



Institute of Gas Technology's P-V-T apparatus diagrammed in Figure 2.

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## Techniques for P-V-T measurements

Uses of experimental P-V-T composition data are reviewed briefly to show the need for increased accuracy in new data.

*"It is an inescapable fact that in research, the quality of a conclusion is expressible in terms of one or more measurements. Without such a reduction to elementary considerations, no experiment is repeatable, no result is verifiable—no basis exists for the entire structure."*

This statement (1) is especially true for our field—chemical engineering. In recent years, it has also become increasingly evident that measurements of a given accuracy have a definite place in time in the development of a given area of physical science. As theoretical and empirical methods of representing behavior are improved and come abreast of data accuracy, it may be pertinent to inquire as to whether an addition to the literature represents new information or measurement error. Frequently an increase in the accuracy of experimental data may be necessary to implement the next step in theoretical or analytical developments. Such steps have frequently characterized developments in the field of physics.

Those working on the P-V-T behavior of fluids should seek such

improvements. Re-examination of their approach might be worthwhile for many university and industrial laboratories. It would seem that many investigators overlook the uses that others will try to make of their data after they become part of the literature—even though the investigator may have stated intended limits of use. In many cases, in considering service to the profession, it might be worth the extra effort to improve a piece of apparatus to the point that another significant figure can be added to the values reported. It might be worthwhile for more university laboratories to emulate the practice of a noted laboratory in Europe. In this, the number of apparatus construction activities is reduced to a minimum; a single apparatus is built and it is as refined as possible. In this approach, masters degree candidates would engage in fewer apparatus construction activities; more would spend their time on taking high quality data, data analysis, and carrying out calculations with these data. It might also be hoped that the more mature investigators in industrial laboratories

would seek to add all possible refinement to their efforts. In short, this is a plea for excellence in the P-V-T investigations that may be planned in the future.

Such a plea requires defense because it would certainly mean reduction in the number of thesis investigations of intermediate sophistication—those with the objective of building a piece of equipment and obtaining some data primarily for experience. A generation ago, densities of little better than two-figure accuracy provided the level of information on fluid behavior generally necessary. Since then, equations of state and other methods of representation have been improved to the point that data of such accuracy now seldom add much to the useful information in the field. The requirements for modern equation of state development, second and third interaction virial coefficient determination, and phase equilibrium prediction work are such that accuracies in excess of four significant figures are frequently worthwhile. At times this may require expensive duplication of work done not too many years before unless the earlier investigator is quite foresighted. A further impetus for internally consistent liquid, gas, and dense fluid P-V-T work is provided by the success which has been realized in representing nonequilibrium (transport)

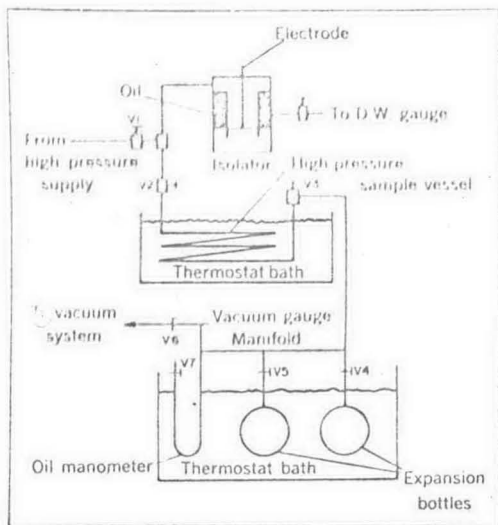


Figure 1. Schematic diagram of constant-volume P-V-T apparatus typical of that used by Dodge (15).

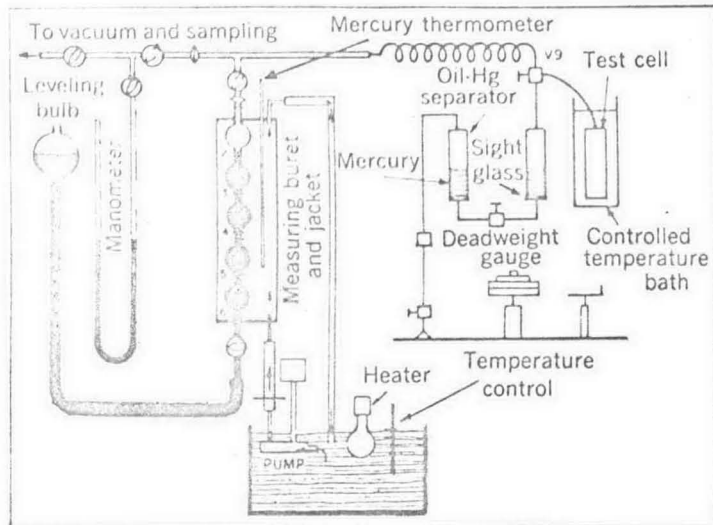


Figure 2. Schematic diagram of constant-volume P-V-T apparatus of Solbrig and Ellington (16).

