Compressions of Liquids

This three-part paper reports on the first step of a study of the liquid state initiated in 1954 by Union Carbide Chemicals Company. The ultimate objectives of this program are to elucidate the mechanism of the flow process and to write an equation of state that is valid continuously from the melting point through the ideal-gas region.

Only the compressions of the *n*-alkanes (ratios of the volumes under the pressures of measurement to the volume under the initial pressure at the same temperature) are here considered. An accuracy of four significant figures in the measurement was sought to enable the subsequent calculation of the thermodynamic properties of these liquids to be made with equivalent accuracy.

I. Apparatus and Method of Measurement

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A novel type of piezometer used to measure the compressions of liquids from 20° to 300°C. and from 1 to 4,000 kg./sq. cm. is described. The accuracy anticipated is 4 parts in 10,000.

The four essential operations involved in the determination of the compressions of liquids are measurements of volume, pressure, temperature, and mass of the sample. Of these the determination of volume with an accuracy better than one part in 10,000 under pressures up to 4,000 kg./sq. cm. and temperatures up to 300°C. was the most difficult problem experimentally. Several known methods of measurement were considered and rejected. For example the method of Beattie (*1*), which depends upon the accuracy of the calibrated mercury injector and the sample bulb, was not applicable beyond the pressure range of 0 to 500 kg./sq. cm. The piston-displacement method of Bridgman (*2*) has limited accuracy in the lower pressure range because of friction and is not easily adapted for temperatures higher than 100°C. The accuracy of the method of metallic bellows (*3*) suffers from the inelastic hysteresis of the bellows. The glass piezometer of Adams and Gibson (*4*) allows determination of only one volume at one filling and therefore is too slow. The glass piezometer with sealed-in contacts used extensively by Michels (*5*) and his co-workers has high accuracy but is not operable above 200°C. because the mercury dissolves the platinum contacts at the higher temperatures. Since none of these and other known methods were entirely satisfactory for the purpose of this investigation, a novel type of piezometer was developed.

Although the piezometer is the most critical part of the apparatus, the other components such as the pressure plant, the pressure gauge, and the temperature control will also be described because they are all functionally interconnected.

APPARATUS

The piezometers to be described were based on the idea that the displacement of a small iron core could be measured from the outside of a pressure container made of an austenitic, nonmagnetic steel by means of a linear differential transformer (*6*). The iron core floated on the surface of mercury enclosing the liquid under test.

The piezometers were made of lengths (about 19 in.) of precision-drawn, thin-walled stainless steel (type 321) tubing (0.097-in. O.D., 0.005-in. wall) terminated by screw closures at the top and mercury valves at the bottom. During measurements the piezometer was positioned in a pressure container consisting of thick-walled, high-pressure stainless steel (type 316) tubing (0.375-in. O.D., 0.125-in. I.D.) which was filled with light mineral oil as a pressure-transmitting medium. The pressure was transmitted to the sample via a column of mercury which communicated with the oil medium in the mercury cup at the bottom of the apparatus (Figure 1).

The construction of the piezometer is shown in detail in Figure 2. The top, which was silver-soldered to the stainless steel piezometer tube, was provided with a closure consisting of a steel socket set screw (No. 2-56, ½ in. long) fitting into a cone seat with a 60 deg. angle. The sample, introduced into the piezometer through the top with a long hypodermic syringe, filled it to the cone seat. Then the socket screw was put in and tightened with a miniature wrench. Repeated tests with a helium-leak detector proved that this seal remained completely tight over the whole temperature range.

The small lateral dimensions of the piezometer resulted in a considerable saving on the volume of sample and in a great reduction of the thermal capacity of the entire apparatus. The length of the sample column was sufficient to allow accurate determination of the compression; in a typical arrangement the sample column was approximately 100 mm. long, its length being determined by readings on the external micrometer directly to 0.01 mm. (Five microns can be estimated on the dial.)

Volume Measurement

The volume of the sample in the piezometer was essentially the volume between the electromagnetic centers of the plug at the top and the float that rode on the mercury column.

