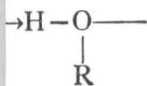


$p/4$, where ΔE_{vap} is per unit molecule. these energies of or 40,000 cal., so n at temperatures position temperature. a whole polymerized molecules would be would never soften molecule had to flow ss.

olecules containing OH rdinarily called ab- s. Among the other n higher viscosities from the size and . This abnormally due to the hydrogen uids. If it were not cture H_2O and NH_3 about the same vis- id CH_3CH_3 ; phenol, e maximum possible ds per molecule is d NH groups in the

hydrogen bonds super- uids and eventually se, glycerol, glycol, e, betol, and prac- oids, many phenolic s, etc. Glucose, for ps and can form as ls. A large molecule ve a large energy of er Waals and dipole y of activation for uch as 80,000 cal. e a maximum coordi- t that ethyl alcohol same viscosity indi- must possess a large n two-coordination. of chains



d 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 writer² 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°C , $1\frac{1}{2}$ at 50° , 1 at 100° and $\frac{1}{2}$ at 150° . 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

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

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 Eyring¹ 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 Smallwood²⁸ has done.

Figure 10, taken from the work of Ferry and Parks²⁹ 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

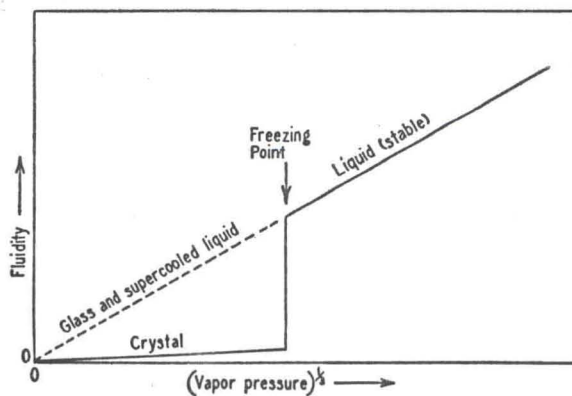


FIG. 12. Schematic representation of the fluidity and vapor pressure relations of liquids, crystals and glasses.