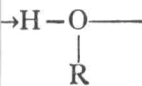


$p/4$ , where  $\Delta E_{vap}$  is per unit molecule. these energies of or 40,000 cal., so at temperatures position temperature. a whole polymerized molecules would be would never soften molecule had to flow ss.

is  
molecules containing OH ordinarily called alcohols. Among the other higher viscosities from the size and weight. This abnormally due to the hydrogen bonds. If it were not structure  $H_2O$  and  $NH_3$  about the same viscosity and  $CH_3CH_3$ ; phenol, the maximum possible number of hydrogen bonds per molecule is about 4 and  $NH$  groups in the

hydrogen bonds superliquids and eventually ice, glycerol, glycol, urea, betol, and paraffins, etc. Glucose, for example, can form as many as 12 hydrogen bonds. A large molecule may have a large energy of activation for breaking van der Waals and dipole bonds. The energy of activation for such as 80,000 cal. For a maximum coordination number of 4 that ethyl alcohol has the same viscosity indicates that it must possess a large number of two-coordination. of chains



is roughly parallel in  
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the liquid, or possibly rings containing three or four molecules linked in similar fashion.

Quantitative calculation of the viscosity of these associated liquids is not possible because the relative contribution to the energy of vaporization of van der Waals, dipole, hydrogen bond and repulsive forces is not known. A study of the viscosity and its temperature variation can, however, throw some light on the question. The writer<sup>2</sup> was able to use viscosity data to estimate the number of hydrogen bonds per molecule in water and it was concluded that the average number of bonds was about  $2\frac{1}{2}$  per molecule at  $0^\circ\text{C}$ ,  $1\frac{1}{2}$  at  $50^\circ$ , 1 at  $100^\circ$  and  $\frac{1}{2}$  at  $150^\circ$ . Heavy water is about 27 percent more viscous than ordinary water. This is easily explained by the fact that deuterium bonds are somewhat stronger than hydrogen bonds. It would require only a very small increase in the energy of activation of flow to account for a difference in viscosity of only 27 percent. This is a good illustration of the exceptional sensitivity of the viscosity to structural differences, compared to the relative insensitivity of most physical properties.

#### Non-Newtonian Flow and the Viscosity of Rubber

If  $\sinh f\lambda_2\lambda_3\lambda/2kT$  in Eq. (2) is expanded in the most general way we have

$$\eta = \frac{\lambda_1 h}{\lambda^2 \lambda_2 \lambda_3} \frac{F_n}{F_a^*} e^{\Delta E_a/kT} \left[ 1 + \frac{1}{6} \left( \frac{f\lambda_2\lambda_3\lambda}{2kT} \right)^2 + \frac{1}{120} \left( \frac{f\lambda_2\lambda_3\lambda}{2kT} \right)^4 + \dots \right], \quad (13)$$

which reduces to Eq. (3) when  $f\lambda_2\lambda_3\lambda/2 \ll kT$ . This inequality may be taken as a theoretical definition of Newtonian flow. For higher shearing stresses, however, the viscosity decreases with increasing shearing stress, which is in accord with experimental fact. This effect should occur in any flowing material, but in substances of low viscosity, turbulence sets in before the shearing stress has become high enough, and then the hydrodynamic definition of viscosity is no longer valid. Homogeneous substances of low viscosity are therefore called Newtonian liquids, because their regime of nonturbulent flow is always in

the region of low shearing stress. More viscous substances will show Newtonian flow at sufficiently small stresses, but at higher stresses they will show non-Newtonian flow, i.e., a variation in the ratio rate of shear/shearing stress with shearing stress. For very viscous substances even the smallest stresses giving conveniently measurable deformations may be in the non-Newtonian range.

In cases where  $f\lambda_2\lambda_3\lambda/2$  is sufficiently large the backward rate of flow can be neglected in comparison with the forward rate of flow as Eyring<sup>1</sup> has pointed out (see Fig. 2). For this case

$$\eta = \frac{f\lambda_1}{\lambda} \frac{h}{kT} \frac{F_n}{F_a^*} e^{(\Delta E_a - \frac{1}{2}f\lambda_2\lambda_3\lambda)/kT}. \quad (14)$$

This same result is obtained by making the approximation  $\sinh x \cong e^x$  for  $x \geq 1.5$  in Eq. (2), as Smallwood<sup>28</sup> has done.

Figure 10, taken from the work of Ferry and Parks<sup>29</sup> on the viscosity of polyisobutylene, shows an example of flow over a wide range of shearing stress. The region of Newtonian flow appears to extend up to a torque of about 200,000 dyne-cm. The reciprocal of the slope of this "consistency" curve at any point multiplied by the constant of the instrument is the viscosity. Sometimes these viscosities which are not independent of shearing stress are called "apparent viscosities," but this development makes it clear that they are all true viscosities. However, the slope of the linear portion of the curve at small shearing

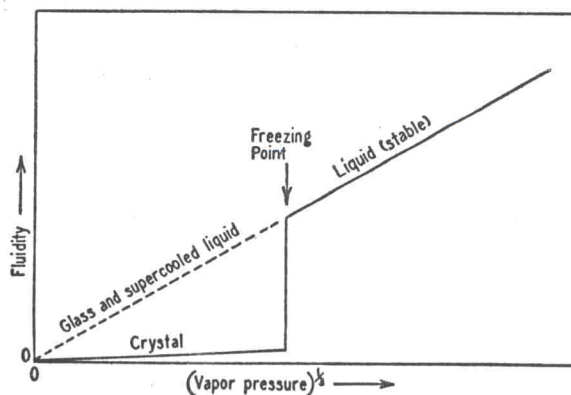


FIG. 12. Schematic representation of the fluidity and vapor pressure relations of liquids, crystals and glasses.