The Viscosity of Silicate Glasses

The structures of several inorganic glasses have been studied, principally by Warren and his co-workers. Silica glass[24] has a random structure with each silicon surrounded by four oxygens tetrahedrally at a distance of 1.60A. It is obvious that whatever the unit (or units) of flow may be, four $Si-O$ bonds will have to be broken per unit of flow. The energy of an $Si-O$ bond is known to be about 100,000 cal. from thermal data, and so ΔE_{vis} should be a half of four times this energy, or 200,000 cal. at any temperature at which this four-coordinated structure is complete. The slope of the curve in Fig. 8 multiplied by $2.303R$ gives $\Delta E_{vis}=175{,}000$ cal.

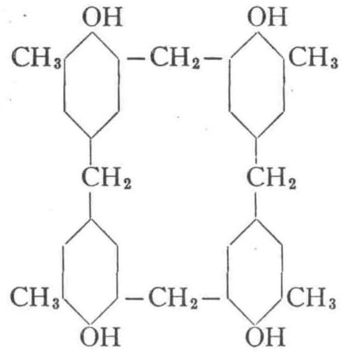
The addition of metal oxides to SiO_2 greatly reduces the viscosity. Soda-silica glasses[25] have a structure in which some of the $Si-O-Si$ bridges are replaced by the electrostatically bound ONa_2O bridges shown diagrammatically in Fig. 9, taken from Warren and Loring's paper.[25] The sodium and O_1 oxygens are univalent ions and the interionic distances are believed to be the following: $Na-O_1=2.35$, $Na-Na=3.85$, and $O_1-O_1=2.65$A. Four attractions and two repulsions, all electrostatic, are involved in this bridge, and a simple calculation shows that the bridge breaks most easily into two ONa groups as indicated by the dotted line in Fig. 9 and that this requires 70,000 cal. Whatever the unit of flow may be, it will certainly involve four bonds. If three of these are $Si-O$ bonds and one is an ONa_2O bridge, the activation energy will be 185,000 cal.; if two are $Si-O$ bonds and two are ONa_2O bridges, the activation energy will be 170,000 cal., etc. The higher the soda content the lower will be the activation energy and the lower the viscosity. The change of viscosity with composition in Na_2O-SiO_2 glasses can be accounted for roughly quantitatively in this way.

Similar considerations apply to other binary glasses, such as $PbO-SiO_2$ glasses, which have a replacement of $Si-O-Si$ bridges by $Si-O-Pb-O-Si$ bridges.[26] The energy required to break this bridge is probably about 40,000 cal. The viscosity measurements of Bair[26] on $Pb-SiO_2$ glasses and of Taylor and Dear[27] on Na_2O-SiO_2 glasses show that PbO is much more potent in reducing the viscosity of silicate glasses than Na_2O is.

The Viscosity of Resins

Resins which have (2,3) or greater reactivity, such as phenol-formaldehyde, glycerol-phthalic anhydride, etc., are called hardening, convertible or infusible resins. When completely polymerized, such resins form a three-dimensional network of covalent bonds and are entirely analogous to silica glass in every respect. Flow in such a resin involves breaking several $C-C$ or $C-O$ bonds, each of which have energies of about 80,000 cal. This makes the activation energy for flow nearly as great as that of silica glass, and no softening would occur below a red heat at the lowest. Naturally the resin decomposes before that temperature is ever reached, and so they are called hardening or infusible resins.

Resins such as cresol-formaldehyde and some others which have only (2,2) reactivity are presumed to form complexes of limited size, but a three-dimensional network is impossible. The following diagram



illustrates the type of structure, although the complexes in a resin will be much larger. Such resins are called nonhardening, nonconvertible or fusible resins. Flow in such a resin involves breaking a number of hydrogen bonds, (at 6000 cal. each) formed between the complexes through the OH groups, plus a fairly large energy of activation due to van der Waals and dipole forces for such large molecules. Such a resin will therefore be very viscous, even hard and glassy at low enough temperatures, depending on the size of the complexes, but its energy of activation for flow will be of an entirely different order of magnitude from that of the (3,2) reactive resins,