

Fig. 5. Compression $(v_0-v)/v_0$ versus pressure for n-dodecane (PSU 528), n-pentadecane (PSU 532), n-octadecane (PSU 537), 1-alpha-naphthylpentadecane (PSU 174), and 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16-dodecahydrochrysene (PSU 574) at 135°C.

hydrocarbons, PSU 174 and 574. PSU 174 and 528 were, respectively, the least and most compressible compounds in this present study and serve to illustrate the range of compression found in this study. PSU 574, a fused ring compound (whose PVT data were obtained by Lowitz³⁰ as part of a study of viscosity-temperature-pressure surfaces) proved to be even more incompressible.

Compression data for ten compounds are summarized in Fig. 6. All ten of these hydrocarbons contain 25 carbon atoms per molecule and are, therefore, of approximately the same molecular weight. From an examination of Fig. 6 one can obtain the effect of

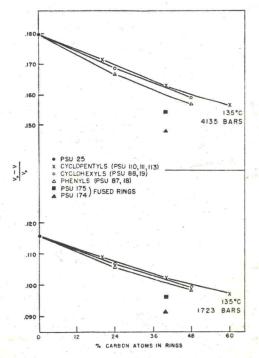


Fig. 6. Compression versus percent carbon atoms in rings.

³⁰ D. A. Lowitz, Ph.D. dissertation, The Pennsylvania State University (1955).

progressive cyclization on the compression. Increasing cyclization decreases the compression. The decrease in compression is a function, not only of the percent carbon atoms in rings, but of the type of rings as well. Fused ring cyclization, as exemplified by naphthyl and decalyl structures, produced the greatest decrease in the compression. The next most effective structural change in decreasing the compression was cyclization to phenyl rings followed in order by cyclization to cyclohexyl rings and cyclization to cyclopentyl rings.

The compression and the percent carbon atoms in rings form an almost linear relationship in the case of the cyclopentyls. The relationships for the other types of rings are not as well defined because these studies were not extended to the same number of compounds as in the case of the cyclopentyls. Nevertheless, the trend of decrease in compression with increasing cyclization is definitely established for the phenyl and cyclohexyl groups.

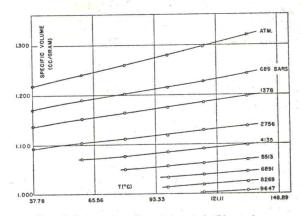


Fig. 7. Isobars for 9(2-cyclohexylethyl)heptadecane.

The most compressible compounds found in the studies of the higher molecular weight hydrocarbons possess the straight chain structure. The rotational freedom characteristic of straight chains results in a flexible, or nonrigid, structure that is relatively easy to compress. Next in order of compressibility come the branched chains. The branched chain is also a relatively nonrigid structure but has lost some of the flexibility of the straight chain structure. In going from the chain structures into ring structures the compression decreases and the key factor in this decrease is the rigidity of shape that comes with loss of rotational freedom. The fused ring compounds possess this rigidity of shape to an even higher degree than the nonfused aromatics and cycloalkanes, and proved to be decidedly less compressible than the nonfused compounds. In comparing the aromatics with the corresponding cycloalkanes it was noted that the aromatics, at atmospheric pressure and under similar temperature conditions, were always more dense. Therefore the aromatic molecules pack more closely at atmospheric pressure than do the molecules of the cycloalkanes.