These electromagnetic centers were located from without the apparatus by means of two small linear differential transformers, which slid with small clearance over the surface of the pressure vessel. These two coils were mounted securely on a stainless steel rod so that their distance apart was fixed (a in Figure 1). An Invar wire passing over a pulley connected the coil suspension with a precision micrometer slide. It was necessary to use two coils because the micrometer slide commercially available did not have a span large enough to cover the whole length of the sample column directly.

The transformers were connected to an A.C. 1,000 cycles/sec. bridge with a vacuum-tube voltmeter as a null indicator (*7*). Either coil might be switched into this circuit at will. To balance the bridge, one of the coils was moved until either the plug or the float, depending on which coil was moved, lay in the exact electromagnetic center of that coil. This position, indicated by a very sharp minimum deflection of the voltmeter, could be located easily to within 5 μ on the dial scale of the micrometer. Manipulation of the dial thus permitted one to center the top coil on the plug and the bottom coil on the float.

The difference between these two readings x established the distance X

between the float and the plug. Thus if a was the difference between two coils and x the difference between the two readings of the micrometer, the length of sample in the piezometer would be $X = x + a$. The volume of sample contained in the instrument at the temperature and pressure of measurement could then be determined from the length X, the cross-sectional area A of the piezometer, and the initial volume.

Measurement of Mass

The mass of the sample contained in the piezometer was measured by direct weighing of the piezometer before and after filling it with the sample.

A simple plug valve at the bottom of the piezometer made it possible to introduce the predetermined amount of mercury; then the piezometer was weighed before being filled with sample, as described above. After the two weights had been obtained, this valve was opened by rotating it with a key until a small inner hole lined up with a similar hole in the wall of the piezometer. This was done with the piezometer dipping into the mercury reservoir at the base of the apparatus (Figure 1).

The weight of the sample was also checked by weighing the filling pipette (hypodermic syringe) before and after the sample was transferred to the piezometer. By either method the mass could be weighed to 0.2 or 0.3 mg, but on a sample weight of 0.3 g. this represented accuracy of only one part in 1,000, which is at least an order of magnitude less than the accuracy attainable in the measurements of pressure, volume, and temperature. For this and other reasons the mass of sample was determined by indirect methods, as described in a companion paper (8).

Temperature Control and Measurement

Because the steel piezometer with its surrounding pressure vessel represented a relatively small mass of low heat capacity, the temperature control was simplified with respect to both changing from one temperature to another and maintaining a fixed temperature accurately during a set of volume measurements at various pressures.

The pressure vessel containing the piezometer and surrounded by the two differential transformer coils was immersed in an oil bath 3 in. in diameter and extending approximately 8 in. above and 5 in. below the sample. The bath was insulated with magnesia-pipe insulation and asbestos soaked with water glass. Two heaters were employed; one, an electric heating tape, was wound spirally around the outside of the oil bath container, and the other was an immersion heater inside the oil bath. Dow-Corning No. 710 fluid was used as the heat transfer medium, and a small electric stirrer provided adequate circulation. The external heater was controlled manually by a variac; the immersion heater was connected to a thyratron controller, but it was found that even better temperature control could be maintained during the period of a run by manual operation of the variac. The vertical temperature gradients were checked by means of three thermocouples attached to the steel tube containing the piezometer, and the variations never exceeded a few hundredths of a degree. The temperature was maintained uniform to within ± 0.1°C., but the actual temperature was measured to five significant figures at the moment of each measurement of volume. Temperatures were measured with a platinum resistance thermometer and Mueller resistance bridge.

Pressure Measurement

The dead-weight or free-piston gauge was chosen for the measurement of high pressures because of its accuracy and its ability to maintain the pressure constant during operation. In such a gauge the internal pressure in a system is balanced by the force of a known weight acting upon a piston of known area. Two conditions must be satisfied for the practical application of this principle: first, there must be negligible friction between the piston and the cylinder walls, and, second, there must be little leak of the pressure-transmitting oil. These conditions are resolved by the rotation of the piston above the critical velocity so that a continuous film of oil is maintained.

