

stresses gives the viscosity which is to be compared to the Newtonian viscosities of other liquids.

Smallwood<sup>28</sup> has applied Eq. (14) in the form

$$\eta = A f e^{(a-bf)/T} \quad (15)$$

to the experimental data of Mooney<sup>30</sup> on the viscosity of raw rubber as a function of temperature and shearing stress. A graphical evaluation of the constants gave:  $A = 1.65 \cdot 10^{-4}$ ,  $a = 5100$ ,  $b = 1.28 \cdot 10^{-5}$ . Using these constants the equation gave good agreement with experiment for shearing stresses between 840,000 and 1,880,000 dynes/cm<sup>2</sup> and at temperatures of 70 to 140°C.

The constant  $a$  is equal to  $\Delta E_{vis}/R$ , so that  $\Delta E_{vis} = 10.1$  kcal. Raw rubber consists of linear polymers of isoprene of the order of 1000 isoprene units per chain. Such a chain would not move a whole chain length per unit flow process, but probably only the length of several isoprene units as Smallwood has suggested. The energy of vaporization of isoprene at 25° is 5.7 kcal./mole. At the higher temperatures of these experiments this energy would be less, and also the energy of vaporization per isoprene unit in rubber would be somewhat less than the energy of vaporization for an isolated isoprene molecule. If we assume then that the energy of vaporization of rubber per isoprene unit is about 4 kcal. and that  $n=4$  for this molecule, the energy of activation for flow per isoprene unit would be 1 kcal. This leads to the conclusion that during the flow process, the rubber molecule moves about 10 isoprene units.

The constant  $b$  is equal to  $\lambda_2 \lambda_3 \lambda / 2k$  and substituting the experimental value we have

$$\begin{aligned} \lambda_2 \lambda_3 \lambda / 2k &= 1.28 \cdot 10^{-5}, \\ \lambda_2 \lambda_3 \lambda &= 3.51 \cdot 10^{-21} \text{ cc.} \end{aligned}$$

Now assume the length of the isoprene unit,  $\lambda_2$ , is 5A and the thickness,  $\lambda_3$ , is 4A. The last paragraph showed that  $\lambda = 10\lambda_2$ , or  $\lambda = 50A$ . These values give  $\lambda_2 \lambda_3 \lambda = 1 \cdot 10^{-21}$  cc, in fair agreement with the above experimental value. The factor of 3.5 might mean, as Smallwood suggests, that a bundle of 3 or 4 hydrocarbon chains moves as a unit.

Equation (14) represents the viscous behavior

of a non-Newtonian liquid, or more accurately of a non-Newtonian state of flow. The equation has, however, both upper and lower limits of applicability. On the side of very small stresses the equation is not valid when  $f \lambda_2 \lambda_3 \lambda / 2kT < 1$  and on the side of large stresses the whole development is invalid when  $f \lambda_2 \lambda_3 \lambda / 2 = \Delta E_a$ .

### Flow in Crystals

When a liquid crystallizes the viscosity usually increases by a factor of approximately  $10^{12}$ . The energy of activation for flow is obviously much greater in the crystal, and it seems likely that the regular structure of the crystal requires a whole molecule-sized hole, and therefore all the energy of vaporization (sublimation) to activate the flow process, compared to the  $\frac{1}{3}$  or  $\frac{1}{4}$  the energy of vaporization in the case of liquid. Since the best of fusion is relatively small,  $\Delta E_{vis}$  for the crystal should be about 3 or 4 times  $\Delta E_{vis}$  for the liquid, if the two entropies of activation for flow are the same.

The only substance for which viscosity measurements on both liquid and crystal are available is menthol, shown in Fig. 11. The slope of the liquid line gives  $\Delta E_{vis} = 12,000$  cal. and the slope of the crystal line gives  $\Delta E_{vis} = 34,000$  cal. Since the entropies of activation for flow are probably be different for liquid and crystal, the approximate ratio of 3 between the two values of  $\Delta E_{vis}$  is satisfactory. The energies of vaporization of liquid and crystalline menthol have never been measured.

The high viscosities of glasses and crystals differ in an important respect. High viscosity of a glass is accompanied by a corresponding small vapor pressure, while the vapor pressure of a crystal is relatively high. Fig. 12 illustrates this point. When a liquid is cooled the fluidity and the vapor pressure both decrease as discussed in an earlier section. At the freezing point the liquid may crystallize decreasing the fluidity enormously (by a factor of about  $10^{12}$ ), while the vapor pressure remains unchanged. However, if the liquid supercools, the fluidity and the vapor pressure continue to decrease with any discontinuity (dotted line in Fig. 12), and only when the vapor pressure has become exceedingly small does the fluidity become very small.

**Conclusion**  
The conclusion of this article can be stated quantitatively in one application.

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