KINETICS OF THE GLASS TRANSITION IN A CALCIUM-POTASSIUM NITRATE MELT

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The kinetic parameters governing the structural relaxation of enthalpy in the glass transition region of a 40 mol % Ca(NO₃)₂ - 60 mol % KNO₃ melt have been determined by analysis of heat capacities measured on a differential scanning calorimeter during rate heating. The activation enthalpy governing the structural relaxation is 141 kcal/mol, the same as that for the shear viscosity. The rate of enthalpy relaxation is markedly slower than that for shear stress.

I. INTRODUCTION

There are many examples of glass formation by fused salts, particularly in systems with complex anions or cations (nitrates, acetates, sulfates, pyridinium ions, etc.), with cations of different valence (Ca²⁺, K⁺, Pb²⁺-Na⁺, etc.), or with network character (BeF₂, ZnCl₂). As with other glasses, these fused salts are frequently characterized by a glass transition temperature, Tg, a temperature in the vicinity of which the heat capacity Cp or thermal expansion coefficient α exhibits a fairly abrupt change over a narrow temperature region while heating or cooling at a rate of a few degrees per minute. The glass transition as observed in this fashion is kinetic in nature and represents the inability of the liquid structure at low temperatures to equilibrate on the experimental time scale following a temperature change. In the present paper we report a study of the kinetics of the glass transition monitored in terms of the macroscopic property enthalpy, H, for a nitrate glass (40 mol % Ca(NO₃)₂ - 60 mol % KNO₃) on
which a number of previous relaxational studies have been carried out.

II. KINETICS OF STRUCTURAL RELAXATION

The phenomenology of the kinetics of the glass transition used here has been described in detail in previous papers and will be summarized only briefly in this section. In Fig. 1 is shown schematically the response of a macroscopic property, the enthalpy, of a liquid initially at its equilibrium value at temperature to an instantaneous change of temperature, at time . The system exhibits an immediate enthalpy change, , associated primarily with solid-like vibrational degrees of freedom. This is followed by a further change with time by an amount due to rearrangement of the liquid structure to the equilibrium value at the new temperature. The equilibrium liquid and glass heat capacities, and , may then be defined

\[ C_{pg} = \lim_{\Delta T \to 0} \frac{\Delta H_g}{\Delta T} \]  
\[ C_{pe} = \lim_{\Delta T \to 0} \frac{(\Delta H_g + \Delta H_r)}{\Delta T} \]

where the limitation to small is introduced to take into account that and may in general be temperature dependent.

Rather than describe the structural relaxation in terms of the macroscopic property itself - enthalpy in the present example - it is convenient to express the property in temperature units by means of the fictive temperature, . In terms of Fig. 1 for the case in which and are not appreciably temperature dependent over the range , is defined such that

\[ \frac{H - H_e}{\Delta H_r} = \frac{T_f - T_1}{\Delta T} \]  

A more general definition of , applicable to the characterization of the structural state during any arbitrary temperature-time program, is, again for the property enthalpy,

\[ H(T) = H_e(T_f) - \int_T^{T_f} C_{pg} \, dT' \]  

where is the equilibrium value of the enthalpy at temperature . thus has the property that at equilibrium at temperature , . Differentiation of Eq. (4) relates the temperature coefficient of to the heat capacity.
\[ \frac{dT_f}{dT} = \frac{(C_p - C_{pg})}{(C_{pe} - C_{pg})} \]  \[ (5) \]

The variation of \( T_f \) with time \( t \) during structural relaxation following a single temperature step \( \Delta T \) from equilibrium at temperature \( T_0 \) may be described by a relaxation function, \( \phi(t - t_1, t) \):

\[ T_f(t) = T_0 + \Delta T [1 - \phi(t - t_1, t)] \]  \[ (6) \]

