

A unified theory for studying chemical relaxation by using light scattering or ultrasonic absorption experiments

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A unified theory for studying dissolution of oxides in glass melts by using light scattering or ultrasonic absorption experiments has been derived from irreversible thermodynamic fluctuation theory: The study of such reactions will permit the identification of changes in cation coordination number and changes in reaction rates. From this theoretical model one can predict the physical and chemical properties of glass which are governed by the reaction.

1. Introduction

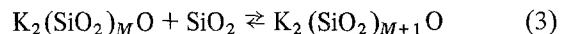
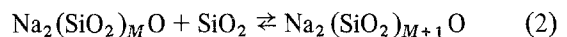
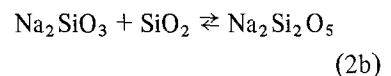
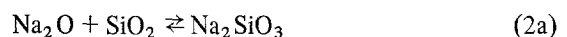
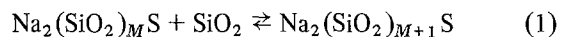
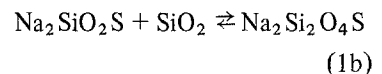
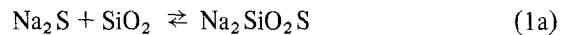
Since chemical reactions are so important in determining the forming characteristics as well as the physical and chemical properties of a glass, it seems that a more quantitative study of the chemical reactions in glass is desirable.

Recently Ray [1] has shown that increasing the coordination number of the cation would increase the glass transformation temperature in a highly cross-linked oxide glass like silica. Topping [2] also showed that changes of cation coordination in the reaction of an oxide with an oxide glass system would affect the elastic properties of the glasses, such as modulus.

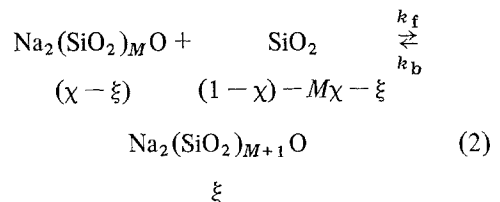
A unified theory for studying chemical reactions by using light-scattering or ultrasonic-absorption experiments has been derived from irreversible thermodynamic fluctuation theory. Use of the theory assumes that only one reaction dominates the situation in any system to which it is applied. Predicted results were compared with literature results for sodium borate and sodium germanate glasses. Good agreement was found.

2. Chemical reactions and thermodynamic fluctuation theory

Several chemical reactions in the melting of glass batch have been investigated [3, 4]. The following equations present a few of these involving dissolution of solid silica in glass melts.



In particular, if we consider Reaction 2, we can write the reaction as



Then if the total mole fraction Na_2O , considered either to be in the form $\text{Na}_2(\text{SiO}_2)_M\text{O}$ or $\text{Na}_2(\text{SiO}_2)_{M+1}\text{O}$ is χ , and ξ is the mole fraction of the latter species, the rate equation is

$$\frac{d\xi}{dt} = k_f(\chi - \xi)[(1 - \chi) - M\chi - \xi] - k_b\xi \quad (4)$$

Here k_f and k_b are the forward and backward reaction rates and $[(1-\chi) - M\chi - \xi]$ is the concentration of "free" silica molecules in the solution. At equilibrium

$$(\chi - \xi^{(0)})[(1-\chi) - M\chi - \xi^{(0)}] - \frac{1}{K} \xi^{(0)} = 0 \quad (5)$$

where

$$K \equiv \frac{k_f}{k_b} = \exp(-\Delta G^*/RT) \quad (6)$$

ΔG^* is the Gibbs free energy difference between the left-hand side and right-hand side of the reaction, R is the gas constant, and T is the temperature. Solving Equation 5 gives

$$\xi^{(0)} = \frac{1}{2} \left(1 - M\chi + \frac{1}{K} \right) - \frac{1}{2} \left\{ \left(1 - M\chi + \frac{1}{K} \right)^2 - 4\chi[1 - (M+1)\chi] \right\}^{1/2} \quad (7)$$

In the present case, knowledge of the mole fraction of $\text{Na}_2(\text{SiO}_2)_{M+1}\text{O} = \xi$ at equilibrium should define the thermodynamic state of the chemical reaction concerned. If it is assumed that this reaction totally dominates all other possible reactions, then knowledge of ξ closely approximates the thermodynamic state of the whole system. ξ is thus the only important ordering parameter for the system.

