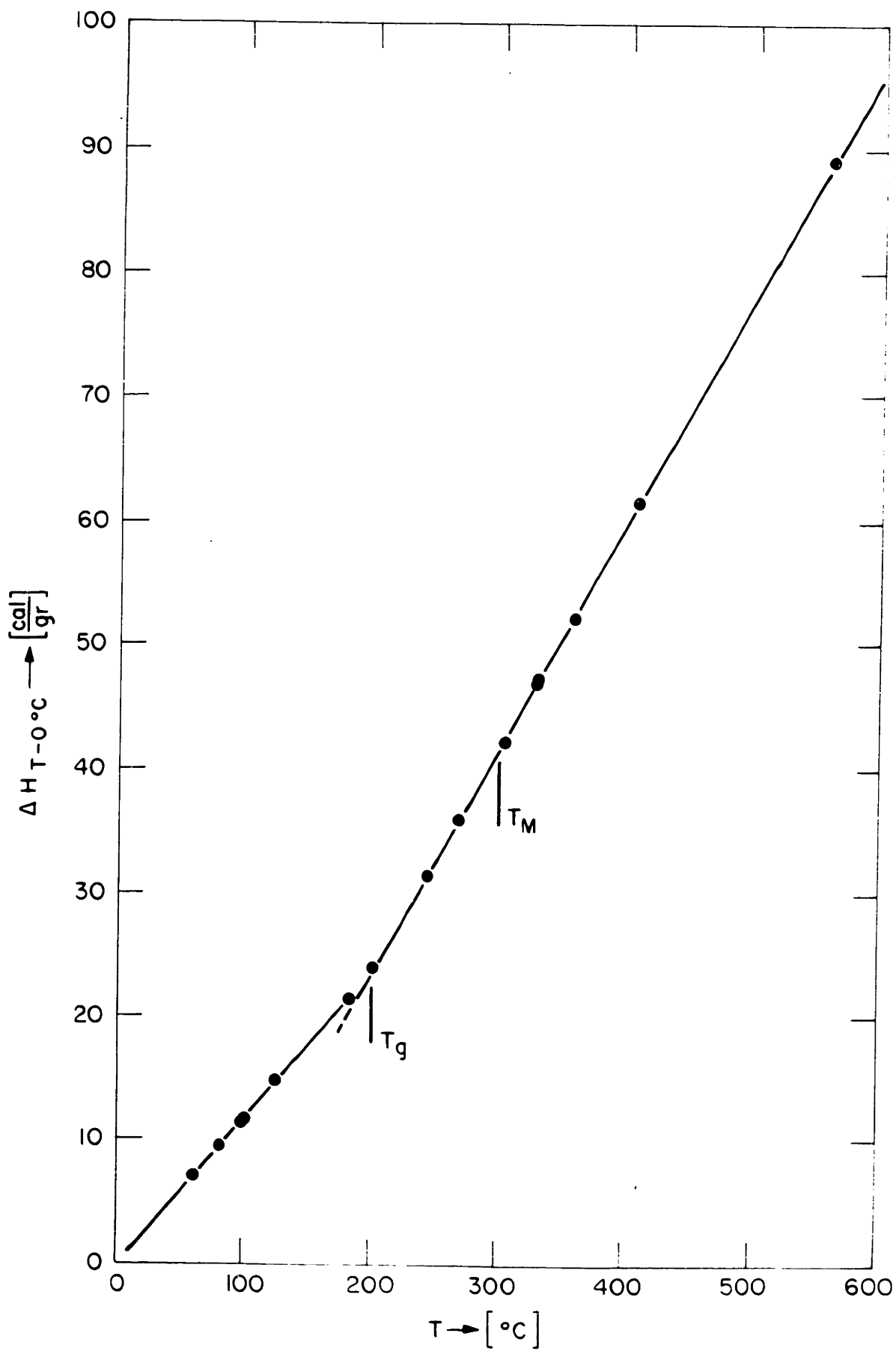
$$\frac{1}{\tau_{\text{eff}}} \equiv - \frac{1}{V-V_{\infty}} \frac{d(V-V_{\infty})}{dt} = - \frac{1}{L-L_{\infty}} \frac{d(L-L_{\infty})}{dt} .$$

The value of $\delta_V = \frac{V-V_{\infty}}{V_{\infty}}$ does not equal that of $\delta_L = \frac{L-L_{\infty}}{L_{\infty}}$, and it can be shown that

$$\delta_V \approx 3 \delta_L .$$

All graphs and calculations have been made using length as the basis.

The relaxation of length resulting from a sudden change of temperature from 475°C to 500°C is shown in Figure 19. τ_{eff} 's were

Fig.13 Enthalpy of As_2S_3

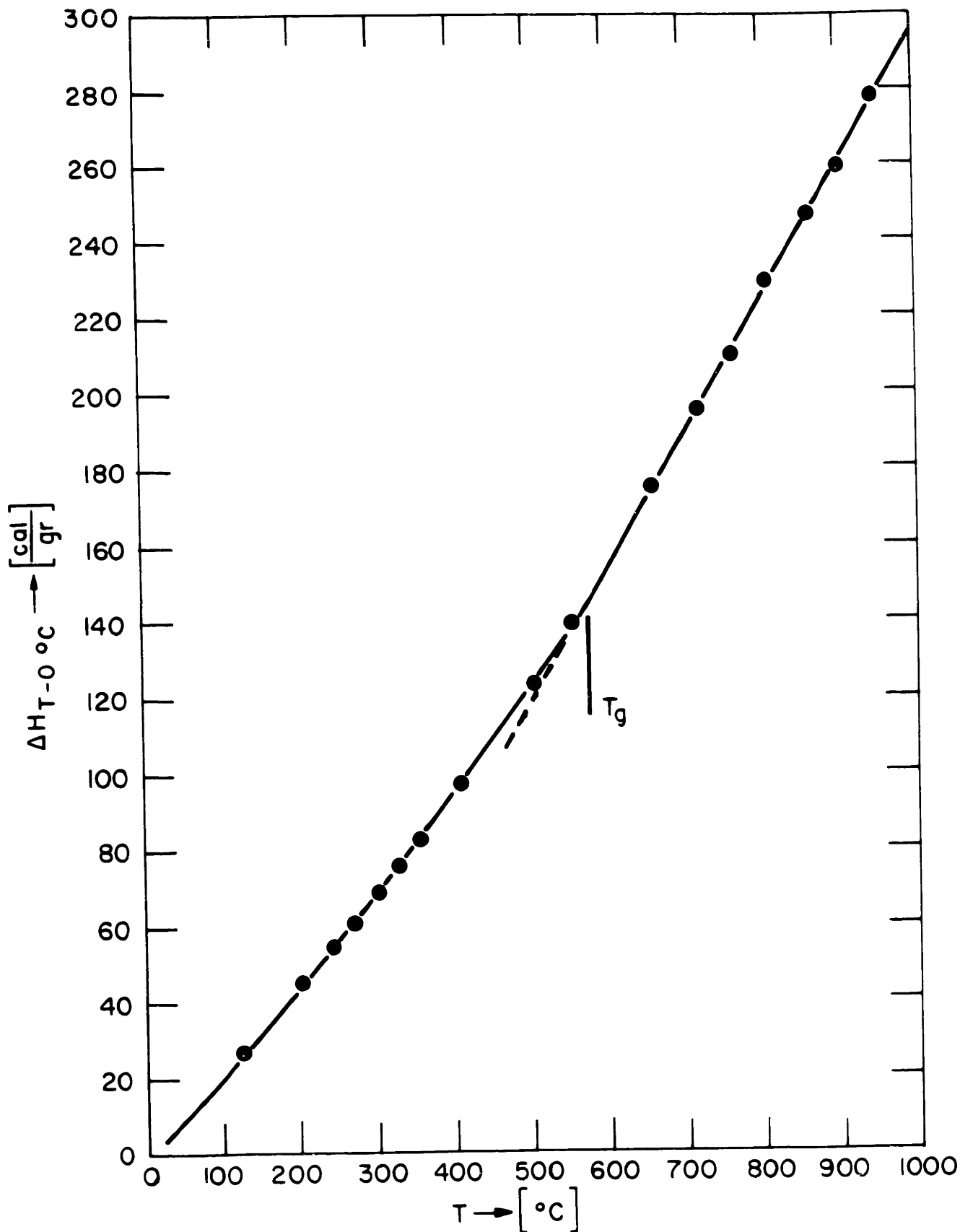


Fig. 14 Enthalpy of Lillie No. 1

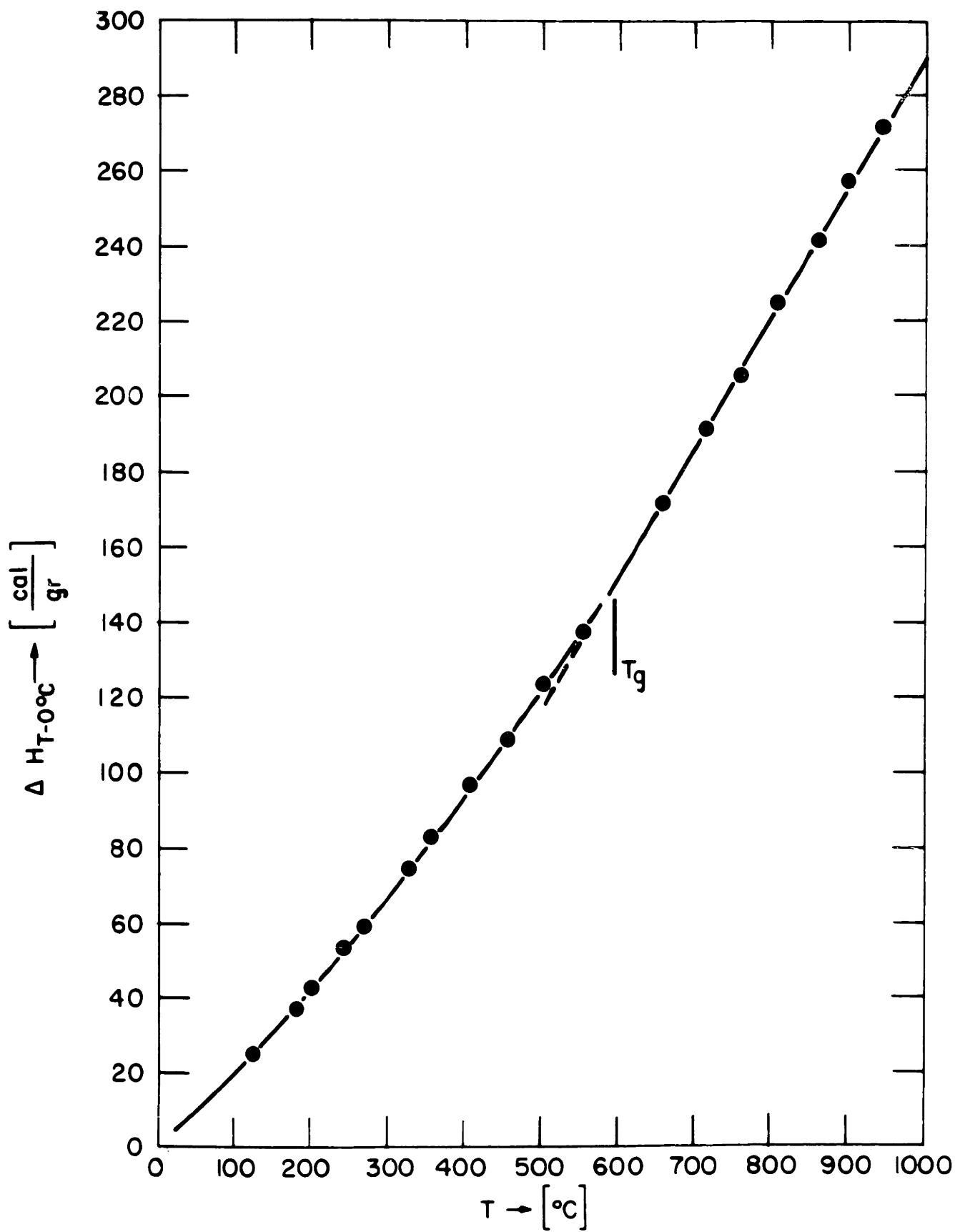
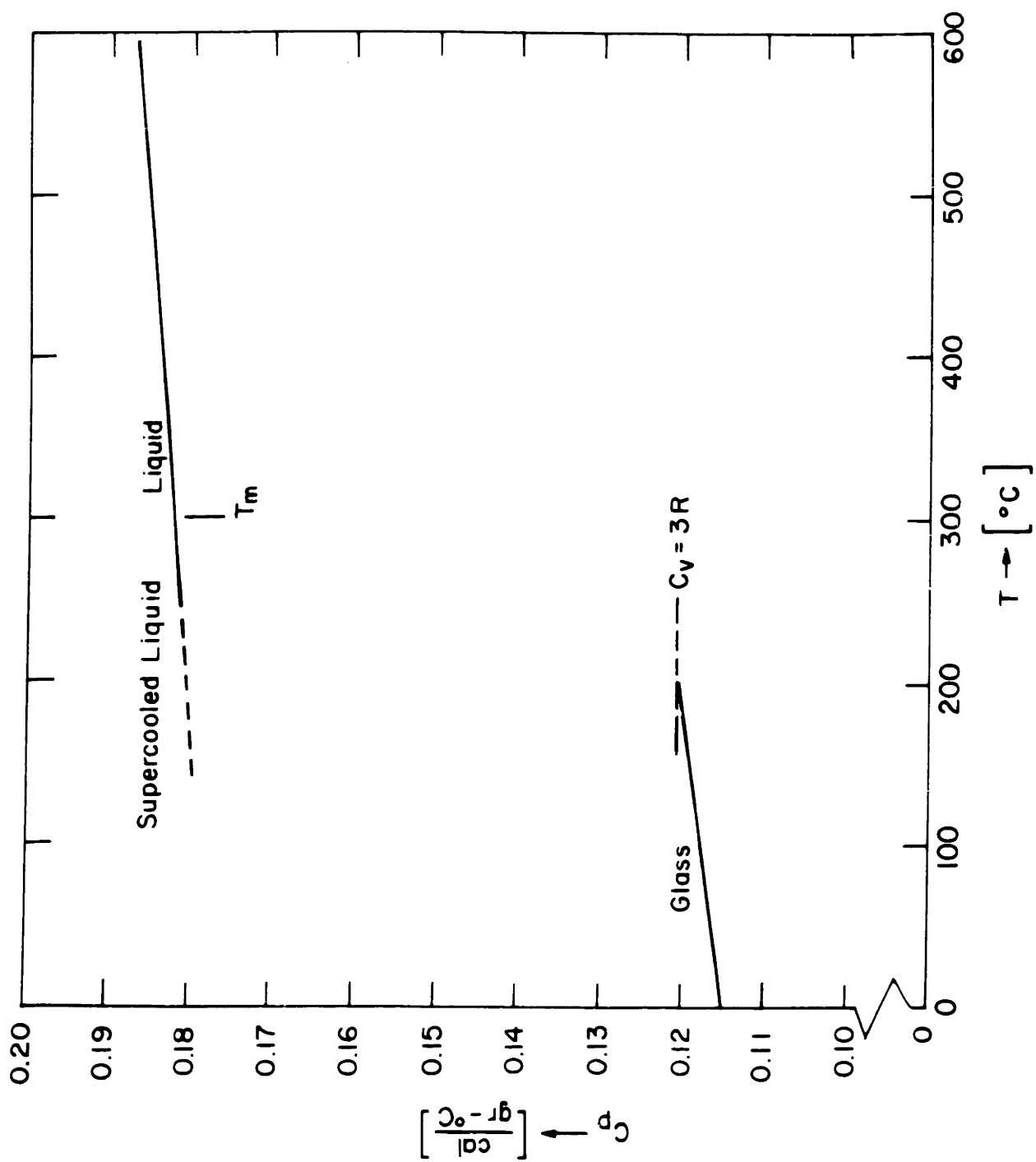


