

The quantity $T(\delta P/\delta T)_v + B$ was examined in this study for a number of the hydrocarbons and the results support the finding that $T(\delta P/\delta T)_v + B$ is solely a function of volume. Details of the investigation of this function have been reported.²³

Variation of Internal Energy with Pressure and Volume

It is known from thermodynamics that $(\delta E/\delta v)_T = T(\delta P/\delta T)_v - P$ where E is the internal energy of the liquid. $(\delta P/\delta T)_v$ is a positive quantity and at low pressures, where the magnitude of $T(\delta P/\delta T)_v$ is greater than the magnitude of P , $(\delta E/\delta v)_T$ is, therefore, positive. That is, as the volume is initially decreased under pressure, the internal energy decreases also. However, when the pressure becomes great enough that its magnitude exceeds $T(\delta P/\delta T)_v$, $(\delta E/\delta v)_T$ becomes negative and the internal energy increases with decreasing volume.

A similar analysis results when one considers the variation of internal energy with pressure. It is known that $(\delta E/\delta P)_T = -T(\delta v/\delta T)_P - P(\delta v/\delta P)_T$ and since $(\delta v/\delta T)_P$ is positive and $(\delta v/\delta P)_T$ is negative, the two terms in the right-hand member of this equation are opposite in sign. At lower pressures $T(\delta v/\delta T)_P$ is greater in magnitude than $P(\delta v/\delta P)_T$ and $(\delta E/\delta P)_T$ is negative; that is, the internal energy decreases with increasing pressure. However, the magnitude of $P(\delta v/\delta P)_T$ becomes increasingly great as the pressure increases and eventually makes $(\delta E/\delta P)_T$ positive and the internal energy then increases with increasing pressure.

The physical interpretation, in terms of molecular forces, of the phenomena described above is as follows. The resultant forces under low-pressure conditions are attractive and as the volume decreases the potential energy of mutual forces decreases. When the volume has undergone a sufficient decrease the repulsive forces become preponderant and further decreases in the volume increase the internal energy of the liquid.

It can be shown that both $(\delta E/\delta P)_T$ and $(\delta E/\delta v)_T$ change sign when the pressure exceeds the magnitude of $T(\delta P/\delta T)_v$. From the slopes of the isochores the pressure for which $P = T(\delta P/\delta T)_v$ can be found if it is within the experimental range. For example, for PSU 88 this pressure was 7240 bars at 135°C and 8270 bars at 115°C and for PSU 87 was 9100 bars at 135°C.

Bridgman²² and Hildebrand²⁴ have speculated that since $(\delta E/\delta P)_T = (\delta E/\delta v)_T = 0$, when $P = T(\delta P/\delta T)_v$,

giving a minimum energy for the liquid, that the volume of the liquid at this pressure should correspond to the volume of the liquid at 0°K. The following comparison was made for PSU 87 and 88. PSU 87; specific volume at 135°C and 9100 bars, 0.99 cc/gram, specific volume at 0°K (extrapolated linearly from known densities) 0.96 cc/gram. PSU 88; specific volume at 135°C and 7240 bars, 1.04 cc/gram, at 115°C and 8270 bars 1.02 cc/gram, and at 0°K 0.98 cc/gram.

SUMMARY

Experimental evidence has been presented to establish the following characteristics of the volumetric behavior of liquid hydrocarbons of high molecular weight.

1. Pressure-volume isotherms can be described adequately by either the Tait equation or, for pressures above a certain minimum, whose value depends on the compound, by the Hudleston equation.

2. For the Tait equation the parameter C can be predicted, for hydrocarbon liquids, from the relation $C = 0.2058v_0$.

3. Compressibility, for a given hydrocarbon, decreases with increasing pressure at constant temperature and increases with increasing temperature at constant pressure.

4. The compression, and compressibility, of the liquid hydrocarbons are strongly dependent on molecular structure. Cyclization, which decreases the rotational freedom characteristic of open chain hydrocarbons, introduces a rigidity of molecular shape which decreases the compressibility markedly. Furthermore, fused ring cyclization as exemplified by naphthyl and decalyl structures has a considerably greater effect in decreasing compressibility than cyclization to nonfused rings such as cyclopentyl, cyclohexyl, or phenyl, even at equivalent carbon atom in ring percentages.

5. The coefficient of thermal expansion, $1/v_0(\delta v/\delta T)_P$, for a given hydrocarbon, decreases with increasing pressure at constant temperature.

6. $(\delta^2 v/\delta T^2)_P$ undergoes a sign change at a certain pressure, whose value depends on the compound; $(\delta v/\delta T)_P$ increases with increasing temperature below this pressure and decreases with increasing temperature above this pressure.

7. The pressure coefficient, $(\delta P/\delta T)_v$, is not a function of volume alone but is also dependent on the temperature and pressure.

8. $T(\delta P/\delta T)_v + B$ evidently is solely a function of volume.

9. The pressure for which $(\delta E/\delta v)_T$ and $(\delta E/\delta P)_T$ are zero can be observed experimentally for compounds that can be studied to sufficiently high pressures.

²³ Cutler, Webb, and Schiessler, *J. Chem. Phys.* **23**, 2466 (1955).

²⁴ J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1936), Chap. V.