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juenched from liquidus tema compressibility data on the ults indicate that the pressure h the glass point, but thermal characteristic of the applied t predicted at 25°C and load ow the glass point should be s released before pressure, or e, because thermal relaxation cient. For SiO2 the glass comlap field parameter ($\beta = 1.37$) glass compressed at various P dues calculated for permanent mpression is partly elastic and e glasses, configurational trapanent compression. The direct ows that the model of H. M. ral changes at high P followed existing data.

olding up the vitreous network of that the Si-O bond angles are igh the nearest neighbor Si-O disto remain unchanged. The folded e mechanically stable at room temt the original density can be renealing at high temperatures. The ect is similar, though opposite in increase of density observed in upidly chilled glasses at ordinary idgman and Simon therefore sugthere exists an equilibrium conor a glass at any temperature and high- and low-density metastable cterized by the trapping of displaced ad relatively strong potential barist.

d Roy [1961] showed that the perisification of SiO₂ and other glasses ied by an increased refractive index, found to be continuously proporressure at temperatures greater than room temperature they found a ressure of about 20 kb for SiO₂ glass.

PERMANENT COMPRESSION OF SILICATE GLASSES

considerably lower than the value reported by Bridgman and Simon.

Boyd and England [1963] have observed similar increases in the refractive indices of glasses of albite (NaAlSi₃O₈) and diopside (CaMgSi₂O₆) quenched from above the liquidus at high pressures; their experiments were done with a solid pressure-medium apparatus in which samples could be rapidly quenched to low temperatures at pressure [Boyd and England, 1960]. They found a continuous increase of refractive index with applied pressures of up to 50 kb. These experiments are similar to the experiments of Tammann [1933, p. 66 ff.], who supercooled liquids at different pressures and observed glasses with different volumes when the pressures were released. That is, the observed increase in refractive index of a glass reflects, at least to some extent, the density increase due to the permanent compressibility. A large body of theoretical and experimental work on glasses has developed since Tammann's work, but no quantitative discussion of the effects of permanent compression on density and refractive index of glasses has been attempted. In this paper I describe a very simple model that reproduces the observations on albite, diopside, and quartz glass with remarkable success.

THERMODYNAMIC CONSIDERATIONS

In applying the normal thermal and mechanical coefficients to thermodynamic calculations on glasses, it must be recognized that these coefficients are not uniquely defined, since a glass, by definition, is not a stable thermodynamic phase in internal equilibrium. Rigorously defined, a glass is a supercooled disordered phase in which the configurational contributions to its properties have been frozen out at a higher temperature [Jones and Simon, 1949; Davies and Jones, 1953; Stevels, 1962]. Thus we can describe volume changes by the usual equation

 $d \ln V = \alpha \, dT - \kappa \, dP \tag{1}$

where α is the thermal expansion coefficient and κ is compressibility. The values of α and κ will, however, normally vary somewhat with the history of the glass even at temperatures at which vibrational contributions dominate the configurational effects. At higher temperatures

at which configurational changes can occur, e.g. during a thermal process, the coefficients will also vary with the rate at which the process is carried out.

Tammann [1933] showed that the configurational quenching that produces a glass occurs at a viscosity of 10¹³ poises in all glass-forming substances; this viscosity is encountered at a characteristic transformation temperature or 'glass point' at which the viscous relaxation time is of the order of minutes or less and secondorder transitions occur. A schematic illustration of the effects on compressibility and volume, which are of particular concern in the discussion to follow, is shown in Figure 1. In all glasses the compressibility and heat capacity decrease rapidly on cooling through the glass point; the thermal expansion coefficient shows a similar discontinuity but can increase or decrease [Davies and Jones, 1953]. As the liquid supercools below $T_{\mathcal{M}}$, however, the volume, entropy, and other state functions are continuous across T_{M} and T_{g} ; between these temperatures the liquid is a metastable, equilibrium phase, but below T_{σ} the glass is an unstable phase because it retains the high-temperature configuration frozen in at T_{g} . The dashed lines



Fig. 1. Variation of compressibility and volume with temperature in crystal, liquid, and supercooled liquid (SCL). T_{M} is the melting point and T_{σ} is the glass point.

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