

The energy of vaporization of a liquid under pressure has its most definite meaning in terms of the equation

$$\Delta E_{\text{vap}} = Vp_{\text{internal}} = V(\partial E/\partial V)_T = V(T(\partial p/\partial T)_V - p) \quad (7)$$

due to Hildebrand.<sup>6</sup> If this is substituted in Eq. (6) we get

$$\eta = 1.090 \cdot 10^{-3} \frac{M^3 T^{\frac{1}{2}}}{V^{5/2} (\partial p/\partial T)_V} \cdot \exp [V(\partial p/\partial T)_V/nR]. \quad (8)$$

Eqs. (6) and (8) are general equations for calculating the viscosity of a pure liquid at any temperature and pressure. Table III and Fig. 6

TABLE III. Computation of the viscosity of ether as a function of pressure at 52.5°, using Eq. (8).

$p$ KG/CM <sup>2</sup>	$V$ CC/MOLE	$(\partial p/\partial T)_V$ KG/CM <sup>2</sup> DEG.	$\eta$ (CALC.) MILLI- POISES	$\eta$ (OBS.) MILLI- POISES
1	109.9	6.73	1.80	1.83
1000	—	—	—	3.61
2000	90.25	13.50	5.35	5.64
3000	86.70	16.00	8.00	—
4000	84.00	18.00	10.7	10.50
5000	81.80	19.80	14.0	—
6000	80.05	21.40	17.7	17.58
7000	78.50	22.85	22.0	—
8000	77.15	24.20	26.3	27.75
9000	76.05	25.40	30.9	—
10000	75.05	26.50	35.8	42.69
11000	74.10	27.50	40.8	—
12000	73.25	—	—	64.24

show a test of Eq. (8) for ether at 52.5°, using  $n=4$  and dividing the calculated values by 2 as mentioned above in the test of Eq. (4).  $V$  and  $(\partial p/\partial T)_V$  were evaluated from the PVT data of Bridgman.<sup>7</sup> The observed viscosities under pressure were also taken from Bridgman.<sup>8</sup> It is seen that the equation fails above about 7000 kg/cm<sup>2</sup>. This failure may be due to the failure of Eq. (7) or to any of several other causes which need not be discussed here, but the close agreement up to 7000 kg/cm<sup>2</sup> gives striking confirmation to the fundamental correctness of the theory.

Equation (6) will give approximate results for pressures below 2000 kg/cm<sup>2</sup> when the ordinary energy of vaporization measured at atmospheric pressure is used, thus requiring PV data only at

the temperature in question. This is possible because the internal pressure and energy of vaporization change very little for pressures up to about 2000 kg/cm<sup>2</sup>. Eq. (6) can also be used to calculate the internal pressures of liquids if experimental values of the viscosity under pressure are available—just the reverse of the calculation in the last paragraph. The original paper<sup>2</sup> illustrates both these applications.

An obvious application of Eq. (8) is to the calculation of the viscosity of lubricants under high pressures. The fact that the viscosity of liquids increases rapidly with pressure is, of course, of great importance in many lubricative problems. Mineral lubricating oils are mixtures of many molecular species, and since Eq. (8) is true only for pure liquids, no attempt will be made here to calculate the absolute viscosities of oils under pressure. However, a calculation of the relative viscosities at two different pressures seems more likely to succeed. Eq. (8) gives

$$\frac{\eta_{p_2}}{\eta_{p_1}} = \frac{(V_r^{5/2}(\partial p/\partial T)_V)_{p_1}}{(V_r^{5/2}(\partial p/\partial T)_V)_{p_2}} \cdot \exp \frac{M}{nRd_0} \left[ \left( V_r \left( \frac{\partial p}{\partial T} \right)_V \right)_{p_2} - \left( V_r \left( \frac{\partial p}{\partial T} \right)_V \right)_{p_1} \right]$$

where  $V_r$  = relative volume,  
 $d_0$  = reference density,  
 $n=4$ ,

and  $R$  must be in the appropriate energy unit.

Table IV shows the results of testing the equation.  $(\partial p/\partial T)_V$  and  $V_r$  were evaluated from the PVT data of Dow<sup>9</sup> on a Pennsylvania oil and the observed viscosities were interpolated from the data of Dow<sup>10</sup> on another Pennsylvania oil, whose molecular weight was  $485 \pm 10$  percent. The value of the molecular weight in such a calculation is the most uncertain factor. The

TABLE IV. Computation of the viscosity of Pennsylvania oil as a function of pressure at 57.5°C.  $M=485 \pm 10$ ,  $d_0=0.8524$ .

$p$ KG/CM <sup>2</sup>	$V_r$	$(\partial p/\partial T)_V$ KG/CM <sup>2</sup> DEG.	$\frac{\eta_{1500}}{\eta_{375}}$ (CALC.)	$\eta$ (OBS.) POISES	$\frac{\eta_{1500}}{\eta_{375}}$ (OBS.)
375	0.9875	10.81	6.96	0.77	6.95
1500	0.9412	12.78	—	5.35	—