A semiempirical expression for the relaxation function that has been found to give an excellent fit to structural relaxation data is

\[ \phi(t - t_1, t) = \exp[-(t - t_1) / \tau_o] \]  \[ (7) \]

with the relaxation time given by

\[ \tau_o = A \exp[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f}] \]  \[ (8) \]

where \( 0 < \beta \leq 1 \), \( 0 \leq x \leq 1 \), \( A \) and \( \Delta h^* \) are constants and \( R \) is the ideal gas constant. The \( \beta \) parameter is a measure of the width of the spectrum of relaxation times needed to characterize the structural relaxation; the smaller \( \beta \) the broader the spectrum. The \( x \) parameter is a measure of the non-linearity of the relaxation process, i.e., it allows for the dependence of the relaxation time on both the actual temperature \( T \) and on the structure, i.e., on \( T_f \). \( \Delta h^* \) is the activation enthalpy and expresses the temperature dependence of the relaxation time for the linear condition very close to equilibrium \( (T \approx T_f) \):

\[ \frac{d}{dT} (\ln \tau_o)_{T \approx T_f} = \frac{d}{dT} \ln \tau_o = \frac{\Delta h^*}{R} \]  \[ (9) \]

If a system initially at equilibrium at temperature \( T_0 \) is subjected to a series of temperature steps \( \Delta T_1 \) at time \( t_1 \), \( \Delta T_2 \) at time \( t_2 \), ..., \( \Delta T_m \) at time \( t_m \), then the evolution of \( T_f \) for \( t \geq t_m \) may be expressed as a superposition of the responses of the system to the various temperature changes at their respective times:

\[ T_f(t) = T_0 + \Delta T_1 [1 - \phi(t - t_1, t)] \]

\[ + \Delta T_2 [1 - \phi(t - t_2, t)] \]

\[ + ... + \Delta T_m [1 - \phi(t - t_m, t)] \]  \[ (10) \]

In the limit of a continuous change in temperature during heating or cooling at a rate

\[ q = \frac{dT}{dt} \]  \[ (11) \]
the summation in Eq. (1) becomes an integral and we get, using Eqs. (7) and (11),

\[ T_f(T) = T_o + \int_0^T \frac{\sigma}{\sigma_0} dI \left[ 1 - \exp\left[ -\frac{(\sigma/\sigma_0)^{1/2}}{\sigma_0} \right] \right] \]  \hspace{1cm} (12)

with the relaxation time \( \tau_0 \) given by Eq. (8). The integrals in Eq. (12) must be evaluated over the actual temperature-time path followed by the system, starting at a temperature \( T_o \) at which the system is in equilibrium.

In Fig. 2 is shown schematically the variation of enthalpy with temperature, as might be calculated from Eqs. (4) and (12), for a glass cooled and subsequently reheated through the glass transition region. At high temperatures (the region labelled "liquid") the rate of structural relaxation is so rapid that the system remains in equilibrium during heating or cooling, while at low temperatures (the region labelled "glass") the rate of relaxation is so slow as to have effectively ceased on the experimental time scale. Note that there is a hysteresis, so that the heating curve lies below the cooling curve. During the final stages of reheating the \( H-T \) curve approaches the equilibrium liquid curve rapidly from below, leading to a maximum in the measured heat capacity. Note also that via Eq. (4) the value of \( T_f \) at any point on the heating or cooling curve may be taken as the temperature of intersection with the equilibrium liquid \( H-T \) curve of a line drawn through the point parallel to the glass \( H-T \) curve, e.g., the fictive temperature for point a on the cooling curve is \( T_{fa} \). In cooling to low temperatures the fictive temperature eventually reaches a constant limiting value, \( T_f^* \), i.e., at low temperatures the glass structure is completely frozen in. The value of \( T_f^* \) is lower the lower the cooling rate \( q \), the relation between the two quantities being\(^{15,17}\)

\[ \frac{d \ln|q|}{d(1/T_f^*)} = -\Delta h*/R \]  \hspace{1cm} (13)

Note finally that \( T_f^* \) is the extrapolated temperature of intersection of the glass and equilibrium liquid \( H-T \) curves (cf. Fig. 2) and as such corresponds to the temperature frequently designated as the glass transition temperature, \( T_g \).