In reality, $\xi^{(0)}$ can be thought of as an average value of ξ for the particular thermodynamic system when at equilibrium. The true value of ξ at any point in the system has a finite probability of being slightly different from $\xi^{(0)}$ at a given time. This is a dynamic situation in which values of ξ are continually varying on either side of $\xi^{(0)}$ in any given sub-system of the thermodynamic system. If the system is at thermodynamic equilibrium, the summation of these dynamically-varying values of ξ for all of the sub-systems must continually average $\xi^{(0)}$. This fluctuating nature of a thermodynamic system at equilibrium can be characterized by the mean square fluctuation of the ordering parameter for the system.

From the thermodynamic fluctuation theory the mean square fluctuation of an ordering parameter [5, 6] for a chemical reaction is

$$\langle(\Delta\xi)^2\rangle = \frac{kT}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{PT\chi}} = -\frac{kT}{\left(\frac{\partial A}{\partial \xi}\right)_{PT\chi}}, \quad (8)$$

where k is Boltzmann's constant and A the affinity.

Following Bauer [6] and Lamb [7] the ordering coefficient for an ideal mixture is

$$\phi = \left(\frac{\partial A}{\partial \xi}\right)_{PT\chi} = \left[\frac{-kT}{V} \sum_i \frac{(\Delta\nu_i)^2}{\chi_i} - \left(\sum_i \Delta\nu_i\right)^2 \right] \quad (9)$$

where V is the volume, χ_i is the mole fraction of substance i and $\Delta\nu_i = \nu'_i - \nu_i$ is the difference of the right and left stoichiometric coefficients ν'_i and ν_i of substance i .

Hence, from Equations 8 and 9 the mean square fluctuation in the ordering parameter is

$$\langle(\Delta\xi)^2\rangle = V \left[\sum_i \frac{(\Delta\nu_i)^2}{\chi_i} - \left(\sum_i \Delta\nu_i\right)^2 \right]^{-1} \quad (10)$$

3. Theory of light scattering in chemical relaxation

This section will consider how light scattering measurements can be used to experimentally characterize $\langle(\Delta\xi)^2\rangle$.

The total intensity of light scattered by a two-component fluid can be written by [8, 9]

$$\begin{aligned} I_T \propto & \left(\frac{\partial \epsilon}{\partial \rho}\right)_{T\chi}^2 \frac{kT}{V\beta_s} + \left(\frac{\partial \epsilon}{\partial T}\right)_{P\chi} \frac{kT^2 \beta_T}{V\rho C_p \beta_s} \\ & + 2 \left(\frac{\partial \epsilon}{\partial \rho}\right)_{T\chi} \left(\frac{\partial \epsilon}{\partial T}\right)_{P\chi} \frac{kT^2 \alpha}{V\rho C_p \beta_s} \\ & + \left(\frac{\partial \epsilon}{\partial \chi}\right)_{PT}^2 \frac{kT}{N' \left(\frac{\partial \mu}{\partial \chi}\right)_{PT}} \end{aligned} \quad (11)$$

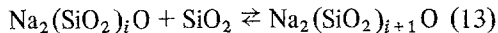
or

$$I_T \propto \left(\rho \frac{\partial \epsilon}{\partial \rho}\right)_\chi \frac{kT\beta_T}{V} + \left(\frac{\partial \epsilon}{\partial \chi}\right)_{PT}^2 \frac{kT}{N' \left(\frac{\partial \mu}{\partial \chi}\right)_{PT}} \quad (12)$$

where ϵ is the dielectric constant, μ is the chemical potential, ρ is the density, N' is the number of moles of solvent, χ is the concentration of the solute, and α , β_T , β_s , and C_p are the thermal expansion coefficient, the isothermal compressibility, the adiabatic compressibility and the specific heat per unit mass at constant pressure.