The Michels dead-weight gauge, or pressure balance, which became available shortly after this project was started, consists essentially of a differential piston moving in a cylinder that contains two coaxial bores. The cylinder is mounted in a frame, and the piston is connected to a weight-carrying shaft at the bottom and a pointer arm at the top. The assembled pressure balance, as made by the 'T Hart Company, is shown in Figure 3.

The piston is a tight fit in the cylinder until pressure is applied, the hydraulic pressure causing a slight expansion in the

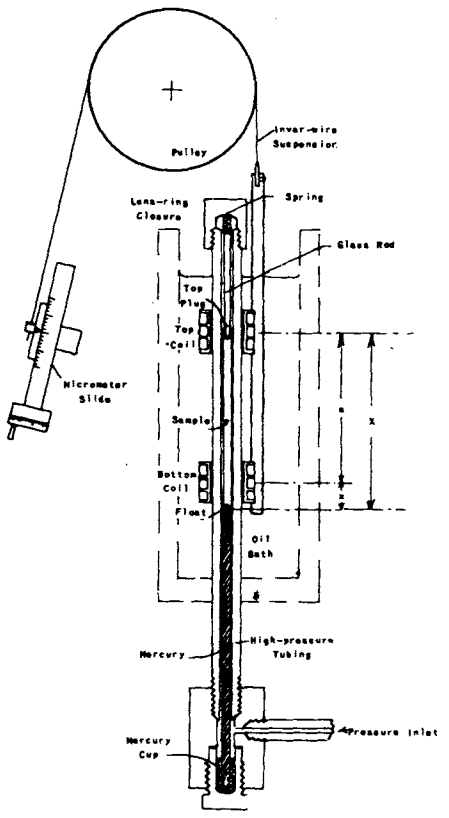

Fig. 1. Schematic diagram of steel piezometer and measuring assembly (not a scale drawing; mechanical details omitted).

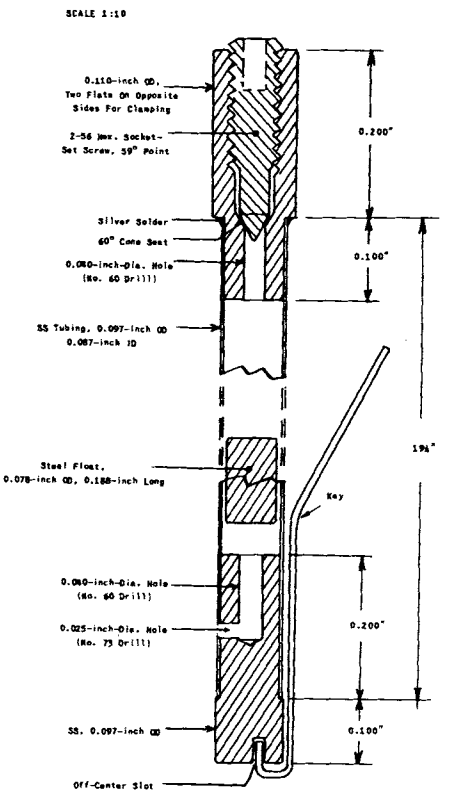

Fig. 2. Steel piezometer.

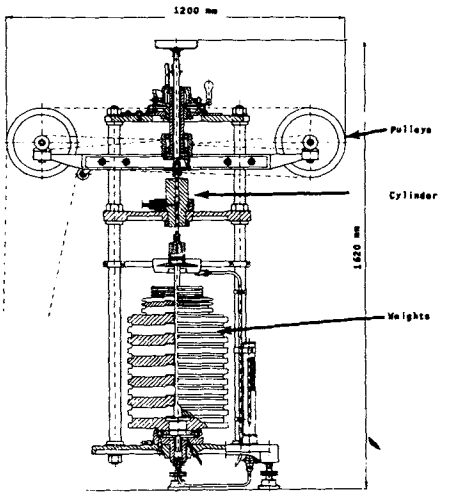

Fig. 3. Michels pressure balance.

