TABLE VIII. $\Delta S_{\pm} = 1/T[\Delta H_{\pm} - \Delta F_{\pm}]$ for six high-purity hydrocarbons.

Pressure (bars)	PSU 25 60°C	98.9°C	PSU 110 60°C	98.9°C	PSU 111 60°C	98.9°C	PSU 113 60°C	98.9°C	PSU 19 60°C	98.9°C	PSU 18 60°C	98.9°C
1	−1.62	−4.46	−0.41	−3.19	+0.08	−2.76	+1.68	−2.08	+3.70	−1.12	+0.35	−2.96
1030	−0.60	−4.29	+0.71	−3.76	1.15	−1.62	4.33	−0.97	7.60	−1.20	2.93	−1.96
2070	+0.30	−3.27	+2.05	−2.84	3.03	−0.51	4.50	+1.03	11.41	+3.78	6.19	+0.08
3100	+0.93	−1.65	+3.17	−0.97	5.65	+0.48	8.49	+3.41	14.70	+7.38	10.60	+3.01

values being associated with the more rigid molecules the diphenyl PSU 18, the dicyclohexyl PSU 19, and the tricyclopentyl PSU 113. The effect of this rigidity is greatly enhanced by higher pressures, as Table VIII indicates.

The behavior of $\Delta S_{\pm}$ for these compounds agrees in general with the pattern indicated by Bondi.[18,19] The energy associated with $T\Delta S_{\pm}$, while not as great as with $\Delta H_{\pm}$, is certainly not negligible compared with $\Delta H_{\pm}$, and they increase together.[24]

The quantity $\Delta V_{\pm} \equiv RT(\partial \ln Z/\partial P)_T$ is interpreted in the Eyring theory as a volume characteristic of the flow process. In the derivative Z is the kinematic viscosity. This relationship is a consequence of the definition of $\Delta F_{\pm}$ as $RT \ln(\eta V/Nh)$. Bondi[19] has observed parallel relationships between $\Delta V_{\pm}/V$ and $(\Delta H_{\pm} - \Delta H_{\pm}{}^i)$ for a number of compounds. Since $\Delta V_{\pm}$ is found to be but a small fraction of the molecular volume, V, he concludes that long chain molecules flow segment-wise. Of course, the mixture data of the present paper and that cited earlier[6] furnish more direct evidence of segmental flow. The values of $\Delta V_{\pm}$ were calculated for the compounds studied in this paper. These values will not be reproduced here since all the significant information follows from Table II and the fact that $(\partial \ln Z/\partial P)_T$ does not differ significantly from $(\partial \ln Z/\partial P)_T$. The values of $\Delta V_{\pm}$ decrease with increasing pressure in all cases reported here as the curves of $\ln Z$ vs P are concave toward the pressure axis. At any given pressure, $\Delta V_{\pm}$ decreases when the temperature of the isotherm is increased, for all pressures above 200 bars. The values of $\Delta V_{\pm}$ show, of course, the same characteristic structural dependence as do the original data in Table II. For example at 60°C, when the pressure is increased from 165 to 3000 bars, $\Delta V_{\pm}$ decreases 24% for the diphenyl PSU 18, 32% for the tricyclopentyl PSU 113, 34% for the dicyclohexyl PSU 19, and 41% for the branched paraffin PSU 25. The higher pressures enhance the differences in $\Delta V_{\pm}$ at all temperatures with PSU 19 having the highest value and PSU 25 the smallest value.

It should be pointed out that the pressure coefficient $[(1/\eta)(\partial \eta/\partial P)]_T$ might become an increasing function at higher pressures than those employed in this work

[24] Further studies of $\Delta S_{\pm}$ data on more compounds and over a wider range of temperature will be submitted for publication in the near future.

for others have found the $\ln\eta$ vs P becomes convex toward the pressure axis in many cases when the pressures are carried to 10 000 bars.[12] The magnitude of $\Delta V_{\pm}$ varies from 10% to 16% of the molar volume at 165 bars and 37.8°C and from 5% to 9% at 3000 bars and 135°C. The largest values are associated with the dicyclohexyl, PSU 19, and smallest values with the monocyclopentyl, PSU 110, in each case.

As was previously stated no choice of the parameters of the Eyring equation was found that reproduced the data of this report quantitatively. An empirical equation was therefore sought that would do so. It seemed reasonable to try to adapt the semiempirical equation

$$\eta = A \exp(B/RT) \qquad (7)$$

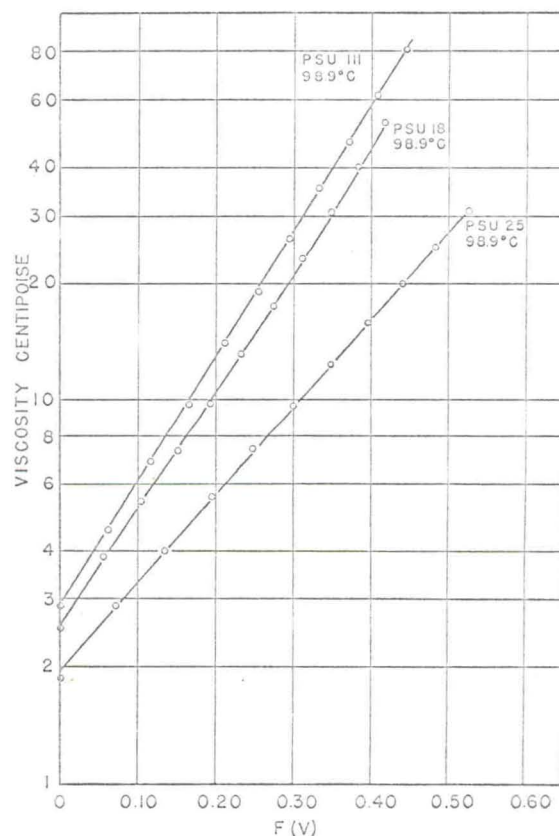discussed previously, to the pressure data as this

FIG. 1. Absolute viscosity versus $F(v) = [(v_0/v)^4 - (v_0/v)^2]$ for PSU 25, 18, and 111 at 98.9°C.