

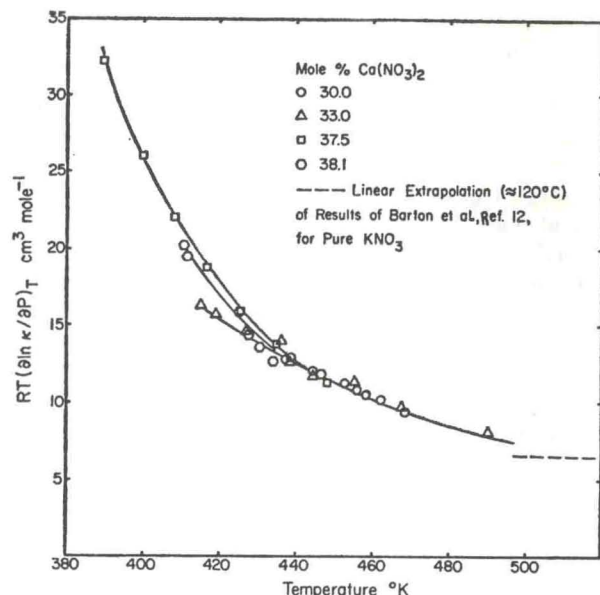


FIG. 7. Dependence of the "activation volume," $RT(d \ln \kappa / dP)_T$ between 1 and 1000 bar] on temperature for $\text{Ca}(\text{NO}_3)_2 + \text{KNO}_3$ solutions.

The data of Fig. 6 suggest T_0 may be the only pressure-dependent parameter in the transport equation, Eq. (2). If the dependence on pressure is linear, as suggested by our limited data and also various previous studies of the pressure dependence of the experimental glass transition temperature,^{36,37} then Eq. (2) can be modified to describe pressure as well as temperature dependence, according to

$$\Lambda = A_\Lambda T^{-1/2} \exp\{-k/[T - (T_0 + bP)]\}, \quad (6)$$

where b is a constant, ($8^\circ\text{K}/\text{kbar}$ in this instance).

Equation (6) provides an explanation of the non-linearity of the lower-temperature plots of Figs. 1-3 since differentiation after taking logs yields

$$(\partial \ln \Lambda / \partial P)_T = -bk / (T - T_0 - bP)^2. \quad (7)$$

Thus when $T - T_0$ is small, the pressure term will lead to decidedly pressure-dependent slopes for $\log \Lambda$ vs P plots. The linearity observed¹⁰⁻¹² at high temperatures (more accurately, at high T/T_0 values) is analogous to the Arrhenius behavior observed at high temperatures for constant pressure measurements. The parallel implies that the meaning of the "activation volume" parameter is no less obscure than that of the "activation energy" parameter now often referred to non-committally as the "Arrhenius coefficient". For sake of comparison with other data, however, we plot in Fig. 7 the "activation volumes" obtained from the average slope over the first 1000 bar pressure for each composition studied, as a function of temperature. The contrast between "high" (alkali nitrates above T_m)

and "low" (present results) temperature behavior is further emphasized by the strong and nonlinear temperature dependence of this volume parameter (cf., a weak linear dependence for alkali nitrates).^{11,12}

An interesting feature of Fig. 7 is the common value for the "activation volume" and (less certainly) its temperature dependence which is reached by the various compositions at higher temperatures, a result which is also expected from Eq. (7) for $T \gg T_0$ when b and k are only weakly dependent on composition and pressure. This common value seems to be approaching that of pure KNO_3 ,¹² a result which lends some support to the idea, employed above, of estimating solution compressibilities from data on pure KNO_3 .

An equation similar to Eq. (6) has previously been proposed by one of us³⁸ to describe the joint effects of composition and temperature changes on the equivalent conductance in this system. It was found then that a choice of T_0 varying linearly with mole % $\text{Ca}(\text{NO}_3)_2$ at a rate of $2.01^\circ\text{K}/\text{mole } \%$ was sufficient to reduce all the composition-temperature data to a single straight line in a Fig. 6 type plot. The T_0 values themselves were definable by the linearity to $\pm 2^\circ\text{K}$.^{7a} It would seem appropriate then to combine the two equations to obtain a simple (one constant per variable) description of conductance in this system. However, recent determinations³⁹ of the experimental glass transition temperature, T_g , between 25% and 45% $\text{Ca}(\text{NO}_3)_2$ find T_g varying at the rate of only $1.6^\circ\text{deg}/\text{mole } \%$. It is readily shown that when k is small the composition dependence of T_0 must give the composition dependence of T_0 more accurately than it can be analyzed from the conductance data (the changes in T_0 neces-

³⁶ J. M. O'Reilly, J. Polymer. Sci. 57, 429 (1962).