Fig. 15 Enthalpy of Pyrex

Fig. 16 Heat Capacity of As_2S_3

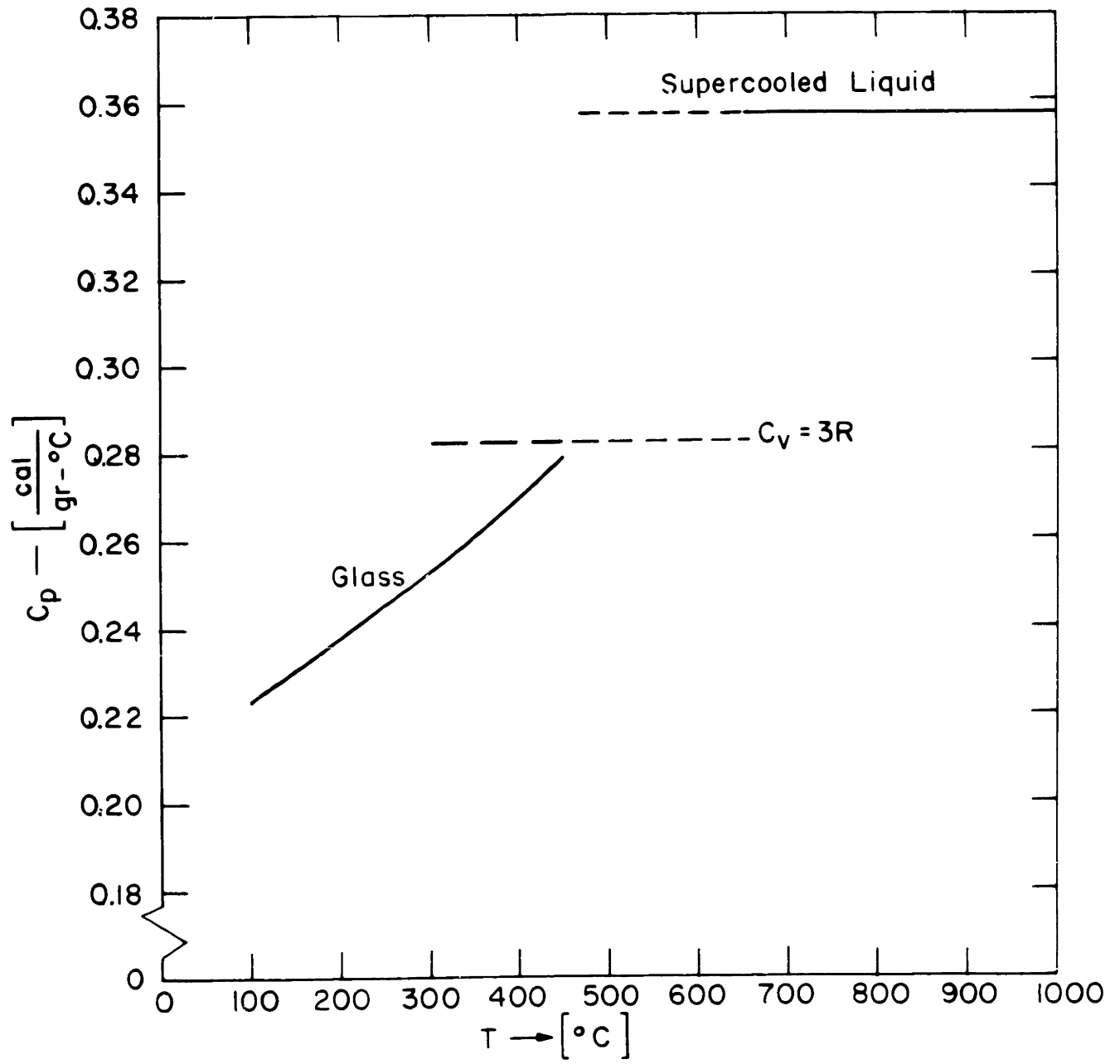


Fig.17 Heat Capacity of Lillie No.1

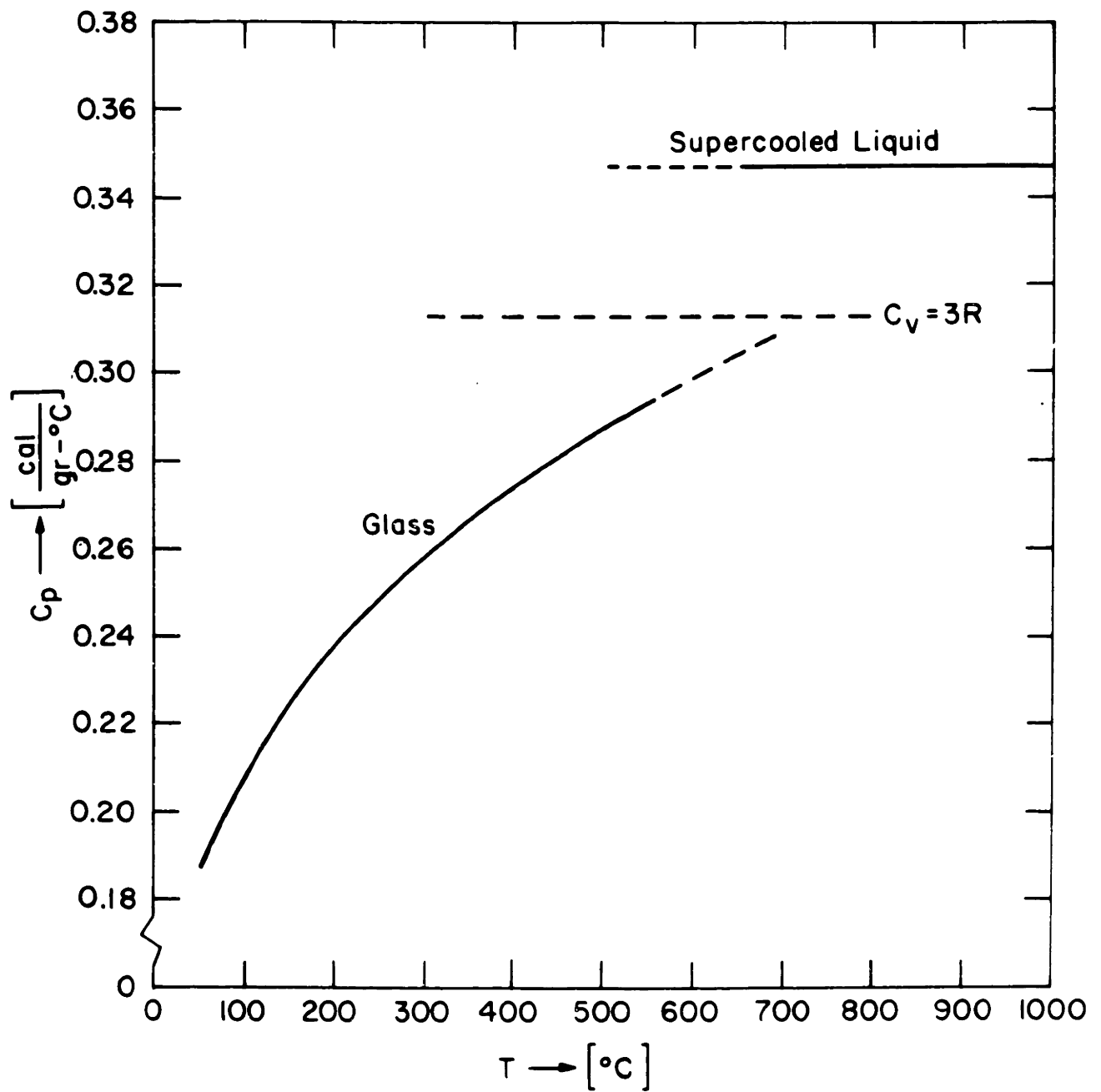


Fig. 18 Heat Capacity of Pyrex

calculated at several $(L-L_{\infty})$'s by graphically finding the slope of the smooth line drawn through the experimental points with the use of a front surfaced mirror. The mirror was placed on the paper and rotated until the visible portion of the line and its reflection appeared to form a continuous line. The plane of the mirror is perpendicular to the tangent of the curve at this orientation. Once the normal was established, the tangent was readily determined either mathematically from the equation of the normal line, or graphically. When the length is plotted vs. $\log(\text{time})$ as it was in Figure 19, τ_{eff} is calculated as

$$\frac{1}{\tau_{\text{eff}}} = - \frac{\text{slope of tangent}}{2.303 \, t(L-L_{\infty})}$$

The values of $\log(\frac{1}{\tau_{\text{eff}}})$ calculated for all relaxation experiments made on Lillie No. 1 are shown in Figure 20. The nominal stabilized and soak temperatures are shown on the figure for each run; the measured values of initial and final temperatures for these runs are summarized in Table 3, along with the τ_{eff} 's extrapolated to $\delta_L = 0$. Linear expressions were fitted to the observed $\log(\frac{1}{\tau_{\text{eff}}})$ vs. δ_L data, since it was felt that the curvature observed in some runs was well within the error expected from the graphical differentiation treatment. It should be remarked that even though the technique of finding the slope by means of a mirror appears to be quite reproducible,

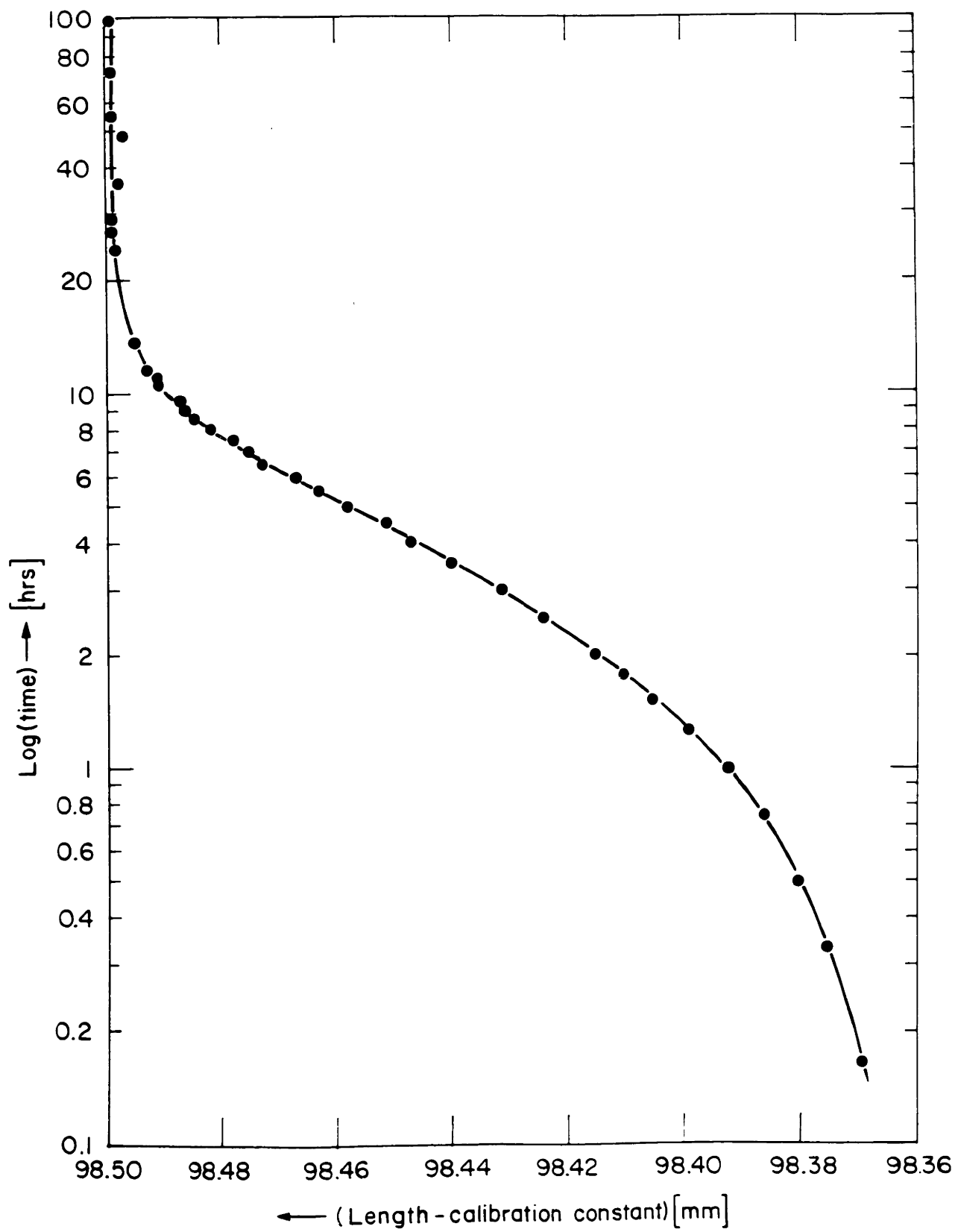


Fig. 19 Length Relaxation of 500° C of a Lillie No.1 Sample Initially Stabilized at 475° C

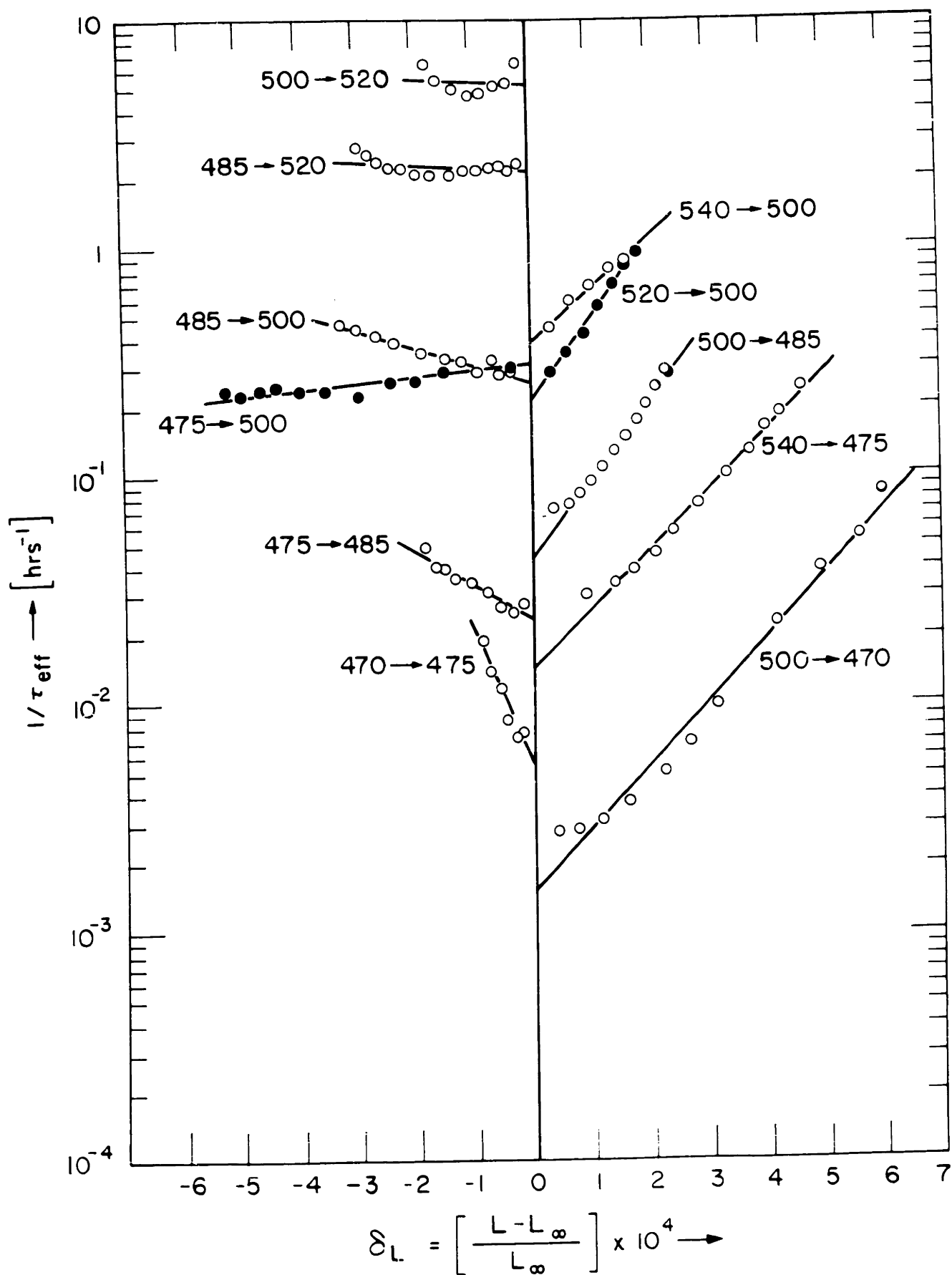


Fig. 20 Effective Time Constants for Structural Relaxation of Lillie No. 1

provided that an inflection point is not nearby, that the calculated τ_{eff} 's are quite sensitive to the particular smooth line drawn through the experimental points and also to the exact value of L_{∞} used. The errors due to an incorrect choice of L_{∞} were increasingly large as $L \rightarrow L_{\infty}$ and thus τ_{eff} 's were not calculated for equivalent to $(T-T_f)$'s smaller than approximately 2°C . It was found that if the points were plotted on semi logarithm paper, as in Figure 19, that frequently a poor line was drawn through the early points, and since the initial slope is comparatively small, large errors in τ_{eff} frequently resulted. Often the τ_{eff} 's for early points were calculated from plots on linear graph paper.