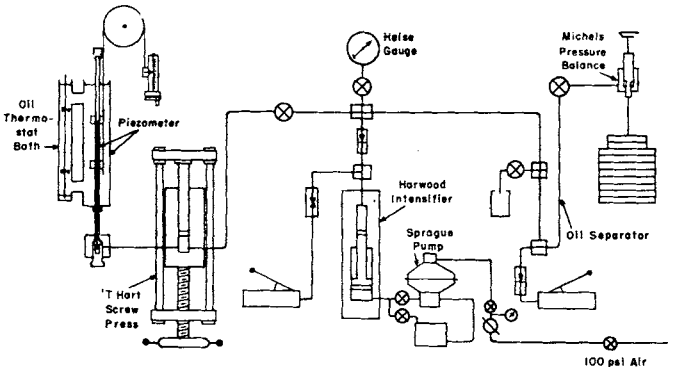

Fig. 4. Pressure plant.

cylinder walls and also a slight decrease in the area of the piston. Under these conditions the piston can rotate freely, and there is sufficient leakage to ensure continuous oil-film lubrication. A motor-driven pulley system rotates the piston and the column of weights above the critical velocity of about 50 to 60 rev./min. At the time of measurement a clutch is disengaged, and the piston and weights can therefore rotate freely by their own momentum. A mixture of 75% Shell Talpa 30 and 25% Shell Diala AX (by volume), having a viscosity of approximately 80 centipoises at 25°C., was found to be satisfactory. Under pressure the piston and weights can fall through 2 cm. of free travel. With an oil of proper viscosity a good cylinder with piston and weights rotating freely takes 5 to 10 min. to fall this 2 cm.

The Michels pressure balance has a series of six measuring cylinders that cover a range from 118 to 4,000 kg./sq. cm. There are twelve 50-kg., one 10-kg., two 5-kg., and five 1-kg. weights, all calibrated to 0.1 g.

For low pressures a Bourdon-tube gauge was employed which, over the range of 0 to 250 kg./sq. cm., had an accuracy of better than 1 part in 1,000, as demonstrated repeatedly by checks against the Michels pressure balance.

Pressure Plant

The diagram of the pressure plant is shown in Figure 4. Pressures up to 8,000 kg./sq. cm. can be generated by means of a Harwood intensifier operated by a 1,500-kg./sq. cm. Sprague air/oil booster pump or by a Blackhawk hand pump. A screw press allows fine adjustments of volume and pressure directly on the high-pressure side (up to 4,000 kg./sq. cm.).

The high-pressure vessel consists of a vertical section of 3/8-in. O.D. by 1/8-in. I.D. cold-drawn stainless steel tubing, approximately 40 in. long, connected to the various components of the system through 5/16-in. O.D. by 1/16-in. I.D. cold-drawn stainless steel (type 316) tubing which was proof tested by the supplier at 130,000 lb./sq. in. The rupture pressure is 20,000 to 40,000 lb./sq. in. above the proof test. Harwood series 5 M fittings, designed for service to 100,000 lb./sq. in., are used for connecting the various components.

The pressure-transmitting fluid is Shell Diala AX, which has a viscosity of approximately 30 centipoises at 25°C. and can withstand the maximum operating temperature (300°C.) without excessive decomposition. Its viscosity rises rather rapidly with pressure. Thus in the upper limit of the working range (4,000 kg./sq. cm.) the time necessary to reach equilibrium between the pressure gauge and the pressure vessel may be a minute or more, which makes it difficult to obtain pressure equalization throughout the system in the time allowed for the piston to sink freely on the leaking oil film.

Since the pressure balance requires a different type of oil for satisfactory operation, a fluid separator, consisting of a 4-ft. vertical section of the same 3/8-in. O.D. by 1/8-in. I.D. high-pressure tubing, was inserted. A second Blackhawk pump supplied fresh balance oil from a reservoir through a high-pressure check valve.

CALIBRATION

Volume-Measuring Instrument

The cross-sectional areas of the piezometers were determined at atmospheric pressure by weighing small increments of mercury released from the instrument and observing the corresponding drop in the level of the steel float by means of the sensing coil. From the density of mercury the volume of mercury released is computed. This volume divided by the corresponding difference in level is equal to the area of cross section. The precision-drawn polished stainless steel tubing was found to be uniform to better than ± 0.05% in cross section over the length used.