III. EXPERIMENTAL SECTION

A sample of 40 mol % Ca(NO\(_3\))\(_2\) - 60 mol % KNO\(_3\) glass was prepared as described previously\(^7\). A portion of this glass of mass 21.7 mg was crimp sealed into an Al sample pan, placed in a Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC), and a series of heat capacity scans carried out in the following fashion without removing the sample from the DSC. The sample was first heated to a temperature
well above the glass transition to erase its prior thermal history, after which it was cooled on the DSC at a constant rate to a temperature (300K) well below the glass transition. Immediately following this the heat capacity of the sample was measured while heating at a rate of 10 K/min through the same temperature range. Measurements were carried out following cools at seven different rates ranging from 0.31 to 20 K/min. Single crystal Al₂O₃ was used as a heat capacity calibration standard.

IV. RESULTS AND ANALYSIS

Typical heat capacity results for three prior cooling rates are shown in Fig. 3. The glass heat capacities, Cpg, were taken to be a linear function of temperature and fit to an equation of the form

\[ C_{pg} = a_g + b_g(T(K) - 300) \]

The equilibrium liquid heat capacities, Cpe, were taken to be constant. Values of \( a_g \), \( b_g \), and Cpe for the data of Fig. 3 are given in Table I. The Cpg and Cpe values obtained are in good agreement with those reported previously.

| prior cooling rate (K/min) | \( a_g \) (cal/gK) | \( b_g \) (cal/gK²) | Cpe (cal/gK) | T_f° (K) |
|---------------------------|-------------------|-------------------|--------------|----------|
| 0.62                      | 0.216             | 0.00031           | 0.359        | 335.0    |
| 2.5                       | 0.213             | 0.00049           | 0.361        | 337.8    |
| 10                        | 0.212             | 0.00040           | 0.355        | 339.1    |

The limiting fictive temperatures, \( T_f° \), attained by the glasses on cooling through the transition region were calculated by integrating Eq. (5) from a temperature \( T* \) (cf. Fig. 2) well above the transition region where \( T_f(T*) = T* \) to a temperature well below the transition region where \( T_f = \) constant = \( T_f° \). More complete details on this calculation are given in Ref. 17. \( T_f° \) values for the data of Fig. 3 are given in Table I. In Fig. 4 an Arrhenius plot of \( \log|q| \) where \( q \) is
the cooling rate, versus $10^3/T_f$ is shown; the plot is linear within experimental error, as suggested by Eq. (13). Also shown in Fig. 4 is an Arrhenius plot of the shear viscosity $\eta$ in the glass transition region. Within experimental error the two plots are parallel, so that the activation enthalpy $\Delta h^*$ for the structural relaxation (cf. Eq. (13)) may be taken equal to the activation enthalpy obtained from the more extensive shear viscosity data, 141 kcal/mol.

The other kinetic parameters for the structural relaxation in Eqs. (8) and (12), $A$, $x$, and $\beta$, can be determined by the method described in Ref. 18, summarized briefly as follows. Trial values of $A$, $x$, and $\beta$ are selected and Eq. (12) is integrated numerically to give $T_f(T)$ over a $T$-$t$ path starting at a temperature $T_0$ above the transition region and proceeding through the cooling and subsequent reheating at the experimental rates. Numerical differentiation of $T_f(T)$ gives $dT_f/dT$, which in turn via Eq. (5) gives the calculated $C_p$ versus $T$ curves during cooling and subsequent reheating. The $A$ parameter is varied to bring the calculated and experimental $T_f$ values into agreement, and the $x$ and $\beta$ parameters are varied to give agreement between the shapes of the calculated and experimental $C_p$ heating curves. The solid lines in Fig. 3 are the $C_p$ heating curves calculated in this fashion; the corresponding kinetic parameters are listed in Table II.