TABLE 3

INITIAL AND FINAL TEMPERATURE FOR STRUCTURAL RELAXATION RUNS
ON LILLIE NO. 1 WITH EXTRAPOLATED EQUILIBRIUM RELAXATION TIMES

Run	Initial $T^{\circ}\text{C}$	Final $T^{\circ}\text{C}$	τ_{eff} @ $\delta_L = 0$ [hrs]
500 \rightarrow 520	498.7	521.1	0.196
485 \rightarrow 520	483.2	519.4	0.459
485 \rightarrow 500	485.9	502.2	3.95
475 \rightarrow 500	474.7	498.7	3.23
520 \rightarrow 500	520.2	499.9	4.72
540 \rightarrow 500	538.7	500.6	2.555
475 \rightarrow 485	474.0	485.1	42.6
500 \rightarrow 485	500.6	485.1	21.85
470 \rightarrow 475	469.4	474.4	189.0
540 \rightarrow 475	539.5	474.7	64.1
500 \rightarrow 470	499.9	469.4	644.0

In Figure 21 the logarithms of τ_{eff} at $\delta_L = 0$ and the shear relaxation time defined as the quotient of the viscosity divided by the shear modulus are plotted vs. the reciprocal of the absolute temperature for Lillie No. 1. The shear viscosities were measured over this temperature range by Lillie.⁽⁸⁴⁾ The shear modulus for this glass has not been measured; however, a value for $G = 3 \times 10^{11}$ dyne/cm² was found in Morey⁽¹⁰²⁾ for a glass of similar composition. It can be seen that both sets of data are fit over the narrow temperature range within the apparent scatter by straight lines. The slopes of the lines represented by equations of the form

$$\log(\tau_i) = A_i + B_i \frac{1}{T}$$

are

$$B_{\text{structural}} = 36.032 \pm 2.398 \times 10^3 \text{ (}^\circ\text{K)}$$

$$B_{\text{shear}} = 33.497 \pm 1.756 \times 10^3 \text{ (}^\circ\text{K)}$$

If it is assumed that the relaxation times are correctly represented in terms of activation energies, they can be calculated to be

$$E_{\text{structural}} = 164.0 \pm 10.9 \frac{\text{kcal}}{\text{mole}}$$

and

$$E_{\text{shear}} = 152.6 \pm 8.0 \frac{\text{kcal}}{\text{mole}}$$

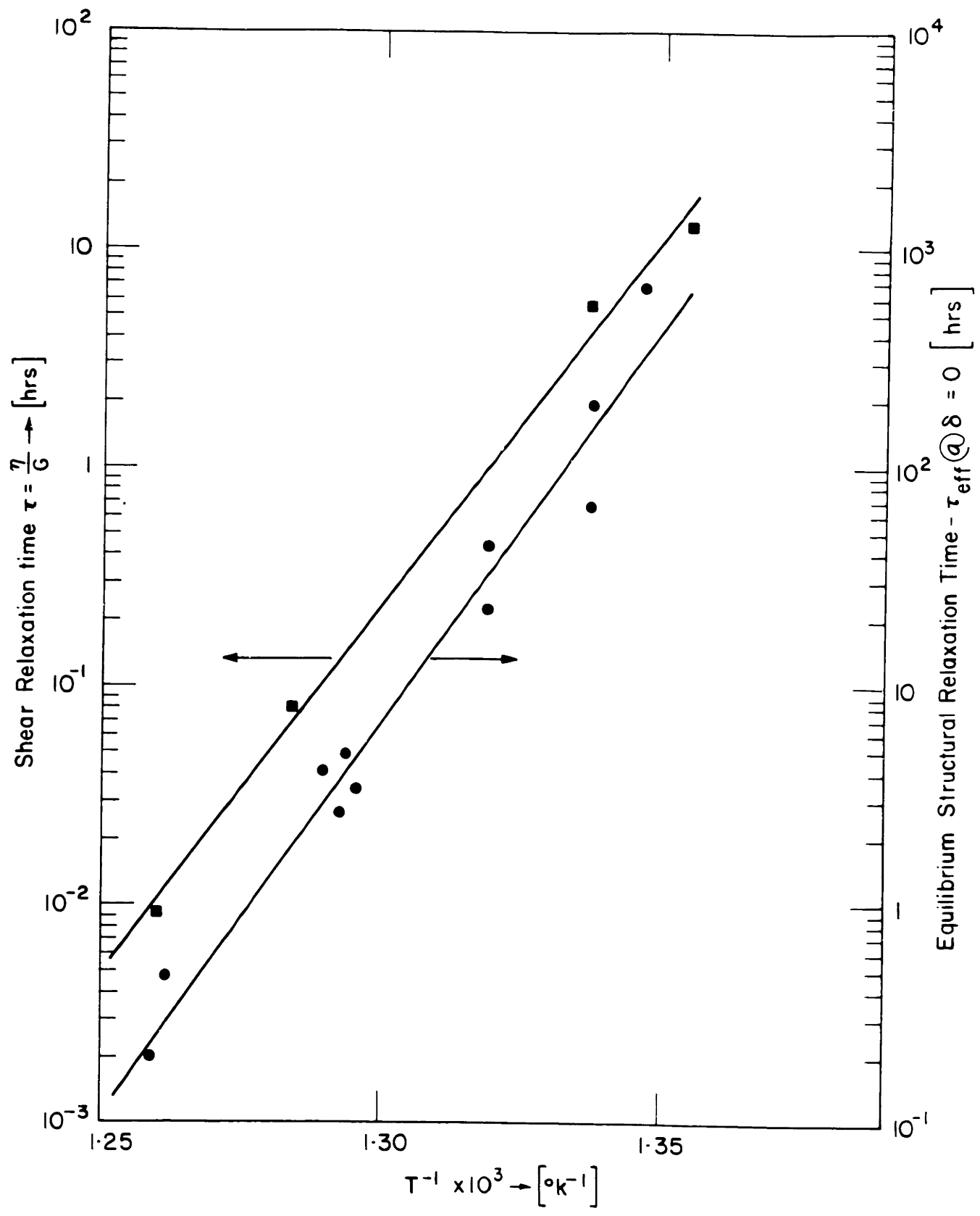


Fig. 21 Equilibrium Structural and Shear Relaxation Time for Lillie No.1

It is obvious from the calculated values of the activation energies and their standard deviations that the two overlap and that the activation energy could be the same for both relaxation processes. To check this hypothesis, the "Students T" test⁽¹⁰³⁾ was applied to the two activation energies. This test gives the probability that a sample could have come from a population whose mean value is \bar{X} and whose standard deviation is $\sigma_{\bar{X}}$.

In this case

$$\bar{E} = \bar{X} = 158.3 \left(\frac{\text{kcal}}{\text{mole}} \right)$$

$$\sigma_{\bar{E}} = \left(\frac{\sigma_{E_1}^2 + \sigma_{E_2}^2}{n^2} \right)^{1/2} = \left(\frac{(10.9)^2 + (8.0)^2}{2^2} \right)^{1/2} = 6.76 \left(\frac{\text{kcal}}{\text{mole}} \right) (5)$$

$$t \equiv \frac{\text{difference in mean}}{\text{standard deviation of mean}} = \frac{(164.0 - 158.3)}{6.76} = \frac{(158.3 - 152.6)}{6.76}$$

$$t = 0.84$$

The table of the significance of the difference between two sample means⁽¹⁰⁴⁾ indicates that there is a 60% probability that the two activation energies come from the same sample, or were equal. Thus the conclusion derived from the test is that the two relaxation processes probably have the same activation energy $E = 158.3 \text{ kcal/mole}$.

It can be seen from Figure 21 that although the slopes of the curves are apparently the same, the equilibrium structural relaxation time exceeds the shear relaxation time by approximately a factor of thirty at any temperature level.

The relaxation experiments were not made over a wide enough temperature range with either Pyrex or As_2S_3 to make meaningful calculations of the activation energies for τ_{eff} at $\delta_L = 0$. Precise viscosity measurements of As_2S_3 have not been reported and those for Pyrex have been made only down to temperatures about 50°C above the transition region. Thus to make a comparison of the shear and volumetric time constants an extrapolation of the viscosity must be made. The time constant for structural relaxation of Pyrex for the quench from 566 to 468°C is 50 hours at $\delta_L = 0$. The extrapolated viscosity at this temperature is 4.17×10^{15} poise and the value of the shear modulus is calculated to be 2.615×10^{11} dyne/cm² from values of E and μ tabulated by Corning Glass Co. The time constant for shear relaxation is thus 4.43 hours which is approximately eleven times less than the structural relaxation time constant. There is no reason to expect that the ratios of the two time constants should be equal for the two glasses, but it was found that for both Pyrex and Lillie No. 1, the so-called equilibrium structural relaxation times are at least an order of magnitude larger than the shear relaxation times, but apparently have the same temperature dependence.

VI. DISCUSSION OF RESULTS

A. Glassy Thermal Expansivity

The first evaluation of the results of the thermal expansion measurements made in this experimental program is by comparison with the results obtained by others for the same glasses. The thermal expansion behavior of As_2S_3 between 50 and 175°C has been studied⁽¹⁰⁵⁾ and its reported expansivity is 23.7×10^{-6} (cm/cm $^\circ\text{C}$). The best value found for the data obtained in this program was $23.29 \pm 0.28 \times 10^{-6}$ (cm/cm $^\circ\text{C}$) where the error indicated is the probable error as calculated from the standard deviation of the slope. It can be seen that the maximum probable value for the expansivity just equals that observed by Glaze et al at the National Bureau of Standards and the two values differ by 1.28 percent. Since no error limits were indicated by Glaze et al, the values can be considered to be equal.

Corning Glass Works reports⁽¹⁰⁶⁾ the thermal expansivity of glass number 7740 (Pyrex) to be 33×10^{-7} (cm/cm $^\circ\text{C}$) over the temperature range 0 to 300°C . The equivalent average expansivity is calculated to be 34.1×10^{-7} when the values for the two observed linear regions are averaged over the temperature ranges that apply.

This value deviates from that reported by Corning by 3.2 percent.

There appears to be no reported value for the thermal expansivity of the soda-lime glass, Lillie No. 1. Bestul⁽⁸⁷⁾ measured its expansivity in conjunction with a study of the applicability of the W.L.F. equation to the viscosity of silicate glasses, but reported only the value he measured for $\Delta\alpha$, the difference between the liquid and glassy volumetric expansivities. Comparison of its expansivity with those calculated from the numerous empirical additive expressions appearing in the literature appears pointless since they vary considerably in their predicted expansivities and generally include no temperature dependence of thermal expansivity.

It can be seen from the above discussion that the observed values for thermal expansivity are in good agreement with those reported for As_2S_3 and Pyrex. It is not possible to make any comparisons other than the percentage difference between the observed values since no probable error was indicated for the other measurements. The difference between the observed average expansivity and that reported by Corning for Pyrex is difficult to access, since it was found that the data resulting from this experimental program was best fit by two straight lines which intersect at a temperature within the temperature range over which the average expansivity is given by Corning. Since the temperature

dependence of Pyrex's expansivity is not indicated and the average expansivity is given only to two significant figures, the agreement between the observed and reported expansivities is considered adequate.

The differences between the glassy expansivities of the three systems studied can be interpreted only qualitatively in terms of the factors which have been discussed. The thermal expansion behavior of vitreous SiO_2 is not well enough understood to thoroughly pursue the effects on thermal expansion of substitutions into the silica network. Introduction of B_2O_3 into silica has less effect on thermal expansion than the introduction of CaO and Na_2O since the expansivity of Pyrex is approximately one third that of Lillie No. 1. Even though this result is consistent with the correlation of the effect of bond strength of the introduced ion on expansivity, it must be argued that the B^{+3} ions are able to enter the silica network with less effect on the proposed vibrational mode with a negative γ_i than either Ca^{+2} or Na^{+1} ions. The presence of modes with negative γ_i 's in Pyrex is indicated by two observations. The first is a large negative expansion coefficient at temperatures above $5^\circ\text{K}^{(107)}$ and secondly its compressibility increases with increasing pressure^(20,108). The soda-lime glasses, on the other hand, behave in a more typical manner with respect to compressibility and low temperature thermal

expansion, in that the compressibility decreases with increasing pressure⁽¹⁰⁹⁾ and the expansion coefficient is essentially greater than zero for all temperatures greater than the absolute zero of temperature⁽¹⁰⁷⁾. In the paper by White⁽¹⁰⁷⁾ it is reported that the expansivity of a soda-lime glass becomes negative at approximately 14°K and reaches a minimum value of -2×10^{-8} (cm/cm°C) at 11°K a borosilicate glass with the Pyrex composition has an approximate expansivity of -60×10^{-8} (cm/cm°C) while SiO₂ and Vycor have expansivities of approximately -85×10^{-8} (cm/cm°C). The negative expansivity of the soda-lime glass is essentially negligible. It appears from these observations that the vibrational modes with negative γ_i 's can be essentially suppressed by the introduction of Na₂O and CaO into the silica network.

It is tempting to attribute the large expansivity of As₂S₃, compared with the siliceous glasses, to the lack of vibrational modes with negative γ_i 's. This assumption cannot be justified by the calculated $\bar{\gamma}$ which will follow shortly. Rather the differences in the siliceous and As₂S₃ glass structures appears to be responsible for its relatively large expansivity. The structure of vitreous As₂S₃ has been reported^(110,111) to be one in which each arsenic atom is surrounded by three sulphur atoms and each sulphur atom by two arsenic atoms, the total structure consisting of chains, bands or layers. It appears that the high expansivity

of As_2S_3 is directly attributable to the existence of weak intermolecular bands between the chains, bonds or layers while the siliceous glasses are made up of a continuous network, bound by primary bonds. The existence of negative γ_i 's in the siliceous glasses serves to increase the difference in expansivity between a material influenced by bonds of secondary strength and one which contains only primary bonds.

The harmonic oscillator model predicts that, like specific heat, the thermal expansion coefficient should be zero at 0°K and, providing no modes with negative γ_i 's exist, should increase with temperature and asymptotically approach a constant value at high temperatures. Even with the inclusion of negative γ_i 's, the expansivity should approach a constant value once all modes of vibration exceed their characteristic temperatures. The asymptotic constant value of expansivity can be positive or negative, depending on the distribution of γ_i 's, but in the case of siliceous glasses it is a relatively low positive number. Since the modes of vibration with γ_i 's in siliceous glasses have low characteristic temperatures^(20,24), their expansivities would be expected to be increasingly negative from 0°K , reach a minimum, then increase to a constant value with increasing temperature.

Thermal expansion measurements were not made at temperatures below 25°C and the resulting data was fit only to polynomial

expressions with a maximum of three terms so it is not possible to interpret the results of this experimental program in terms of the behavior discussed above. It is obvious from the results reported by White⁽¹⁰⁷⁾ that the low temperature behavior is qualitatively correct for the soda-lime and Pyrex glasses. No low temperature expansion measurements are reported for vitreous As_2S_3 . The measurements made for these glasses would indicate that over the temperature range investigated the expansivity of As_2S_3 is constant, that of Lillie No. 1 increases and that of Pyrex decreases with increasing temperature. The behavior exhibited by As_2S_3 and Lillie No. 1 is normal if it is considered that As_2S_3 has reached its characteristic temperature and Lillie No. 1 is approaching its.

