any viscous system is determined partly by the temperature alone, and partly by the structure at that temperature. The more important the structural contribution the more severe the linearity problem for a given p- or T-jump magnitude. Since these factors are usually not known in advance, the need for experimental demonstration of linearity in each case can be appreciated.

Feasibility of certain experiments in which the consequences of T jumps of 1°C produced in 1 μsec by xenon flash lamps are determined by spectroscopic monitoring of temperature-sensitive, optically active structural elements, has recently been demonstrated [116]. There is reason to believe the responses in such experiments will also fall in the linear regime.

It was originally believed, though is now disproven by experiment, that some volume relaxation measurements made by Macedo and Napolitano [117] using the sensitive refractive index monitoring technique after small temperature jumps (<1°C) may have been made sufficiently close to equilibrium for the responses to have been linear.

11.3 RELAXATION SPECTROSCOPY OUTSIDE THE LINEAR RESPONSE REGIME: TEMPERATURE STEP AND TEMPERATURE RAMPING STUDIES

Above we have considered the responses of liquid and vitreous systems to displacements from equilibrium which are so small that the responses are linear in the displacements. Such measurements depend on response monitoring techniques which are intrinsically very sensitive. There are, however, response functions of great interest which cannot, unfortunately, be conveniently monitored with great sensitivity. For instance, it is of vital concern to glassmakers to understand the rate at which a glass recovers its equilibrium state after suffering a perturbation due to changes in the temperature or pressure variables. Although it is possible to monitor volume changes very sensitively, particularly by index of refraction measurements [117], it remains difficult to follow changes induced by changes of temperature small enough (<1°C) for the system to be considered in equilibrium throughout the relaxation process. It is still more difficult to monitor enthalpy changes under linear response conditions, and only rarely
possible to determine linear changes in spectroscopic absorption coefficients by means of which the relaxation of selected structural units within the glass can be monitored. Thus, there has developed a need for analytical methods for extracting relaxation functions from data acquired under nonlinear conditions. Many authors [118] have attempted to analyze the relaxational responses of glasses following sudden temperature changes or during rate heating and cooling but until recently none had dealt successfully with the problem posed by the dependence of the relaxation rate on the structural state, hence the thermal history, of the glass. Recently, however, an approach to this problem for the case of temperature jump, which is basically simple and leads to an excellent description of experimental findings, has been proposed by Narayanaswamy [119] and Narayanaswamy [120] and developed by Moynihan, Macedo, and co-workers [121-124] for the description of temperature-ramping (i.e., continuous perturbation) experiments.

Temperature-ramping experiments, properly analyzed, provide a very efficient means of surveying the relaxational behavior of a system, and are of special value for optical monitoring studies where the change in observed property is not easily determined for small temperature jumps.

It has long been recognized [51,118] that the recovery rate after displacements from equilibrium due to temperature changes depends on both the temperature, and on the magnitude of the displacement. Assuming that the dependence of the strain relaxation on strain itself was the only source of nonlinear behavior Narayanaswamy [120] has shown formally how the relaxation data can be effectively linearized by writing \( \tau \) or \( \tau_o \) of Eq. (18) as quantities dependent on both temperature and "fictive" temperature, \( T_f \), where the latter measures the departure from equilibrium, in the form

\[
\tau \text{ or } \tau_o = A \exp \left( \frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right)
\]

where \( A, x (0 \leq x \leq 1) \), and \( \Delta h^* \) are constants and \( R \) has its usual meaning. When \( T_f \to T \), i.e., when the displacement from equilibrium is very small, Eq. (38) becomes identical with the ordinary Arrhenius form which so frequently describes \( \tau \) or \( \tau_o \) in the vicinity of \( T_g \). \( T_f \), which is a measure of the instantaneous strain for the system in any T-jump or P-jump experiment, is defined by the departure of the property \( Y \) being monitored from its equilibrium value, \( Y_e \). For enthalpy displacements, for instance,

\[
H(T) = H_e(T_f) - \int_{T}^{T_f} C_{pg} \, dT
\]  

(the prime is to distinguish the variable) from which it is clear that a state of equilibrium is defined by the condition \( T_f = T \).