| prior cooling rate (K/min) | $10^8 A$ (s) | $\Delta h^*$ (kcal/mol) | $\beta$ | $x$ | $<t_H^e>$ (s) at 338K |
|-------------------------|-----------|---------------------|------|----|------------------|
| 0.62                    | 1.24      | 141                | 0.42 | 0.33| 5.4 x $10^3$    |
| 2.5                     | 1.08      | 141                | 0.48 | 0.36| 3.5 x $10^3$    |
| 10                      | 1.21      | 141                | 0.48 | 0.24| 4.0 x $10^3$    |

The three heat capacity curves of Fig. 3 are independent sets of data on the same system and should yield on analysis the same kinetic parameters within experimental uncertainty. Within these limits the agreement among the three sets of parameters in Table II is acceptable, particularly the relaxation times. In the last column of Table II the average equilibrium enthalpy structural relaxation times, $<t_H^e>$, at 338K (approximately the mean value of $T_f$ or $T_g$ for these data) are compared, where $<t_H^e>$ has been calculated from the expression.
and \( x_0 \) is the value of \( \tau_0 \) in Eq. (8) at equilibrium, i.e., for \( T_f = T \):

\[
\tau_{oe} = A \exp(\Delta h^*/RT)
\]

(16)

The mean value of \( <\tau_{He}> \) at 338K is \((4.3 \pm 1.0) \times 10^3 \) s, which corresponds via Eqs. (15) and (16) to an uncertainty in the position of the calculated Cp curves along the T axis of about 0.3K, i.e., approximately the thickness of the solid lines in that figure.

IV. DISCUSSION

The agreement between the \( \Delta h^* \) values for enthalpy structural relaxation and for shear viscosity is typical; similar agreement has been observed for a wide variety of other glass-formers including network oxide glasses\(^{15-17,20,21}\), chalcogenide glasses\(^{22}\), organic liquids\(^1\), and amorphous polymers\. This presumably indicates that somewhat similar molecular motions are involved in viscous flow in response to imposed shear stresses and in the rearrangement of the structure of the vitreous system in response to temperature changes. On the other hand, the time scales for the two types of response are markedly different. In Fig. 4 is shown an Arrhenius plot of the mean relaxation time, \( <\tau_s> \), for shear stress in response to imposed shear strains calculated from the data of Ref. 11 and the relation

\[
<\tau_s> = \eta / G_o
\]

(17)

where \( G_o \) is the solid-like shear modulus. This may be compared with a similar plot for the mean equilibrium enthalpy structural relaxation time calculated from the parameters of Table II and Eqs. (15) and (16). \( <\tau_{He}> \) is longer than \( <\tau_s> \) by a factor of about 330. This result, \( <\tau_{He}> > <\tau_s> \), is also typical of other glasses of a wide variety of types\(^{20,21}\) and reflects in part that the two times are not strictly comparable\(^{21,23}\). That is, \( <\tau_s> \) is a relaxation time for a stress in response to an imposed strain, while \( <\tau_{He}> \) is a relaxation time for a "strain" (\( \Delta H \)) in response to an imposed "stress" (\( \Delta T \)).

The \( \beta \) parameter in Eqs. (7) and (12) is a measure of the width of the spectrum of relaxation times needed to describe the relaxation process. For the linear case close to equilibrium (\( T_f = T \)) the iso-thermal relaxation function of Eq. (7) would become

\[
\phi_e(t-t_1) = \exp\left\{-\left[(t-t_1)/\tau_{oe}\right]^{\beta}\right\}
\]

(18)
This could be written equivalently in terms of a spectrum of relaxation times

$$\phi_e(t-t_1) = \int_{-\infty}^{\infty} \frac{d\ln(t)}{t_{oe}} g(\frac{t}{t_{oe}}) \exp\left\{-\frac{(t-t_1)}{\tau}\right\}$$

