# Vapor Pressures for the System 1-Butene, Isobutane, and 1,3-Butadiene

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An apparatus capable of determining vapor pressures with a probable error of ±0.05% over a range of 40–160 °F and 20–160 psia is demonstrated by a significant amount of new vapor pressure data for pure 1-butene, isobutane, and 1,3-butadiene and their mixtures. These new data are compared with existing data from the literature.

The design of commercial distillation columns to separate the components of a system of close boiling chemicals requires extremely accurate vapor–liquid phase equilibrium data. One method of acquiring these data is to measure the vapor pressures over liquid mixtures of the components to be separated, and then calculate the associated vapor compositions using the Gibbs–Duhem equation and some assumptions on the volumetric behavior of both phases. The real advantage of this technique is the relative ease with which it can be applied.

In this paper an apparatus capable of determining vapor pressures with a probable error of ±0.05% over a range of 40–160 °F and 20–160 psia is described. The viability of the equipment is demonstrated by producing a significant amount of new vapor pressure data for 1-butene, isobutane, and 1,3-butadiene and their mixtures.

## Experimental Section

The experimental apparatus used in this study is that designed and constructed by Manley and Walker (14). Their combined efforts have developed a simple cell and transducer system suitable for measuring the vapor pressures of liquid mixtures with great precision over a wide range of pressures, temperatures, and compositions.

Figure 1 (not drawn to scale) shows a view of the pressure transducer and differential transformer with internal details. The cell consists of a male and a female disk which, when assembled, engage a flexible stainless steel diaphragm and securely crimp it in place. The face of the male disk is dished about 2° from each edge for a distance of about 0.1 in. The remainder is machined flat. The face of the female disk is machined flat for $\frac{1}{16}$ in. radially, dished about 0.1 in. from each side, and machined flat to the center. A Teflon coating is sprayed around the perimeter of the diaphragm to ensure a proper seal. The flexible diaphragm is cut from 0.001 in. 302 stainless steel shim stock, and placed between the dished faces of the cell. The assembly is then secured by 12 no. 6-32 socket head machine screws spaced at equal intervals around the perimeter of the assembly and tightened uniformly. The transducer is 2 in. in diameter, has an effective cavity diameter of about 1.6 in., and a total cavity displacement of about 0.014 in. The female disk is connected directly to the high pressure cell, which contains the hydrocarbon mixture. The male disk is connected to half of an Autoclave Engineer's positive bite coupling which is silver soldered to the outer side of the disk. A $\frac{1}{8}$ in. stainless tubing is connected at the coupling and holds the external gas (nitrogen). This tubing also contains the $\frac{1}{16}$ in. diameter stainless rod which moves up or down with deflection of the diaphragm.

The zero pressure differential, or null point of the transducer, is sensed by means of the stainless steel rod which follows the movements of the diaphragm within the transducer. A large external nitrogen pressure deflects the diaphragm downward while an external vacuum moves the diaphragm upward. The null point occurs, of course, when the diaphragm is totally undeflected. The stainless steel rod drives a steel core whose position can be sensed by a Trans-Tek differential transformer. A nylon spacer is positioned so as to maintain a constant distance along the tubing between the transformer and the body of the transducer. The transformer produces a voltage which is linear with respect to the displacement of the core.

The transducer has several properties desirable for the measuring of hydrocarbon vapor pressures. It weighs only 219 g so that it can be weighed on a 240-g capacity Mettler balance to precisely determine mixture compositions by weight. The null point is insensitive to temperature and pressure and a reproducibility of 0.01 psi differential can be obtained between 40 and 160 °F and 20 and 160 psia (equivalent to ±0.05% at 20 psia). The drift in the null point of the transducer is significantly less than the desired sensitivity range of 0.01 lb in.$^{-2}$ difference. The transducer was easy to use because of its sturdy yet simple construction, and the null point was not affected by "over pressures" encountered during the normal course of the experiments.