Graphical methods of determining limiting values of \( T_f \) characteristic of glasses cooled below \( T_g \) at different rates, have been described by Moynihan et al. [121]. \( T_f \) will usually depend on the property in terms of which it is defined, since a general finding is that different properties relax towards their equilibrium values at different characteristic rates. Likewise, some processes are more nearly linear, or less structure-dependent than others, a characteristic which is reflected by relatively large values of \( x \) in Eq. (38).

For Eq. (38) to hold over a range of \( T \), as is so far generally found to be the case, a certain simplicity of relaxational behavior is required, particularly when \( \beta \neq 1 \) in Eq. (18) for \( \tau \). Specifically, the nonlinearity parameter, \( x \), must be temperature-independent, and the relaxation process must be Arrhenius, with the same activation energy, for both temperature- and structure-dependent parts. Furthermore, for \( \beta \neq 1 \), as almost invariably is the case, \( \beta \) must be independent of temperature, i.e., every component of the spectrum of relaxation times must have the same activation energy. Given this degree of simplicity, however, it then becomes possible to extract the characteristic nonlinearity and nonexponentiality characteristics not only for single or double step perturbations, but also from measurements taken during rate-heating.

Using Eq. (39) the results of a relaxation measurement (e.g. \( V \) vs. \( T \) (Fig. 1)) are cast in the form of \( T_f \) vs. \( T \) for purposes of
analysis. This scheme has dimensional simplicity since the stress, $\Delta T$, has dimensions of temperature. For a single step perturbation in a system which is assumed to have an equilibrium response function of the now-familiar Eq. (18) fractional exponential form, we have analogous to Eq. (1)(except that the strain rather than stress is relaxing)

$$T_F(t) = T_0 + \Delta T [1 - \phi(t)]$$  \hspace{1cm} (40)

where $\phi(t)$, instead of the linear regime function Eq. (18)

$$\phi_e(t) = \exp(-t/\tau_0)$$  \hspace{1cm} (41)

(where the subscript e denotes "near equilibrium"), is now

$$\phi(t) = \exp[-(\int_0^t dt'/\tau_0)^{\beta}]$$  \hspace{1cm} (42)

in which $\tau_0$ is given by Eq. (38). When $T_F$ is very close to $T$, Eq. (42) reduces to Eq. (41). Computer programs can be written to obtain best fit values of $\beta$, $\Delta h^*$, $x$ and $\tau_0$ from input $T_F$ vs. $T$ data.

For two successive perturbations occurring at $t_1$ and $t_2$, $T_F$ is written as an additive function of the perturbations, as under linear response conditions,

$$T_F(t) = T_0 + \Delta T_1 [1 - \phi(t-t_1, t)] + \Delta T_2 [1 - \phi(t-t_2, t)]$$  \hspace{1cm} (43)

where the $\tau_0$ in the functions $\phi(t-t_1, t)$ and $\phi(t-t_2, t)$ are again written as Eq. (38). In evaluating the integrals in Eq. (43) the effect of changes in both $T_F$ and $T$ on the relaxation times Eq. (38) must be taken into account.

For temperature-ramping (rate-heating) experiments the analysis [122] is conducted by treating the continuous perturbation as a succession of infinitesimal T-jumps $dT$ separated in time by isothermal equilibrations of duration $dt = dt'/q$ (where $q$ is the heating [or cooling] rate) and developing the series of which Eq. (43) is a two-membered example into an integral expression. For the evolution of $T_F$ with temperature, commencing at some initial temperature $T_0$, where $T_F = T$, i.e. in the equilibrium liquid, DeBolt et al. [122] obtain

$$T_F(T) = T_0 + \int_{T_0}^{T} dT' \left[ 1 - \exp\left[-\left(\int_{T'}^{T} dT''/q_0 \beta \right) \right]\right]$$  \hspace{1cm} (44)

Moynihan and co-workers process experimental data on enthalpy, volume, log (conductance), etc. obtained during rate-heating experiments, by integrating Eq. (44) numerically as described in Ref. 122 for assumed sets of fitting parameters and displaying the calculated curve on a video screen where it is compared with the experimental curve. The curves are sufficiently complex that, with data for more than one value of $q$ available, the fitting parameters are well-defined. Alternatively, the $\Delta h^*$ parameter may be fixed from viscosity-temperature studies. Figure 25 shows the excellent agreement of calculated curves of the heat capacity with the experimental points for $B_2O_3$ with the parameters $A = 1.51 \times 10^{-33} s$, $\Delta h^* = 90 \text{ kcal/mole}$, $x = 0.40$ and $\beta = 0.65$. The spectrum is of comparable shape to those for $B_2O_3$ we have seen earlier. More detailed comparisons follow.