(19)

where $g(\ln(t_{oe}))$ is the probability density function for relaxation times, i.e.,

$$g(\ln(t_{oe})) \frac{d\ln(t_{oe})}{t_{oe}} = \text{fraction of relaxation times with values between } \ln(t_{oe}) \text{ and } (\ln(t_{oe}) + d\ln(t_{oe}))$$

A measure of the width of the spectrum of relaxation times is then the standard deviation of the logarithm of the relaxation times from their mean:

$$D(\ln(\tau)) = \int_{-\infty}^{\infty} \frac{d\ln(t_{oe})}{t_{oe}} g(\frac{t}{t_{oe}}) \ln^2(t) - \left[ \int_{-\infty}^{\infty} \frac{d\ln(t_{oe})}{t_{oe}} g(\frac{t}{t_{oe}}) \ln(t) \right]^2$$

$$= \left[ \langle \ln^2(\tau) \rangle - \langle \ln(\tau) \rangle^2 \right]^{1/2}$$

(20)

where the brackets $\langle \rangle$ denote, as usual, mean values. Values of $D(\ln(\tau))$ as a function of $\beta$ have been calculated and reported in previous publications $^{19,24}$.

In Table III values of $\beta$ and the corresponding $D(\ln(\tau))$ for the enthalpy structural relaxation are compared for a number of glasses.

| Glass                  | $\beta$ | $D(\ln(\tau))$ | Reference |
|------------------------|---------|-----------------|-----------|
| $B_2O_3$               | 0.65    | 1.50            | 16,18     |
| 0.25 Na$_2$O/K$_2$O-0.75SiO$_2$ | 0.66    | 1.46            | 20        |
| 5-phenyl-4-ether       | 0.70    | 1.31            | 21        |
| As$_2$Se$_3$           | 0.67    | 1.42            | 21        |
| poly(vinylacetate)    | 0.51    | 2.15            | 22        |
| 0.4Ca(NO$_3$)$_2$-0.6KNO$_3$ | 0.42-0.48 | 2.74-2.33      | present work |

The spectrum of enthalpy structural relaxation times in 0.4 Ca(NO$_3$)$_2$-0.6 KNO$_3$ glass is much broader than that observed for molecular glasses (5-phenyl-4-ether) and network glasses ($B_2O_3$, As$_2$Se$_3$, alkali silicate) and somewhat broader even than that for the amorphous polymer poly(vinylacetate).
The thermodynamics of the structural relaxation, i.e., of the glass transition, are frequently explained in terms of an order parameter model in which it is presumed that the state of the vitreous system needs to be specified in terms of \( N \) order parameters, \( Z_1, Z_2, \ldots, Z_N \), in addition to \( T \) and \( P \), so that the Gibbs free energy is of the form

\[
G = G(T, P, Z_1, Z_2, \ldots, Z_N) \tag{21}
\]

The microscopic significance of the order parameters at present cannot be unambiguously specified, but might correspond to such things as the number of "holes" and the number of flexed bonds in polymers, the number of cations with a given nearest neighbor coordination configuration in a fused salt, etc. It is presumed that the change of the order parameters in response to changes in \( T \) and \( P \) is kinetically impeded. Hence at point \( (T_0, P_0) \) on the equilibrium liquid free energy surface subjecting the liquid to instantaneous changes in \( T \) and/or \( P \) freezes in the order parameter at the equilibrium value at \( (T_0, P_0) \). Since the equilibrium liquid is never thermodynamically unstable with respect to the glass, the condition must apply

\[
G_g \geq G_e \text{ for } (T, P) \neq (T_0, P_0) \tag{22}
\]