The peripheral equipment, used for metering the hydrocarbons into the cell, is shown in Figure 2. In order to fill the cell with the appropriate hydrocarbon, the system was first evacuated. An inverted sample bottle was gently heated and the hydrocarbon was transferred first to the metering pump and then to the cell. Since the sample bottles were inverted, any residual air which
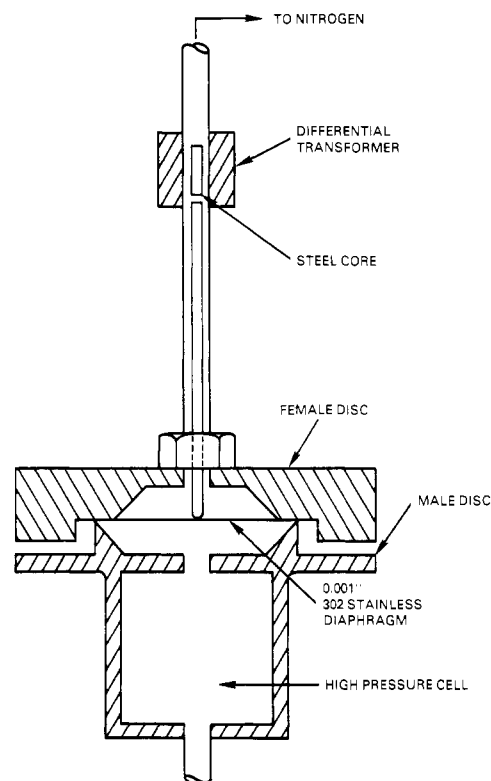


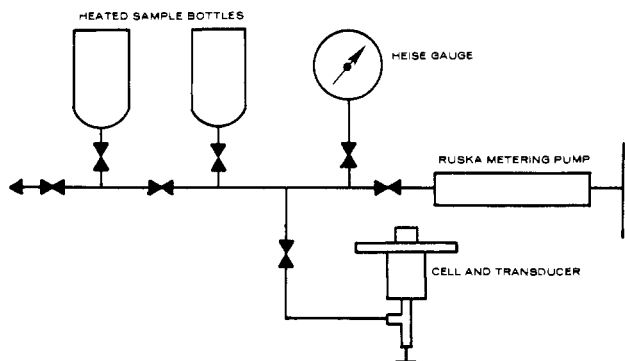**Figure 1.** Cell and transducer for vapor pressure measurement.

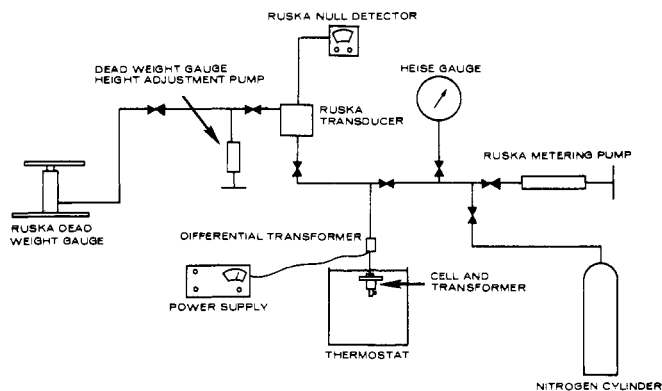Figure 2. Schematic of system for making sample mixtures.



Figure 3. Schematic of system for measuring pressure.

## Table I. Vapor Pressure Data for Isobutane, 1-Butene, and 1,3-Butadiene

| Isobutane | | 1-Butene | | 1,3-Butadiene | |
|---|---|---|---|---|---|
| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
| 39.88 | 26.57 | 40.02 | 21.92 | 40.05 | 20.59 |
| 70.20 | 45.50 | 70.02 | 38.24 | 70.27 | 36.30 |
| 99.72 | 72.33 | 99.86 | 62.29 | 99.97 | 59.33 |
| 130.10 | 110.74 | 130.21 | 96.83 | 130.10 | 92.57 |
| 159.90 | 161.32 | 159.86 | 142.63 | 159.27 | 136.22 |
| 160.10 | 161.68 | 160.12 | 143.09 | 159.30 | 136.29 |
| 129.98 | 110.59 | 130.12 | 96.74 | 130.19 | 92.72 |
| 99.59 | 72.22 | 99.66 | 62.08 | 99.95 | 59.36 |
| 69.93 | 45.32 | 69.95 | 38.19 | 70.32 | 36.34 |
| 40.32 | 26.84 | 40.18 | 21.98 | 40.02 | 20.56 |