(A) Enthalpy and Volume Studies

The interesting parameters of the analysis are $x$, which measures the importance of pure temperature as opposed to structure in determining the relaxation time, and $\beta$ which, as we have seen earlier, characterizes the shape of the relaxation spectrum (frequency domain) or of the decay function (time domain). Moynihan et al. [123] have tabulated values of $x$, $\beta$, and also $\zeta(r) = (2\pi r^3)^{-1}$ at the same temperature for relaxation of $H$, $V$, shear stress, etc., in those cases for which reliable data are now available. Their interesting results and other data added recently [124] are reproduced in Table 2. They show several significant and sometimes puzzling features.

Firstly, the characteristic frequency is always highest, or the relaxation time always shortest, for the relaxation of shear stress - though part of the difference is due to the fact that the other processes for which data are given in Table 2 are strain relaxations at constant stress. There is also a suggestion in Table 2 that the higher frequencies for shear relaxation are associated with lower
TABLE 2
Mean Isothermal, Isobaric Equilibrium Relaxation Times in the Glass Transition Region and Structural Relaxation Kinetic Parameters for Various Materials

<table>
<thead>
<tr>
<th>System</th>
<th>Relaxing property</th>
<th>In response to changes in</th>
<th>Notation</th>
<th>T(K)</th>
<th>$\langle \tau \rangle(s)$</th>
<th>$\langle f \rangle(s^{-1})$</th>
<th>$\Delta H^*$(J/mole)</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Phenyl 4-Ether</td>
<td>H</td>
<td>T</td>
<td>HT</td>
<td>250</td>
<td>5.2 $\times 10^{-2}$</td>
<td>5.0 $\times 10^{-7}$</td>
<td>322</td>
<td>0.70</td>
<td></td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>long. strain</td>
<td>long. stress</td>
<td>Ln Ls</td>
<td>250</td>
<td>5.1 $\times 10^{-3}$</td>
<td>3.1 $\times 10^{-7}$</td>
<td>385</td>
<td>0.65</td>
<td></td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>shear stress</td>
<td>shear strain</td>
<td>Ss Sm</td>
<td>250</td>
<td>1.6 $\times 10^{-1}$</td>
<td>9.9 $\times 10^{-1}$</td>
<td>292</td>
<td></td>
<td></td>
<td>123</td>
</tr>
<tr>
<td>BeO</td>
<td>H</td>
<td>T</td>
<td>HT</td>
<td>536.4</td>
<td>9.7 $\times 10^{3}$</td>
<td>1.6 $\times 10^{-5}$</td>
<td>376</td>
<td>0.65</td>
<td>0.40</td>
<td>122</td>
</tr>
<tr>
<td>B</td>
<td>V</td>
<td>P</td>
<td>VP</td>
<td>536.4</td>
<td>1.7 $\times 10^{4}$</td>
<td>9.4 $\times 10^{-6}$</td>
<td>385</td>
<td>0.85</td>
<td>0.5</td>
<td>123</td>
</tr>
<tr>
<td>n</td>
<td>long. strain</td>
<td>long. stress</td>
<td>Ln Ls</td>
<td>585.</td>
<td>1.1 $\times 10^{2}$</td>
<td>1.5 $\times 10^{-4}$</td>
<td>385</td>
<td></td>
<td></td>
<td>110</td>
</tr>
<tr>
<td>V</td>
<td>shear stress</td>
<td>shear strain</td>
<td>Ss Sm</td>
<td>536.4</td>
<td>1.1 $\times 10^{3}$</td>
<td>1.5 $\times 10^{-4}$</td>
<td>385</td>
<td></td>
<td></td>
<td>117</td>
</tr>
<tr>
<td>AsS3Se3</td>
<td>H</td>
<td>T</td>
<td>HT</td>
<td>450</td>
<td>5.4 $\times 10^{2}$</td>
<td>2.9 $\times 10^{-4}$</td>
<td>342</td>
<td>0.67</td>
<td>0.49</td>
<td>123</td>
</tr>
<tr>
<td>P</td>
<td>V</td>
<td>T</td>
<td>VT</td>
<td>450</td>
<td>1.0 $\times 10^{2}$</td>
<td>1.6 $\times 10^{-3}$</td>
<td>342</td>
<td>0.80</td>
<td>0.25</td>
<td>123</td>
</tr>
<tr>
<td>shear stress</td>
<td>shear strain</td>
<td>Ss Sm</td>
<td>450</td>
<td>4.5 $\times 10^{1}$</td>
<td>3.5 $\times 10^{-3}$</td>
<td>284</td>
<td></td>
<td></td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>0.125Na2O</td>
<td>H</td>
<td>T</td>
<td>HT</td>
<td>727</td>
<td>2.1 $\times 10^{2}$</td>
<td>7.6 $\times 10^{-4}$</td>
<td>410</td>
<td>0.66</td>
<td>0.70</td>
<td>125</td>
</tr>
<tr>
<td>-0.125K2O</td>
<td>long. strain</td>
<td>long. stress</td>
<td>Ln Ls</td>
<td>727</td>
<td>5.0 $\times 10^{1}$</td>
<td>5.3 $\times 10^{-3}$</td>
<td>380</td>
<td>0.57</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>-0.75K2O</td>
<td>shear stress</td>
<td>shear strain</td>
<td>Ss Sm</td>
<td>727</td>
<td>7.8</td>
<td>2.0 $\times 10^{-2}$</td>
<td>385</td>
<td></td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>2Ca(NO3)2•2KNO3</td>
<td>H</td>
<td>T</td>
<td>HT</td>
<td>538</td>
<td>5.2-5.5 $\times 10^{3}$</td>
<td>2.9-3.5 $\times 10^{-5}$</td>
<td>590</td>
<td>0.42-0.48</td>
<td>0.25-0.35</td>
<td>125</td>
</tr>
<tr>
<td>-3</td>
<td>shear stress</td>
<td>shear strain</td>
<td>Ss Sm</td>
<td>538</td>
<td>1.4 $\times 10^{1}$</td>
<td>1.1 $\times 10^{-2}$</td>
<td>585</td>
<td></td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>
experiment is that of the mode to which the system offers no restoring force. Liquid systems are nonpolarizing to shear stresses. Thus, if the liquid structure becomes in any way "grainy" or microheterogeneous as temperatures approach $T_g$ (as many studies suggest may be the case), then it is plausible that the shear stress may be relaxed by motion of the more mobile elements of the structure before any energy can be dissipated by shear motion within the less mobile elements. The broader the spread of relaxation times indicated by a relaxation experiment for which the system is polarizing, the more likely it becomes that the shear time will fall at the low end of the relaxation time spectrum due to the above mechanism. The extreme case would be that of a glass in which actual phase separation has occurred in which the enthalpy relaxation or volume (compressional stress) experiments would be sensitive to the properties of both phases and show either a very wide relaxation frequency range or two separate ranges, while the shear stress relaxation time would be determined mainly by the relaxation of the more mobile phase (assuming interconnection of phases).

