

jectory to room temperature and pressure via the equilibrium supercooled phase, and  $A^*$  can be returned to  $A$  or by heating the liquid via  $D^*$  and then compressing it. The density with pressure and temperature are equal to the equilibrium-phase  $\kappa$  and  $\alpha$  at 25°C and  $T$ , and at 1 bar and  $P$ . The  $A^*$ - $B$ - $C$ - $D$ - $A^*$  is a reversible cycle involving a glass instead of the supercooled liquid. Points  $B$  and  $C$  will scatter somewhat during a number of cycles due to variations in rates of cooling or heating. A cycle is drawn for a 'normal' silicate (side-albite).

Consider the diopside-albite experiment in which temperature is quenched at the liquid is at  $A^*$  ( $T$ ,  $P$ ) and is at point  $B$  (25°,  $P$ ) with  $\Delta V$  proportional to the thermal expansion coefficient at temperature drops through the glass. The volume (density, refractive index) changes to 25°C and pressure  $P$  is at point  $B$ , via the reversible thermal contraction. The potential energy barrier is now too high for pressure relaxation at low temperature so that pressure release is irreversible. Properties at point  $B$  are locked in to the glass. Thus, any point on any trajectory at any  $T$  and  $P$ , will, in this process, be equal to the 25° trajectory  $C$ - $B$  and  $C$ - $B$  at the pressure at which temperature was quenched. As discussed in the case of the diopside-albite results, this follows from the equality  $(\partial\alpha/\partial P) = -(\partial\kappa/\partial T)$ . The  $A^*$ - $B$ - $C$ - $D$ - $A^*$  is drawn for normal silicates in which  $\alpha_p < \alpha_0$  and  $\kappa_T > \kappa_{25}$ . After release from above the glass point  $D$ , the trajectory  $D$ - $A^*$  follows the isotherm, with subthermal relaxation to point  $C$ , the uncompressed glass. If the pressure is released at a high temperature below the glass point, the pressure effect may be locked in with thermal contraction at 1 bar. This is shown in Figure 4 by the area  $C$ - $D$ - $A^*$ - $B$ . For  $\text{SiO}_2$  glass, in which  $C$ - $B$  is now assumed to be the 25°C compression slope for the glass, the compressed glass sample at 600°C is at point  $D$  below the glass point  $T_g$  (as, for example, reached by cooling at pressure from the liquid). When the pressure is released,

the pressure deformation is trapped by viscosity, as configurational changes are required for pressure relaxation. However, thermal relaxation is dominantly a vibrational effect and occurs with the  $\alpha$  value characteristic of ambient pressure, in this case  $\alpha_0$ . The trajectory is  $E$ - $F$ , this difference being equal to  $D$ - $C$ , and the points from compression along an isotherm  $D$ - $E$  will plot on the isotherm  $C$ - $F$  with a slope given by  $\kappa$  at the isotherm temperature. (At 600°C, however, the difference  $C$ - $D$  is only 0.1% on density, so that the difference between the two lines cannot actually be observed.) For normal silicates, the trajectory  $C$ - $F$  would, of course, lie above  $C$ - $B$  because of the higher compressibility at higher temperature.

At still lower temperatures it is evident from Figure 3 that  $\text{SiO}_2$  glass is partly elastic, with some rebound along  $D$ - $E$  on decompression; subsequent cooling then produces a trajectory from  $C$  below  $C$ - $F$  as is observed. Although shear effects may be involved in the degree of elasticity observed, Cohen and Roy [1965, Figure 6 and Table 2] observed quite similar effects in hydrostatic compression in argon up to 10 kb. Samples compressed at 600°C and above scatter between the 25° and 600°C isotherms in Figure 3 (the quenching cycle is not described), whereas partial or total elasticity was observed at lower temperatures.<sup>3</sup>

Cohen and Roy [1961, 1965] have proposed that the densification of glass is independent of the compressibility and involves an irreversible, second-order structural change at high pressure, followed by completely elastic volume relaxation of the new phase. It is evident, however, that the relationships between densification and compressibility shown in Figures 2 and 3 are incompatible with such a model. Configurational

trapping of pressure deformation is clearly adequate to explain the permanent compression of the glasses studied here.

Recent work dealing with pressure effects on refractive index in elastic compression [Waxler and Weir, 1965, and references therein] has dealt with some substances in which the molar polarizabilities actually change with pressure, so that  $R$  in (2) cannot be considered constant. Discussions of possible effects of this type in glasses [Waxler and Weir, 1965; Vedam et al., 1966] have, so far, been confined to models based on the Lorentz-Lorentz or Drude law, rather than on equation 2, which allows an intermediate overlap field. It is clear that the more general refraction model given by equation 2 should be used as the basis for further studies of polarizability changes. Fortunately, pressure effects on polarizability do not seem to be important in the glasses studied here.

This study was originally undertaken in the hope that meteoritic glasses might yield some information on conditions under which they were quenched. Although the results indicate this is unlikely, it should be of interest to study the quenching conditions in tektites. By simply heating tektite samples above the glass point and cooling, and comparing the refractive index before and after, it would be possible to see if a pressure deformation has been trapped in the glass; if so, measurement of the compressibility as a function of temperature might yield some interesting information.

*Note added in press.* In the *Annual Report of the Geophysical Laboratory for 1967-68*, E. C. Chao and P. M. Bell have recently reported data on refractive index as a function of pressure to 50 kb, for three feldspar glasses quenched at pressure. The  $n$ - $P$  relation for oligoclase ( $\text{An}_{25}$ ) is given exactly by the Lorentz-Lorentz law, using the crystal compressibility, and the relationship for orthoclase is given exactly by the Drude law; compressibility data for their third glass were not available. The oligoclase curve is essentially linear, and it seems clear that with very precise data a plagioclase glass of some composition can be found that will give a precisely linear curve and should be most useful for an experimental barometer. Measurement of the actual feldspar glass compressibilities, together with the  $n$ - $P$  curves, would provide very interesting data on

<sup>3</sup> Note added in press. G. J. Wasserburg has drawn my attention to two papers by Kennedy et al. [1961, 1962] in which permanent increases in refractive index were observed in  $\text{SiO}_2$  glass quenched under hydrostatic pressures up to 10 kb in a hydrothermal system. Kennedy et al. [1962] showed that the refractive index of the quenched glass was approximately given by the Lorentz-Lorentz equation and attributed this to a permanent 'set' in the high-pressure density. Their data (0-10 kb) fit the 25°C,  $\beta = 1.37$ , calculated curve in Figure 3 very closely.