The setting constant a, which represents essentially the distance between the electromagnetic centers of the two sensing coils, can be determined by filling the sample space with a known volume of liquid. The difference between the top and bottom coil readings added to the length of the column of liquid is equal to the setting constant. As long as the distance between the coils is mechanically fixed, and if the float and the plug are not changed, the value of the setting constant is fixed except for the change resulting from the thermal expansion of the apparatus. The accuracy of the measurements, reduced as explained in the succeeding papers, does not depend on the accuracy of the setting constant, since the extrapolated zero-pressure volumes are shown to be far more accurate than the initial volumes computed from low-pressure measurements by use of the setting constant.

The change in the cross-sectional area of the piezometer as a result of the thermal expansion of the metal must be taken into account, but any change in the length of the piezometer or in the column of mercury inside it is immaterial, since the length of the column of sample is measured independently of its surroundings.

The temperature dependence of the setting constant results from the linear expansion of the section of the stainless steel suspension rod between the sensing coils; the value of $1.62 \cdot 10^{-5}$ deg.$^{-1}$ was used for the thermal expansion coefficient of the steel used (type 321). Similarly the thermal expansion causes an increase of the cross-sectional area of the piezometer at a rate of $3.24 \cdot 10^{-5}$ deg.$^{-1}$

Hydrostatic pressure decreases the cross-sectional area of the piezometer tubing by a factor of approximately $(1 - 3.9 \cdot 10^{-7} p)$, where p is in kg./sq. cm. A series of test runs with pure water up to pressures of 3,000 kg./sq. cm. indicated that the compression is actually smaller than the value estimated from the formula above and below the limits of observational accuracy.

The combined experimental errors involved allowed the measurements of volume to be made with an accuracy of one part in 10,000 at all temperatures and at all pressures except those in the neighborhood of 1 atm. The loss of accuracy at very low pressures is presumably occasioned by a change in the shape of the meniscus at the mercury-sample interface.

Temperature-Measuring Instrument

The platinum resistance thermometer was calibrated by the manufacturer by comparison with a platinum resistance thermometer certified by the National Bureau of Standards. One check of the resistance at the ice point agreed exactly with the manufacturer's calibration; which assures an accuracy in the measurement of temperature of at least one part in 10,000.

Pressure-Measuring Instrument

The calibration of the dead-weight gauge was supplied by the manufacturer. Certificates of calibration by The Netherlands Bureau of Standards

accompanied the weights and cylinders, guaranteeing an accuracy of one part in 10,000 in the measurement of pressure.

Over-All Accuracy

When one combines the errors in the measurement of temperature and volume, a conservative estimate of the probable over-all accuracy of measurement may be placed at 4 parts in 10,000, which assures four significant figures in specific volume. [Statistical analyses of the data on two compounds, *n*-heptane and *n*-eicosane, described in a companion paper (*8*), indicate that the over-all accuracy for the entire range of temperatures and pressures is more likely to be of the order of 3 parts in 10,000.]

Over 4,000 measurements of volume under pressure were made in the course of this program. The presentation and complete evaluation of these and other liquid *n*-alkane data is the subject of the companion papers (*8*, *9*).

ACKNOWLEDGMENT

J. A. Beattie of the Massachusetts Institute of Technology and A. Michels of the University of Amsterdam served as consultants on the experimental phases of this project and contributed to its successful outcome in many ways. R. W. Zwanzig of Johns Hopkins University and J. C. Poirier of Duke University were retained as consultants on other phases of the project. The experimental work was carried out at Ohio State Research Foundation, Columbus, Ohio (preparation of *n*-triacontane and *n*-tetracontane) and at Arthur D. Little, Inc., Acorn Park, Cambridge, Massachusetts (measurements of volume under pressure), under contracts with Union Carbide Chemicals Company.

II. Critical Evaluation of New *n*-Alkane Data: *n*-Heptane to *n*-Tetracontane

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New measurements of the volumes of liquid *n*-alkanes of 7, 9, 11, 13, 17, 20, 30, and 40 carbon atoms over a range of temperatures from 20° to 300°C. and pressures from 0 to 4,000 kg./sq. cm. have been made. These volume measurements are here reduced to compressions $(vol^{p}_{T})/(vol^{o}_{T})$, and the accuracy of the measurements has been determined. Analysis of the data for *n*-heptane and *n*-eicosane shows that the order of accuracy of the compressions of each of these compounds appears to be approximately 3 parts in 10,000. Evaluation of random multiple measurements on the remaining six compounds indicates that their over-all accuracy is likewise of this same order.