³⁷ E. Pasaglia and G. M. Martin, J. Res. Natl. Bur. Std. 68A, 273 (1964).

³⁸ C. A. Angell, J. Chem. Phys. 46, 4673 (1967).

³⁹ C. A. Angell, J. Wong, and D. B. Helphrey (unpublished).

sary to give the new dependence are within the assigned uncertainties). Now if T_0 changes with composition at 1.6 rather than 2.01 deg/mole % $\text{Ca}(\text{NO}_3)_2$ then k cannot be independent of composition, and in fact must increase 12% in the range 33%–45% $\text{Ca}(\text{NO}_3)_2$. Thus while it is possible to describe with good accuracy the available conductance data by an equation with T_0 the only variable, it seems undesirable to do so.

It is wholly possible that pressure studies of T_0 to be performed later will reveal a similar correction necessary to dT_0/dP , and accordingly a small pressure dependence of k in Eq. (6). However, here an interesting check is possible. If, as Gibbs and co-workers suggest^{13,19} T_0 is the temperature of a second order thermodynamic transition, the following relationship (due to Ehrenfest)⁴⁰ should hold

$$dT_0/dP = T_0 V_{T_0} (\Delta\alpha/\Delta C_p), \quad (8)$$

where V_{T_0} is the molar volume at T_0 and $\Delta\alpha$ and ΔC_p are the changes in expansion coefficient and molar heat capacity accompanying the transition. Goldstein²⁸ points out that the equivalent of Eq. (8) should hold at the experimental transition temperature, T_g , also if the transition occurs at some critical value of the excess heat content or entropy. Experimentally it is found that Eq. (8) is obeyed at T_g by a variety of glass-forming materials.³⁶ On this basis we predicted in our preliminary communication of these results¹⁴ a value for ΔC_p for 38% $\text{Ca}(\text{NO}_3)_2 + 62\%$ KNO_3 glass of 20.0 cal mole⁻¹·deg⁻¹ or 0.16 cal g⁻¹·deg⁻¹. Based on our later assessment of dT_0/dP of 8 ± 2 deg kbar⁻¹, the predicted value of ΔC_p becomes 0.10 ± 0.02 cal g⁻¹·deg⁻¹. To check this value de Neufville,⁴¹ working in Turnbull's laboratory, has kindly determined a ΔC_p for this glass by differential scanning calorimetry. Their

⁴⁰ P. Ehrenfest, Commun. Kamerlingh Onnes Lab. Univ. Leiden, 756 (1933); H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960).

⁴¹ J. de Neufville (private communication).

value of 0.12 ± 0.01 cal g⁻¹·deg⁻¹ is within the uncertainty limits and thus tends to confirm that k in Eq. (6) is at worst a rather weak function of pressure.

Since it seems clear at least that T_0 is a linear function of the composition and pressure variables, it is worth emphasizing the implied equivalence of these factors in changing the thermodynamic state of the liquid. One kbar increase of pressure is evidently as effective in reducing S_c towards zero as is 8.0/1.6, or 5.0, mole % increase of $\text{Ca}(\text{NO}_3)_2$, each of which is equivalent to 8.0°K drop in temperature.

Concluding Remarks

It is somehow impressive that the magnitude of a thermodynamic quantity (ΔC_p) should be predictable from transport measurements performed, at the nearest point, almost 100°C above the temperature of the event with which the prediction is concerned. This encourages belief that the recently noted⁴² return of some liquids to Arrhenius behavior at high viscosities, in conflict with the requirements of Eq. (1), indicates a need for refinements to, rather than abandonment of, theories with T_0 as a basic parameter. In support of this position we note⁴³ that T_0 parameters extracted from transport data covering the first 1–3 orders of magnitude of charge of transport constants with decreasing temperature, are in pleasing agreement with estimates, from thermal data alone, of the temperature [$T_0(\text{cal})$] at which the total entropy of the amorphous phase at equilibrium would reach that of the crystalline phase at the same temperature, i.e., $S_c \approx 0$, $S_{\text{vib}}(\text{glass}) = S_{\text{vib}}(\text{crystal})$. These estimates of T_0 , unlike those from transport data near the glass transition temperature⁴² are almost independent of the temperature interval over which the liquid heat capacity is measured.

⁴² P. B. Macedo (private communication); W. T. Laughlin and D. R. Uhlmann (private communication).

⁴³ C. A. Angell and C. T. Moynihan, *Characterization and Analysis in Molten Salts*, G. Mamantov, Ed. (Marcel Dekker Inc., New York, to be published).