

where

$$\Delta F_{\pm} = RT \ln(\eta V/Nh) \quad (4)$$

$$\Delta H_{\pm} = R \frac{\partial(\ln Z)}{\partial(1/T)_p} = \frac{\partial(\Delta F_{\pm}/T)}{\partial(1/T)_p} \quad (5)$$

$$\Delta S_{\pm} = - \left(\frac{\partial(\Delta F_{\pm})}{\partial T} \right)_p \quad (6)$$

In these equations ΔF_{\pm} is the Eyring free energy of activation for viscous flow, ΔH_{\pm} the enthalpy of activation for viscous flow, ΔS_{\pm} the entropy of activation associated with the flow and Z the kinematic viscosity, equal to η/d .

The values of ΔF_{\pm} were computed from the data of Table II and Eq. (4) in order to compute ΔH_{\pm} and ΔS_{\pm} , and a quantity ΔH_{\pm}^i to be discussed later in this paper. Table VI is an abbreviated list of the values of ΔF_{\pm} ; a complete list is not given since ΔF_{\pm} gives no information not contained in Table II. From Table VI it is seen that the variation of ΔF_{\pm} with temperature is small at any fixed pressure indicating approximate conformance to the De Guzman or Andrade type of equation even at high pressures.^{16,17} It should be noted that although the viscosity is always a decreasing function of temperature that ΔF_{\pm} is not. In fact ΔF_{\pm} exhibits minimums in some cases, e.g., PSU 110. Using the data of Schiessler, Whitmore, and co-workers for the heats of vaporization the ratios $E_{\text{vap}}/\Delta F_{\pm}$ were calculated and found to vary from 3.9 to 4.5 at atmospheric pressure. These values agree with those previously observed.²

The several differential coefficients used in the Eyring theory have significance independent of the particular theory used since they describe the variation of the viscosity with the variable of differentiation. The enthalpy of activation, ΔH_{\pm} , has been computed by Lowitz for the compounds reported here and for others whose viscosities as a function of pressure have been studied in this laboratory. The results of these studies are reported in another paper.²² An analysis of ΔH_{\pm} into two parts has been made by Eyring *et al.*² One part, $\Delta H_{\pm}^i \equiv R[\partial(\ln Z)/\partial(1/T)]_p$ has been interpreted as representing the energy to move a molecule into a vacancy which has already been created. The second part of ΔH_{\pm} called ΔH_{\pm}^h and equated to the difference between ΔH_{\pm} and ΔH_{\pm}^i has been interpreted as the energy required to form the hole.^{2,18,19,23} Values of ΔH_{\pm}^i have been determined at intervals of 0.01 g/cm³ in the density for six of the compounds. The ranges of pressures and temperatures, shown in Table II, were such that ten densities were available for four compounds and nine densities for two compounds. The derivatives were obtained by measuring the slopes of

²² Lowitz *et al.* submitted for publication to J. Chem. Phys.

²³ References 17 and 18 represent a study by Bondi of the several differential coefficients of the Eyring theory using the extensive data, mostly at atmospheric pressure, found in the literature for many compounds, including lubricating oils.

curves $\ln Z$ versus T at constant density. Although the values of ΔH_{\pm}^i were determined for at least seven different temperatures for each compound, only those for one temperature, 71.1°C (160°F) are listed in Table VII. These are typical of the others obtained. In every case ΔH_{\pm}^i increases with density at constant temperature as would be expected (see Table III), since this represents an isothermal increase in pressure from atmospheric to 3300 bars. When the data at all temperatures are examined, it is found that the increase in ΔH_{\pm}^i ranges from a factor of 1.9 to 3.1 with 2.2 representing a rough average. On the average, the cyclohexyl, PSU 19, has the highest factors while the dicyclopentyl, PSU 111, has the lowest. One might expect the branched paraffin, PSU 25, to have the lowest if ΔH_{\pm}^i represents the work to move into a vacancy. At temperatures other than that of Table VII one observes similar behavior but the magnitudes of the ratios of the maximum to the minimum values may be in a different order from those of Table VII. This seems difficult to correlate with an interpretation of ΔH_{\pm}^i as an energy to move into a vacancy.

It might seem logical to compare the values of ΔH_{\pm}^i at equal densities and equal temperatures. With $d=0.8800$ at $T=71.1^\circ\text{C}$ the order of increasing magnitude of ΔH_{\pm}^i is PSU 18, 111, 113, 110, 19, and 25. It would seem reasonable to suppose the "hole" size to be about equal under these conditions yet the *simplex structure (and the structure with greatest freedom of intramolecular and intermolecular rotation) shows the greatest ΔH_{\pm}^i value.* The smallest value of the density available for PSU 18 was 0.9100 but even so and in spite of its two phenyl rings its ΔH_{\pm}^i value is still the lowest for these conditions. It should be noted that while PSU 25 is at the highest pressure for this density that PSU 110 is at a higher pressure than PSU 19 and PSU 111 is at a higher pressure than PSU 113.

When all of the data for ΔH_{\pm}^i are examined one finds that for fixed density levels and increasing temperatures there are 13 instances of monotonic decrease of the ΔH_{\pm}^i values, 19 of decrease to constant value, 4 of no significant change, and 22 minimums occurring. The minimums were not very marked, however.

ΔS_{\pm} , the Eyring theory entropy of activation, was calculated at two temperatures and four pressures by use of the Gibbs-Helmholtz equation and the values of ΔH_{\pm} and ΔF_{\pm} already calculated. The values obtained from ΔS_{\pm} are listed in Table VIII. From Table VIII it is immediately apparent that ΔS_{\pm} increases with an increase of pressure. An examination of the changes in the relative viscosity with temperature at the higher pressures compared with corresponding changes at lower pressures, Table II, would lead one to expect this result. Table VIII shows that there is always a decrease of ΔS_{\pm} with an increase in temperature, with the magnitude of this decrease usually being greater at the higher pressures. The quantity ΔS_{\pm} is seen to be very structure dependent with the larger

Pressure (bars)	PSU 25 60°C
1	-1.62
1030	-0.60
2070	+0.30
3100	+0.93

values being assigned to the diphenyl PSU 19, the tricyclopentyl, PSU 111, is greatly enhanced as indicated.

The behavior is general with the energy associated with ΔH_{\pm} , is constant, ΔH_{\pm} , and they increase.

The quantity ΔH_{\pm}^i in the Eyring theory of flow process. I viscosity. This definition of ΔH_{\pm}^i observed parallel ($\Delta H_{\pm} - \Delta H_{\pm}^i$) ΔV_{\pm} is found to volume, V , he c segment-wise. O paper and that dence of segme calculated for t These values w significant infor fact that $(\partial \ln Z / \partial \ln Z / \partial P)_T$. T creasing pressu curves of $\ln Z$ e axis. At any gi temperature of sures above 20 course, the sam as do the origi 60°C, when th 3000 bars, ΔV_{\pm} 18, 32% for the dicyclohexyl P paraffin PSU 2 differences in Δ having the highe

It should be p $[(1/\eta)(\partial\eta/\partial P)]_T$ at higher pressu

²⁴ Further studie wider range of ten the near future.