

to make the hole in which the molecules pass each other. At high pressures we must add on to  $\Delta E_{\text{vap}}/nRT$  the term  $P\Delta V/RT$  where  $P$  is the external pressure and  $\Delta V$  the volume of the hole formed against it.  $\Delta V$  will be some fraction  $V/n'$  of the molecular volume, giving

$$\eta = (\pi RMT)^{1/2} N^{-1/2} (u_0/u_1) V_1^{-1/2} \times \exp(\Delta E_{\text{vap}}/nRT + PV/n'RT). \quad (16)$$

$n'$  will often vary over the experimental pressure range because as the liquid becomes compressed and the molecular volume decreases, a different fraction of the molecular volume is needed to give the same amount of space for the passing of molecules. Liquids such as water undergo structural changes under pressure that would naturally alter rapidly the free space available for molecular passage without making an additional hole, thus affecting  $n'$ .

Solids unlike liquids are not able to introduce a hole a fraction the size of a molecule without profoundly altering the crystal structure in the neighborhood of the molecules passing each other. This alteration in structure could take the form of a compression of neighboring molecules. In this case it can be estimated from the well-known thermodynamic expression for the free energy of compression. This way of obtaining the necessary cavity permitting viscous flow would be expected to be more extravagant of free energy than the method of over-all expansion possible in the comparatively structureless liquids. In fact in solids it may be cheaper from the free energy point of view to diffuse only where a molecule is omitted from the lattice than by distortion of a perfect lattice.

The procedure followed in the computations is to use the experimental viscosity, the energy of vaporization, the velocity of sound in both the liquid and the gas, and the other terms on the right-hand side of Eq. (15) to determine  $n$ , giving

TABLE I.

SUBSTANCE	$n$ , E. AND E.	$n$ (THIS PAPER)	$n'$ (MEAN VALUE)	$n'/n$ (THIS PAPER)	$\eta$ (obs.) $\eta$ (COMPUTED)
<i>n</i> -Pentane	3.5	4.4	7.8	1.8	1.1
Diethyl Ether		4.5	7.8	1.6	1.9
Benzene	2.6	3.3	5.5	1.7	0.6
Iso-Pentane		4.4	8	1.8	1.9
Mercury	20	11	23	2.1	2.8

the proper temperature variation of viscosity. This is done over as wide a temperature range as the data warrant and at atmospheric pressure employing the sound velocity data of Freyer, Hubbard and Andrews,<sup>10</sup> and other data from *Landolt-Bornstein Tabellen*. The values of  $n$  obtained in this way, given in Table I, are the values used in Eq. (16) in order to obtain values of  $\eta$  at a given temperature and different pressures. The viscosity and P-V-T data are those given by Bridgman.<sup>8</sup> By the use of the P-V-T data, the energies of vaporization were in all cases corrected to the particular pressure in question. A summary of the results for  $n'$  is given in Table II.

The values of  $n$  given in column three of Table I lie in a slightly different range than those of Ewell and Eyring<sup>5</sup> shown in column two because a different evaluation of the free volume has been used here. Column six of Table I shows that the value for  $n$  which gives the right temperature coefficient of viscosity also gives the absolute value to within better than an average factor of 2 for liquids other than those classed as "hydrogen-bonded."

TABLE II. Values of  $n'$  as computed from the data at various pressures.

PRES-SURE kg/cm <sup>2</sup>	<i>n</i> -PEN-TANE 30°C	DIETHYL ETHER 52.5°C	BEN-ZENE 25°C	ISO-PEN-TANE 50°C	MER-CURY 0°C	WATER 0°C
1,000	6.0		5.5	8		124
2,000	6.9	4.7			25.0	14
4,000	8.5	6.0			23.0	8
6,000	9.7	6.8			24.2	(5000)12
8,000	10.4	7.2				
10,000	10.8	7.6				
12,000		7.9				

The individual computations of  $n'$  are shown in Table II. The treatments possible for benzene and for iso-pentane warrant giving only one value for  $n'$ . It will be noted that  $n'$  for *n*-pentane, ether, and mercury does not vary greatly over the entire experimental pressure range, but that  $n'$  for water ranges from 124 at 1000 kg/cm<sup>2</sup> to 7.2 at 5000 kg/cm<sup>2</sup>. This variation is interpreted as follows: at low pressures water has an open, four-coordinated structure

<sup>10</sup> Freyer, Hubbard and Andrews, *J. Am. Chem. Soc.* **51**, 759 (1929).

<sup>11</sup> J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 5 (1933).

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