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,  $Z$ ,

$$(\partial P/\partial T)_v = (ZR/V) + (RT/V)(\partial Z/\partial T)_v \quad (2)$$

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

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

$$(\partial V/\partial T)_p = (R/P) \times [Z + T(\partial Z/\partial T)_p] \quad (4)$$

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

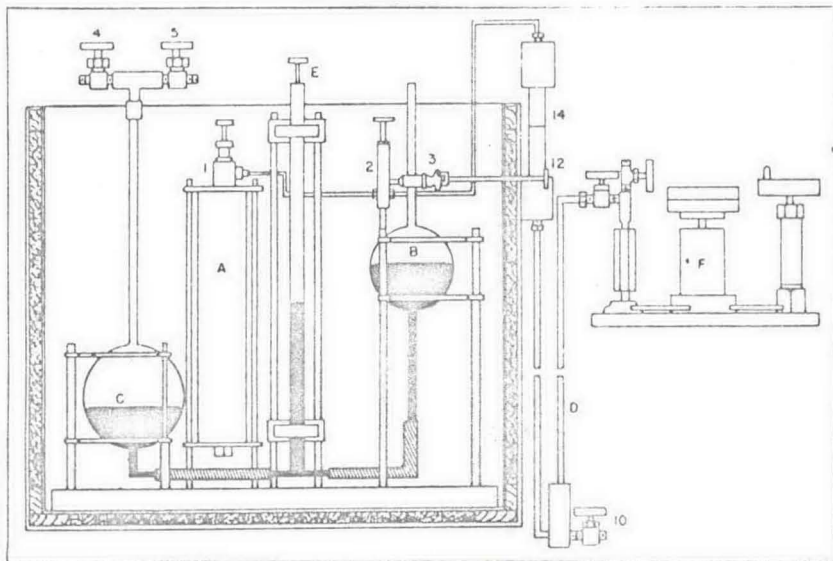


Figure 3. Bean variable-volume P-V-T apparatus (18).

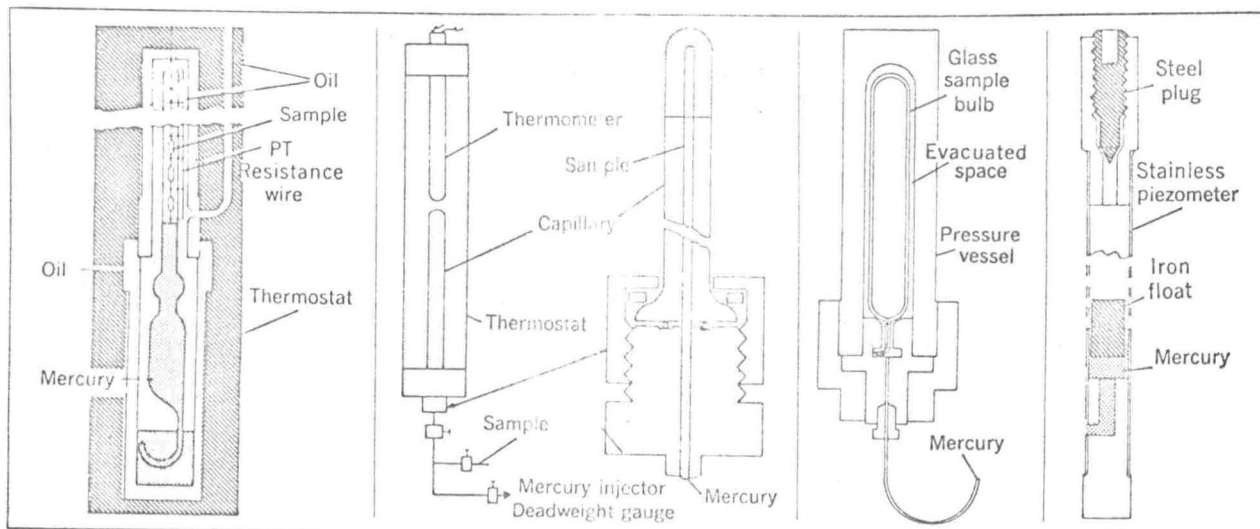


Figure 4. Michels' type variable-volume P-V-T apparatus (20).

