Variable volume—constant mass

In this method, combinations of *P-V-T* conditions are obtained by confining a certain constant mass of test fluid in a vessel at constant temperature and determining the change in volume of the sample with change in pressure. Its use dates from antiquity with respect to experimental thermodynamics. In the 16th century, glass cells containing a test liquid confined with mercury and a gold foil mercury position indicator were lowered into the ocean to secure high pressures. General use of the method dates from Amagat's work (1893). Some of the most accurate data yet reported have been obtained by use of this method.

The form of apparatus which has yielded some of the best information is that due to Michels and Gibson (20), Figure 4. It has been used more recently by Schamp, *et al.* (21). This consists essentially of an inverted glass buret of bulbs joined by capillary tubing to magnify volume changes and into which platinum contacts have been fused. The bulbs may be arranged so that all but the first are the same size, or sequenced in size (22). The buret is placed in a pressure vessel in which the bottom part is filled with mercury and the top part outside the buret filled with oil from the pressure generator. The entire pressure vessel is immersed in a thermostat bath.

Pressures to 3,000 atm.

The quantity of gas placed in the buret above the mercury is determined with great care. Then, the pressure of the oil is increased to drive mercury into the buret and compress the sample. As the mercury contacts each electrode, the volume occupied by the sample is known for the pressure existing at that time. This type of application of the method has many inherent advantages. Pressure has no effect on the buret until levels are reached at which the compressibility of the glass must be taken into account. It has been used effectively to pressures as high as 3,000 atm. Errors of no more than 1:10,000 are estimated for some of this work (20). However, it is not generally used for temperatures above 200°C because the mercury dissolves the platinum contacts.

A different adaptation of this basic method was employed by Connolly and Kandalic (23), Figure 5, in which a calibrated glass capillary served as the pressure vessel with mercury the confining fluid. The volume of the sample at any time was determined from the length of the capillary not
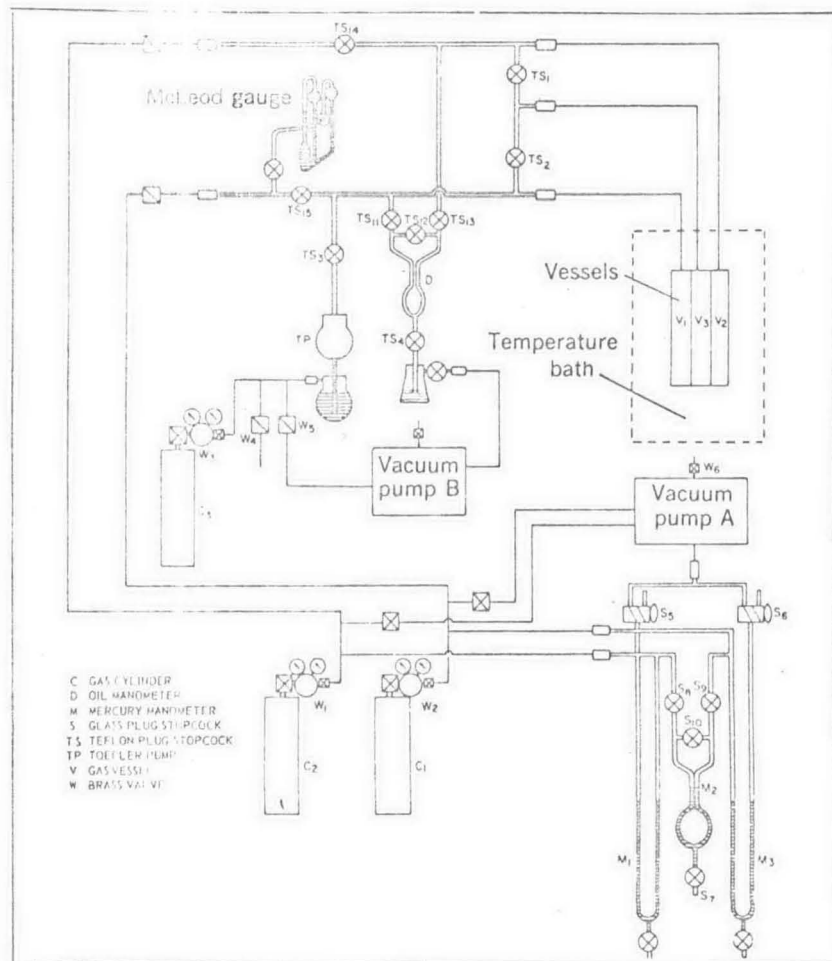

Figure 15. Differential apparatus for determining interaction of second virial coefficients directly (6).

filled with mercury. Estimated errors were less than about 3:10,000 for data obtained around 10 atm. and 1:1,000 for that around 25 atm.

A somewhat similar adaptation has been used by Douslin, *et al.* (24), Figure 6, to obtain data estimated to be accurate within 3:10,000 for temperatures near ambient and 3:1,000 at 300°C and 400 atm. In this case, the sample container consists of a pressure vessel, within which is placed a glass liner or pipette of measured volume containing a carefully weighed amount of sample. To begin a run, the space between the pipette and vessel is evacuated, filled with mercury and the tip of the pipette broken off. From this point, the pipette volume minus the amount of mercury pumped into the vessel including various corrections yields the sample volume.

Another variation was used by Doolittle, *et al.* (25), for measurements on liquids, Figure 7. In this, a stainless steel piezometer contained the sample instead of the glass vessel employed by Michels; it was closed at the top with a steel plug. A rising

mercury column compressed the test fluid as in Michels' apparatus. The position of the column was determined by use of a differential transformer connected to a 1000 cycles/sec. bridge with a vacuum tube voltmeter as a null indicator; the differential transformer was moved to detect the position of an iron slug which floated on the mercury. Doolittle estimated that volume measurements were accurate to 1:10,000 except around 1 atm.; over-all errors in density were estimated to be less than 4:10,000 to pressures of 4,000 kg./sq. cm.

Hydrocarbon systems

A version incorporating a magnetically driven stirrer, resistance bridge liquid-vapor interface locator and ports for sampling both phases has been used by Sage and Lacey (26) for hydrocarbon systems, Figure 8. The estimated uncertainty in volume measurements is 5:10,000, with this being the greatest error in the measured variables.

Bridgeman (27) suggests two further embodiments for high pres-