

in Figure 1 show the equilibrium paths of supercooled liquid below T_g ; this liquid continues to maintain internal equilibrium and is metastable relative to the solid. At normal pressure the volume of the glass is greater than that of the supercooled liquid, and at constant temperature all fluctuations will tend to decrease the volume (and increase the compressibility) to those of the supercooled liquid phase at the same temperature. On the other hand, if the glass is rapidly compressed, the volume can be made less than that of the supercooled liquid, and, on release of pressure, fluctuations will tend to increase it irreversibly toward the liquid volume at a rate dependent on temperature. The equilibrium configuration suggested by Bridgman and Simon, which can be approached from both high- and low-density states, thus corresponds to the supercooled liquid at the same temperature.

The temperature T_g is to some extent a function of the cooling rate, so that the compressibility, thermal expansion, and volume of the glass will vary somewhat depending on the conditions under which the glass is formed and on the extent to which the glass has been annealed. For borosilicate and lime glasses and normal silicates, such as diopside and albite, T_g is about 550°C, but for SiO₂ glass it is 1200°C. In addition, T_g is a function of pressure because it actually defines a viscosity. If the temperature and pressure dependence of viscosity are assumed to be of the form $\exp(E/RT)$ and $\exp(AP)$, respectively, and if the crude estimates of $E = 100$ kcal/mole and $A = 10^{-4}$ bar⁻¹ [Clark, 1966] are used, then dT/dP for constant viscosity is about 1°C/kb as the approximate P - T slope of T_g . Thus, in the measurements of Boyd and England on diopside and albite at pressures up to 50 kb T_g remains well below the liquidus at all pressures and increases by only some 50°C at the highest pressures.

The compressibility variation shown in Figure 1 indicates that κ for the glass is much closer to the value for the crystal than to the equilibrium value of the supercooled liquid. This relationship is observed for α and heat capacity [Davies and Jones, 1953, pp. 378-379]; it reflects the loss of the configurational contribution to the liquid coefficients and the fact that the remaining contribution is principally vibrational in both glass and crystal. Although very few

data are available on compressibilities, it is a fair guess that a similar relationship is true for κ . For natural silicate minerals data are available only for quartz, but the compressibility of SiO₂ glass is identical to that for α quartz (both at 25°C) and is only 30% greater than that of β quartz (both at 600°C); also, the compressibilities of crystalline and glassy diopside are essentially identical at 25°C [Birch, 1966]. No compressibility data are available for diopside and albite glass, so that in the following treatment it has been necessary to use the crystal compressibilities for these minerals under the assumption that they do not differ significantly from the values for the glasses.

REFRACTIVE INDEX CALCULATIONS

According to dielectric theory, the refractive index (n) and molar volume (V) of a condensed phase can be related by a general molar refraction function

$$R = V/[\beta + 4\pi/(n^2 - 1)] \quad (2)$$

where R is actually the sum of the individual molar polarizabilities of the constituent ions multiplied by their mole fractions and is constant for processes in which the polarizabilities do not change [Ritland, 1955]. The 'overlap field' parameter β is a measure of the nearest-neighbor interaction field and must be determined experimentally; the limiting values of β are 0 and $4\pi/3$. In the case of point dipoles in a random or cubic lattice the nearest-neighbor interaction vanishes and only the 'distant-neighbor' or Lorentz field is effective; $\beta = 4\pi/3$ and the molar refraction law can be written

$$R_{LL} = V(n^2 - 1)/(n^2 + 2) \quad (3)$$

which is the Lorentz-Lorenz refraction equation [Brown, 1956]. When large deformable ions are considered, there is an 'overlap' nearest-neighbor field of opposite sign, which reduces the polarization interaction; when this field equals the Lorentz field, $\beta = 0$, and the refraction law becomes simply

$$R_D = V(n^2 - 1) \quad (4)$$

which is the Drude refraction equation. (R_{LL} and R_D are $4\pi/3$ and 4π times the R defined in equation 2.) Equations 3 and 4 are discussed by Mott and Gurney [1940] and Ritland [1955], who show that they are limiting laws