The behavior of Pyrex is anomalous since it has been argued that all vibrational modes with negative γ_i 's have low characteristic temperatures, hence it would be expected that its expansivity should increase with increasing temperature. It was further found that its expansion behavior was best fit by two intersecting lines, which would indicate the presence of a phase transition. It is evident that if a phase transition is taking place at approximately 260°C , it cannot be of the first order, since there is no discontinuity in volume across it. Even though it is thermodynamically possible for a solid phase to undergo a polymorphic second order phase transition with a negative $\Delta\alpha$, it is felt that the most probable explanation of the

discontinuity in slope is that Pyrex is a two phase glass and at approximately 260°C one of the phases undergoes a glass transition.

It is well known that borosilicate glasses are prone to phase separation. The fabrication process of Vycor glass has as a necessary step the leaching out of the high borate phase after phase separation has occurred. Recently Charles⁽¹¹²⁾ studied the A.C. and D.C. electrical properties of a Vycor type glass and commercial Pyrex. It was his conclusion from this study that normal Pyrex glass should be considered as completely phase separated rather than phase separable. He further concluded from his measurements that the high borate phase is continuous throughout the glass and has an estimated characteristic pore diameter of 20\AA . The equality of the activation energies for conduction for Pyrex and the phase separated Vycor type glass suggested that the high borate phases of the two glasses were of virtually the same composition which he estimated to be $1 \text{ Na}_2\text{O} \cdot 2.4 \text{ B}_2\text{O}_3 \cdot 0.2 \text{ SiO}_2$. He made no estimate of the volume fraction of the high borate phase other than to suggest that it should contain virtually all of the sodium.

Intuitively one might expect that because the expansivity of a liquid is generally higher than that of its glass, the expansivity of a phase separated "composite" body ought to increase when one component goes through a glass transition. It can be shown that the change in the expansion coefficient can be either positive or negative depending

on the microstructure of the two phases and on their relative values of expansivities and compressibilities before and after one phase has undergone a transition from a solid to a liquid. It appears that the high silica phase must be continuous in Pyrex and that the high borate phase must have a higher thermal expansion coefficient than the high silica phase to be consistent with the observed negative $\Delta\alpha$. The results of the thermal expansion measurements by themselves give no indication as to whether the high borate phase is continuous; however, when combined with those of Charles it appears that both phases are continuous. It is evident that in the case of Vycor that the high silica phase must be continuous since the body remains intact after the high borate phase is leached out.

It is apparent that since the low temperature thermal expansivity of Pyrex must be treated as one of a composite body, the glassy expansivity should be influenced by the thermal history of the glass. Differences in both the high and low temperature regions were observed among the three Pyrex samples which were greater than that expected from the standard deviations. It is not possible to make any correlation with thermal history regarding the differences observed since the exact thermal histories of the three samples is not known. All were taken from commercial Pyrex rods and heated to temperatures in the vicinity of 550°C for short periods, then soaked at slightly lower temperatures for periods ranging from several hours to several

hundred hours. Also it is not clear that sufficient points were included in each temperature region to insure a representative sample of the error and thus to predict a correct probable error in the slope from the observed standard deviations.

A large variation in the apparent transition temperature was also observed in the three samples; however, it appears to be accounted for by experimental error. The average transition temperature of $259.7 \pm 35.2^{\circ}\text{C}$ is very close to the glass transition temperature observed by Thomas and Parks⁽⁴²⁾ for B_2O_3 with calorimetric measurements. Thus, it is consistent with the thermal expansion experiments that the phase undergoing a glass transition has a very high B_2O_3 concentration, but it is not possible for them to make a judgment regarding the composition suggested by Charles.

B. Glassy Specific Heat.

No attempt has been made to analyze the observed glassy specific heats for the three systems studied in terms of the Debye or Einstein models other than to compare the observed heat capacities with the expected maximum $3R$ value per gram atom. This stems primarily from the fact that detailed interpretation need be made in terms of the heat capacity behavior from cryogenic temperatures to those exceeding the characteristic temperature. This information was not available for

the glasses studied, and in view of the difficulty of successful interpretation of the specific heat of vitreous $\text{SiO}_2^{(20)}$, it appeared to be out of the question to attempt a similar analysis for the multicomponent siliceous glasses. This is particularly true for Pyrex where the compositions of the two phases is not known.

It can be seen from the standard deviations of the least square curve fits that the enthalpy data is well represented by the given expressions. In the worst case, Pyrex, the standard deviation between the expression representing enthalpies up to 140 calories per gram is only approximately half a calorie per gram. As was pointed out in the presentation of results, the relatively narrow temperature range and the rounding errors made during calculations introduced significant potential errors into the values of the constants. One of the features of the computer program used for the four term least square curve fitting was an indication of error in the calculated constants. Unfortunately for the calculation of specific heats by differentiation of the enthalpy expressions, the largest potential error was indicated to be in the values of A and D. When the expressions for $\Delta H(T)$ are differentiated, the A's disappear; however the value of D remains, and it is the term containing D which introduces the curvature into the $C_p(T)$ curve. Thus the details of the curvature of the $C_p(T)$ curves shown in Figures 17 and 18 for Lillie No. 1 and Pyrex must be interpreted with caution. The four term expression was found to fit

the enthalpy data for As_2S_3 so poorly that a three term polynomial expression was used, hence no curvature of the heat capacity curve is indicated.

On the basis of their compositions Lillie No. 1 was calculated to have 2.8926 gram atoms per mole and Pyrex 3.2552. Arsenic trisulfide has 5. The expected maximum heat capacities of 3R calories per gram atom are 0.282, 0.313, and 0.1205 calories per gram per degree centigrade for Lillie No. 1, Pyrex and As_2S_3 glasses respectively. It can be seen from Figures 16, 17 and 18 that the observed heat capacities are quite close to the 3R values in the transformation region. It appears from the B_2O_3 and glycerin examples where the observed C_p 's at their glass transitions are only 0.6 and 0.25, the classical 3R values respectively, that this cannot be considered to be a general rule.

No discontinuity in the enthalpy temperature curve of Pyrex was apparent as was the case with its volume temperature curve. While the $\Delta\alpha$ resulting from one phase of a two phase glass going through a glass transition could be positive or negative, the ΔC_p must be positive. There are at least three reasons why it was not observed though it must have been present. In this temperature range, the heat capacity of siliceous glasses increases with increasing temperature. The enthalpy-temperature curve will show a positive curvature whether or not one phase goes through a glass transition and thus it would be expected to be difficult to locate a point where the slope discontinuously increases, particularly if the curvature decreases after the transition as is indicated by the specific heat curve of Pyrex. This effect is especially

troublesome if the phase going through the transition is a low volume fraction one as was indicated by Charles.⁽¹¹²⁾ Finally the rapid cooling rates associated with a drop calorimeter would be expected to shift and smear out the transition. For these reasons it would be anticipated that a discontinuity in the enthalpy-temperature curve would be difficult to observe with a drop calorimeter. It is probable that if a sufficient number of drops were made in the low temperature region with samples that were not canned as these were, that with the more precise measurements and a proper statistical analysis the effect could be demonstrated, though it would not be expected to be large.

C. The Grüneisen Constant

According to White⁽¹⁰⁷⁾ the observed value for the Grüneisen constant $\bar{\gamma}$ at any temperature is the weighted mean of the individual γ_i 's and is defined by

$$\bar{\gamma} = \frac{\sum_{i=1}^{3N} \gamma_i C_i}{\sum_{i=1}^{3N} C_i}$$

where the weighting factors C_i are the contribution of each mode of vibration to the heat capacity. It is clear that it represents an average which reflects both the number fraction and the fraction of total strength of each mode as a function of temperature. The value of $\bar{\gamma}$ is calculated from the following expression.

$$\bar{\gamma}(T) = \frac{V(T) \alpha(T)}{\beta(T) C_V(T)}$$

Compressibility measurements as a function of temperature have been

made for Pyrex⁽¹¹³⁾ and As_2S_3 ⁽¹⁰⁵⁾ glasses. The elastic properties of the Lillie glass have not been reported, so typical values for β for a soda-lime glass was taken from the literature to make a single calculation for $\bar{\gamma}$ at 100°C.

It is significant that the $\beta(T)$ for Pyrex obtained by Birch⁽¹¹³⁾ shows a minimum at approximately 250-270°C. The increase in compressibility is consistent with one phase of a two phase glass behaving as a liquid. The decrease of compressibility with increasing temperature results apparently only from a low thermal expansivity⁽²⁰⁾ which is consistent with the hypothesis that modes with negative γ_i 's are operative in Pyrex. Values of $\bar{\gamma}$ for Pyrex were calculated for the temperature range from 100 to 250°C. It was felt that it was not safe to use the expressions for heat capacity at temperatures below the lowest experimental point and it is clear that the value of $\bar{\gamma}$ has little meaning if one phase is acting as a liquid. The results of these calculations are shown in Figure 22. The variation of $\bar{\gamma}$ with temperature should probably not be considered significant since the $\beta(T)$ values were taken from a very coarsely plotted graph and the $C_p(T)$ and $\alpha(T)$ values are subject to experimental error. An average value for $\bar{\gamma}$ in this temperature region is 0.167. The low value of $\bar{\gamma}$ is indicative of the operation of modes with low or negative γ_i 's. Previous observations would suggest that negative γ_i 's exist in Pyrex.

It was necessary to use as a value for the compressibility of Lillie No. 1 one which results from an empirical expression in Morey for a soda-lime glass⁽¹¹⁴⁾ since no reported measurements of its elastic

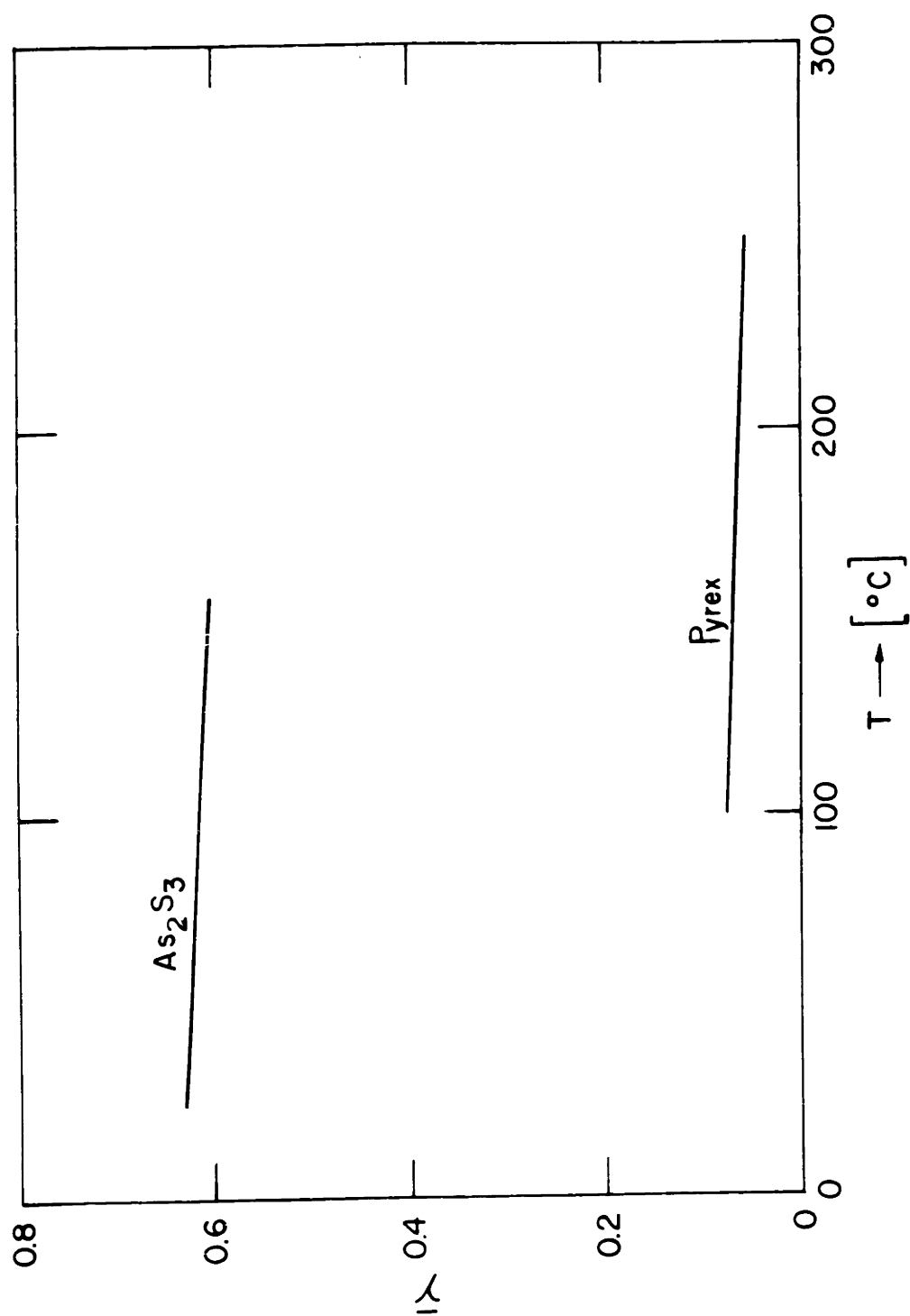


Fig. 22 Grüneisen Constants for As_2S_3 and Pyrex

properties were found in the literature. When this value is combined with those observed for C_p , α and V , $\bar{\gamma}$ is calculated to be 0.545 at 100°C . The only significance that should be attached to the calculated $\bar{\gamma}$ for Lillie No. 1 is that it is over three times that observed for Pyrex at the same temperature. It appears from these observations that the higher thermal expansivity of the soda-lime glass results from the suppression of modes with negative γ_i 's in the SiO_2 network.

Glaze et al⁽¹⁰⁵⁾ have measured the shear and Young's moduli as well as the Poisson's ratio of vitreous As_2S_3 . Combination of any two of these properties permits the calculation of the compressibility. The $\bar{\gamma}$'s plotted in Figure 22 result from combining these calculated compressibilities with the observed values for C_p , α and V . Like that observed for Pyrex the slight temperature variation of $\bar{\gamma}$ is not considered significant since it is probably within that expected from experimental errors. The low average $\bar{\gamma} = 0.616$ is considered to be anomalous since it was not anticipated that modes with low γ_i 's should be present and thus a more typical $\bar{\gamma}$ in the range of 1 to 3 was expected. The calculated $\bar{\gamma}$ for vitreous B_2O_3 is 1.6 at 25°C which is within the observed range of $\bar{\gamma}$'s for ionic compounds⁽¹¹⁵⁾. Since the structures of As_2S_3 and B_2O_3 are alike, at least in their gross features, the reason for the low $\bar{\gamma}$ observed for As_2S_3 is not evident. Two basic differences between the glasses are in the fractional ionic character of their bonds and in the ratio of the molecular weights of the ions in triangular coordination to those

surrounding it. It can be seen from the electronegativity scale⁽¹¹⁶⁾ that the fractional ionic characters of B_2O_3 and As_2S_3 are 0.4 and less than 0.1 respectively. The ratio $\frac{M_{AS}}{M_S} = 2.34$ while $\frac{M_B}{M_O} = 0.675$. The full significance of these differences is not understood. However, it is obvious that a comparison of the $\bar{\gamma}$ for As_2S_3 with those of ionic compounds is not justified, and that the large differences in the ratios of the molecular weights of the component ions in B_2O_3 and As_2S_3 will certainly produce different lattice dynamics. At least one sulfur compound, ZnS , is known to contain vibrational modes with negative γ_i 's as is evident by the negative $\bar{\gamma}$'s observed at low temperatures.⁽²⁰⁾ Extension of the property measurements needed for the calculation of $\bar{\gamma}$ to cryogenic temperatures should be useful in explaining the low $\bar{\gamma}$ observed for As_2S_3 .

D. Thermal Expansion and Heat Capacity of Supercooled Liquids

It was concluded from the literature survey of the thermal properties of liquids that although the Eyring liquid model should be regarded as empirical, it is the most successful equation of state for liquids at temperatures in the vicinity of their melting points. The agreement between observed and calculated thermodynamic properties becomes increasingly poor as the boiling point is approached. All indications suggested that the Eyring liquid model should be as successful for supercooled liquids as those near their melting points.