This in turn may be shown to lead to an expression known as the Prigogine-Defay condition:

\[
\Pi = \frac{\Delta C_p}{\Delta \kappa_T} \frac{\Delta \kappa_T}{TV(\Delta \alpha)^2} \geq 1 \tag{23}
\]

where \( \kappa_T \) is isothermal compressibility, \( V \) is volume, \( \Delta C_p = C_{pe} - C_{pg} \), and similarly for the differences between equilibrium liquid and glass thermal expansion coefficients and isothermal compressibilities, \( \Delta \alpha \) and \( \Delta \kappa_T \). The equality in Eq. (23) applies either (a) when only a single order parameter is needed to specify the state of the system or (b) when two or more order parameters are needed which satisfy the condition for all \( i \) and \( k \):

\[
\frac{\partial \Pi}{\partial Z_i} / \left( \Delta \Pi / \Delta Z_i \right) = \frac{\partial \Pi}{\partial Z_k} / \left( \Delta \Pi / \Delta Z_k \right) \tag{24}
\]

The inequality applies for the case of two or more order parameters which do not satisfy this condition.

For 0.4 Ca(NO₃)₂ - 0.6 KNO₃ glass using the data in the present paper and in the literature in or near the glass transition region we have

\[
\begin{align*}
T &= 340K \\
V &= 4.56 \times 10^{-4} \text{ m}^3/\text{kg} \\
\Delta C_p &= 5.4 \times 10^2 \text{ J/kg K} \\
\Delta \alpha &= 2.3 \times 10^{-4} \text{ K}^{-1} \\
\Delta \kappa_T &= 6.9 \times 10^{-11} \text{ m}^2/\text{N}
\end{align*}
\]
so that $\Pi = 4.5$. Sufficient data exists in the literature to evaluate $\Pi$ accurately for two other glasses in the transition region\textsuperscript{20,28}: $\text{B}_2\text{O}_3 (\Pi=4.7)$ and poly(vinylacetate) ($\Pi=2.2$). Hence it appears in general that $\Pi > 1$ for glass forming liquids, i.e., the state of these systems requires a description in terms of two or more order parameters which do not satisfy Eq. (24).

A connection between the thermodynamics and the kinetics of the structural relaxation may be made by expressing the rate of change of $V$ or $H$ during the structural relaxation in terms of the rate of evolution of the order parameters:

$$\frac{dV}{dt} = \sum_{i=1}^{N} \frac{\partial V}{\partial Z_i} \frac{dZ_i}{dt} \tag{25}$$

$$\frac{dH}{dt} = \sum_{i=1}^{N} \frac{\partial H}{\partial Z_i} \frac{dZ_i}{dt} \tag{26}$$

One may then attribute the apparent distribution of structural relaxation times to the fact that the various order parameters relax with different relaxation times, i.e.,

$$\frac{d\ln(Z_i - Z_{i\epsilon})}{dt} = -\frac{1}{\tau_i} \neq \frac{d\ln(Z_k - Z_{ke})}{dt} = -\frac{1}{\tau_k} \tag{27}$$

For a system, such as the one studied here, for which $\Pi > 1$ Eq. (24) is not satisfied, so that the ($\partial V/\partial Z_i$) and ($\partial H/\partial Z_i$) in Eqs. (25) and (26) are not proportional term for term. This in turn leads one to expect different kinetic parameters (i.e., different $\alpha$ and $\beta$ values) for the structural relaxation monitored in terms of enthalpy and volume. At present there is no accurate set of relaxational data for both $H$ and $V$ for a glass-forming system for which the value of $\Pi$ is accurately known. Acquisition of such a complete set of data may be counted an undertaking of some importance, since it will provide a test of the connection between the thermodynamics and kinetics of the structural relaxation suggested here.