However, if there is any chemical reaction, such

as the dissolution of silica in an oxide melt (see Equation 2), one is forced to abandon the concept of a simple binary mixture and to regard the solution as a multicomponent system composed of silica and a number of solvated species, typically $\text{Na}_2(\text{SiO}_2)_i\text{O}$ with $i = 0, 1, 2, \dots, m$. The equilibrium concentration of each species $\xi_i^{(0)}$ is determined by the equilibrium of a set of dissolution reactions of the form;



Therefore, Hsich *et al.* [8] concluded that fluctuation in these concentration variables lead to fluctuations in the dielectric constant $\Delta\epsilon$ (in addition to those resulting from fluctuations in temperature and pressure). A convenient set of variables in which to expand $\Delta\epsilon$ are the mole fraction of solute χ and the concentrations of the solvated species $\xi_1, \xi_2, \dots, \xi_m$:

$$\Delta\epsilon = \left(\frac{\partial\epsilon}{\partial\chi}\right)_{PT\xi} \Delta\chi + \sum_{i=1}^m \left(\frac{\partial\epsilon}{\partial\xi_i}\right)_{PT\chi\xi_j'} \Delta\xi_i \quad (14)$$

Where the subscript ξ denotes differentiation holding all the ξ_j constant and ξ_i' holding all but $\xi_j = \xi_i$ constant. The quantities $\Delta\xi_i = \xi_i - \xi_i^{(0)}$ are the fluctuations in concentration of the i -solvated species and can be regarded as fluctuations in the progress variables describing the Reactions 13. The fluctuation $\Delta\epsilon$ in Equation 14 leads to the scattered light intensity caused by the total concentration fluctuation of all solvate species. Therefore, the second term of Equation 12 can be rewritten as

$$\begin{aligned} I' &\propto \left(\frac{\partial\epsilon}{\partial\chi}\right)_{PT\xi}^2 \langle(\Delta\chi)^2\rangle + \\ &2 \left(\frac{\partial\epsilon}{\partial\chi}\right)_{PT\xi} \sum_{i=1}^m \left(\frac{\partial\epsilon}{\partial\xi_i}\right)_{PT\chi\xi_j'} \langle\Delta\chi\Delta\xi_i\rangle \\ &+ \sum_{i,j=1}^m \left(\frac{\partial\epsilon}{\partial\xi_i}\right)_{PT\chi\xi_j'} \left(\frac{\partial\epsilon}{\partial\xi_j}\right)_{PT\chi\xi_i'} \langle\Delta\xi_i\Delta\xi_j\rangle \quad (15) \end{aligned}$$

However, if only one chemical reaction dominates in the reaction process, there is only one ordering parameter ξ which is important in the system. If in addition, fluctuations in ξ are uncorrelated with those in χ , the total intensity due to the dissolution reaction is

$$I_\xi = \left(\frac{\partial\epsilon}{\partial\xi}\right)_{PT\chi}^2 \langle(\Delta\xi)^2\rangle \quad (16)$$

When we put Equation 10 in the above equation, then

$$I_\xi \propto \left[\sum_i \frac{(\Delta\nu_i)^2}{\chi_i} - \left(\sum_i \Delta\nu_i \right)^2 \right]^{-1} \quad (17)$$

Thus, for the reaction given by Equation 2, the Rayleigh intensity due to the mean square fluctuation of the ordering parameter for the chemical reaction is

$$I_\xi \propto \left[\frac{1}{\chi - \xi^{(0)}} + \frac{1}{(1-\chi) - M\chi - \xi^{(0)}} + \frac{1}{\xi^{(0)}} - 1 \right]^{-1} \quad (18)$$

Following the method of Hsich *et al.* [8], the total scattered light intensity other than the intensity caused by the chemical reactions can be calculated from the Rayleigh and Brillouin light scattering spectra. Then the additional intensity due to the chemical reaction can be calculated by using Equation 18.

4. The theory of ultrasonic absorption in chemical relaxation

Ultrasonic absorption measurements can also be used to characterize $\langle(\Delta\xi)^2\rangle$ for a system.

The maximum ultrasonic absorption per wavelength μ_{\max} is given by [10, 11]

$$\mu_{\max} = \frac{\pi}{2} \left(\frac{\delta\beta_s}{\beta_s} \right) \quad (19)$$

where $\delta\beta_s = \beta_s - \beta_s^\infty$ is the difference between the equilibrium and instantaneous adiabatic compressibilities.