The volumes of small samples of eight *n*-alkanes, from 7 to 40 carbons, were measured by Simon and Cornish at a number of temperatures from 20° to 300°C. and over a range of pressures from 0 to 4,000 kg./sq. cm., with the apparatus and method described in the prior paper (*10*). This method has the advantage of very high accuracy in the measurement of volumes under pressure, but it does not afford equivalent accuracy in the direct measurement of the weight of the material whose volume is being measured. It is therefore necessary to resort to indirect means of determining the sample weight.

Also this procedure measures volumes very accurately under high pressure, but somewhat less accurately at low pressures. Therefore, to realize the full advantage of the method it is necessary to establish the values of the zero-pressure volumes with more certainty than is possible by extrapolating the lower pressure values alone.

A procedure was devised for making an indirect extrapolation to zero pressure of the volumes measured at higher pressures which gives values fully as accurate as the measurements. When applied to the Simon and Cornish data, this procedure permits the results to be reported as compressions or ratios of the volume at the pressure of measurement to the zero-pressure volume $(vol^{p}_{T})/(vol^{o}_{T})$.

PURITY OF SAMPLES

The preparation and characterization of the samples of *n*-heptane, *n*-nonane, *n*-undecane, *n*-tridecane, and *n*-heptadecane used in this study have been described elsewhere (*11*). The remaining pure compound *n*-eicosane, was synthesized as follows. Decanol-1, was purified and brominated with anhydrous hydrogen bromide at 100°C. The purified 1-bromodecane was converted to *n*-eicosane by a Wurtz reaction with sodium. The crude distilled product was hydrogenated and fractionated, the fractions of common density being combined. The composite had a freezing point of 36.51°C.; the freezing point of pure *n*-eicosane is reported (*12*) to be 36.8°C.

The other two samples were characterized as follows: *n*-tricontane freezing point 65.512°C., purity (*13*) 99.48%; *n*-tetracontane freezing point 81.030°C., purity 98.6%.

DETERMINATION OF ZERO-PRESSURE VOLUME

Linear extrapolation of the volumes of sample under pressure is satisfactory at temperatures well below the normal boiling point of the substance being measured, but this method fails in the neighborhood of the normal boiling point and is obviously inapplicable above this temperature. An indirect extrapolation procedure was therefore devised which makes use of a pressure-volume relationship that has so far received very little attention in this country. This relationship used by Bett, Weale, and Newitt (*14*) for evaluating data on the compression of liquids, was originally proposed by Hudleston (*15*):

$$\ln \frac{P(vol^{p}_{T})^{2/3}}{(vol^{o}_{T})^{1/3}-(vol^{p}_{T})^{1/3}} = C_1 + C_2[(vol^{o}_{T})^{1/3}-(vol^{p}_{T})^{1/3}]$$

One of the features of the Hudleston equation is that at low pressures the left-hand member of the equation is very sensitive to small changes in the zero-pressure volume. As the pressure is reduced in the low-pressure region, $(vol^{p}_{T})^{1/3}$ approaches $(vol^{o}_{T})^{1/3}$ and the denominator becomes vanishingly small. A slight error in $(vol^{o}_{T})^{1/3}$ therefore makes a large difference in the quotient at the limit. Since the fit of data to the Hudleston equation is determined principally by the higher pressure points, deviations of the lower pressure points generally suggest an error in the value assigned to $(vol^{o}_{T})^{1/3}$. This feature of the Hudleston equation makes it ideal for the indirect extrapolation of the volumes to the zero-pressure value, as it involves simply trying different values of $(vol^{o}_{T})^{1/3}$ until a value is found that provides the best fit of the lower pressure points to the line determined by the higher pressure points. In this way the best fitting values of (vol^{o}_{T}) were determined for each compound at all temperatures of measurements, thereby enabling the compressions to be calcu-

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