that have the same basic symmetry, the viscosity is an additive function of the parts of the molecule, independent of whether these parts are in the same or different molecules.

Since the chief external effect of the increase in pressure is the decrease in specific volume, a qualitative explanation of the variation of the effect of pressure on viscosity among different compounds may be related to their diminished free volume. The intermolecular forces, which are related to the chemical type, are known to vary inversely as a high power of the intermolecular radii and the work required to move the liquid molecules past one another, that is the viscosity, must rise sharply as this distance decreases.[15] While the rigidity of a molecule would not be expected to be a rapidly varying function of pressure, the effect of a given degree of rigidity would become increasingly important at high pressure. If the molecule be able to deform easily (with a small change in internal energy) then adaptation to a variety of hole shapes is possible within a short time and a low viscosity is evidenced.

It has been known for many years that the viscosity of a substance could be described over a short temperature range by the equation

$$\eta = \exp(B/RT),$$

when η is the absolute viscosity and A and B are characteristic of the substance.[16,17] Because of the practical and theoretical importance of viscosity, many attempts have been made to obtain a general expression for it as a function of temperature and pressure. One of the best known theoretical approaches is that of Eyring and his co-workers.§ The equation they suggest for expressing the viscosity as a function of pressure is

$$\eta = N/V \, (2\pi m k T)^{\frac{1}{2}} v_f^{\frac{1}{3}} \exp \frac{\Delta E_{\text{vis}} + PV/n'}{RT},$$

where v_f is a "free volume," ΔE_{vis} an energy associated with viscous flow, n' a numeric in the range 6–8, and the other symbols have their usual significance. This equation was tested with the data of the research reported herein. Agreement as to direction of variation and order of magnitude was found *but no choice of the parameters reproduced the data quantitatively.*

[15] R. W. Schiessler, Ph.D. dissertation, The Pennsylvania State University (1944).
[16] E. N. da C. Andrade, Phil. Mag. 17, 497, 698 (1934).
[17] J. de Guzman, Anales soc. espan. fis. y quím. 11, 353 (1913).
§ Reference 2 summarizes the work of Eyring and his co-workers and contains a complete bibliography of their work published up to the time of the publication of reference 2.
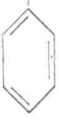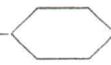[18] A. Bondi, Ann. N. Y. Acad. Sci. 53, 870 (1951).
[19] A. Bondi, J. Chem. Phys. 14, 591 (1946).
[20] E. Brunner, J. Chem. Phys. 17, 346 (1949).
[21] Brunner has criticized the appearance of Planck's constant in an equation for an nonquantum phenomenon and suggested a different pre-exponential coefficient. Bondi in reference 18 expresses preference for the form suggested by Brunner. Both forms contain the volume in the denominator and since to fit the data the other factor must be empirically determined anyway, we choose to use the form suggested in reference 2.

TABLE VI. $\Delta F_{\pm}$, Free energy of activation for viscous flow (kcal/mole).

| Sample | °C | Pressure (bars) | | | |
		Atmos	1034	2067	3101
PSU 25	37.8	5.54	6.35	6.99	7.54
C_8—C—C_8	60.0	5.56	6.33	6.95	7.48
|	98.9	5.69	6.44	7.00	7.49
C_8					
PSU 18	37.8	5.73	6.60	7.42	8.20
C_8—C—C_2—	60.0	5.69	6.51	7.26	7.95
|	98.9	5.76	6.51	7.13	7.72
C_2					
PSU 111	37.8	5.95	6.86	7.65	8.35
C_5—C—C_3	60.0	5.87	6.79	7.54	8.20
|	98.9	5.95	6.80	7.50	8.11
C_3					
PSU 110	37.8	5.70	6.53	7.24	7.85
C_8—C—C_8	60.0	5.70	6.48	7.16	7.74
|	98.9	5.80	6.58	7.17	7.72
C_3	135	5.99	6.75	7.31	7.82
PSU 113	37.8	6.18	7.28	8.22	
	60.0	6.11	7.15	8.03	8.81
$[[\ ]$—C_3—$]$ C$_3$	98.8	6.13	7.07	7.88	8.59
	135	6.27	7.18	7.90	8.57
PSU 19	37.8	6.36	7.65	8.78	
C_8—C—C_2—	60.0	6.23	7.44	8.47	9.4
|	98.9	6.19	7.27	8.19	9.04
C_2	135	6.30	7.32	8.13	8.90

A less specific form of the Eyring equation is[18–21]

$$\eta = (Nh/V)\exp(\Delta F_{\pm}/RT) = (Nh/V)\exp\frac{\Delta H_{\pm} - T\Delta S_{\pm}}{RT},$$

(3)