

eresis in

quenched from liquidus tem-
n compressibility data on the
lts 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
e released before pressure, or
e, because thermal relaxation
cient. For SiO₂ the glass com-
lap field parameter ($\beta = 1.37$)
glass compressed at various P
lues calculated for permanent
mpression is partly elastic and
e glasses, configurational trap-
anent 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
ugh the nearest neighbor Si-O dis-
t remain unchanged. The folded
e mechanically stable at room tem-
t the original density can be re-
nealing at high temperatures. The
ect is similar, though opposite in
increase of density observed in
apidly chilled glasses at ordinary
idgman and Simon therefore sug-
there exists an equilibrium con-
or a glass at any temperature and
high- and low-density metastable
eterized by the trapping of displaced
ad relatively strong potential bar-
rist.

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

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 ob-
served 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 at-
tempted. In this paper I describe a very simple
model that reproduces the observations on
albite, diopside, and quartz glass with remark-
able success.

THERMODYNAMIC CONSIDERATIONS

In applying the normal thermal and mechan-
ical 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 thermo-
dynamic phase in internal equilibrium. Rigor-
ously 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

$$d \ln V = \alpha dT - \kappa dP \quad (1)$$

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 configura-
tional 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 second-
order transitions occur. A schematic illustra-
tion of the effects on compressibility and vol-
ume, which are of particular concern in the
discussion to follow, is shown in Figure 1. In
all glasses the compressibility and heat capa-
city 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_M , however, the volume,
entropy, and other state functions are contin-
uous across T_M and T_G ; between these tem-
peratures the liquid is a metastable, equilibrium
phase, but below T_G the glass is an unstable
phase because it retains the high-temperature
configuration frozen in at T_G . The dashed lines

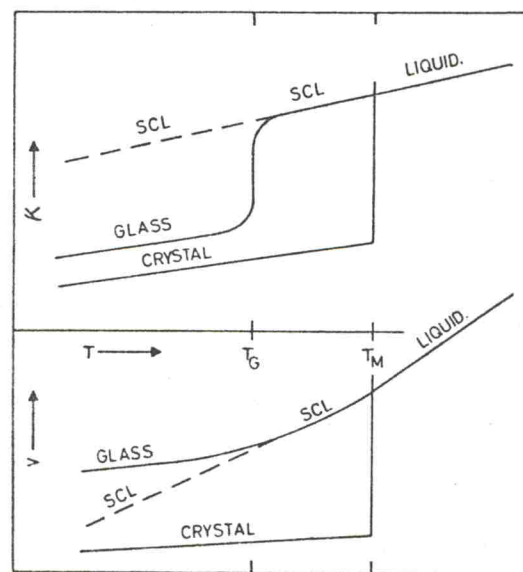


Fig. 1. Variation of compressibility and volume with temperature in crystal, liquid, and supercooled liquid (SCL). T_M is the melting point and T_G is the glass point.