Following Bauer [9] $\delta\beta_s$ is given by

$$\delta\beta_s = -\frac{1}{V} \left(\frac{\partial V}{\partial\xi} \right)_{PS\chi}^2 \left(\frac{\partial\xi}{\partial A} \right)_{PS\chi} \quad (20)$$

The pertinent expressions can be expressed in terms of thermodynamical quantities as follows [9]:

$$\left(\frac{\partial V}{\partial\xi} \right)_{PS} = \Delta V - \frac{\nu^* a^\infty}{C_p^\infty} \Delta H \quad (21)$$

and

$$\left(\frac{\partial\xi}{\partial A} \right)_{PS} = \frac{C_p^\infty}{C_p} \frac{1}{\left(\frac{\partial A}{\partial\xi} \right)_{PT\chi}} \quad (22)$$

In Equations 21 and 22, $\Delta V = (\partial V/\partial \xi)_{PT\chi}$ indicates the amount by which the volume changes during an isothermal, isobaric unit reaction step,

$$\Delta H = \left(\frac{\partial H}{\partial \xi} \right)_{PT\chi}$$

is the heat of reaction change at constant temperature and pressure, C_p^∞ is the instantaneous heat capacity at constant pressure, α^∞ is the instantaneous thermal expansion, and ν^* is the molar volume. From these it follows that

$$\mu_{\max} = -\frac{\pi}{2V\beta_s} \frac{C_p^\infty}{C_p} \left[\Delta V - \frac{\nu^* \alpha^\infty \Delta H}{C_p^\infty} \right]^2 \frac{1}{\left(\frac{\partial A}{\partial \xi} \right)_{PT\chi}} \quad (23)$$

If Equation 20 is rewritten as follows

$$\delta\beta_s = \frac{1}{V} \frac{C_p^\infty}{C_p} \left(\frac{\partial V}{\partial \xi} \right)_{PS\chi}^2 \left(\frac{\partial \xi}{\partial A} \right)_{PT\chi} \quad (24)$$

$$= \frac{1}{kTV} \frac{C_p^\infty}{C_p} \left(\frac{\partial V}{\partial \xi} \right)_{PS\chi}^2 \langle (\Delta \xi)^2 \rangle \quad (25)$$

Then, Equation 19 can be rewritten as

$$\mu_{\max} = \frac{\pi}{2kTV\beta_s} \frac{C_p^\infty}{C_p} \left(\frac{\partial V}{\partial \xi} \right)_{PS\chi}^2 \langle (\Delta \xi)^2 \rangle \quad (26)$$

or

$$\mu_{\max} = \frac{\pi}{2kTV\beta_s} \frac{C_p^\infty}{C_p} \langle \Delta V(\xi)^2 \rangle \quad (27)$$

where

$$\Delta V(\xi) = \left(\frac{\partial V}{\partial \xi} \right)_{PS\chi} \Delta \xi$$

Equation 26 shows that changes in the chemical reaction ordering parameter ξ which lead to volume fluctuations cause excess ultrasonic attenuation. Equation 16 indicated that changes in ξ produce variations in the dielectric constant which lead to excess light scattering intensity. Thus, the mean square fluctuation of the chemical reaction ordering parameter $\langle (\Delta \xi)^2 \rangle$ plays an important role in both experiments.

5. Results and discussion

A detailed discussion of the effects of fluctuations in the ordering parameter describing a chemical

reaction in light scattering intensity and ultrasonic absorption has been given. This discussion has been thermodynamic in nature; it is now appropriate to consider briefly the kinetics of the reaction. In particular, the influence of fluctuations on the shape of the scattered light spectrum and on the frequency dependence of the ultrasonic absorption will be examined.

Following Lamb [11], assume a sinusoidal perturbation caused by a sound wave of frequency $f (= \omega/2\pi)$, causes $\delta\xi$ and δK , the amplitudes of the variations in ξ and K . Then replacing the time differential by $i\omega$, Equation 4 becomes approximately

$$i\omega d\xi = k_b(\chi - \xi^{(0)}) [1 - (M+1)\chi - \xi^{(0)}] \times \left[\delta K - \frac{1 + K(1 - M\chi - 2\xi^{(0)})}{(\chi - \xi^{(0)})[1 - (M+1)\chi - \xi^{(0)}]} \right] d\xi \quad (28)$$

$$\delta\xi = \frac{\xi^{(0)} \delta(\ln K)}{1 + K(1 - M\chi - 2\xi^{(0)})} \frac{1}{1 + i\omega\tau} \quad (29)$$

where the relaxation time τ is

$$\tau^{-1} = k_b + k_f(1 - M\chi - 2\xi^{(0)}) \quad (30)$$

From Landau and Lifshitz [5] the time correlation function of the chemical reaction ordering parameter is

$$\begin{aligned} \psi(t) &= \langle \Delta \xi(t_0) \Delta \xi(t_0 + t) \rangle \\ &= \langle (\Delta \xi)^2 \rangle \exp(-t/\tau) \end{aligned} \quad (31)$$

Then the line spectrum is just the Fourier transform of the time correlation function

$$I_\xi(\omega) \propto \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \psi(t) = \langle (\delta \xi)^2 \rangle \frac{\tau/\pi}{1 + \omega^2 \tau^2} \quad (32)$$

Therefore, the line shape of the light scattering intensity from the chemical reaction is a Lorentzian function centred at the position of the Rayleigh component. The half-width is equal to the inverse of the relaxation time τ .

