sures. One, Figure 9, contains the test fluid in a bellows which is surrounded by the pressure generating fluid. The change in length of the bellows is measured by use of a slide wire and potentiometer and the change in internal volume is calculated. Some investigators feel that the accuracy of the method suffers because of inelastic hysteresis of the bellows. The second embodiment utilizes a free piston, Figure 10, which slides up and down the barrel of the cylindrical compressibility cell. The volume occupied by the test is determined from the position of the piston. Bridgeman used a piston which fitted the vessel barrel so closely as to preclude fluid bypass and determined piston position with the slidewire technique. Several petroleum company laboratories utilize further modifications which include "O"-ring or "chevron" packings between the piston and cell, measurement of piston position with a ruled rod attached to the piston and extending through a packing gland, trunion mounting for rocking to facilitate mixing, and a bulls-eye port for observing liquid-vapor interfaces and estimating the volume of each phase. Less accuracy is obtainable with these units, but highly useful information has been obtained with them.

Variable volume—variable mass

Burnett (28) evolved a method for obtaining P-V-T data without direct volume measurements. Figure 11 and Figure 12 show a refinement of the equipment in which the two sample containers operate under balanced pressure. In operation, the test gas, Figure 11, is contained at a measured pressure in one chamber, V1, of a double pressure vessel which is in a constant temperature bath. The second chamber is evacuated and valved off. Then the sample is expanded to fill both chambers, the pressure measured, the second chamber again closed off and evacuated, and the expansion process repeated a number of times until near-atmospheric pressure is obtained. With the equation of state written, in terms of the compressibility factor, first for the original mass in Vessel V1 and then in both vessels, one obtains:

$$P_o V_1 = Z_o n_o RT \qquad (10)$$
$$P_1(V_1 + V_2) = Z_1 n_o RT \qquad (11)$$

This can be rearranged to give
$$(P_1/P_o)N = (P_1/P_o)(V_1 + V_2)/V_1$$
$$Z_1/Z_o \qquad (12)$$

where N is an apparatus constant which depends only on the dimensions of the equipment. After a series of j successive expansions,

$$(P_j/P_o) N^j = Z_j/Z_o \qquad (13)$$
$$P_j N^j = P_o Z_j/Z_o \qquad (13a)$$

The limit of the ratio P_j/P_o as $P_j \rightarrow 0$ is the cell constant, which must usually be considered to be a function of temperature. If the isotherm for a given series of expansions is sufficiently linear, the extrapolation often may be performed graphically; frequently it must be performed by fitting a function to the data.

As regards accuracy of results, it should be noted that any error in P_o/Z_o is introduced directly into each Z_j. Therefore, accurate low pressure measurements are essential unless the isotherm exhibits linearity to relatively high pressures. Also, because the cell constant N is raised to the power j in determining Z_j, the effect of any error in N is magnified considerably;

to a first approximation the error in $P_j N^j$ from an error in N is j times the error in N. Therefore, the crux of accurate Burnett apparatus work is very accurate determination of the apparatus constant. Detailed discussions of the use of this equipment have been given by Bloomer (19), Mueller, et al. (29) and Schneider (7); data treatment has been discussed by Pfefferle, et al. (30), Schneider, et al. (31), Silberberg, et al. (32), and Canfield (33). Error estimates range from 2:1,000 in Z for use of the industrial units (32), to 1:10,000 in cell constant N for very careful work and special units (33).

Recently, Burnett (34) reported on the adaptation of this approach to the determination of the compressibities of multicomponent systems for conditions within the two-phase region. In this apparatus, two expansion valves are needed between the two chambers; one at the top for vapor and another at the bottom for liquid. The system is set on a rocking mount so that the fluid in the chambers can be mixed to assure constant mixture composition. This is a new technique and error analyses have not been presented.

A modification of the method has been used to obtain compressibility factors accurate within about 0.01% for pressures near atmospheric, Figure 13 (14). Data are obtained at two or three different pressures by confining a sample of gas in successively larger volumes at constant temperature over mercury. Each pure gas or first mixture component was taken into the expansion system, Figure 13, to fill one of the measured volumes, and its pressure measured carefully. Other components were then taken successively into the mixture preparation bulbs, measured in like manner and then forced into the expansion system and mixed. The sample pressure was then measured as it filled successively one, two and three bulbs.

The data were treated with the equation of state truncated after the second virial, i.e.,

$$[PV/(1+aP)]_1 = [PV/(1+aP)]_2$$
$$= (PV/Z)_1 = PV_{P\rightarrow 0} = RT$$
$$(14)$$

The data for several expansions were fitted to:

$$PV = (PV)_o (1+\beta P) \qquad (15)$$

Then β was corrected for variation with pressure to give the second virial at 60°F and 1 atm. by introducing the third virial.

Special methods

It is especially worthwhile to note that several investigators have developed experimental approaches that
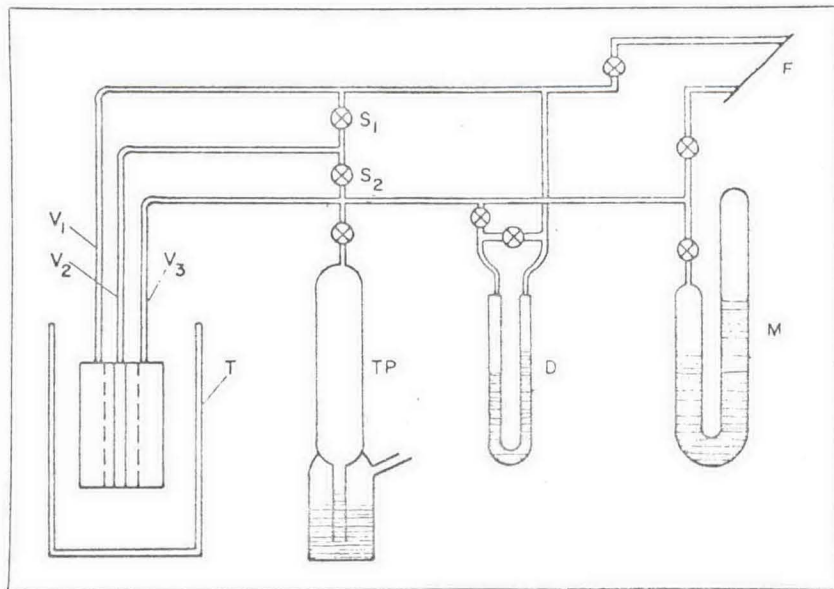

Figure 16. Details of a differential P-V-T apparatus (6).