## Table II. Antoine Constants

| | $A$ | $B$ | $C$ |
|---|---|---|---|
| Isobutane | 12.1465 | −4170.45 | 430.529 |
| 1-Butene | 12.0502 | −4067.26 | 413.786 |
| 1,3-Butadiene | 12.1118 | −4126.44 | 414.039 |

remained in the vapor space of the bottle was not transferred to the pressure cell. The metering pump allowed approximate determination of mixture compositions, as well as an indication of how full the cell was. Calculations showed that filling the cell about 80% full minimized errors in the liquid phase composition (the liquid composition was assumed to be the same as the
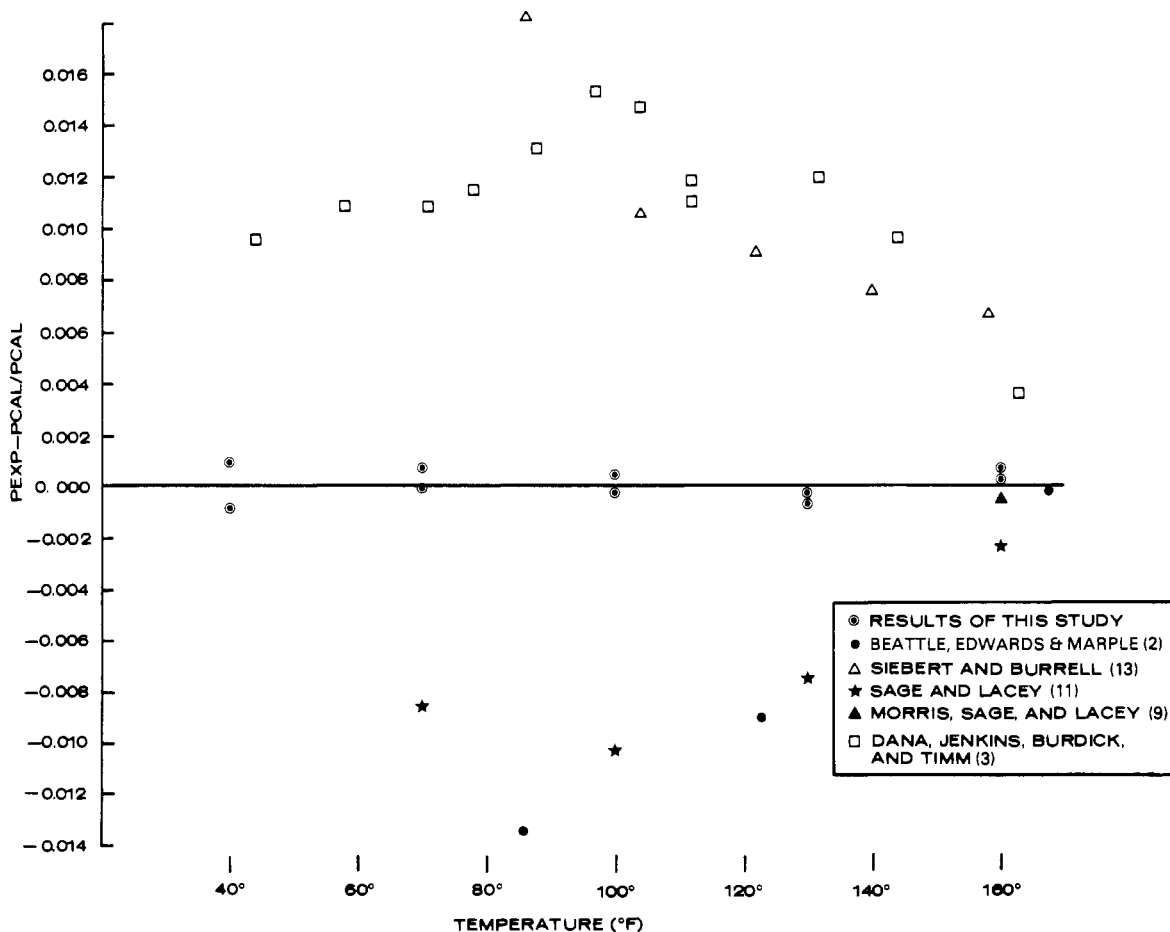


Figure 4. Literature study of isobutane.

Figure 5. Literature study of 1-butene.

overall composition so errors increased as the amount of vapor increased) and errors due to residual air (these errors increased as the amount of vapor was decreased).

Figure 3 shows the equipment used to measure the vapor pressures. The temperature was maintained to within ±0.03 °F (equivalent to a ±0.05% error in the pressure at 100 °F) by a Neslab Instruments RTE 4 circulating temperature bath and was measured with a Leeds and Northrup platinum resistance thermometer in conjunction with a Rubicon Instruments Mueller bridge. The bridge circuit was balanced using a Leeds and Nor-

thrup DC null detector. Pressure was measured with a Ruska dead weight gauge and a Heise gauge. The range of the dead weight gauge was 6–6000 psi, with increments of 0.01 psi.