This result differs from that previously obtained by Berne and Frisch [12] and Yeh and Keeler [13]. It appears that they may have oversimplified the chemical reaction model and obtained an expression for τ which was valid only in the low concentration limit.

It is interesting to note that Equation 18 predicts that the dissolution reaction intensity maximizes the concentration $\chi = [1 + (M+1)]^{-1}$. In

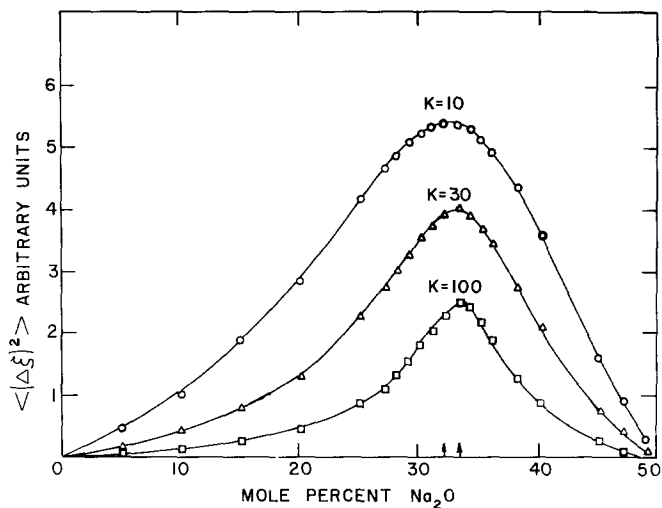


Figure 1 The fluctuation intensity $\langle (\Delta\xi)^2 \rangle$ plotted as a function of concentration for the reaction $\text{Na}_2(\text{SiO}_2) + \text{SiO}_2 \rightleftharpoons \text{Na}_2(\text{SiO}_2)_2\text{O}$.

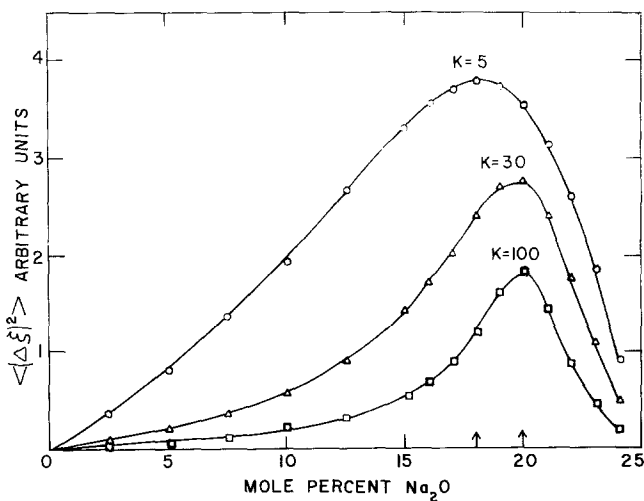


Figure 2 The fluctuation intensity $\langle (\Delta\xi)^2 \rangle$ plotted as a function of concentration for the reaction $\text{Na}_2(\text{SiO}_2)_3\text{O} + \text{SiO}_2 \rightleftharpoons \text{Na}_2(\text{SiO}_2)_4\text{O}$.