The expressions given below for the volumetric thermal expansion coefficient and heat capacity are the corrected ones resulting from the derivation given in the literature survey and are not the same as those appearing in the original Eyring references⁽³⁾. The so-called hole expansivity and heat capacity are the differences between the supercooled liquid and glassy values. The $\Delta\alpha$ and ΔC_p notation for these terms will be used throughout the remainder of the discussion. The expressions for $\Delta\alpha$ and ΔC_p resulting from the corrected Eyring model are

$$\Delta\alpha = \frac{1}{\sigma} \frac{\epsilon_h}{kT^2} e^{-\frac{\epsilon_h + PV_h}{kT}}$$

and

$$\Delta C_p = \frac{nk}{\sigma} \left(\frac{\epsilon_h}{kT} \right)^2 e^{-\frac{\epsilon_h + PV_h}{kT}}$$

where n is equal to the ratio of the volume of a molecule to that of a hole and σ is defined by

$$\ln \sigma = - \frac{S_h}{k} .$$

Independent measurements of $\Delta\alpha$ and ΔC_p at the glass transition permit the evaluation of ϵ_h and n provided some estimate of σ can be made. It can be shown that $\epsilon_h \gg PV_h$, so the pressure term will be dropped with future usage of the expressions.

The free volume (V_f) can be defined as the difference between the liquid volumes and the occupied volume. Thus

$$V_f = V - V_o \left[\alpha_g T + 1 \right]$$

and

$$V_f = V_o \int_0^T \Delta \alpha \, dT = \frac{V_o}{\sigma} e^{-\frac{\epsilon_h}{kT}}$$

are equivalent expressions. If V_f can be calculated from experimental data and then plotted as $\ln V_f$ vs. $1/T$, the extrapolated intercept at $1/T = 0$ will equal V_o/σ . V_o is roughly defined as the occupied volume. It has been more precisely defined either as the specific volume of the ions in a close packed structure or the Van der Waal's volume. (117)

The two definitions do not give equal numerical values but their maximum difference is only of the order of ten percent. Thus from experimental measurements of $V(T)$ a value for σ can be calculated.

In terms of the extrapolation described above, B_2O_3 is a unique glass forming liquid since its specific volume has been measured over a temperature range extending from its glass transition to almost its boiling point. (68,69,70) When a value of $V_o = 0.336 \text{ cm}^3/\text{gr}$ is used in conjunction with the data for $V(T)$ used in Figure 3 in the literature survey, the plot of $\ln V_f$ vs. $1/T$ shown in Figure 23 results. The value

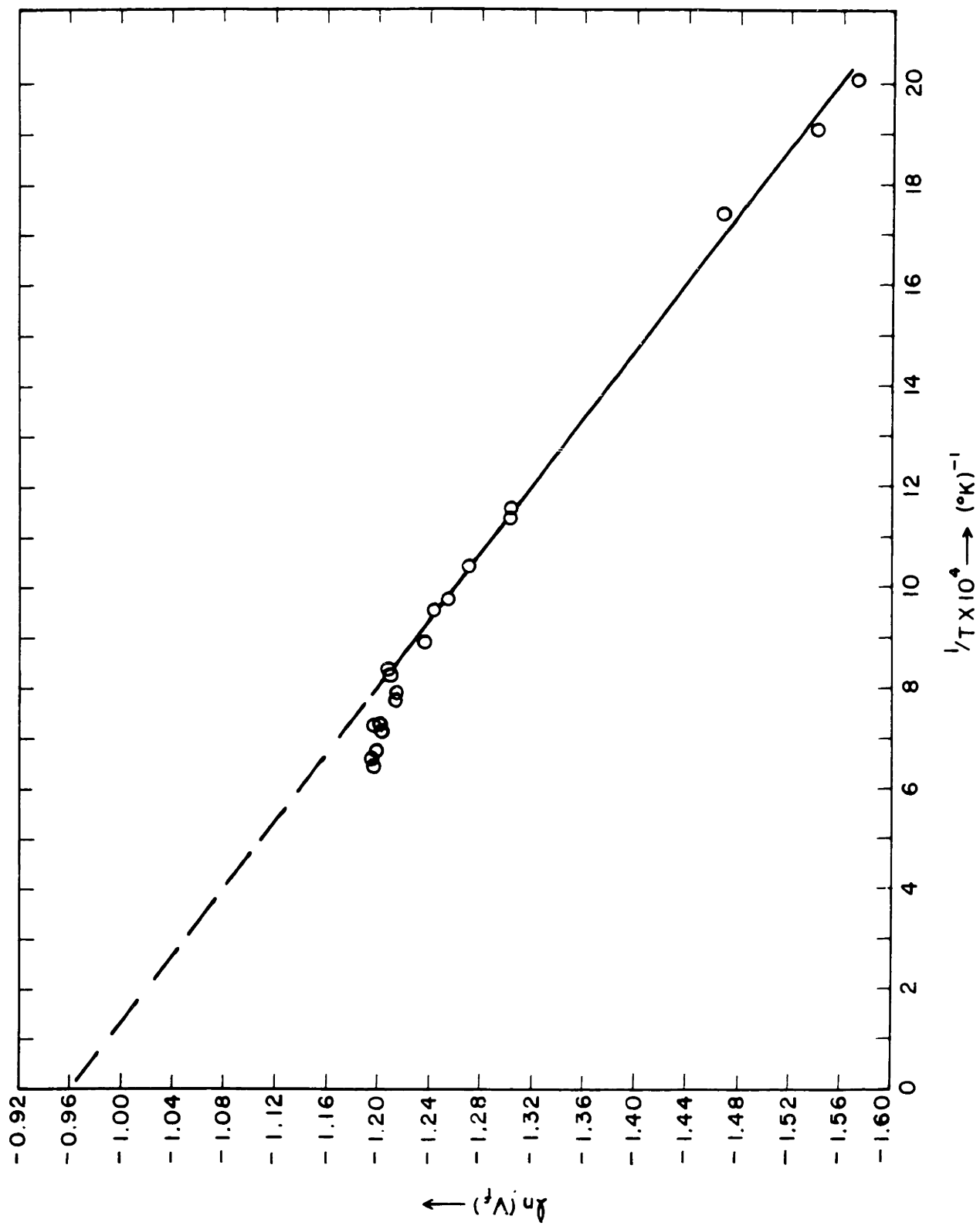


Fig. 23 \ln (free volume) vs. Reciprocal of Absolute Temperature

of V_0 is the average of those calculated both ways mentioned above. The extrapolation of the line drawn through the points closest to and including the transition region, extrapolates to give a value for $1/\sigma = 1.1$. The suggestion by Eyring⁽³⁾ that σ was approximately equal to one appears justified, and σ was set equal to one in all subsequent calculations. With this approximation the values of ϵ_h and n can be calculated directly from the observed values of $\Delta\alpha$ and ΔC_p at the glass transition.

In general both the values of $\Delta\alpha$ and ΔC_p would be expected to be dependent on the transition temperature. It was found that linear expressions fit both the glassy and supercooled liquid length-temperature curves best for both Pyrex and As_2S_3 , so $\Delta\alpha$ is independent of T_g for these systems. The glassy length-temperature curve for Lillie No. 1 was found to be best fit by a three term polynomial, so $\Delta\alpha$ for this glass is dependent on T_g for this system. The value of $\frac{\epsilon_h}{RT_g}$ is quite insensitive to small variations in $\Delta\alpha$ so a value corresponding to a $T_g = 500^\circ\text{C}$ will be used to calculate ϵ_h for Lillie No. 1. The observed values of ΔC_p for all three systems vary with T_g as is shown in Figures 24, 25, and 26. With a fixed value for $\frac{\epsilon_h}{RT_g}$, the value of n is directly proportional to ΔC_p , so the value of n must be specified in terms of a transition temperature.

In Table 4 a summary of the experimental values for the three systems studied plus B_2O_3 are given along with the derived values for

