

representations so that the various properties calculated using them will have adequate accuracy.

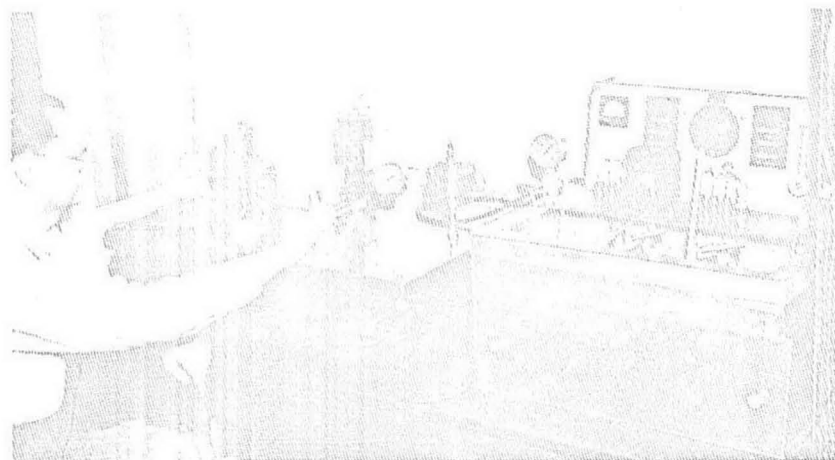
Methods of measurement

The methods of determining the $P-V-T$ behavior of a fluid may be generalized as to the basic restraint placed upon the fluid. There are the constant-volume pycnometers and variable-volume cells for constant-sample mass, the expansion system arrangements for variable-sample mass, special configurations of each, and differential apparatus designed to screen out first-order effects. Each will be discussed as a class and some significant works with that method described briefly. It is hoped that this will aid the new investigator in selecting an approach which will meet his objectives.

Constant volume—constant mass

Conceptually, this method is probably the simplest of those employed to obtain combinations of $P-V-T$ conditions. Basically, it involves charging a known mass of the fluid under test to a pycnometer or cell of known volume and measuring the pressure and temperature of the material, or vice versa. There are many variations of the method, some for high pressure work, some for high or low temperatures, and some based on the state of the fluid.

The simplest versions are those for determining the densities of liquids or gases near atmospheric pressure. These employ glass vessels, whose volume has been determined as accurately



Tests being performed using the Burnett apparatus diagrammed in Figure 11.

as possible, filled with the test fluid. The volume determination is usually effected by weighing the vessel full of mercury or specially prepared water at a measured temperature, thus the accuracy of this value depends ultimately upon the purity of the mercury or water used, the knowledge of its temperature coefficient, the accuracy of measurement of the weighing temperature, and the accuracy of the weighing itself (10). The variable of barometric pressure can be measured with acceptable accuracy with relative ease; the temperature also can be measured with assailable accuracy. Use of this method for pressures much above atmospheric is obtained by the increased weight of the cell. The end result is that with every refinement, errors can be reduced to the order of 0.005% (5:100,000) for gases, but even

achieving errors of less than 0.1% is difficult; achieving errors of the order of 1:1,000,000 is possible for liquids.

Density balance

Another apparatus for low pressures is the density balance. This consists of a vessel, with a window in one end, containing a balance beam with a pointer on one end and a quartz bulb or balloon on the other. The chamber is evacuated and then filled with a reference gas to such a pressure that the beam is exactly balanced. If the chamber is again evacuated and then filled with a test gas to such a pressure that the beam is again in balance, the densities of the gases are equal for the two sets of conditions. Errors with this method may be reduced to the order of 0.1% (1:1,000) with careful work (11, 12).

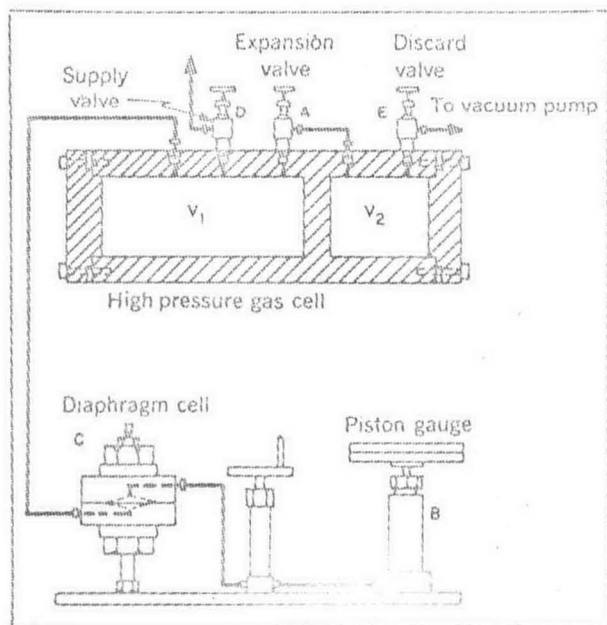


Figure 11. Diagram of commercial Burnett apparatus (34).

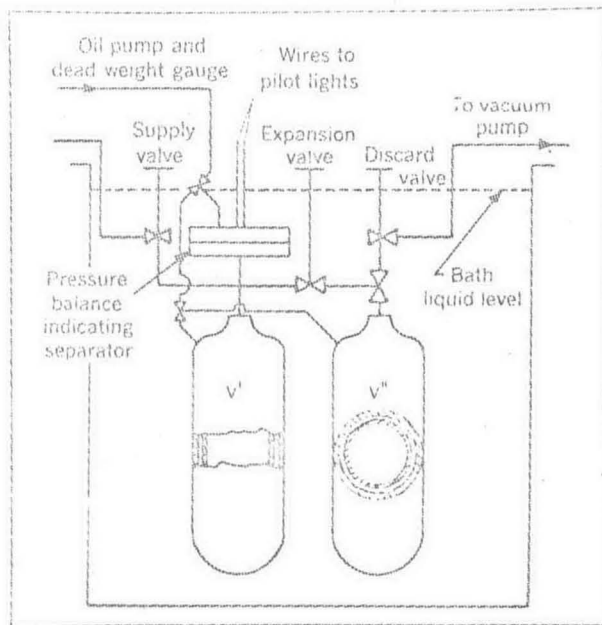


Figure 12. Burnett apparatus with balanced-pressure cells.