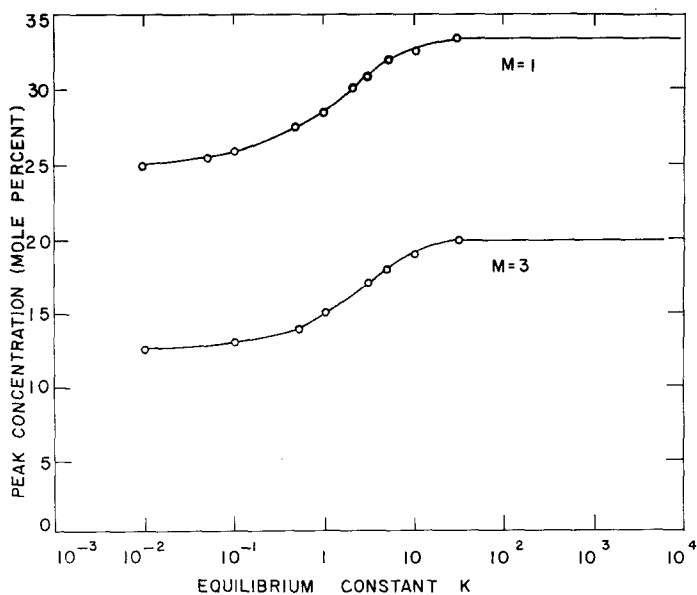


Figure 3 The position of the peak of the $\langle (\Delta\xi)^2 \rangle$ versus concentration curve χ plotted as a function of equilibrium constant K for both the $M=1$ and $M=3$ reactions.

addition as shown in Fig. 1, the shape of the curve depends rather sensitively on the equilibrium constant K . The mean square fluctuation of the chemical reaction ordering parameter $\langle(\Delta\xi)^2\rangle$ for two separate reactions, i.e. $M = 1$ and $M = 3$, was calculated from Equation 18 and is shown in Figs. 1 and 2. The results show that when the thermal equilibrium constant K is larger than certain values (in these two cases $K = 30$), then the peak of $\langle(\Delta\xi)^2\rangle$ is fixed at the mole fraction $\chi = [1 + (M + 1)]^{-1}$. Changing the value of K under these conditions affects only the strength and width of the maximum. When K is less than this certain value, i.e., $K < 30$, the peak shifts to the low concentration side as is shown in Fig. 3. For $K < 10^{-2}$ the plot of $\langle(\Delta\xi)^2\rangle$ versus χ showed two peaks. Whereas the appearance of a single peak at the stoichiometric concentration is easily understood in terms of optimizing the formation of the product of the reaction, there appears to be no simple picture that satisfactorily accounts for the appearance of two peaks when K is small. This approach differs slightly from that of Andreoe *et al.* [14] in that they have made a rather severe linearizing approximation in deriving their results. No such approximation was made in this work.

Light scattering intensity and ultrasonic absorption attenuation are only two of the properties which will be strongly influenced by fluctuations of the chemical reaction ordering parameter. If the model is a valid one for a given system, any of its physical properties which are dependent upon structure should show peaks in the properties which correlate with the dominant chemical reaction.

For example, as mentioned above, the mean square fluctuation of the thermodynamic ordering parameter, $\langle(\Delta\xi)^2\rangle$ is associated with changes of volume and compressibility as the chemical reaction occurs. As shown in Equation 25, $\langle(\Delta\xi)^2\rangle \propto \delta\beta_s$, where $\delta\beta_s$ is the difference between compressibilities in the equilibrium and non-equilibrium states. The physical properties of the glass were frozen in a non-equilibrium state when it was super-cooled from a higher temperature. Therefore, the compressibility of the glass is below the equilibrium state value. On the other hand, modulus, acoustic velocity, viscosity, and other physical properties could be increased by the chemical reactions. Their characteristic behaviour would parallel the behaviour of the mean square fluctuation of the ordering parameter $\langle(\Delta\xi)^2\rangle$ as shown

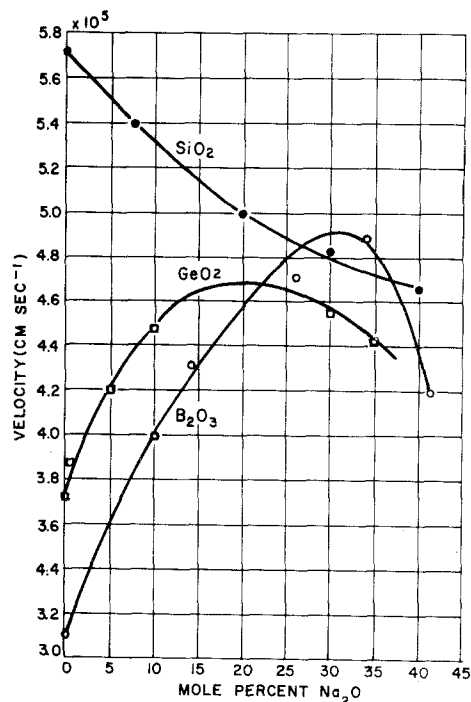
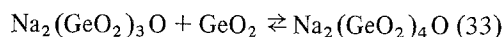


Figure 4 After Kurkjian and Krause, acoustic velocity versus composition at 25°C for sodium silicate and borate glasses from [16] (longitudinal) and sodium germanate glasses from this investigation (shear).