The hydrocarbons used in this study were supplied by the Phillips Petroleum Company. Phillips reported a purity of 99.99% for the isobutane, 99.96 for the 1-butene, and 99.86% for the 1,3-butadiene. Gas chromatography confirmed the absence of impurities. The hydrocarbons were degassed by a freezing-evacuating-thawing cycle. The cycle was repeated eight to ten times. After degassing, the vapor phase was analyzed for air by



Figure 6. Literature study of 1,3-butadiene.

## Table III. Vapor Pressures for the Binary System

| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
|---|---|---|---|---|---|

### (a) Composed of Isobutane (1) and 1-Butene (2)

$x_1 = 0.7483$    $x_1 = 0.5019$    $x_1 = 0.2464$
$x_2 = 0.2517$    $x_2 = 0.4981$    $x_2 = 0.7536$

| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
|---|---|---|---|---|---|
| 69.96 | 43.96 | 40.21 | 24.87 | 40.18 | 23.52 |
| 99.75 | 70.52 | 100.00 | 68.52 | 69.98 | 40.52 |
| 130.70 | 109.05 | 129.87 | 104.77 | 99.57 | 65.27 |
| 159.81 | 157.81 | 159.95 | 153.90 | 130.08 | 101.14 |
| 159.94 | 157.99 | 160.17 | 154.30 | 159.85 | 148.73 |
| 129.63 | 107.52 | 129.47 | 104.23 | 159.95 | 148.82 |
| 99.84 | 70.58 | 99.86 | 68.43 | 130.16 | 101.25 |
| 69.95 | 44.01 | 69.87 | 42.41 | 99.84 | 65.54 |
| 40.13 | 25.84 | 40.59 | 25.05 | 70.07 | 40.58 |
|  |  | 40.18 | 24.85 | 40.05 | 23.50 |
|  |  |  |  | 40.23 | 23.55 |

### (b) Composed of 1-Butene (2) and 1,3-Butadiene (3)

$x_2 = 0.2509$    $x_2 = 0.5022$    $x_2 = 0.7523$
$x_3 = 0.7491$    $x_3 = 0.4978$    $x_3 = 0.2477$

| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
|---|---|---|---|---|---|
| 40.02 | 21.20 | 70.37 | 38.09 | 40.30 | 22.01 |
| 69.84 | 37.10 | 99.70 | 61.62 | 69.93 | 38.15 |
| 99.66 | 60.65 | 130.08 | 96.01 | 100.13 | 62.52 |
| 129.83 | 94.50 | 160.01 | 142.11 | 129.98 | 96.49 |
| 159.66 | 139.96 | 160.04 | 142.21 | 160.19 | 143.19 |
| 159.95 | 140.45 | 130.12 | 96.10 | 160.21 | 143.26 |
| 129.89 | 94.51 | 99.66 | 61.60 | 129.99 | 96.51 |
| 99.70 | 60.74 | 70.28 | 38.10 | 100.22 | 62.58 |
| 70.05 | 37.31 | 40.34 | 21.87 | 69.93 | 38.09 |
| 40.16 | 21.28 |  |  | 40.30 | 22.05 |

### (c) Composed of Isobutane (1) and 1,3-Butadiene (3)

$x_1 = 0.2525$    $x_1 = 0.5120$    $x_1 = 0.7522$
$x_3 = 0.7475$    $x_3 = 0.4880$    $x_3 = 0.2478$

| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
|---|---|---|---|---|---|
| 40.11 | 23.67 | 39.91 | 25.42 | 40.00 | 26.45 |
| 70.09 | 40.74 | 70.11 | 43.65 | 70.30 | 45.29 |
| 99.47 | 65.30 | 99.38 | 69.33 | 99.57 | 71.64 |
| 130.12 | 101.35 | 130.16 | 107.21 | 130.19 | 110.24 |
| 159.43 | 148.01 | 159.18 | 155.19 | 159.30 | 159.22 |
| 159.61 | 148.34 | 159.21 | 155.26 | 159.34 | 159.35 |
| 130.10 | 101.33 | 130.14 | 107.21 | 130.17 | 110.22 |
| 99.41 | 65.26 | 99.39 | 69.34 | 99.63 | 71.71 |
| 70.09 | 40.72 | 70.07 | 43.62 | 70.34 | 45.31 |
| 40.07 | 23.63 | 39.91 | 25.44 | 39.97 | 26.41 |

