Figure 4. Michels' type variable-volume P·V·T apparatus (20).

Figure 5. Variable-volume apparatus of Connolly, et al. (22).

Figure 6. Compressibility cell, Douslin (24).

Figure 7. Piezometer of Doolittle (25).

PV measurements must have a precision of about one part in 1,000.

Partial enthalpies

To calculate similar properties for mixtures, it is necessary to know the effect of composition on the contribution of each component, such as partial enthalpies; $\overline{H}_1 = (\partial H/\partial n_1)_{T, P, n_1, n_2,} \cdot \cdot$ To derive partial enthalpies for mixture components, differentiations of the PV product with respect to both temperature and composition are required, and the initial measurements must have an accuracy of about one part in 10,000 to yield partial enthalpy values accurate to one part in 100. Thus, for mixtures, precision in the P-V-T data is even more important than for pure components.

The change of isobaric heat capacity with pressure is given by:

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \qquad (5)$$

This equation involves second differentiation of the PV product for the pure component or given mixture, and provides a means of evaluating heat capacities at high pressure without the use of calorimetric or Joule-Thomson data. Again, the evaluation of the second derivative requires P-V-T data with a precision of about one part in 10,000 to yield values accurate to one part in 100. In the case of vapor-liquid equilibrium, the fugacity or thermodynamic pressure of each component must be balanced in each of the coexisting phases. The fugacity of a component in a mixture at constant temperature and constant composition is given as:

$$RT \ d(\ln f_i) = \overline{V}_i \ dP \qquad (6)$$

where f_i is the fugacity and $\overline{V}_i$ is the partial molal volume of the ith component. To evaluate the partial molal volume, it is necessary to differentiate the saturated liquid and vapor volumes with respect to composition. Thus, to obtain the ratio of vapor composition to liquid composition at equilibrium (K-factors) accurate to one part in 100, the original P-V-T-composition measurements must be accurate to about one part in 2,000.

Equations of State

During the last decade a high level of activity has continued in equation of state development. The objectives of this work are twofold; first there is the engineering objective of improved representation of existing data on fluids for thermodynamic property calculation and design and, secondly, there is the fundamental objective of expanding knowledge of the molecular behavior of fluids. Recent efforts to improve representation of data may be thought to date from the work of Beattie and Bridgeman and Benedict, Webb and Rubin. The success achieved with these equations has resulted in use for ranges beyond those for which they were developed. There have been so many developments of polynomial fits to various sets of data that new offerings may almost be presented with apology. Nevertheless, the objective of adequately representing the behavior of both single and multicomponent systems for the liquid, gas, dense fluid, and liquid-vapor regions with a single relationship still remains unat-

tained. The primary requirement for continued progress toward this goal is internally consistent, accurate data for all of these regions. It is extremely disturbing for the investigator trying to do analytic work to find that important sets of data are displaced from each other or show divergent trends. Even more trying is the task of analyzing experimental methods and determining which set of data shall be used, on the basis of a terse journal article.

Voids in experimental data which are assuming increased importance are those near phase boundaries and for the dense fluid. In particular, if an equation is to be used to represent saturated densities or to predict vapor-liquid equilibria, difficulty may be expected if considerable extrapolation beyond the range of the data is required to reach the phase boundary. From the preceding discussion, it is evident that a valid equation of state must fit an adequately large field of data with sufficient accuracy that the values of the first and second derivatives at any point meet calculation requirements. This places increased dependence upon the higher order terms and hence the accuracy of the data fitted.

Virial coefficients

To improve knowledge of the molecular behavior of fluids, efforts have been concentrated on the virial form of the equation of state developed from statistical mechanics. The second virial coefficient can be calculated from consideration of two-body interactions if the intermolecular potential