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;  $\bar{H}_i = (\partial H / \partial n_i)_{T, P, n_1, n_2, \dots}$ . 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:

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

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:

$$RT \, d(\ln f_i) = \bar{V}_i \, dP \quad (6)$$

where  $f_i$  is the fugacity and  $\bar{V}_i$  is the partial molal volume of the  $i$ th 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

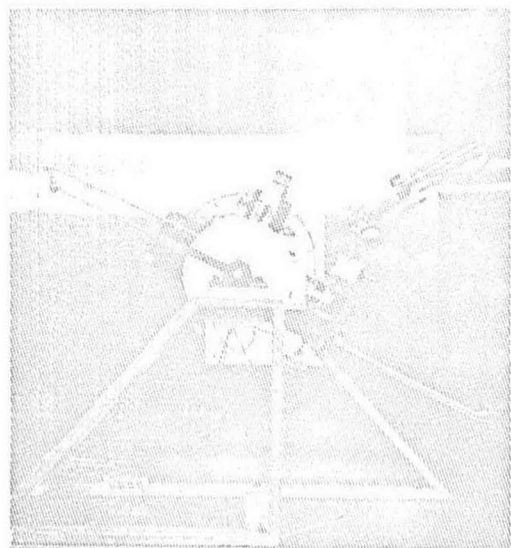
During the last decade a high level of activity has continued in equation of state development. The objectives of this work are twofold; first there is the engineering objective of improved representation of existing data on fluids for thermodynamic property calculation and design and, secondly, there 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



Multipurpose free-piston P-V-T and phase equilibrium test cell.

function is known. If highly accurate values of the second virial coefficient are available, new information can be obtained regarding the adequacy of the various potential functions and combining rules (5, 6). Although the calculations are extremely difficult for all but the simplest potential functions, the third virial can be calculated by consideration of all possible two-body interactions in the three-body system.

Extensive and very accurate P-V-T data are required to yield second virial values accurate to better than 1% (7). Accuracies considerably better than this are desirable if information is to be extracted regarding interaction coefficients for mixtures and especially if potential function parameter combining rules are to be tested (6). In addition to the use of

least-squares P-V-T data to obtain second virial values, it is often convenient to obtain values graphically by use of compressibility factor data, i.e., rearrangement of the virial equation yields,

$$(Z-1)V = B + C/V + D/V^2 + \dots \quad (7)$$

From this, the second virial may be found by plotting  $(Z-1)V$  versus  $1/V$  and extrapolating to the ordinate to obtain:

$$\lim_{(1/V) \rightarrow 0} (Z-1)V = B \quad (8)$$

This method is very sensitive to errors in density at low densities, so that the extrapolation can be extensive and the values obtained rather questionable. In like manner the third virial can be evaluated by graphically determining:

$$\lim_{(1/V) \rightarrow 0} (Z-1)V^2 - BV = C \quad (9)$$

This plot is very sensitive to the value of  $B$  and will blow up rather than extrapolate with negligible curvature if an erroneous value of  $B$  has been used. It is because of these difficulties that the experimental methods which screen out first-order effects may become more widely used.

#### Transport properties

Recent correlation efforts have shown that relationship between the nonequilibrium properties, e.g., viscosity and thermal conductivity, and the equilibrium P-V-T property continues to gain support. On the basis of suggestions by Russian writers, Owens and Thodes (8) and others have made extensive use of the relationship between residual thermal conductivity and the density of a fluid to correlate data to a single curve. Eakin and

Ellington (3) and Starling and Ellington (2) have shown that liquid, gas, and dense fluid viscosities can be correlated similarly. The dependence has been shown (2) to have fundamental basis in the modern molecular theory of fluids.

It is significant that these efforts yield continuity of states in the correlations. The correlations also show that for extensive ranges of conditions a single viscosity value results for a single density, whether that density represents a highly compressed gas, dense fluid, or a liquid at elevated temperature and low pressure. This has been shown to obtain for both pure components and mixtures (9). This situation is especially important in the extra emphasis that it places on the need for accurate prediction of densities of all fluid phases and preferably with a single relationship. Further confirmation of this need has been found because of the significant composition dependence of the correlation, both from the viscosity mixing rule standpoint and that of the density. In a case or two, erroneous sample analyses were detected through these sensitivities.