gas chromatography which indicated that no air was present. The chromatograph was capable of measuring air mole fractions as low as 0.001, equivalent to a partial pressure of air in the final pressure measurement of 0.02 psi.
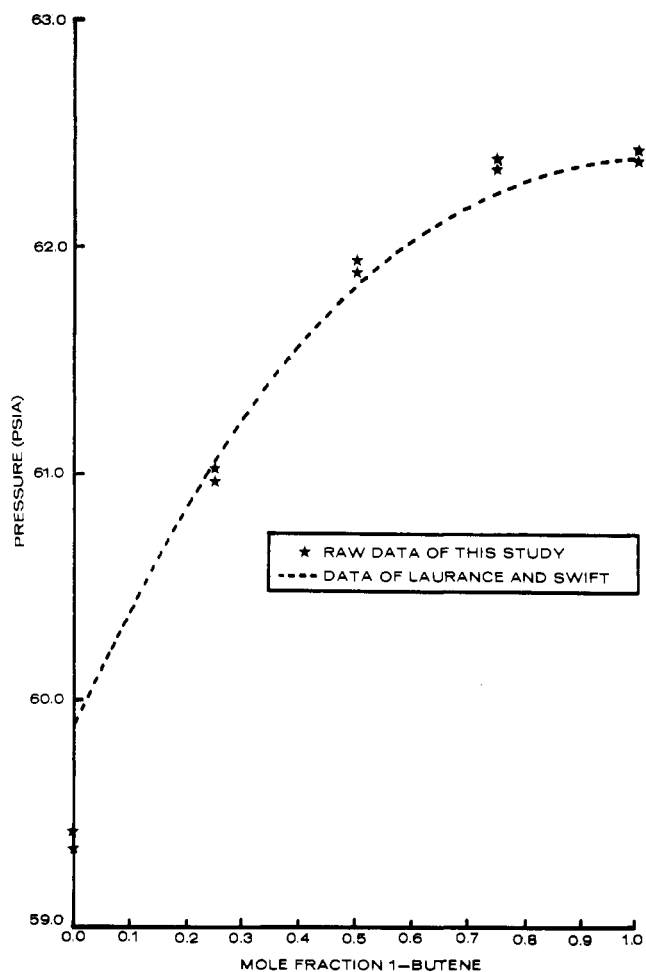


**Figure 7.** Pressure vs. mole fraction for 1,3-butadiene–1-butene at 100 °F.

## Results and Discussion

The raw vapor pressure data for the three pure components are presented in Table I. The vapor pressures were read twice for each data point to verify the reproducibility of the apparatus. The raw data were fit to the Antoine equation:

$$P_{cal} = \exp\left(A + \frac{B}{C + T}\right)$$

where $T =$ °F and $P_{cal} =$ psia. Values of the constants, $A$, $B$, and $C$ for the three components, are given in Table II. Figures 4, 5, and 6 show the fractional deviation from pressures calculated by the Antoine equation for the data from this study, as well as

## Table IV. Vapor Pressures for the Ternary System Composed of Isobutane (1), 1-Butene (2), and 1,3-Butadiene (3)

| $x_1 = 0.2513$ | | $x_1 = 0.5014$ | | $x_1 = 0.2448$ | | $x_1 = 0.3359$ | |
| $x_2 = 0.4985$ | | $x_2 = 0.2515$ | | $x_2 = 0.2568$ | | $x_2 = 0.3313$ | |
| $x_3 = 0.2502$ | | $x_3 = 0.2471$ | | $x_3 = 0.4984$ | | $x_3 = 0.3328$ | |
| $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) | $T$ (°F) | $P$ (psia) |
|---|---|---|---|---|---|---|---|
| 40.32 | 23.95 | 40.13 | 25.28 | 40.13 | 23.79 | 40.04 | 24.52 |
| 70.23 | 41.18 | 70.23 | 43.31 | 70.14 | 40.97 | 70.21 | 42.13 |
| 99.48 | 65.85 | 99.73 | 69.20 | 99.59 | 65.72 | 99.59 | 67.27 |
| 130.30 | 102.35 | 130.16 | 106.39 | 130.08 | 101.73 | 130.30 | 104.23 |
| 159.70 | 149.30 | 159.32 | 154.35 | 159.54 | 148.76 | 159.65 | 151.78 |
| 159.79 | 149.52 | 159.45 | 154.61 | 159.59 | 148.89 | 159.68 | 151.87 |
| 130.26 | 102.28 | 130.14 | 106.35 | 130.03 | 101.67 | 130.25 | 104.08 |
| 99.47 | 65.84 | 99.65 | 69.03 | 99.63 | 65.73 | 99.54 | 67.24 |
| 69.87 | 40.94 | 70.28 | 43.33 | 70.25 | 41.06 | 70.20 | 42.12 |
| 40.09 | 23.89 | 40.11 | 25.22 | 40.13 | 23.80 | 40.13 | 24.52 |