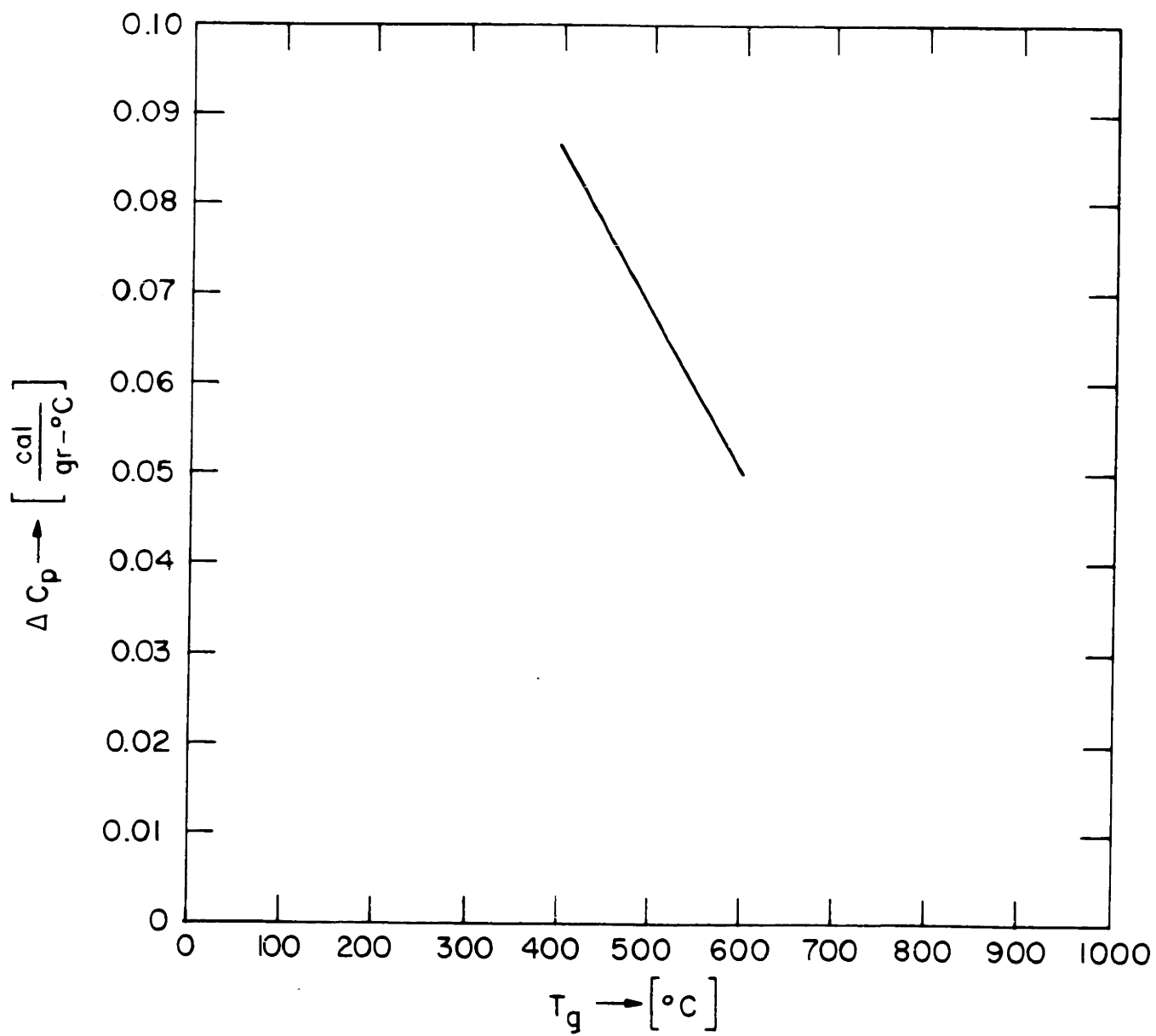


Fig. 24 ΔC_p as a Function of T_g for Lillie No. 1

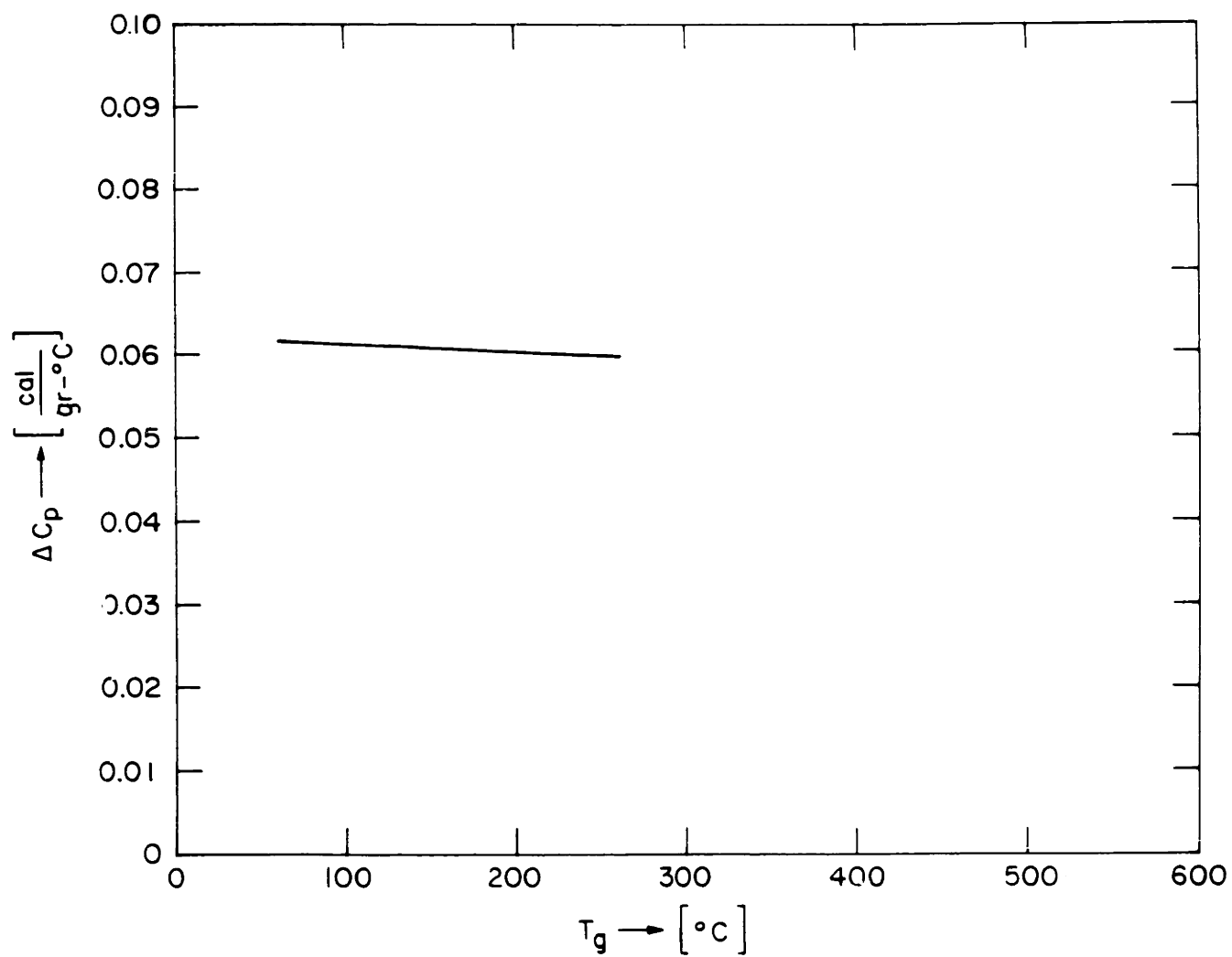


Fig. 25 ΔC_p as a Function of T_g for As_2S_3

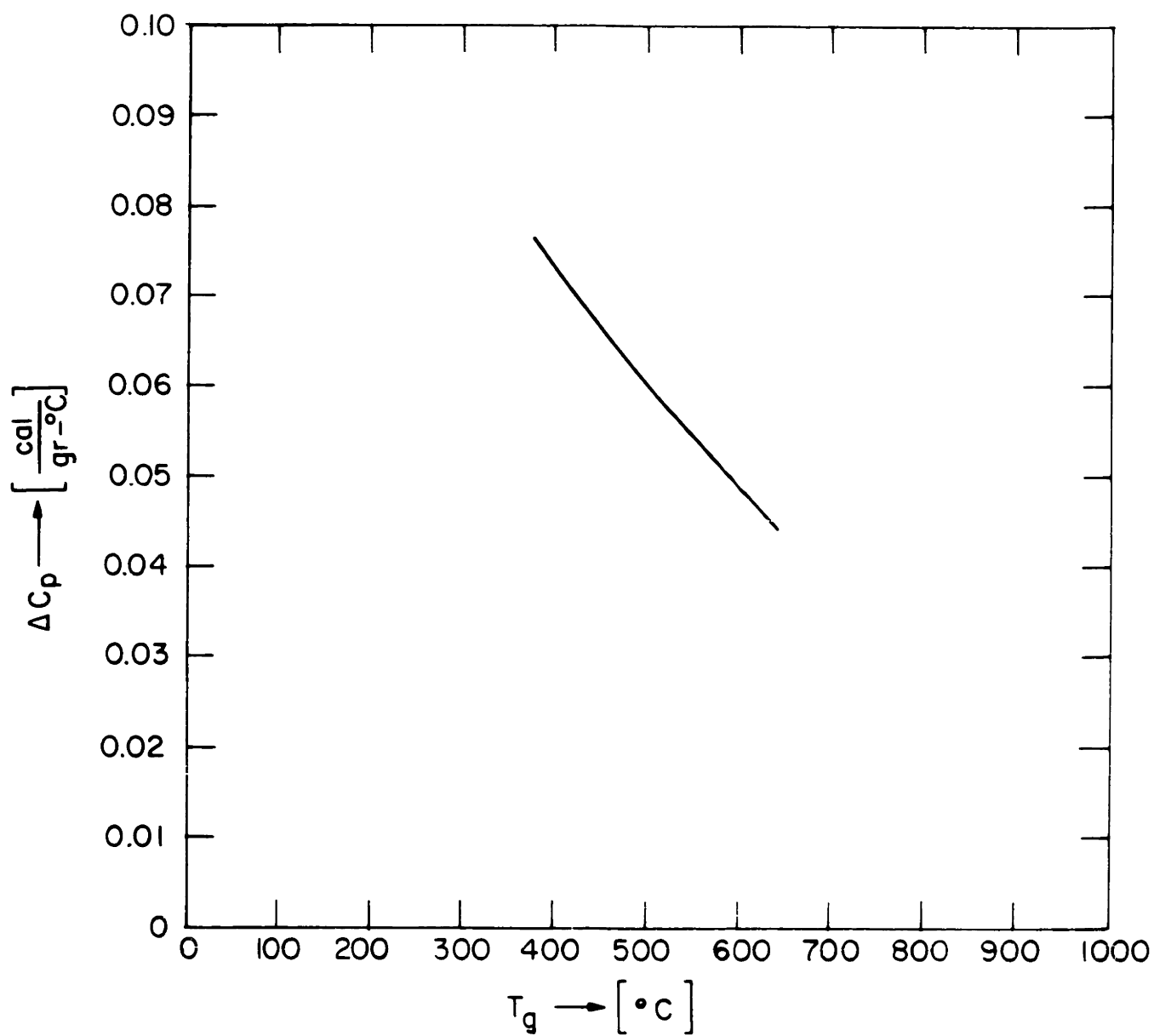


Fig. 26 ΔC_p as a Function of T_g for Pyrex

TABLE 4

SUMMARY OF RESULTS ANALYZED IN TERMS OF EYRING LIQUID MODEL

System	T_g °K	$\Delta\alpha \times 10^6$ cm ³ /cm ³ °C	$\frac{\epsilon_h}{RT_g}$	$\frac{V_f}{V}$	ΔC_p cal/gr °C	n	$d_h \times 10^8$ cm
As ₂ S ₃	443	319.0	3.08	0.046	0.067	19.1	2.35
Lillie No. 1	773	71.55	4.36	0.016	0.0682	8.75	2.08
Pyrex	773	16.09	6.21	0.002	0.0605	24.5	1.53
B ₂ O ₃ **	520	550.0	1.845	0.158	0.14	9.1	2.37
Lexan Poly-carbonate*	416	378.0	2.91	0.054			
Polyvinyl Chloride*	353	310.0	3.43	0.032			
n-Propanol*	95	400.0	4.84	0.007			
Glycerol*	183	240.0	4.70	0.009			
Polyvinyl Acetate*	298	400.0	3.31	0.036			
Natural Rubber*	205	400.0	3.82	0.024			
Polyisobutene*	198	450.0	3.90	0.020			
ZnCl ₂ ***	375	173.0	4.15	0.016			

* Data taken from O'Reilly⁽⁶⁾** Data taken from Parks⁽¹¹⁸⁾*** Data taken from Goldstein⁽⁸¹⁾

$\frac{\epsilon_h}{RT_g}$, n , free volume fraction and the hole diameter d_h . Also included in the table are the configurational thermal expansion coefficients and the glass transition temperatures for a number of other glass forming systems. With the exceptions of B_2O_3 and Pyrex, application of the Eyring expressions for $\Delta\alpha$ leads to similar values for $\frac{\epsilon_h}{RT_g}$ for a wide variety of glass formers. The numerical values for $\frac{\epsilon_h}{RT_g}$ are approximately the same as those Wunderlich⁽⁷¹⁾ calculated from heats of vaporization. One third of the values he observed for 35 organic systems lay between 3.0 and 3.4.

It would appear from these results that in terms of the Eyring liquid a correlation between the glass transition temperature and energy of hole formation exists. A uniform value of $\frac{\epsilon_h}{RT_g}$ leads to a constant free volume fraction at T_g which in the past has been suggested as a criterion for the glass transition. With few exception the free volume fractions calculated from the Eyring expressions are within an order of magnitude agreement with the 2.5 percent value that has been taken as the critical free volume fraction where a supercooled liquid transforms into a glass.

Another correlation that has been observed⁽¹¹⁹⁾ at the glass transition is that the ratio

$$\frac{H_v}{RT_g} \approx 44$$

where H_v is the molar heat of vaporization. The observation by Eyring⁽³⁾ that

$$n = \frac{V_o}{V_h} \approx \frac{H_v}{\epsilon_h}$$

permits comparison of the observed $\Delta\alpha$ and ΔC_p data to this correlation. If the Eyring expression for ΔC_p is divided by $RT_g \Delta\alpha$ and the above approximation is made, the quotient is $\frac{H_v}{RT_g}$. Substitution of the experimental values leads to the quotients 58.7, 37.9, 152 and 17.2 for As_2S_3 , Lillie No. 1, Pyrex and B_2O_3 respectively. The values for As_2S_3 and Lillie No. 1 are consistent with the variation shown by Turnbull⁽¹¹⁹⁾, but it is found in terms of this correlation Pyrex and B_2O_3 are again exceptions.

A final comparison of this data is with the so-called rule of constant heat capacity increment proposed by Wunderlich⁽⁷¹⁾. It was demonstrated by him that a uniform value for ΔC_p of $2.7 \pm .5$ cal/mole^oC was observed for a large number of organic glass formers if they were compared on the basis of the molecular weight of the fundamental or smallest molecular unit whose movements may change the hole equilibrium. He proposed that in oxide glasses the oxygen ions be taken as the fundamental unit. For Lillie No. 1 there are 1.6995 oxygen ions per mole of glass, thus the "bead molecular weight" is 35.9 which gives $\Delta C_p = 2.44$ cal/mole^oC in agreement with Wunderlich's observation. The similarly calculated values for As_2S_3 , Pyrex and B_2O_3 are 3.3, 1.80 and

3.23. Thus, all but Pyrex are included by his indicated standard deviation. The value for Pyrex is within the spread of values observed by him and since the value for ΔG_p would be expected to be low on the basis that one phase already exists as a liquid, it is considered to be consistent with the behavior for other glass forming materials.

In the one case where Pyrex and B_2O_3 were considered on the basis of their heat capacities alone, they were found to behave in a manner which was consistent with that observed for other glass formers when analysed in terms of the Eyring model. This suggests that their failure to agree with the other two correlations stems from an inadequacy of the Eyring liquid to properly describe their thermal expansion. As was pointed out in the literature survey, the Eyring liquid fails completely as a description of liquids which contract with heating. Water is a well known example of a liquid which behaves in this manner over a limited temperature range, and silica is believed to behave similarly. The reasons for the failure of the Eyring model to describe B_2O_3 are not evident; however, there are at least two factors which would make the expansion of Pyrex too complex to be described adequately by the Eyring model. It should be noted though that when the value for $\Delta\alpha$ of B_2O_3 , which Bestul⁽⁸⁷⁾ found necessary to fit the viscosity data by the W.L.F. equation is used in the above calculations, the behavior of B_2O_3 at the glass transition is consistent with the

correlations observed for the other materials. If it is presumed that the Pyrex composition is still within the immiscibility region after the transition to a supercooled liquid, then since the expansion measurements of the supercooled liquid were made by soaking till the presumed equilibrium structure was attained, it is probable that the compositions of the two phases had time to change with changing temperature and would thus affect the specific volume of the two phase liquid in a complex manner. A second factor to be considered is that the composition of the phase going through a transition at approximately 500°C will have a high silica concentration. With Charles' (112) estimate of the composition of the minor phase and the suggestion that it contained all of the Na_2O , the silica concentration in the major phase would be 96.7 mole percent. Even though it is not consistent with the Pyrex expansion measurements that Charles' estimates are numerically correct, the silica content of the major phase will clearly be high and thus might be expected to be influenced by the same factors which make supercooled silica an anomaly in terms of the Eyring liquid.

The best test of the Eyring liquid is by comparison of observed and calculated volumes and enthalpies. It was pointed out earlier that the calculated volumes for B_2O_3 were within 5% of the observed values from the glass point to 200°C above the melting point when a constant energy of hole formation was assumed. At higher temperatures the agreement became increasingly poor. Specific volumes at temperatures

well above the glass points of the three systems studied have not been reported so it is not possible to make a similar comparison for them.

The enthalpies of these systems were measured over a wide enough temperature range to check the correctness of the Eyring specific heat equations. According to the Eyring derivation the heat capacity of a liquid is the sum of the vibrational specific heat of the atoms plus the hole specific heat. It was observed that at the glass transition the hole specific heat could be set equal to the difference between the supercooled liquid and glassy heat capacities, ΔC_p . When differentiated, the Eyring expression for ΔC_p gives

$$\frac{d\Delta C_p}{dT} = \frac{nR}{T} \left(\frac{\epsilon_h}{RT} \right)^2 e^{-\frac{\epsilon_h}{RT}} \left\{ \frac{\epsilon_h}{RT} - 2 \right\},$$

thus with the values for $\frac{\epsilon_h}{RT_g}$ observed for these systems the derivative should be positive. It can be seen from Figures 24, 25 and 26 that the rate of change of the ΔC_p 's calculated from extrapolations of the least square expressions are negative. The variation of ΔC_p for these systems arises from the variation of the glassy heat capacity since with the exception of As_2S_3 which has a small second order temperature dependence, the liquid enthalpy curves were fit best by linear equations. It would appear that since the supercooled liquid enthalpy measurements were made at temperatures well above those where the vibration heat capacity should

have reached a maximum constant value of $3R$, that the rate of change of heat capacity with temperature predicted by the above expression should be compared with that observed for the supercooled liquids. The rates of change for ΔC_p predicted by the Eyring expression when evaluated at the glass transition temperature are 0.090, 0.058 and 0.095 percent per degree Centigrade for As_2S_3 , Lillie No. 1 and Pyrex respectively. It is obvious from the results of these calculations that the heat capacities of the supercooled liquids should have been practically constant and it is not surprising that with the experimental error and the rounding errors made during computations that curvature in the enthalpy-temperature curves was not detected for Lillie No. 1 and Pyrex. The heat capacity of As_2S_3 liquid was observed to increase by 0.01 percent over the temperature range of 200 to $600^{\circ}C$, which compares reasonably well with an averaged calculated value of 0.035 percent. These calculations indicate that if the vibrational component of the supercooled liquid specific heat is considered to be constant, the Eyring model will agree well with experimentally observed enthalpies.

It can be concluded from these observations that application of the Eyring liquid to the thermal expansivity and heat capacity properties of the three systems that were studied leads to numerical correlations which are either consistent with or whose differences are resolvable with those observed by others. The agreement of the

specific heat relations were better than those of the expansion relations. The failure of the thermal expansion relations clearly stems from the model's being a gross oversimplification of the molecular rearrangements involved in the changes of specific volume. Like any other empirical relation, it is impossible to derive information regarding molecular processes from it.

E. Davies and Jones Expansion

As discussed in the Introduction, Davies and Jones⁽²⁾ demonstrated that at the glass transition the difference between the supercooled liquid and glassy compressibilities, expansivities and specific heats are related by the expression

$$\frac{\Delta\beta}{\Delta\alpha} \geq V T_g \frac{\Delta\alpha}{\Delta C_p} .$$

Goldstein⁽⁵⁾ has shown that either term could be equal to the rate of change of the transition with pressure depending on which excess thermodynamic property governs the transition. The inequality exists so long as more than one ordering parameter is needed to describe the thermodynamic state of the glass. Without the compressibility measurements it is impossible to make this comparison of the terms for the three systems studied. The right hand term can be calculated from the measurements that have been made and is presented for the three glasses in Figure 27 as a function of the transition temperature. If the observations of Goldstein⁽⁵⁾ and O'Reilly⁽⁶⁾ apply to these three

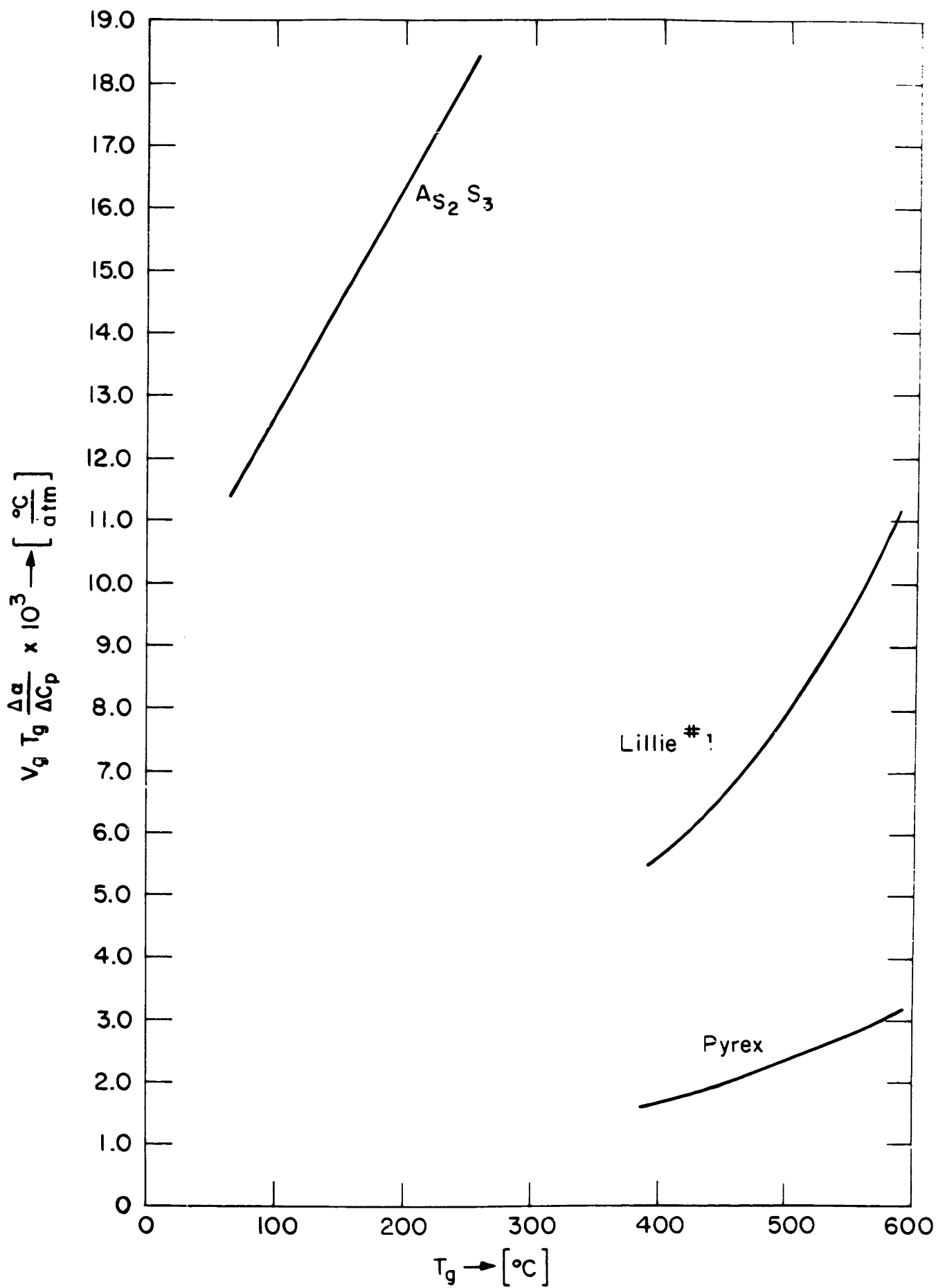


Fig. 27 $V T_g \Delta \alpha / \Delta C_p$ as a Function of T_g

materials, then the values of the term plotted in Figure 27 are equal to the pressure dependence of the glass transition temperature which is indicative that either excess entropy or enthalpy controls the transition.

