

This better packing results in less free space between molecules and reduces the compressibility of the aromatics as compared with the corresponding saturated hydrocarbons.

Isobars

The isobars with specific volume as a function of temperature were plotted for each compound at 345-bar intervals. The isobars for each hydrocarbon had the same general form and were almost linear. Representative isobars are shown in Fig. 7.

The slopes of the isobars were determined from large-scale graphical plots by the use of a tangentometer. These slopes revealed a change in sign of $(\delta^2v/\delta T^2)_P$ at elevated pressures, a phenomenon previously noted by Bridgman.^{12,13} This effect is observed by noting that at lower pressures the magnitude of the slope of the isobar, $(\delta v/\delta T)_P$, increases with increasing temperature but above a certain pressure, the value of $(\delta v/\delta T)_P$ decreases with increasing temperature. Bridgman reported this sign reversal of $(\delta^2v/\delta T^2)_P$ in the range 3100–4100 bars and also reported that the pressure of reversal appeared to decrease with increasing molecular weight. Representative values of the pressure range in which the sign reversal of $(\delta^2v/\delta T^2)_P$ has been observed in the present study are as follows:

PSU 174	1030–1380 bars,
PSU 87	1030–1380 bars,
PSU 528	2410–2760 bars,
PSU 532	1720–2070 bars.

It was difficult to ascertain accurately the pressure of reversal for $(\delta^2v/\delta T^2)_P$ because of scatter inherent in the isobars and the small magnitude of $(\delta^2v/\delta T^2)_P$.

The sign reversal of $(\delta^2v/\delta T^2)_P$ may be attributed to nonlinearity in the intermolecular forces. Large thermal expansion accompanies departure from linearity in the intermolecular forces. Or in other words, thermal expansion depends upon the anharmonic terms in the potential energy.³¹ At high pressures and low temperatures the molecules may be so crowded together that the departure from linear intermolecular forces is greater than at high temperature and the same pressure. This would be consistent with a decrease in the thermal expansion as the temperature increased.

It was also noted for a given compound and temperature that the coefficient of thermal expansion, $1/v_0(\delta v/\delta T)_P$, decreases with increasing pressure. This decrease is as much as a factor of 3 or 4 for a pressure range of 6900 bars. For example, for PSU 88 at 110°C the coefficient of thermal expansion at atmospheric pressure is $9.20 \times 10^{-4}/^\circ\text{C}$. while at 6890 bars it is $2.63 \times 10^{-4}/^\circ\text{C}$.

³¹ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York 1953).

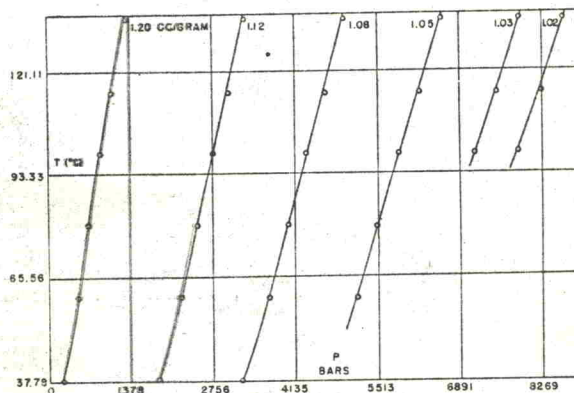


FIG. 8. Isochores for 9(2-cyclohexylethyl)heptadecane.

Isochores

Isochores (curves of constant specific volume) were drawn over the entire range of temperature and pressure for all of the hydrocarbons studied. Isochores were drawn at intervals of 0.01 cc/g with the required pressures having been read from the pressure-volume isotherms. The isochores for various compounds all have the same general form. Representative isochores are illustrated in Fig. 8.

The slopes of the isochores were read with a tangentometer. It was especially noted that the isochores are not straight lines but that the slope of a given isochore decreases with increasing pressure and temperature. Furthermore, the slope of the isochore or pressure coefficient, $(\delta P/\delta T)_v$, for a given temperature, increases with increasing pressure as the volume decreases.

Since the isochores are not straight lines, one can state that $(\delta P/\delta T)_v$ is not a function of the volume alone. If $(\delta P/\delta T)_v$ were a function of volume alone, then $(\delta P/\delta T)_v = f_1(v)$ which could be integrated to give $P = f_1(v)T + f_2(v)$. Van der Waals' equation of state is a special case of the preceding equation. The physical interpretation of $P = f_1(v)T + f_2(v)$ is that pressure can be thought of as resulting from two mechanisms—one a function of volume alone, which at constant volume would be the same for all temperatures, and the other arising from a kinetic mechanism and dependent on the temperature. An equation of the van der Waals type did not hold for the liquids studied here (and probably will not hold for liquids in general) since $(\delta P/\delta T)_v$ is not a function of volume alone, but is dependent on the pressure and temperature. This must mean that the two pressure mechanisms interact. Bridgman¹² stated that this interaction would be expected if one considered molecules themselves to be compressible.

Gibson^{23,32} has examined the quantity $T(\delta P/\delta T)_v + B$, where B is the Tait equation parameter B , and has found this quantity to be a function of volume alone.

³² R. E. Gibson and O. H. Loeffler, *Ann. N. Y. Acad. Sci.* **51**, 727 (1948).