There is, of course, no requirement that $T_S$ ($T_{SS}$ $S_S$) always be smaller than other relaxation times. Indeed, Rekhson et al. [127] have published results showing that in window glass the properties volume and log (shear viscosity) relax to equilibrium according to the same function within experimental error. (The breadth of the spectrum for enthalpy relaxation is not known in this case.) Certainly at higher temperatures dielectric relaxation times and shear stress relaxation times in many (but not all) molecular liquids have been shown essentially the same [10,27].

Referring to $B_2O_3$ again it is noted (Table 2) that for volume (indicated by refractive index n) and enthalpy relaxing in response to temperature change "stresses," the enthalpy relaxation is faster, but is associated with a broader spectrum ($S = 0.65$). This has been tentatively interpreted [123] to mean that chemical bond breaking, which contributes most of the enthalpy effect, must occur before the system can properly redistribute its volume to satisfy thermodynamic equilibrium requirements. It is not obvious at the moment why the spectrum for volume response to a $\Delta T$ stress should be narrower than that for volume response to a $\Delta p$ stress, although the fact that responses to temperature and pressure change should be different is not itself surprising; that systems explore different degrees of freedom under pressure change than under temperature change has been clear for some time from the general finding that the Prigogine-Defay ratio always exceeds unity (Chap. 1). It is reasonable to expect such different explorations to proceed at different rates. Formally [122-124], a different order parameter can be associated with each relaxation in the linear response theory sense that equilibrium fluctuations in each order parameter determine the magnitude of the relaxing property ($\lambda \kappa$, etc.) and also its time correlation function.