It is apparent from Figure 27 that the value of $V T_g \frac{\Delta\alpha}{\Delta C_p}$ varies faster with temperature than is suggested by the appearance of temperature in the expression. The variation shown here is influenced by the dependence of ΔC_p on T_g which arises primarily from the variation of the heat capacity of the glass. Even though the right hand term decreases rapidly with temperature, it is probable that the left hand term is even more strongly influenced by temperature. Compressibility measurements made by Litovitz⁽⁷⁶⁾ on Arochlor indicate that the compressibility of the liquid is so strongly influenced by temperature that it extrapolates to that of the glass ($\Delta\beta = 0$) at temperatures of the order of $T_g - 50^\circ\text{C}$. The direction of the inequality would require that the right hand term approach zero faster than the left term. Clearly at finite temperatures this is achieved only if $\Delta\alpha \rightarrow 0$ faster than $\Delta\beta$ or $\Delta C_p \rightarrow \infty$; both of which are nonsense. Thus it appears that in the event nothing interferes with the extrapolated behavior, suppression of the glass transition temperature would produce conditions which violate the inequality of the Davies and Jones expression.

It is interesting to point out that the strong temperature dependence of the left hand term is due to a variation of a liquid property while that shown by the other appears to result from variation of glass properties with temperature. The expansivity measurements of the supercooled liquids were not extended over a wide enough temperature range to give an indication of their temperature dependence; however, the results shown for B_2O_3 would indicate that it increases as T_g is suppressed. The enthalpy measurements indicate that the heat capacity of the liquid is influenced very little by temperature. The temperature dependence of compressibility of the Eyring liquid is not consistent with this behavior because it can be shown that the left and right hand terms derived from it are equal at all temperatures. This results as a consequence of its being a single ordering parameter liquid.

F. Structural Relaxation

At the beginning of this discussion it should be pointed out that the relaxation experiments were not undertaken for the purpose of developing a phenomenological description of the structural relaxation process but rather as an attempt to determine whether a temperature could be defined by means of an appropriate extrapolation where the relaxation time constant reached an infinite value which presumably would be the glass transition temperature of an infinitely slowly cooled supercooled liquid. It is clear that both goals are

intimately related; however, it appeared from a survey of the available literature that a distribution of relaxation times with a finite maximum could be expected. For purposes of satisfying the latter objective the problem was interpreted as one of extrapolating to a temperature where τ_{\max} approached an infinite value. The experimental program was established to satisfy the latter objective and unfortunately some information which would have been useful for the first objective was lost. No attempt will be made to fit these results to a descriptive equation, but rather where possible they will be compared with existing ones to gain as much insight as possible into the factors affecting the relaxation process.

The Tool equation for structural relaxation can be shown to assume the form

$$\ln \frac{1}{\tau_{\text{eff}}} = \text{constant} + \frac{\delta_L}{h\Delta a}$$

when the substitutions $\delta_L = \Delta a (T_f - T)$ and $\frac{1}{\tau_{\text{eff}}} = \frac{dT_f}{(T - T_f)dT}$ are made. If the relaxation process was correctly described by this relation, a plot of the experimental results in terms of the above equation, as in Figure 20 would appear as straight lines whose slopes were $\frac{1}{h\Delta a}$ and which extrapolate to the value of the "constant" at $\delta_L = 0$. The results of experiments carried out for $T_f > T$ at the same temperature would intersect the $\delta_L = 0$ axis with the same slope at the same point.

It can be seen at a glance that the experimental results shown in Figure 20 are not described by the Tool equation. While it is not apparent from the figure whether the lines intersect the $\delta_L = 0$ axis at the same point, it is clear that lines approach the $\delta_L = 0$ axis with different slopes depending on whether δ_L is positive or negative.

It is also apparent from the four relaxation runs carried out at 500°C that the effective time constant is not a unique function of δ_L which is indicative of the presence of a memory effect. This was pointed out by Goldstein⁽⁷⁾ to be a direct consequence of the existence of a distribution of relaxation times for both linear and nonlinear relaxation processes. The maximum variation between τ 's at the same value of δ_L in Figure 20 is on the order of a factor of three. When the results of the 500°C series are replotted in Figure 28 to include the extrapolated initial τ_{eff} 's, a maximum variation of τ_{eff} 's on the order ten would be expected between the initial values of experiments originating near $\delta = 0$ and those approaching it from large initial δ_L 's. On the basis of the same comparison, Goldstein's⁽⁸¹⁾ results for ZnCl_2 show an apparent maximum variation of the order of two and Kovacs'⁽⁸²⁾ for polyvinyl acetate more than two orders of magnitude. These results for Lillie No. 1 indicated qualitatively that like ZnCl_2 the spectrum of relaxation times is narrow compared to that observed for polyvinyl acetate, and presumably other high polymer glass formers, even though it is not possible to describe the spectrum of a nonlinear process quantitatively.

It appears from the similarity in the dependence of the effective time constants on δ_L observed by Ritland⁽⁸⁰⁾ as replotted by Goldstein⁽⁸¹⁾ and those shown in Figure 20 that the Lillie No. 1 length-time curves could be as well represented by the Ritland equation as Ritland's were. This was not done since the Ritland equation does not take into account the effect of a distribution of relaxation times and it must be concluded that the relatively good fit achieved by this expression results from its having four freely adjustable parameters rather than its being inherently correct.

Like Goldstein's and Ritland's results, the values of τ_{eff} at any one temperature tend to extrapolate to the same value as $\delta_L \rightarrow 0$. This is not as apparent from the curves plotted in Figure 20 where the indicated temperatures are only nominal as in Figure 21 where the equilibrium relaxation times are plotted against the reciprocal of the absolute experimental temperature. Considering that these points are obtained from extrapolations of lines which were drawn through data points derived by graphical differentiation, it is felt that the above statement is consistent with the probable errors. The four 500°C runs indicate that there is no correlation between the points lying above or below the line depending on the direction of approach to $\delta = 0$ since they are equally divided. A point made by Goldstein⁽⁸¹⁾ that the extrapolation is made less sure by the fact that the error in τ_{eff} is larger the closer $\delta_L = 0$ is approached is well taken here; however, it is felt that the conclusion

regarding the extrapolations is valid. As discussed in the literature survey this result is indicative that a maximum value exists in the distribution of relaxation times governing the structural relaxation process.

In the presentation of results, Section V, it was demonstrated that both the shear and structural relaxation time constants were adequately represented over the temperature range shown in Figure 21 by equations of the form

$$\log (\tau) = A + B \frac{1}{T} \quad .$$

It was also shown that there was a 60 percent probability that the difference between the observed slopes was insignificant, or in other words they were the same, considering the experimental errors.

Goldstein demonstrated that the equilibrium relaxation times of ZnCl_2 were fitted within the experimental error by an equation of the above form. Ritland observed that the activation energies for viscosity and structural relaxation time were the same for the borosilicate crown glass he studied. Thus the experimental results for Lillie No.1 are consistent with both those of Goldstein and Ritland in both respects though neither came to both conclusions.

The expressions derived by Eyring⁽³⁾ for the bulk viscosity

and shear viscosity time constants are

$$\tau_B = \frac{h}{kT} \exp \left\{ [\epsilon_j - TS_j(B) - \frac{1}{2} PV_h] / RT \right\}$$

and

$$\tau_S = \frac{h}{kT} \exp \left\{ [\epsilon_j - TS_j(S) + PV_h] / RT \right\}$$

where ϵ_j is the height of the barrier in a diffusion like jump and $S_j(B)$ and $S_j(S)$ are the entropies associated with the jumps in the bulk and shear viscosities. Eyring tabulates the values for $S_j(B)$ and $S_j(S)$ for a number of high polymer liquids which range from 3 to 25 entropy units and the maximum differences between $S_j(B)$ and $S_j(S)$ is 7 entropy units. On the basis of these results and the observation that a S_j of 25 entropy units at 500°C is less than 10 percent of ϵ_j observed for the Lillie glass and that PV_h is completely negligible compared to ϵ_j at one atmosphere, it can be said that Eyring liquid predicts essentially equal temperature dependencies for τ_B and τ_S . According to the Eyring derivation⁽⁵⁹⁾ the structural relaxation time constant is numerical factor times τ_B , so on a logarithmic basis the structural and shear time constants have the same temperature derivative. Thus the observed temperature dependencies for τ_B and τ_S of Lillie No. 1 are consistent with that predicted by the Eyring liquid.

Even though the temperature dependencies of the two relaxation processes are apparently equal in agreement with the prediction of the

Eyring liquid, the prediction of this model that

$$\tau_s > \tau_{\text{eff}}$$

is apparently not correct for Lillie No. 1. The equilibrium structural relaxation time constant exceeds the shear relaxation time constant by approximately a factor of thirty as can be seen from Figure 21. It is obvious that the Eyring model should not be expected to agree in detail since it was derived on the basis that a single relaxation time and not a distribution of τ 's described the kinetics of structural relaxation. A more fair comparison of the time constants in relation to the Eyring model is one of comparing the value of the initial time constant of structural relaxation relative to the shear time constant. The dotted line in Figure 28 represents the initial time constant at 500°C with various fictive temperatures. At $\delta_L = 0$, where the fictive and actual temperatures are equal, the initial time constant for the structural relaxation process is 0.56 hours which compares with a shear time constant of 0.132 hours. The relative values are still wrong, but they are within a factor of four when compared on this basis. It is probable that the dotted line in Figure 28 is low since it was drawn through the points determined by a linear extrapolation through the experimental data. If there is any curvature in the $\log(\frac{1}{\tau_{\text{eff}}})$ vs. δ curves it is certainly concave upward, and thus since the initial portion of the 540 to 500 and 520 to 500 curves was lost during the time the

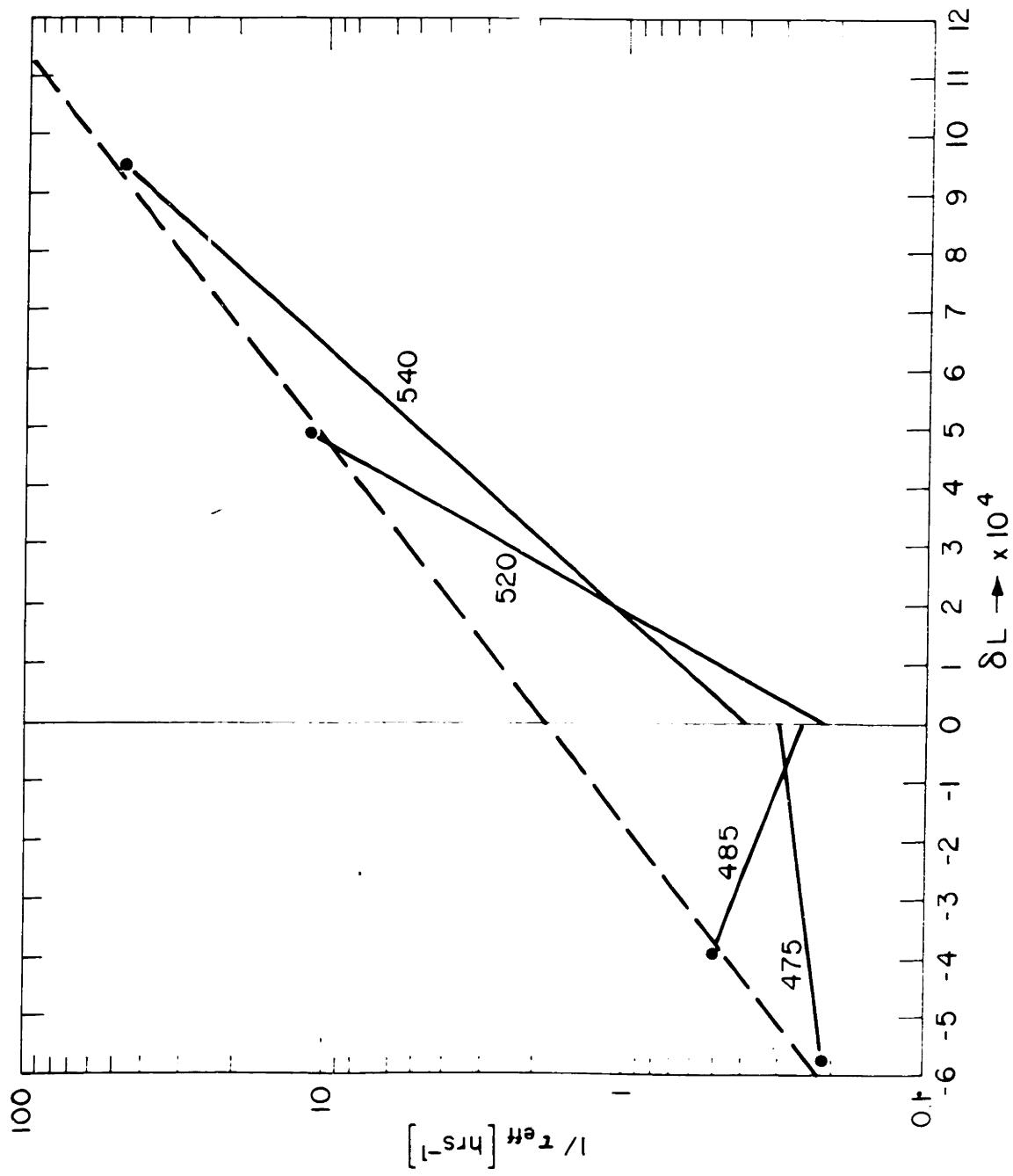


Fig. 28 Extrapolated Effective Relaxation Time Constants
for Lillie No. 1 at 500°C.

furnace stabilized, the extrapolated points will be low. The exact shear modulus of Lillie No. 1 was not known, so a value was taken from Morey⁽¹⁰²⁾ for a similar glass. It is also known that the shear modulus decreases with increasing temperature, so the numerical value of the shear time constant is in doubt; however, it is probable that the values shown on Figure 21 are low. It is not clear that the combined probable low estimate of τ 's and a high estimate of τ_{eff} are enough to reverse the two numbers' relative magnitude, but they should be considered to be numerically close.

The two time constants which have been discussed are defined in terms of experimentally determined parameters. The shear time constant, defined as the quotient of the shear viscosity divided by the shear modulus, behaves in a simple manner for Newtonian fluids. Thus with siliceous glasses, the shear relaxation time constant is uniquely defined at all temperatures and is not time dependent. The structural relaxation time constant is also experimentally defined in a simple manner, by the expression

$$\frac{1}{\tau_{\text{eff}}} \equiv - \frac{1}{L-L_{\infty}} \frac{d(L-L_{\infty})}{dt} .$$

However, its behavior was observed to be complex. It can also be defined in a way equivalent to the shear time constant by

$$\tau_{\text{eff}} = \frac{\eta_B}{M}$$

where η_B is a bulk viscosity and M is a modulus. The phenomenological description equivalent to those obtained for linear viscoelastic problems, of $\tau_{\text{eff}}(t)$, has not been solved. It has been shown that the bulk viscosity is sensitive to the instantaneous thermodynamic state, but without a correct solution for the equation of state of liquids the exact dependence cannot be understood. It should also be pointed out that it is not clear what modulus should be used to represent the driving force which returns the systems to equilibrium. Even if these two factors were understood, the mathematics of nonlinear relaxation with a distribution of relaxation times has not advanced to where a solution could be made, so at this point it appears that the differences between the shear and structural relaxation times cannot be resolved any further.