In recapitulation, great expansion in the uses of P-V-T information in the last decade, particularly in the calculations made possible by high speed computers, has resulted in greater need than ever for high quality P-V-T-composition data for all conditions of fluid existence. There is great need for improved equation of state representation of these data for the full range of conditions and for fundamental studies. Finally, increased accuracy is needed in both the basic data and the various repre-

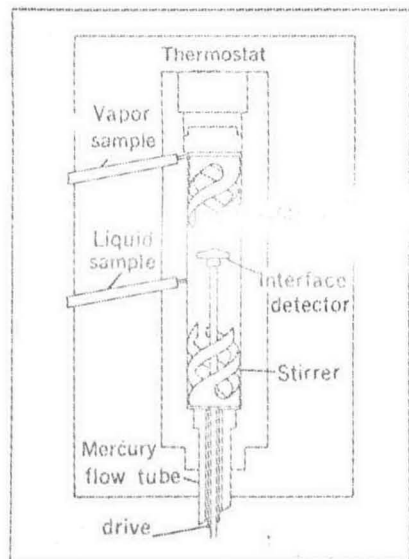


Figure 8. Sage and Lacey cell with liquid surface locator (26).

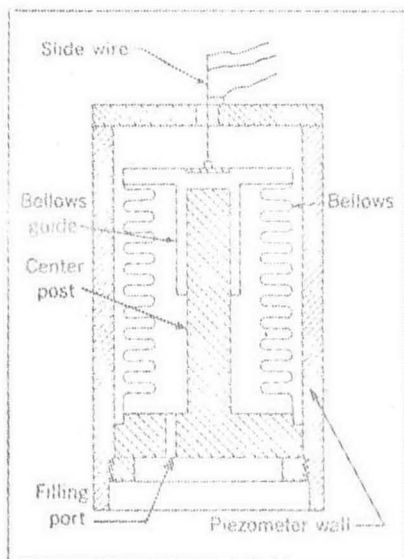


Figure 9. Schematic diagram of Bridgman bellows cell (27).

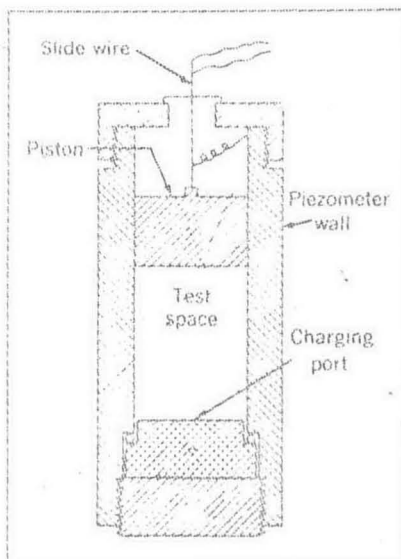


Figure 10. Schematic diagram of Bridgman free piston cell (27).

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

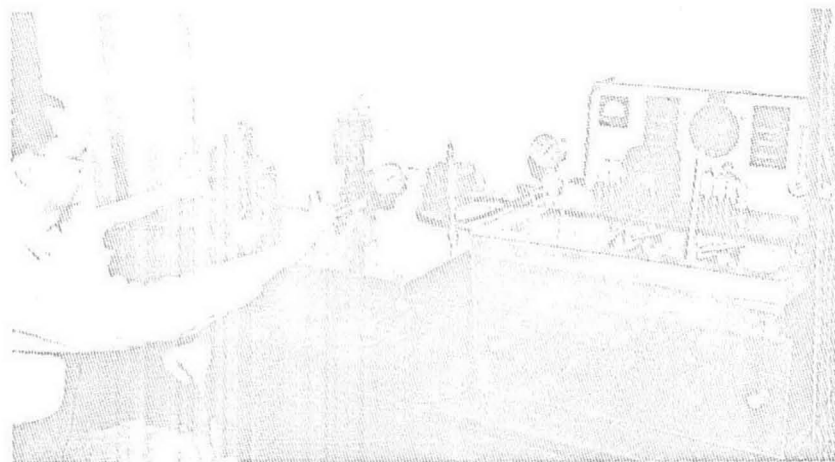
### Methods of measurement

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).