The trends commented on above for $B_2O_3$ ($\beta_{VT} > \beta_{HT}$, $\beta_{VT} > \beta_{VP}$ $\beta_{LNS}$) also apply to the other substances listed in Table 2 for which the relevant data are available.

The very broad $HT$ spectrum (small $\beta$) for the nitrate glass [125], which contains only simple ions, is rather surprising. It evidently cannot be associated with the predominant influence of structure on $\tau(x = 0.25)$, since the same $x$ value* is associated with a large $\beta$ value ($\beta_{VT}$) in the case of $As_2Se_3$. The only other fused salt glass studied so far is $ZnCl_2$, the volume relaxation of which was determined after single temperature steps above and below $T_g$ by Goldstein and Nakoneczny [126]. These authors showed that the relaxation was nonlinear with approximately equal influences of structure and temperature, and this was confirmed by Narayananswamy's subsequent demonstration [120] that their data could be linearized using his approach and apportioning 42% of the $\ln \tau_T$ temperature dependence to the structure-dependent ($1/RT_F$) term. A $\beta$ value for the relaxation is

*We should perhaps define a nonlinearity parameter $\alpha = 1/x$, to indicate the influence of structure on the temperature dependence of $<? or $<\phi$. (Thus, large $\alpha$, large influence.) The larger $\alpha$ is, the more accurately the first Davies-Jones equation (Eq. (7) Chap. 1) should apply to the system [126]. For the nitrate glass, Eq. (7) Chap. 1 is valid within experimental uncertainty (<5%).
unfortunately not available though the spectrum is evidently not very broad. ZnCl₂, however, is not expected to behave similarly to the mixed nitrate glass since it has a tetrahedral network structure, and in many ways behaves as a weakened version of the network glasses SiO₂ and BeF₂ (see Figs. 6 and 7, Chap. 1).

Taken as a whole, the data of Table 2, and the findings described in the following sections, promise the discovery of considerably more variety in relaxation spectroscopy than the earlier sections of this chapter might suggest exists.

(B) Electrical Conductivity Studies
In monitoring the response to temperature or pressure perturbations by volume or enthalpy measurements, one is measuring a total response of all the constituent particles of the system. In such measurements there is no way of deciding unambiguously whether the breadth of a spectrum, such as that of the last-mentioned nitrate glass, is to be associated with a distribution of distinguishable physical processes of different frequencies, or with a single intrinsically nonexponential cooperative process. The comparison of enthalpy and volume relaxation characteristics suggests that there are elemental differences, but to obtain definitive information it will clearly be necessary to monitor the relaxation in some more selective manner.

It has been seen earlier that alkali ions can respond to electrical stresses on a time scale much shorter than that of the characteristic structural relaxation. They may, therefore, act as quasi-independent probes of the structural relaxation process although, being a property which responds to the long-range structure, it seems necessary that the final equilibrium conductivity cannot be determined before the total structure has equilibrated. This does not mean, of course, that the frequency distribution, hence the spectral shape, must be the same, and to investigate the relationship, Saad and Moynihan [124, 129] measured the d.c. conductivity of a 23K₂O·77SiO₂ glass sample during temperature jump experiments analogous to those described in the previous section. Comparing their results for the relaxation of the refractive index n (n = V) for the same glass, they found that ln c approached equilibrium with approximately the same average relaxation time as n but that the spectra were rather different in shape. Thus, $\bar{\sigma}$ for the conductivity monitor was only 0.44 (implying the presence of many rather high frequency elements, or fast processes) vs. ~0.55 for n. $f_{\text{max}}$ on the other hand, was lower ($\sigma_0$ larger) for the conductivity monitor, the two differences compensating to bring <F> to about the same value for the two properties. These distinctions are consistent with expectations for a probe which is intrinsically fast relaxing but is constrained by the long-range structure adjustments.

More such measurements, particularly with glasses of low as well as high conductivities, are greatly needed.