Structural relaxation experiments carried out at the same temperature but with different fictive temperatures permit the comparison of the effect the actual and fictive temperatures have on the initial effective time constant. This is what Kovacs⁽⁸²⁾ refers to as a type "b" experiment. In Figure 28 the dotted line passes through the points corresponding to the initial time constants as the fictive temperature is varied. The ratio $\frac{d \ln \tau}{dT}$ to $\frac{d \ln \tau}{dT_f}$ determines the relative effectiveness of T and T_f . Evaluation of these parameters from the slope of the dotted line on Figure 28 and the slope of the structural relaxation time constant in Figure 21

indicates that temperature influences the initial effective time constant 1.6 times more strongly than the fictive temperature. The comments regarding the probable error in the dotted line made with respect to the comparison of the Eyring shear and bulk time constants apply here with respect to the slope. It is probable that the slope of the dotted line is low, since the extrapolations of τ_{eff} vs. δ_L for $T > T_g$ will be more in error than those for $T < T_g$ because a greater portion of the experimental points was lost during the cooling runs. It is impossible to estimate what the effect would be, but it is felt safer to say that the relative importances of the temperature and fictive temperature are roughly the same rather than putting a numerical value on their relative effectivenesses. This is the same conclusion reached by Goldstein⁽⁸¹⁾ for ZnCl_2 .

It must be concluded from the fit of the lines drawn through the equilibrium structural relaxation times in Figure 21 that with the observed experimental scatter, no significant deviation from the logarithmic representation of τ_{eff} can be inferred, and that these experiments fail to permit an extrapolation which predicts infinite relaxation times at temperatures different from absolute zero. The same observation holds for the shear relaxation time constants shown in Figure 21, yet Bestul⁽⁸⁷⁾ has demonstrated that over a wider temperature range the W.L.F. equation and not a logarithmic one fits the Lillie No. 1 viscosity. Thus, while there is no reason that the

shear and the equilibrium structural relaxation times must have the same temperature dependence, it must also be concluded that the temperature range over which the experiments were made is not wide enough to determine whether the equilibrium structural relaxation times are described by a function other than a logarithmic one. Extension of the experiments to much lower temperatures is impractical since the stabilization run at 470°C too approximately three months too complete. Even with a faster responding furnace the experiments could not be extended to significantly higher temperatures with the techniques employed in these experiments since excessive viscous deformation would occur. It is probable that the question of whether infinite equilibrium structural relaxation times will be attained at finite temperatures cannot be experimentally answered unequivocally.

VII. SUMMARY AND CONCLUSIONS

In terms of the primary objective of this thesis, the study of the Davies and Jones expression for inorganic glass forming systems, it must be conceded that the results are incomplete without the compressibilities of the glasses and supercooled liquids as functions of temperature. At the initiation of the study it was understood that these measurements were to be made by T. A. Litovitz. Unfortunately they have not yet been undertaken. Even though without this data it was impossible to make any conclusion regarding the equality or inequality of the terms of the Davies and Jones expression or which excess thermodynamic property governs the transition, it was possible to make observations and conclusions regarding other aspects of the behavior of the systems studied.

In the area of the glass transition the following observations can be made for all three systems:

- 1) The evaluation of the term $T_g V \frac{\Delta\alpha}{\Delta C_p}$ and its temperature dependence has been accomplished. The term varies in a direction which would tend to preserve the inequality of the Davies and Jones expression, but it was concluded from liquid compressibility measurements on other supercooled liquids that the $\Delta\beta/\Delta\alpha$ term probably varied faster.

- 2) It was not possible to predict a transition temperature for an infinitely slowly cooled liquid by extrapolation of time constants since over the temperature range studied the behavior was adequately represented by a logarithmic expression. It is probable that an unequivocal answer to this question cannot be achieved experimentally.
- 3) Analysis of the $\Delta\alpha$'s and ΔC_p 's observed at the glass transition with the Hirai-Eyring hole model of liquids demonstrated that the experimental results agree with correlations observed for other glass forming materials.

From the analysis of the thermal properties of glasses it can be concluded that:

- 1) Pyrex, Corning Glass #7740, is phase separated. The combined thermal expansion results and results of electrical measurements by Charles suggest that both phases are continuous. Even though the glass transition of the minor phase was not demonstrated with the enthalpy measurements, compressibility measurements were cited which indicate that the transition takes place.
- 2) The values of the Gruneisen constant calculated for both siliceous glasses reflect the effect of substitutions on the modes with negative γ_i 's in the vitreous silica network.

- 3) The Gruneisen constant observed for vitreous As_2S_3 was unusually low. However, without low temperature property measurements no conclusions could be made regarding the reasons for its low value.

From the liquid property measurements it was observed that the Eyring hole model liquid represented the heat capacities of supercooled liquids quite accurately. The thermal expansion measurements were not studied over a wide enough temperature range to make a judgement regarding the usefulness of the Eyring equations as representative of the volume as a function of temperature. It is probable that the Eyring model is not as accurate a representation of the expansion behavior as it is of the heat capacity.

The structural relaxation studies on Lillie No. 1 indicate that:

- 1) A spectrum of relaxation times is present which is dependent on the state of the liquid. Hence the relaxation process is nonlinear;
- 2) A maximum in the distribution of relaxation times exists;
- 3) Fictive and actual temperatures have approximately the same influence on the observed τ_{eff} ;
- 4) The activation energy of the equilibrium structural relaxation time is equal to that of shear viscosity;

- 5) The initial structural relaxation time resulting from an infinitely small change of temperature ($\delta_i \rightarrow 0$) is numerically close to the shear relaxation time at the stabilization temperature, though the equilibrium structural relaxation time is approximately thirty times the value for shear.

VIII. SUGGESTIONS FOR FURTHER WORK

1. The glass and supercooled liquid compressibilities of the three systems studied must be measured in order that both terms of the Davies and Jones expression might be evaluated. Comparison of the relative magnitudes of the two terms is a clear indication of the adequacy of a single ordering parameter description of these glasses.
2. The effect of pressure on the transition temperature should be measured. Its equality to one of the terms of the Davies and Jones expression determines at which, if any, constant excess thermodynamic property the transition occurs. The information for areas of study suggested in items 1 and 2 can easily be obtained from the same experimental program.
3. It is commonly assumed in the literature that all excess thermodynamic properties resulting from sudden changes in pressure or temperature in the transition region will relax along the same path. This has not been demonstrated and there appears to be no reason that this need be true.
Further a comparison of the paths of relaxation resulting from

sudden pressure and temperature changes should be made. There is essentially no data for structural relaxation resulting from changes in pressure for inorganic glass forming systems. The relaxation of volume due to sudden changes in pressure can be made part of the experimental program suggested in items 1 and 2.

4. The heat of fusion of As_2S_3 should be evaluated so the Kauzmann Paradox point of this glass might be calculated. This temperature represents the lowest possible value to which the glass transition temperature can be suppressed.
5. Thermal expansion, compressibility and heat capacity measurements for As_2S_3 glass should be extended to temperatures as close to the absolute zero as practical in order that the relatively low $\bar{\gamma}$ observed for this glass might be explained.
6. It is clear that an understanding of the glass transition, with the associated structural relaxation effects, will only be achieved with a better theoretical model of the liquid state. For this reason, the most important area for future work will be the implementation of suitable approximations within the exact formalism of the statistical mechanical solution for the equation of state for liquids as suggested by Rice⁽⁴⁷⁾.

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APPENDIX A

CALORIMETER OPERATING NOTES

A. Water and Cleaning of Fin Assembly

1. Cleaning

The fin assembly of the calorimeter was cleaned by first rinsing it with acetone to remove oily materials, followed by thoroughly washing it in chemical ware soap and then by rinsing it in distilled water. Precautions were taken to insure that the mercury tube was rinsed after each cleaning operation. The glass vessels were cleaned with chemical ware soap, and chromic acid, then thoroughly rinsed with distilled water.

2. Water

It is obvious that it is not necessary to use purer water than is justified by the cleaning processes used on the components of the calorimeter; however every precaution should be taken to remove dissolved gases. The water used in the calorimeter was deaerated by a vacuum distillation process. It is essential that the water be maintained at a vacuum equal to its vapor pressure until it is introduced into the calorimeter.

B. Filling the Vessels with Water and Mercury

The volumes to be occupied by the mercury and water should first be determined; this is most easily done by filling the inner glass vessel with water, then putting it in place over the fin assembly while allowing the displaced water to run off. The retained volume of water is equal to that which will be occupied by the mercury and water. The volume of mercury should be measured. It should be enough to just come up to, but not touch, the bottom fin. Finally, for filling purposes the volume of water to be introduced into the vessel (the difference between the total volume and the mercury volume) should be placed in the inner vessel and the vessel put into place over the fin assembly. The level of the water on the fins should be noted as it will be critical in the filling procedure.

The distilled, deaerated water is maintained under vacuum in a flask which has two glass tubes passing through a rubber stopper. Tube one extends to the bottom of the flask and tube two extends to just clear the stopper but not enter the water. Both glass tubes have sections of rubber tubing attached to them where tubing clamps can be located. Rubber tube one is connected to glass tube B (see Figure 6) and valve V is opened; the tube clamp on rubber tube one remains closed. A vacuum pump is connected to R and the assembly is pumped down. It is necessary to pump down at

least over night since the relatively large volume to be occupied by the mercury and water must be evacuated through the long small diameter mercury tempering tube.

Once the system has been evacuated, water is introduced by opening the tube clamp on tube one and just cracking slightly and carefully the tube clamp on tube two after the vacuum pump at R has been clamped off. When air is allowed to enter tube two, water will flow through the tubing into the calorimeter vessel. It should be noted that water will also fill the reservoir below R. However, this water may be ignored in the filling since the more dense mercury will flow to the "T" below the reservoir then down the stainless steel tube without displacing the water in the reservoir.

When the water reaches the level which was determined as described above, the valve V is closed. The stopper with tubes one and two is then removed and tube one is inserted into mercury. Care should be taken not to break the column of water which will hold in tube one after it is removed from the water. After tube one is inserted into the mercury, the valve V is opened and mercury will flow into the system until it is filled. It is imperative that the rubber tubing to glass tubing joints not leak air (R, B to tube one, etc.) and so they should be liberally coated with glyptol which can be cleaned off later with acetone.

Spots on the mercury glass interface will no doubt be noticed. This results from the water having been in contact with the glass prior to the mercury and the fact that water wets glass and mercury does not. These spots apparently have no detrimental effect and act like a lubricant for the mercury, making adjustments in the capillary height easier.

After the water is removed from the reservoir below R, and the glass ware cleaned up, the system is ready for operation.

C. Freezing a Mantle

The mantle is frozen about the fin assembly by lowering dry ice into the calorimeter chamber. An open top capsule which is connected to a wire has been found suitable for containing the dry ice. Obviously the capsule should be as close to the internal diameter of the calorimeter well as possible to give good thermal contact. Dry ice should not be dropped directly into the calorimeter as it will rest on the bottom of the well and freeze an excessively thick layer of ice on the bottom fins. The danger exists that the ice about the fins will extend to the wall of the inner vessel, making it possible to break the glass vessel with continued freezing. The final ice configuration should be similar to that shown in Figure 6.

On the first freezing (or any freezing after the unit has been allowed to warm up), a considerable amount of dry ice will be needed to cool the calorimeter to 0°C . Once freezing starts, it proceeds

quite rapidly and should be watched at all times.

D. Wax Joints

The joints between the glass vessels and the type 403 stainless steel flanges were made with Apiezon "W" wax. There are several W type waxes; the one that was used and found satisfactory is the one with the lowest temperature range. It is black in color.

The joints are made by placing the calorimeter and the glass vessels into an oven and heating them to 250-275°C. It was found suitable to turn the calorimeter upside down and coat the inside surfaces of the caps with the wax. The outside ground surfaces of the glass are also coated with the wax. The vessels are then put into place on the caps and the assembled unit is allowed to cool to room temperature inside the furnace so a maximum of stress relaxation occurs.

The wax has a very long working range and even though the "softening point" is about 90°C, it is not very fluid at 275°C and hence must be applied slowly.

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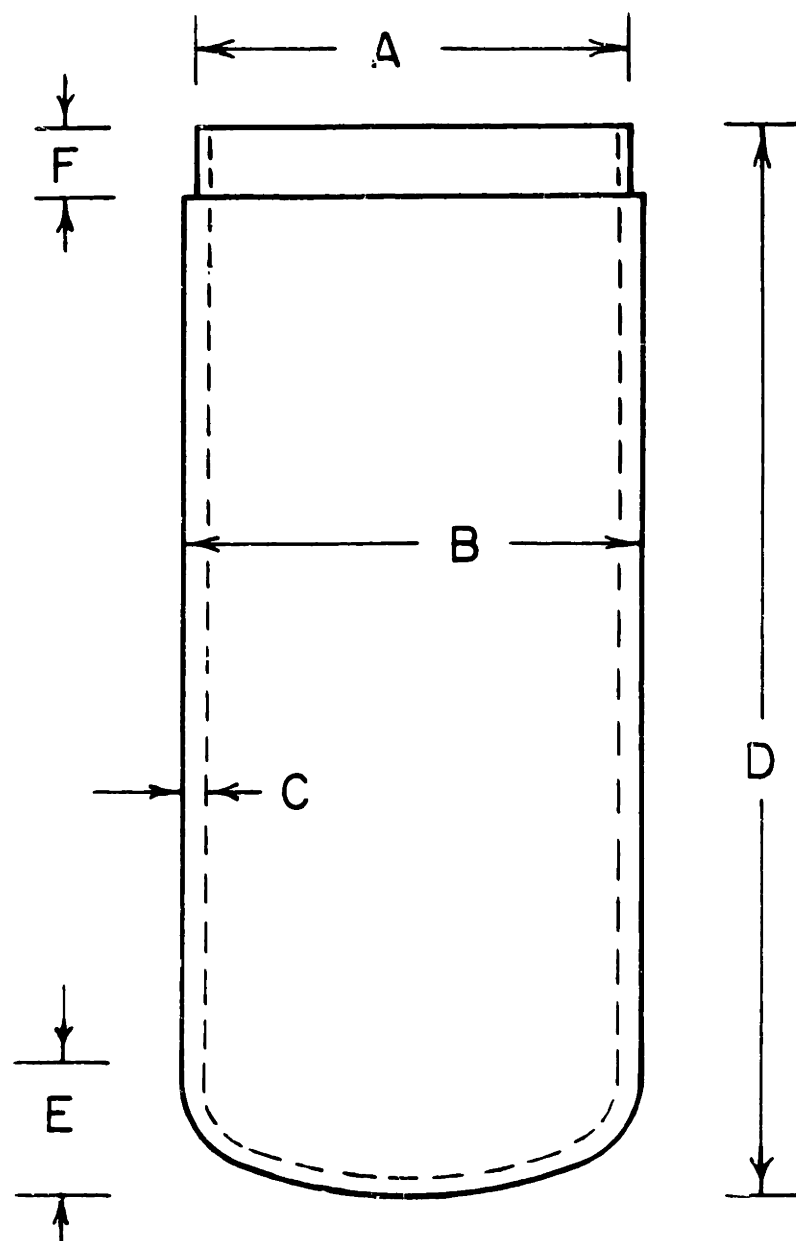
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APPENDIX B. DRAWING OF GLASS VESSELS



	A	B	C	D	E	F
Inner Vessel	3.085 ± 0.002	80 mm	2.4 mm	$9 \frac{1}{8} \pm \frac{1}{8}$	$\frac{3}{4} \pm \frac{1}{8}$	$\frac{5}{8}$
Outer Vessel	3.865 ± 0.002	100 mm	2.4 mm	$11 \pm \frac{1}{8}$	$1 \pm \frac{1}{8}$	$\frac{5}{8}$

All dimensions are in inches with the exceptions of B and C which are in millimeters and are the nominal dimensions of medium wall Pyrex tubing.

APPENDIX C

BIOGRAPHICAL NOTE

The author, John Scarseth Haggerty, was born October 23, 1938. Having attended numerous schools, including L'Ecole International de Suisse, he graduated from Paris American High School, Paris, France, and entered the Massachusetts Institute of Technology in 1957. He received the degree of Bachelor of Science in Mechanical Engineering from M.I.T. in 1961, and received the degree of Master of Science in Ceramics from the same institution in 1963. He is a member of Sigma Xi and the American Ceramics Society.

The author jointly presented a paper with Professor Alfred R. Cooper at the International Conference on Non-Crystalline Solids, Delft, The Netherlands, 1964. The paper, titled "Configurational Thermal Expansion of Three Inorganic Glasses", was later published in The Physics of Non-Crystalline Solids, edited by J. A. Prins, North Holland, Amsterdam, 1965, pages 436 to 443.