

Figure 1. Schematic diagram of constant-volume P-V-T apparatus typical of that used by Dodge (15).

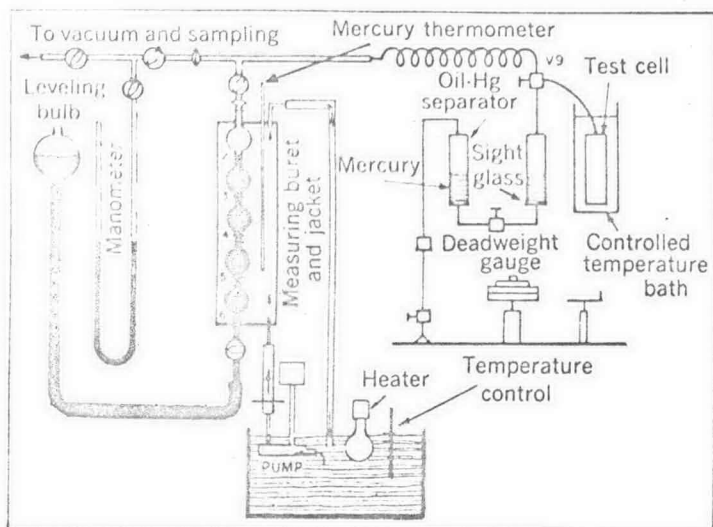


Figure 2. Schematic diagram of constant-volume P-V-T apparatus of Solbrig and Ellington (16).

properties in terms of the equilibrium property, density (2, 3).

In an attempt to present an appraisal of this particular field of work, uses of  $P$ - $V$ - $T$  information will be reviewed briefly, and the major methods of obtaining data described. Some of the characteristics of each method will be cited and their attributes pointed out without defense by detailed error analysis. In this way, it is hoped that new investigators may be assisted to pinpoint accuracy considerations for proposed measurements and obtain data with as long a useful life as possible.

#### Why increased accuracy valuable

Some review of the use of  $P$ - $V$ - $T$  data, to point out areas in which accuracy limitations are already being

felt, should be of merit. It should also help particularize sensitive areas of current information, as determined from some years of work in the field, without detailed documentation.

#### Simple volume calculations

Undoubtedly the first use and need for  $P$ - $V$ - $T$  data were for ordinary density calculations—to know how much of a material could be crammed into a certain vessel at a selected pressure and temperature. This result could, of course, be presented in terms of the conventional compressibility factor by simple algebraic manipulation. There are relatively few instances in which a directly determined density, *per se*, must be accurate to within one-half percent of the true value. An error analysis

based on the defining relationship is simple and it shows that relatively unsophisticated experimental procedures will yield such values.

#### Derivatives in calculations

For the calculation of the thermodynamic properties of a gas, a number of relationships are employed which require integration of terms including the first derivative of functions of  $P$ - $V$ - $T$  behavior, e.g.,

$$dU = C_v dT + [T(\partial P/\partial T)_v - P]dV \quad (1)$$

and in terms of the compressibility factor,  $Z$ ,

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{ZR}{V}\right) + (RT/V)\left(\frac{\partial Z}{\partial T}\right)_v \quad (2)$$

In the above,  $U$  = internal energy and  $C_v$  = molar constant volume heat capacity. Similarly, for enthalpy,  $H$ :

$$dH = C_p dT + [V - T(\partial V/\partial T)_p]dP \quad (3)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{R}{P}\right) \times [Z + T(\partial Z/\partial T)_p] \quad (4)$$

If one examines these relationships, it immediately becomes apparent that for certain combinations of conditions the term involving the derivative will contribute significantly to the result. It should also be evident that the requirements on  $P$ - $V$ - $T$  data are more stringent for representation of the values of the derivative with a given accuracy for given values of the independent variables than for predicting the pressure, volume, or temperature. For each differentiation of the  $PV$  product there will be a loss of precision of about one order (4). Thus, to obtain derived thermodynamic properties from  $P$ - $V$ - $T$  data on a given component or mixture, accurate to one part in 100, the original

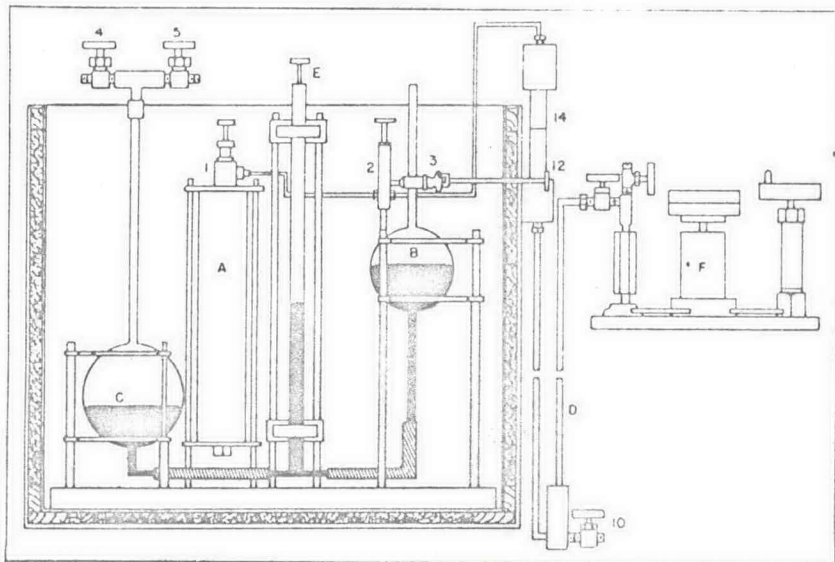


Figure 3. Bean variable-volume P-V-T apparatus (18).