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REFERENCES

1. H. Rawson, "Inorganic Glass-Forming Systems", Academic Press, New York, NY, 1967.
2. C.A. Angell, J. Phys. Chem., 70, 2793 (1966).
3. C.A. Angell, J. Am. Ceram. Soc., 51, 117 (1968).
4. L.G. van Uitert and W.H. Grodkiewicz, Mat. Res. Bull., 6, 283 (1971).
5. L.G. van Uitert, W.A. Bonner, and W.H. Grodkiewicz, Mater. Res. Bull., 6, 513 (1971).
6. A.J. Easteal and C.A. Angell, J. Phys. Chem., 74, 3987 (1970).
7. K.J. Rao, D.B. Helphrey, and C.A. Angell, Phys. Chem. Glasses, 14, 26 (1973).
8. R.H. Doremus, "Glass Science", John Wiley and Sons, Inc., New York, 1973.
9. E. Rhodes, W.E. Smith, and A.R. Ubbelohde, Trans. Faraday Soc., 63, 1943 (1967); Rev. Int. Hautes Temp. Refract., 4, 231 (1967).
10. R. Weiler, R. Bose, and P.B. Macedo, J. Chem. Phys., 53, 1258 (1970).
11. H. Tweer, N. Laberge, and P.B. Macedo, J. Am. Ceram. Soc., 54, 1211 (1971).
12. G.M. Glover and A.J. Matheson, Trans. Faraday Soc., 67, 1960 (1971).
13. F.S. Howell, R.A. Bose, P.B. Macedo, and C.T. Moynihan, J. Phys. Chem., 78, 639 (1974).
14. A. Weitz and B. Wunderlich, J. Polym. Sci: Polym. Phys., 12, 2473 (1974).
15. C.T. Moynihan, A.J. Easteal, J. Wilder, and J. Tucker, J. Phys. Chem., 78, 2673 (1974).
16. C.T. Moynihan, P. Macedo, N. Saad, M. DeBolt, B. Dom, A. Easteal, and J. Wilder, Fizika i Khimiya Stekla, 1, 420 (1975).
17. C.T. Moynihan, A.J. Easteal, M.A. DeBolt, and J. Tucker, J. Am. Ceram. Soc., 59, 12 (1976).
18. M.A. DeBolt, A.J. Easteal, P.B. Macedo, and C.T. Moynihan, J. Am. Ceram. Soc., 59, 16 (1976).
19. C.T. Moynihan, L.P. Boesch and N.L. Laberge, Phys. Chem. Glasses, 14, 122 (1973).
20. C.T. Moynihan, A.J. Easteal, D.C. Tran, J.A. Wilder, and E.P. Donovan, J. Am. Ceram. Soc., 59, 137 (1976).
21. C.T. Moynihan, P.B. Macedo, C.J. Montrose, P.K. Gupta, M.A. DeBolt, J.F. Dill, B.E. Dom, P.W. Drake, A.J. Easteal, P.B. Elterman, R.P. Moeller, H. Sasabe, and J.A. Wilder, Proceedings of the Workshop on the Glass Transition and the Nature of the Glassy State, R. Simha and M. Goldstein, Eds., New York Academy of Sciences, in press.
22. H. Sasabe and C.T. Moynihan, Repts. Prog. Polym. Phys. Japan, in press.
23. N.G. McCrum, B.E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, 1967.
24. L.P. Boesch and C.T. Moynihan, J. Non-Cryst. Solids, 17, 44 (1975).
25. R.O. Davies and G.O. Jones, Adv. Phys., 2, 370 (1953).
26. M. Goldstein, J. Chem. Phys., 39, 3369 (1963).
27. M. Goldstein, J. Appl. Phys., 46, 4153 (1973).
28. P.K. Gupta and C.T. Moynihan, J. Chem.Phys., in press.
Figure 1. Response of enthalpy and fictive temperature to an instantaneous temperature change.

Figure 2. Variation of enthalpy with temperature during cooling and subsequent reheating through the glass transition region.
Figure 3. Heat capacity during heating at 10K/min of 0.4Ca(NO$_3$)$_2$ - 0.6KNO$_3$ glass following cooling at different rates. $C_p$ scales is correct for curve (c); curves (a) and (b) have been displaced upward by 0.2 and 0.1 cal/gK respectively.

Figure 4. Arrhenius plots of cooling rate versus limiting fictive temperature and of mean equilibrium enthalpy relaxation time, shear viscosity, and mean shear stress relaxation time versus temperature for 0.4Ca(NO$_3$)$_2$ - 0.6KNO$_3$ melt.