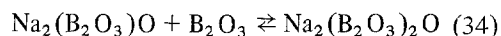
in the following examples.

Application of the model to physical property data from the literature seems to suggest that a dominant reaction can be specified for sodium borate and sodium germanate glasses.

The model will be applied to interpret some of the physical measurements by Kurkjian and Krauss [15], and Shelby [16]. In Fig. 4, which is taken from Kurkjian and Krause, is the data of acoustic velocity versus composition at 25°C for sodium silicate, borate, and germanate glasses. For sodium germanate glass the peak value is at 20 mol % Na₂O, where sodium borate glass is at 33 mol % Na₂O. These behave very similarly to Figs. 1 and 2. Therefore, to explain this abnormal behaviour our chemical reaction model is adapted to show how cation coordination number changes can explain the peak values of sodium germanate and sodium borate glasses.



and



This explanation also agrees with the hypothesis of Kurkjian and Krause [15] that the addition of

Figure 5 After Shelby, compositional dependence of viscosity of alkali germanate glasses (solid line represents $\text{Na}_2\text{O}-\text{GeO}_2$ glasses only).

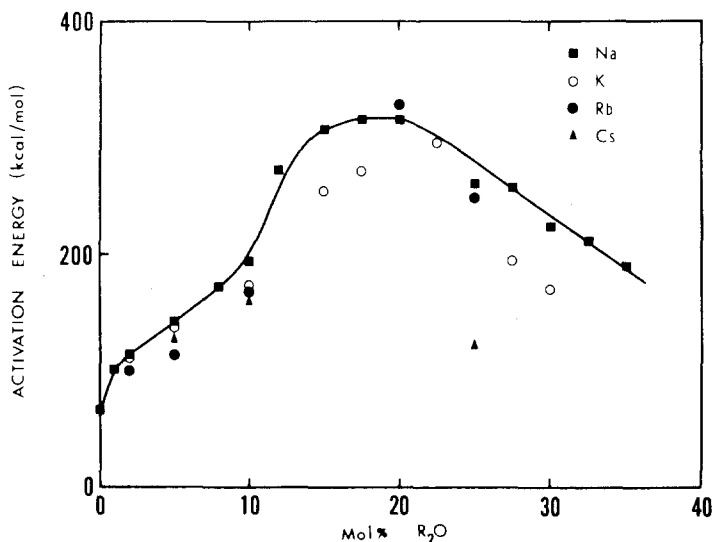
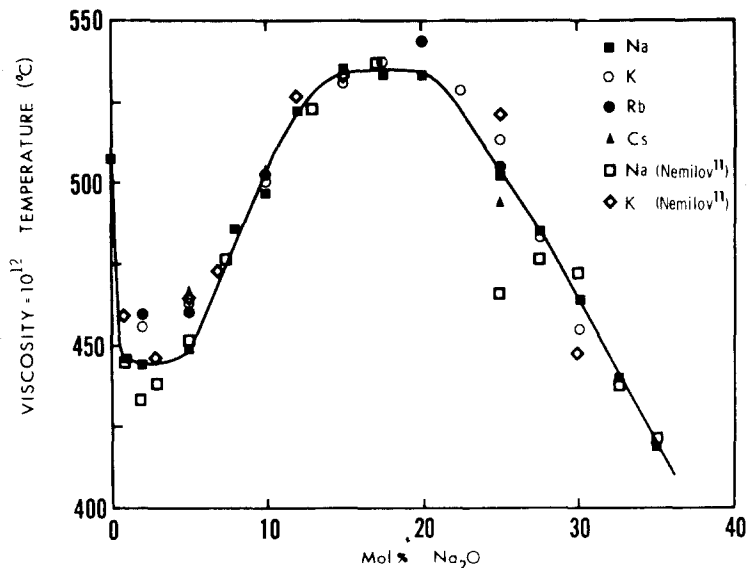


Figure 6 After Shelby, compositional dependence of activation energy for viscous flow of alkali germanate glasses (solid line represents Na_2-GeO_2 glasses only).

