and no extra volume is required for the activated complex for flow to form. As the pressure is increased, the open structure collapses, and at high pressures the activated complex needs as much extra space to form as is required by any other nonspherical molecule. It is probably incorrect to assume that n is constant for these liquids at one temperature and varying pressures, but the value of n' is not greatly affected by a considerable change in n. Table III illustrates

TABLE III. *Values of n' for water for different values of n at 0°C.*

P (kg/cm)	$n=2$	4	5.4
1,000		16.1	124
2,000	32	16	14
3,000	19	11	9.7
4,000	14	8.8	8.0
5,000	10.6	7.7	7.2

that the n' values computed for water using different n's converge to about the same limit at high pressures.

The fifth column of Table I gives the ratio of the mean value of n' over the pressure range to the value of n. The fact that this ratio is nearly constant and equal to 1.6–1.8 for the four nonmetallic liquids in the table is of some significance. It has been previously shown[4] that the energy required to form a hole in a liquid the size of a molecule is equal to the energy of vaporization. Although it might be reasonable to assume a linear relationship between the size of the hole formed and the energy required to form it, the fact that the ratio, n'/n is not unity, but 1.75 indicates that this is not the case. Taking the data for ether as an example, we find an n' of 7, indicating that a hole approximately 1/7 the size of the molecule is required for viscous flow. However, the activation energy is 2/9 times the energy of vaporization. We accordingly have the interesting physical result that there is an energy of dissociation of large holes into smaller ones, i.e., two holes, each 1/7 the size of a molecule cost considerably more energy than one hole 2/7 molecular size. In case of ether, seven holes, each 1/7 the size of a molecule would liberate energy equal to 14/9 the energy of vaporization, on being combined into a single cavity of molecular dimensions.

The ratio n'/n for mercury does not differ greatly from that for the nonmetallic liquids in the Table, but n and n' are themselves much greater. This has been previously explained[5, 12] as being due to movement of the metallic ions in viscous flow, rather than of the atoms. That the ratio of n' to n is again approximately two for a hole as small as 1/23 the size of the atom is an interesting fact.

Figure 1 shows plots of observed and computed viscosities as a function of pressure for ether, mercury, and n-pentane, with constant values of n and n' in Eq. (16). The results of the present work lead us to suggest that viscosities under pressure may be computed with reasonable accuracy by Eqs. (15) and (16) by using only thermodynamic data and viscosity measurements at atmospheric pressure. For normal, nonmetallic liquids n' for use in Eq. (16) is equal to 1.75 times the value of n from Eq. (15). For metallic liquids the factor (n'/n) may be somewhat higher but only one test case is available. Although it is impossible at present to *predict* the pressure effect on viscosity for liquids in which the molecules are bound by directional bonds

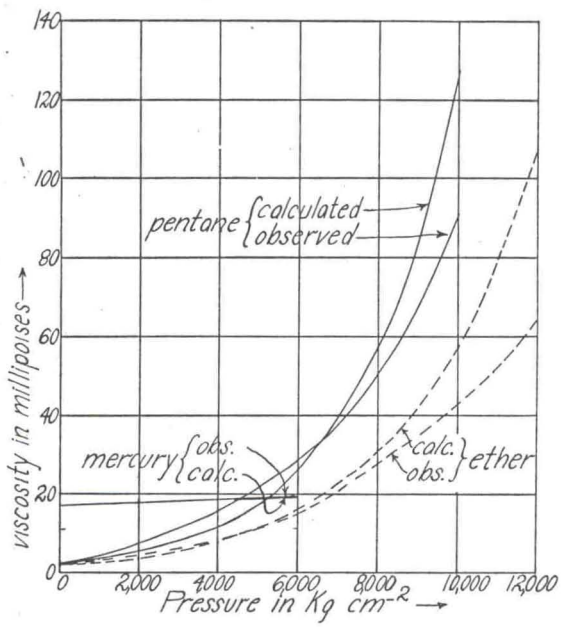

FIG. 1. Comparison of observed viscosities and those computed from Eq. (16). The values of n are 4.5, 12 and 4.4 of n' 8, 23 and 10 for ether, mercury and pentane, respectively.

[12] J. Kincaid and H. Eyring, J. Chem. Phys. **5**, 588 (1937).