for data from the literature. These figures bear out the fact that for the compounds and temperature ranges examined, the data obtained in this study are as good or better than those available elsewhere in the literature.

The raw vapor pressure data for the three binary systems are presented in Table III. To simplify the notation, isobutane, 1-butene, and 1,3-butadiene are referred to as components 1, 2, and 3, respectively.

Binary data for these systems are extremely limited. Karabanov and Zorin (5) measured vapor–liquid equilibrium data for these systems; however, since their temperatures were all below 0 °C their results cannot be directly compared to the data of this study.

Laurance and Swift (6) have thoroughly studied the binary 1,3-butadiene–1-butene system. The results of their study, as shown in Figure 7, are somewhat different from the results of this study, and their pure component vapor pressure data for 1,3-butadiene are high in comparison with most literature sources at 100 °F.

The raw vapor pressures for the four ternary mixtures studied are presented in Table IV.

## Conclusions

An apparatus capable of determining vapor pressures with a probable error of ±0.05% over a range of 40–160 °F and 20–160 psia is demonstrated by a significant amount of new vapor pressure data for the 1-butene, isobutane, 1,3-butadiene

system. The laboratory technique should be of interest to other experimenters, and the new data should help improve correlations of vapor pressures for the systems studied. The data are also of use in calculating equilibrium vapor compositions to be used in the design of separation equipment.

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# Viscosity of Methane, Hydrogen, and Four Mixtures of Methane and Hydrogen from −100 °C to 0 °C at High Pressures

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The absolute capillary method was used to measure the viscosity of methane, hydrogen, and mixtures nominally 20, 40, 60, and 80% hydrogen at 0, −50, −75, and −100 °C at pressures from 4 atm up to 450–500 atm. The maximum probable error of the calculated viscosity is estimated to be 0.5%. The viscosity data were fit by the least-squares method to give 1.193 ± 0.034 for the Hagenbach factor for the kinetic correction in the vicosity formula. The residual viscosity concept was obeyed within ±1% except for hydrogen and the 80% hydrogen mixture. The deviations for these are attributed to first-order quantum effects.

The earliest investigations (21, 36, 37, 41, 43–45) of viscosity were at atmospheric pressure; Michels and co-workers (30, 32) were among the first to extend investigations to high pressures. The first low temperature–high pressure investigation reported was by Ross and Brown (38) in 1957; however, their data are now regarded (9, 14, 25) to be in serious error. A modification of the Rankine type viscometer using positive displacement pumps was used in separate investigations by Flynn et al. (9) at

−78.5 to 100 °C below 200 atm and by Kao and Kobayashi (25) to reach −90 °C below 200 atm.

The falling body viscometer, which is not an absolute instrument, was used by Huang, Swift, and Kurata (17) from −170 to 0 °C up to 5000 psi. Kestin and co-workers (22, 26) have developed the oscillating-disk viscometer for absolute measurements at room temperature and higher. The concentric cylinder viscometer first used by Couette (7) has not been adapted to low temperature–high pressure investigations. Barr (1) gives detailed accounts of the various methods for measuring viscosity.

## Experimental Details

A schematic of the equipment is shown in Figure 1. Earlier investigations at essentially room temperature on a similar installation were reported by Giddings (10, 11) for methane and propane. Placement of the pumps into the same temperature bath as the capillary by Kao et al. (25) led to investigations (23, 24) on helium, nitrogen, and their mixtures. Significant expermental difficulties arose as the temperature of investigation decreased.

The equipment consists of (1) a stainless steel capillary cell in which a Pyrex glass capillary is held, (2) a pair of coupled flow generating pumps maintained in the same temperature bath as the capillary cell, (3) a dead weight gage system for pressure measurement, (4) a differential pressure measuring system, (5)