(C) Spectroscopically Selected Structural Group Relaxation Studies
Electrical monitoring of a glass undergoing relaxation towards its equilibrium state (previous section) can draw enough distinction between the approach rates of different elements of the structure to their equilibrium states, to suggest that important distinctions exist. However, the only satisfactory way to monitor the relaxation of local elements of the structure is to use a local probe. Since probes of local structure have been the subject of all but two of the preceding chapters of this book, it is clear that there are many possibilities. In general, any resonance mode except those which are strictly intramolecular will show some dependence of its characteristic frequency, intensity or bandshape on the liquid structure. To be useful as a probe in kinetic studies, however, the structural element must be temperature-sensitive to the extent of producing changes of at least 0.01 units of absorbance per 10° of temperature change. Within limits, adjustments for weaker temperature dependences can be made by increasing probe concentrations.

Probes which have so far been utilized in this new area of relaxation spectroscopy (chronospectrophotometry) have been (1) cobalt ions, Co²⁺, under conditions in which the Co²⁺ ions are distributed
between octahedral and tetrahedral sites in a temperature-dependent equilibrium, (2) a dye molecule which participates in a temperature-dependent monomer-dimer equilibrium and can be studied in very high dilutions, and (3) the temperature-dependent equilibrium between broken and unbroken intermolecular hydrogen bonds. The latter probe can be a major species of the glass in the interesting cases of H-bonded liquids such as glycerol C₃H₅(OH)₃ and sorbitol C₆H₆(OH)₆.

Barkatt and Angell [130] showed that in mixed nitrate glasses in the presence of small amounts of chloride ions Co²⁺ ions distribute themselves between two well-defined types of site in one of which the Co²⁺ ions are coordinated by four nitrate ions while in the other Co²⁺ is tetrahedrally coordinated by four chloride ions. The two-site equilibrium is temperature-dependent with ΔH = 21.7 kJ mol⁻¹, and since the two coordination groups are characterized by quite different ligand field spectra (Chap. 6, p. 283), the relaxation towards the equilibrium state following a temperature jump can be monitored spectrophotometrically. Initial experiments sufficed to show that the relaxation of this local element of the structure occurred somewhat less rapidly than the shear relaxation process [130], but quantitative developments were prevented by nonlinear effects and slow establishment of temperature equilibrium in the initial technique. Subsequent investigation of this local relaxation was carried out using the temperature-ramping method of the previous sections, with very informative results [131]. Figure 26a shows the variation of optical density 660 nm (one of the band maxima of the [CoCl₄]²⁻ group) as (1) temperature is decreased from the supercooled liquid state through the transformation region into the structurally arrested state well below the DTA-defined Tg, and (2) temperature is raised again to the original value at the same rate (2.5°C min⁻¹). The absorbance behavior shows a typical hysteresis characteristic of most physical property variations in the glass transformation region. Indeed, by taking the derivative of absorbance with respect to T one obtains, with considerable scatter, a plot (Fig. 26b) with the general characteristics of the DTA and DSC traces commonly used to define Tg. Comparison with the corresponding plots for the enthalpy

FIG. 26. (a) Variation of absorbance at 660 nm, A₆₆₀, due to Co²⁺ in tetrahedral sites (Co-Cl₄) as a function of temperature during cooling and heating at -2.5 and 2.5 deg min⁻¹ through the glass transformation region, compared with the variation of enthalpy (expressed as fictive temperature) under the same conditions. (b) Temperature derivative of A₆₆₀ as a function of temperature through the transformation range compared with the variation of heat capacity Cp under the same conditions (dT/dt = 2.5 or -2.5 deg min⁻¹) showing the difference between optical (Co²⁺) and calorimetric glass transition temperatures Tg. (c) Hysteresis spectra for H (or Tg,H) and A₆₆₀, normalized to 1.0, at the maximum separation between heating and cooling curves in each case (or Tg,H).
(Fig. 26a) and heat capacity (Fig. 26b), however, shows that some rather striking differences exist. For instance, $T_g^{*}$ defined in the usual way using the Co$^{2+}$ optical data lies some 8°C below the $T_g$ from the DSC trace.

Since the activation energy for the relaxation time determined from both T-jump experiments [116], and from the analysis of the temperature-ramping data, is essentially the same as for the shear viscosity [28] and the enthalpy relaxation [125], 590 kJ mol$^{-1}$, the 8°C difference in $T_g^{*}$ implies a difference of no less than two orders of magnitude in the characteristic times for the enthalpy and local structure relaxation processes when compared at the same temperature ($\tau_{Co^{2+}}/\tau_H = 127$). Referring to Table 2 we see that $\tau_{Co^{2+}}$ is intermediate between $\tau_S$ and $\tau_H$. The more significant observation, however, seems to be made by comparing what we may call the "hysteresis spectra", viz. the magnitude of the difference in the relaxing property during cooling and heating at equal ramp magnitudes ($q = \Delta T/\Delta t$).

