the sense defined above. For an earlier study of these mixtures at atmospheric pressure see reference 10.

In selecting these hydrocarbons particular attention was given to structural relationships. Because of the structural variations among the compounds selected definite variations in compression with structure were expected. PSU 528, 532, and 537 represent an extension of Bridgman's work on the normal paraffins, his work having extended through *n*-decane.[12]

PSU 25, 87, 18, 88, 19, 110, 111, and 113 all have the same basic symmetry, three groups of eight carbon atoms each, arranged about a central carbon atom. The differences in structure were such that a study could be made of the effect of changing from straight chain groups to one, two, or three cyclopentyl groups, and from straight chain groups to one or two phenyl groups, or one or two cyclohexyl groups. PSU 174 and 175 were included to bring fused ring compounds into the structural study.

The compounds selected cover a molecular weight range of 170 to 351. This represents a fairly wide range over which to study such empirical relationships as the Tait and Hudleston equations and such thermodynamic quantities as $(\delta v/\delta T)_P$, $(\delta P/\delta T)_v$, $(\delta v/\delta P)_T$, $(\delta^2 v/\delta T^2)_P$, $(\delta E/\delta P)_T$, and $(\delta E/\delta v)_T$. Since there is no generally accepted equation of state for liquids involving the three variables, pressure, volume, and temperature, the quantities mentioned previously are important in that their observed behavior should shed light on the validity of any equation of state that might be proposed.

EXPERIMENTAL METHODS AND PROCEDURES

The methods used in this study to measure volume changes and pressures were similar to those employed by Bridgman.[12,13] Bridgman utilized a flexible bellows with attached slide-wire for measurement of volume changes and the changes in the resistance of a coil of manganin wire for measurement of pressure changes.

Pressure System

The pressure generating equipment consisted of a hand operated hydraulic pump, capable of generating a pressure of 1380 bars (approximately 20 000 psi) and two intensifiers. The intensifiers, each of which consisted of a floating piston having a different cross-sectional area at each end, provided multiplication of the pump pressure by theoretical ratios of 4:1 and 9.5:1, respectively.

In operation, the pressure cylinders were preloaded to 1380 bars (20 000 psi) by direct use of the hydraulic pump. Further preloading to 3450 bars (50 000 psi) was carried out using the 4:1 intensifier. Pressures above 3450 bars were produced by driving the high-pressure piston inward, thus compressing the hydraulic fluid in the pressure vessel.

A maximum limit of 10 000 bars was set, although this was not the theoretical limit, to reduce the possibility of equipment trouble and speed the production of data.

Pressure Measurement

Pressures were measured by observing the changes in electrical resistance of a coil of manganin wire. Bridgman has examined the pressure-resistance characteristics of manganin and found its behavior to be linear to 13 000 atmospheres.[14,15] The manganin coil used in this study was wound from B. and S. 40 gauge double silk covered manganin wire, and had an atmospheric pressure resistance of about 120 ohms.

The manganin coil is a secondary pressure gauge and, therefore, required calibration against a standard. The manganin coil used was calibrated against a dead-weight gauge. In this calibration resistances were measured to the nearest 0.001 ohm by use of a Mueller bridge to 3450 bars at 345-bar intervals. The best value of the slope of the straight line relationship between resistance and pressure was obtained by a least squares calculation.

The resistance changes of the manganin coil during a pressure run were measured using a slide-wire Wheatstone bridge. A potentiometric calibration of the slide wire was made to minimize errors arising from the nonlinearity of the slide-wire resistance.

Temperature Regulation and Measurement

The piezometer containing the hydrocarbon under study was immersed in an oil bath whose temperature was regulated to ± 0.1°C of the desired temperature. The bath temperature was measured with a mercury-in-glass thermometer calibrated by the National Bureau of Standards.

Detection and Measurement of Volume Change

The technique used for detection and measurement of the volume change was a modification of the Bridgman[12] bellows technique. Figure 1 is an exploded view showing internal construction of the instrument,[16] hereafter called the piezometer. The piezometer held approximately five cubic centimeters of the hydrocarbon being studied. Although a much larger sample would have been advantageous in volume change determinations, the small sample size was dictated by the scarcity and value of the hydrocarbon samples and by the possibility of sample contamination in a pressure run.

The hydrocarbon to be studied was admitted to the

[12] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949).

[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **66**, 185 (1931).

[14] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 321 (1911).

[15] P. W. Bridgman, Proc. Roy. Soc. (London) **A203**, 1 (1950).

[16] The flexible bellows used in this instrument is a product of the Fulton Sylphon Division of the Robertshaw-Fulton Controls Company Knoxville, Tennessee.