

TABLE V. Temperature dependence of the Tait equation parameter "B",  $B_t = B_{79.4} + a(t - 79.4) + b(t - 79.4)^2$ .

PSU No	$B_{79.4}$ bars	$a$ bars/°C	$b$ bars/(°C) <sup>2</sup>
174	1264	-5.698	0.0094
87	1048	-5.916	0.0121
88	1019	-5.690	0.0107
532	762.8	-4.805	0.0116

of the coefficients of the equations of the form

$$B_t = B_{79.4} + a(t - 79.4) + b(t - 79.4)^2$$

are given in Table V.

### Hudleston Equation

Hudleston<sup>29</sup> proposed an intermolecular force law of the form

$$f = a(l - l_0) \exp b(l_0 - l),$$

where  $f$  is the force between molecules,  $l$  is the distance between molecular centers,  $l_0$  is the distance at which molecules have no effect on each other, and  $a$  and  $b$  are empirical constants. If the distance between force centers is written as  $v^{1/3}$  and the force as  $v^{2/3}P$  the preceding equation can be put in the form

$$\log [v^{2/3}P / (v_0^{1/3} - v^{1/3})] = A + B(v_0^{1/3} - v^{1/3}),$$

where  $v_0$  is the specific volume at atmospheric pressure,  $v$  is the specific volume at pressure  $P$ , and  $A$  and  $B$  are constants.

To check the Hudleston equation with the data obtained in this study  $\log [v^{2/3}P / (v_0^{1/3} - v^{1/3})]$  was plotted against  $(v_0^{1/3} - v^{1/3})$ . If the Hudleston equation is valid the locus of the points plotted should be a straight line having slope  $B$  and intercept  $A$ . For the compounds checked straight lines did result except for some deviations at pressures of 700 bars or lower. These deviations are to be expected, because the mathematical form of the Hudleston equation is such

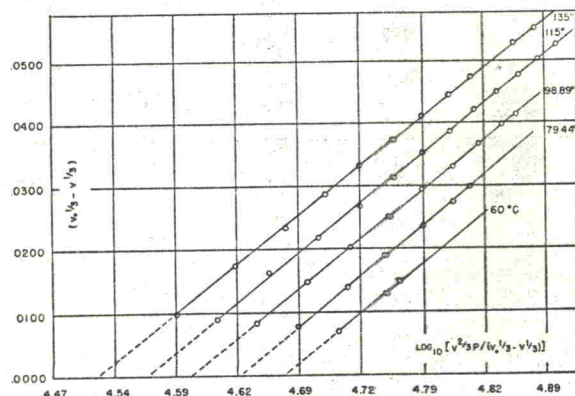


FIG. 2. The Hudleston relation for 1- $\alpha$ -naphthylpentadecane.

<sup>29</sup> L. J. Hudleston, Trans. Faraday Soc. **33**, 97 (1937).

TABLE VI. PSU 88, 135°C.

$P$ (bars)	$k$ (bar) <sup>-1</sup>
Atmospheric	$12.1 \times 10^{-5}$
689	6.27
1378	4.22
3446	2.13
6891	1.18
10 336	0.81

that it could not hold as atmospheric pressure is approached.

For a given compound the plots of the Hudleston equation at a series of temperatures proved to be a family of approximately parallel lines, indicating that  $B$  is constant for a given compound. The intercept  $A$  approximates a linearly decreasing function of the temperature. Using the relations discovered for  $A$  and  $B$  it was possible to write a general Hudleston equation for each compound. Figure 2 is a representative plot of the Hudleston equation for one hydrocarbon.

### Compressibility

Compressibility is defined as  $-(1/v_0)(\delta v / \delta P)_T$ . Since the Tait equation analytically expressed most of the pressure-volume isotherms to within the experimental accuracy of the data, it was deemed adequate to differentiate the Tait equation to get values for the compressibilities. Using the fact that  $C = 0.2058v_0$ , the following expression for  $k$ , the compressibility, is reached:

$$k = (0.08936) / (B + P).$$

An examination of the compressibilities of the hydrocarbons studied led to a number of general conclusions. For a given compound and temperature the compressibility decreases with increasing pressure, the rate of decrease becoming smaller at higher pressures, as Table VI shows. For a given structure and pressure the compressibility increases with increasing temperature. However, this increase is less marked at higher pressures as Table VII illustrates.

Pronounced structural dependence is apparent in the values of the compressibility (the effect of structure will be discussed in detail later). The effect of structure, however, tends to disappear as the pressure increases as shown in Table VIII. The disappearance of structural dependence of the compressibility can be explained by

TABLE VII. PSU 88.

$P$ (bars)	$k$ (37.8°C)	$k$ (135°C)
Atmospheric	$7.01 \times 10^{-5}$	$12.1 \times 10^{-5}$ (bar) <sup>-1</sup>
3446	1.89	2.13