The hysteresis spectra, Fig. 26c, which bear a qualitative resemblance (not accidentally) to the constant frequency loss vs. temperature spectra of earlier sections (e.g. Figs. 2, 8, 20), show clearly that the Co$^{2+}$ relaxation, though faster than the overall enthalpy relaxation, is actually slower than the faster elements of the latter, i.e. the enthalpy relaxation because of its great spectral width surrounds the Co$^{2+}$ relaxation. The latter thus appears to be reflecting just one part of a manifold of processes which constitute the former. Using Table 2 relaxation time data for this system, we estimate that if the shear stress relaxation hysteresis spectrum were available, it would peak about 1.6°C lower in temperature than that for Co$^{2+}$ in Fig. 26, and would also, therefore, fall within the envelope of the enthalpy relaxation spectrum. For Co$^{2+}$ $\beta \approx 0.65$.

These observations are of considerable significance. They imply that, with some ingenuity, local probes of structural relaxation could be chosen which would have characteristic times covering the entire range of the enthalpy relaxation. One probe, which would be of major interest, would be that provided by the nitrate anion itself. Wong and Angell [132] showed some time ago that the $n + \pi^*$ transition of the nitrate anion owed most of its transition energy temperature dependence to structural changes occurring in the liquid, and could, therefore, be used to spectroscopically detect the glass transition. Although the temperature dependence was smaller than convenient, with some care its relaxation could probably be monitored.

One easily monitored spectroscopic probe which may represent a major rather than a minor structural constituent of the system containing it is the broken hydrogen bond. The first overtone, $2\nu_1$, of the free-OH group has a sharp maximum at 1.40–1.42 μm (near IR).

This species participates in a temperature-dependent equilibrium with unbroken hydrogen bonds, the enthalpy change being 9–12 kJ mol$^{-1}$ depending on the system. Barkatt and Angell [116] have monitored the temperature-dependent absorbance of this band during temperature-ramping experiments on sorbitol C$_6$H$_{12}$(OH)$_6$ ($T_g = -9$°C) and find, not surprisingly, that this equilibrium is approached in a manner very similar to that of the equilibrium enthalpy.

The cobalt ion, in a related sorbitol-pyrudinium chloride solution, approaches [Co(OH)$_6^{2-}$] $\rightleftharpoons$ [CoCl$_2^{2-}$] equilibrium a little more rapidly than either the hydrogen bond exchange [ -OH $\rightleftharpoons$ -0-H...0] or the enthalpy H and exhibits a somewhat narrower spectrum, i.e. behaves in a manner qualitatively similar to that described above for the nitrate glass. Equilibrium between monomer and dimer species of the dye stuff pinacyanol chloride doped into pure sorbitol, on the other hand, is only approached at a measurable rate at temperatures 20°–35°C above $T_g$, depending on concentration. In this case, although the loss of, and approach to, equilibrium show the characteristic hysteresis of Fig. 26a, the motions determining the equilibrium in question (essentially diffusion of dye molecules) are so completely uncoupled from those determining structural equilibrium in the host that equilibrium is approached exponentially ($\beta = 1$).

This is reminiscent of, and indeed is causally related to, the exponential relaxation of the large ion-pair dipole in Williams, Davies, and Hains' dielectric relaxation studies (p. 728) and Bartoli et al.'s exponential conductivity relaxation in dilute glycerolic aqueous solutions (p. 759). In each case so many steps are required...
to bring about the relaxation in question that the process acquires Brownian (no memory, hence no information) character.

The optical $T_g$ approaches the DSC $T_g$ with increasing dye concentration since the volume element which the system must explore in order to reach the equilibrium state decreases with increasing concentration. This observation, although not surprising in itself, is very suggestive. It raises the possibility that structural relaxation spectra are broad because of the wide spectrum of system subspaces which must be explored to effectively relax a perturbation. This concept is directly connected with familiar ideas on the increasing size of cooperatively rearranging groups with decreasing temperature in viscous liquids [133] and the ideas behind the environmental relaxation model for conductivity and shear stress relaxation in viscous liquids [134]. Most directly, however, it lends support to the approach to structural relaxation kinetics proposed by Majumdar [135], who suggested that a stress field giving rise to relaxation could be decomposed into elementary modes of wavelength $\lambda$, each with an associated relaxation time $\tau$ proportional to $\lambda^2$. The relaxation is presumed to first occur in small local areas (small $\lambda$ and $\tau$) and then to extend to larger areas (larger $\lambda$ and $\tau$) by adjustment of the mismatch between the local areas. Hence the Co(II) ion rearrangement, for instance, might involve only those modes intermediate in size and time scale between the smallest and the longest modes involved in the enthalpy relaxation.