Na_2O to GeO produces six-fold from four-fold coordinated germanium atoms, while adding Na_2O to B_2O_3 converts three-fold coordinated boron atoms to four-fold coordination. However, there is no peak for sodium silicate glasses. This might be due to the much higher melting temperature of sodium silicate glasses, which could imply that the peak value of the physical properties in sodium silicate glasses would appear at higher temperature. Alternatively, its behaviour could be dominated by Na_2O breaking apart bridging oxygens which entails a reduction in size of the network fragments and thus a decrease of the viscosity and modulus. It is also possible that the model may fail because Si^{4+} ions do not undergo any co-

ordination change as alkali level varies in sodium silicate glasses.

Figs. 5 to 8, which are taken from Shelby, show that viscosity, activation, thermal expansion coefficient, critical point, T_g , and deformation point, T_d , of sodium germanate glasses all have a peak value near 20 mol % Na_2O .

6. Summary

Irreversible thermodynamic fluctuation theory is used to explain the kinetics of dissolution of oxides in glass melts as well as structural changes of glass. The model developed in this study not only permits one to know the rate of the dissolution reaction but also allows one to identify

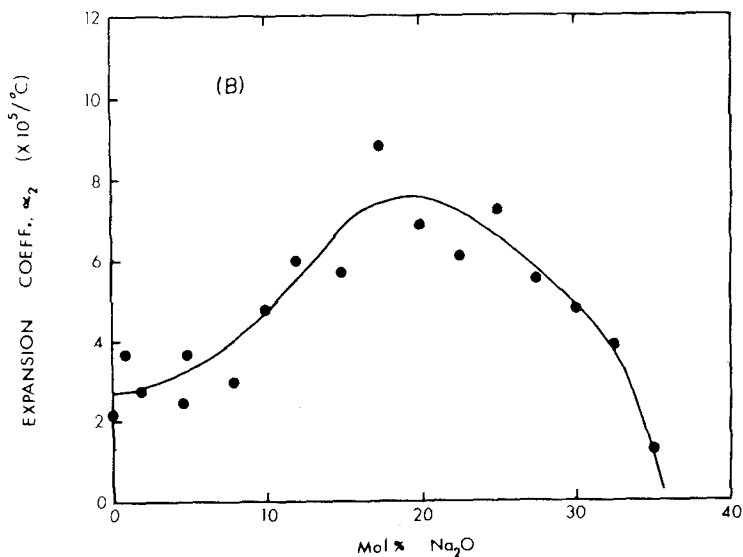


Figure 7 After Shelby, compositional dependence of high temperature thermal expansion coefficients of $\text{Na}_2\text{O}-\text{GeO}_2$ glasses.

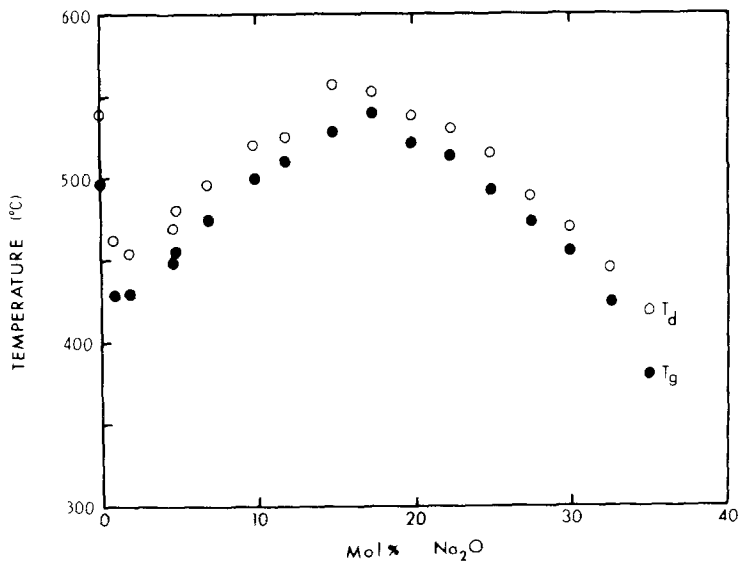


Figure 8 After Shelby, compositional dependence of critical point, T_g and deformation point, T_d .

cation coordination changes associated with the reaction. From this theoretical model one can predict the physical and chemical properties of glass which are governed by the reaction. It is felt that the theory can also be used for the study of chemical fining agents during glass melting on a laboratory scale.

In the present paper, several physical property variations with composition in sodium borate and sodium germanate glasses agreed with predictions of the model.

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Received 31 January and accepted 10 March 1978.