It appears that relaxation studies of properties that are sensitive only to local elements of the structure may be critical to gaining an understanding of the molecular events involved in structural relaxation processes.

11.4 SUMMARY

In this section we recapitulate some of the principal observations and conclusions from this rather broad survey of the relaxation spectroscopy field.

The evidence from dielectric and electrical relaxation studies near $T_g$, and particularly from structurally selective spectroscopic probe relaxation studies, is that any relaxation spectrum contains contributions from a variety of characteristic response modes, which probably are distinguishable by the size of the volume element of the structure in which they occur. With the latter conclusion in mind it is to be emphasized that relaxation measurements fall into two classes depending on whether or not the system ultimately dissipates the stress acting on it (or, alternatively, completely relaxes the strain initially imposed on it). In the former cases, designated nonpolarizing systems, the relaxation measurement may not be sensitive to all the modes of the system and the relaxation spectra will tend to be narrower, and to have higher average frequencies. Outstanding examples are the alkali cation-based electrical relaxation compared with the mechanical relaxation in mixed alkali glasses below $T_g$ and the shear relaxation of liquids in general near $T_g$ compared with the relaxation of volume or enthalpy at the same temperature. These distinctions will be most pronounced in those systems which have intrinsically broad spectra for polarizing relaxations, e.g. compression or T-jump enthalpy relaxation experiments or shear relaxation below $T_g$. The principle involved is that a relaxation experiment will not be sensitive to any mode of motion with a characteristic frequency significantly lower than that of the mode to which there is no restoring force.

For polarizing relaxations, the amount of structure in the relaxation spectra appears to vary strongly with the temperature. At temperature not high enough for the relaxation spectrum to merge with the vibrational spectrum, the relaxation spectrum tends to be narrow, but broadens as thermal excitation decreases ($T \rightarrow T_g$) and different relaxation modes become uncoupled. In some cases a separate (but broad) element in the spectrum may become resolved in the liquid near $T_g$ in dielectric relaxation measurements. Such broad high frequency (secondary) modes are almost always detected in measurements below $T_g$. Fast-relaxing modes phenomenologically related to these are responsible for the electrical conductivity of oxide glasses. In alkali-containing oxide glasses two distinct secondary shear relaxation modes may be observed (unless a high concentration of a
second alkali is present), one due to single alkali cation stress-induced migration, and one due to coupled monovalent species (e.g. Na⁺ - K⁺ impurity, Na⁺ - H⁺ impurity). When the main Tg relaxation is included such spectra may be deemed rich in detail by any standards. Secondary relaxation frequencies have characteristically small temperature dependences, which are always Arrhenius in character, in contrast with primary relaxation temperature dependences. The distinction may reflect the size of the cooperative region involved in the relaxation process, which is believed to be small.

The shape of the relaxation spectrum in the liquid state near Tg is in some cases independent of temperature but in other cases varies in complicated ways. In a great many cases the spectral form can be accounted for rather well in terms of a time domain normalized stress or a strain decay function of the form $\phi(t) = \exp(t/\tau)^S$ where $\tau$ is generally 0.5-0.6. More startling is the very large temperature dependence of the characteristic relaxation frequency. This frequency is the single most sensitive indicator of glass structure and changes thereof available to the glass scientist, although the connection with actual atomic configuration in any given case is indirect and imprecisely known. Likewise, the changes in relaxation spectra which occur near Tg and below are indicators of structural changes which in most cases are too minor to be detected by any conventional structure-monitoring technique. On the other hand, it must be recognized that certain gross structural changes such as the separation of a second thermodynamic phase within the glass structure, may have only minor effects on some relaxation spectra (p. 755).

Relaxation spectroscopy, notwithstanding the great deal of work performed in certain of its areas, is still a young and challenging research field with many important questions waiting for the right experiments to answer them.

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