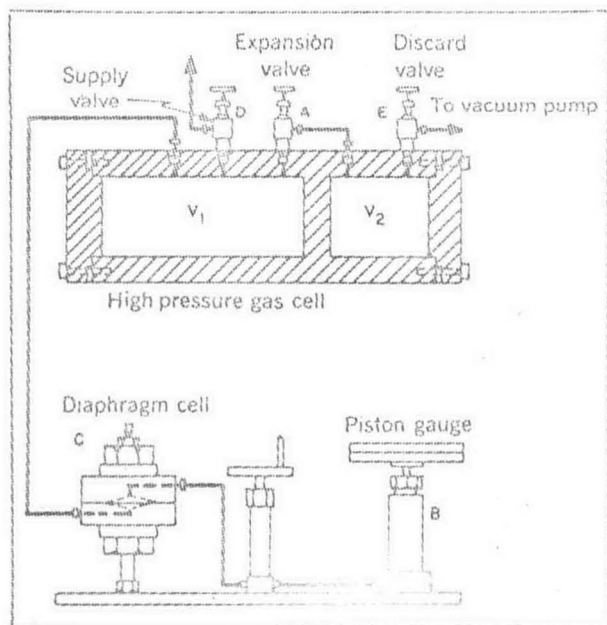


Figure 11. Diagram of commercial Burnett apparatus (34).

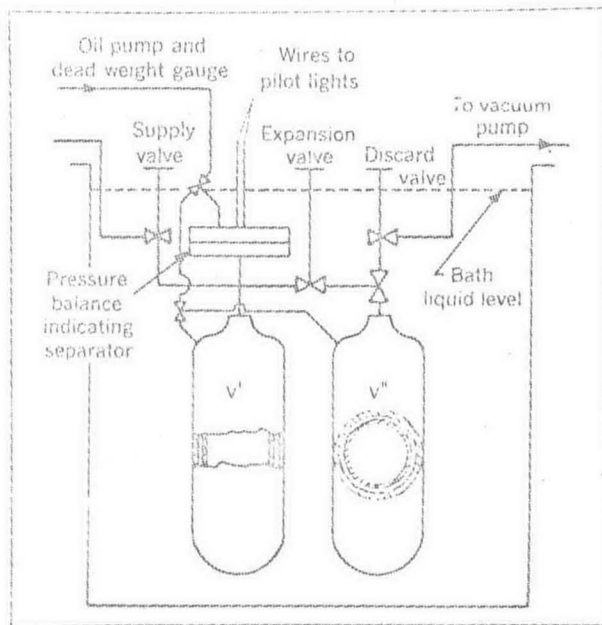


Figure 12. Burnett apparatus with balanced-pressure cells.

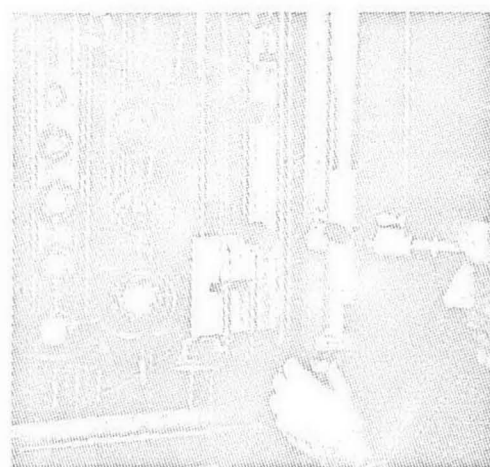
For use at higher pressures, the vessel becomes a heavy-walled metallic container and the measurement of the mass of a gaseous test fluid and the pressure are complicated. A number of investigators, some are listed by Cornings (13), have employed an approach in which the test fluid is charged to the high pressure vessel and its pressure and temperature determined, Figure 1. The mass of the sample is determined afterward by expanding it to atmospheric pressure or below in a large vessel at known temperature. Thus, the mass must be calculated from a second set of  $P$ - $V$ - $T$  measurements at conditions for which the density of the material is known with sufficient accuracy.

Several points should be mentioned regarding this method. One approach is to evacuate the system, close V3, Figure 1, inject the sample, close V1, measure the pressure and thermostat temperature, and then close V2. The sample is then expanded from the measured volume of the sample vessel to low pressure in the vessel plus the measured volume of the expansion vessels and the manifold system. It is clear that, for high accuracy, significant difficulty is encountered in determining the volume of the manifolding and knowing its temperature with sufficient accuracy. Further, ideal gas behavior cannot be assumed for the sample at atmospheric pressure (14), as was done by many earlier investigators, for computing the sample mass. The accuracies obtainable with careful work are represented by those of Bennett and Dodge (15), whose es-

timated errors were less than 4:1,000 for the largest compressibilities ( $PV/P_0V_0$ ) reported. It should also be noted that overcharging of the system yields a single data point.

#### High pressure systems

A variation (16) of this method has been used by Dakin and Ellington for several years for pressures to 3,000 lb./sq. in. and temperature from  $-300^\circ$  to  $310^\circ\text{F}$ , Figure 2. This variation has the advantages that the mass of the sample is determined both as it is charged into the high pressure vessel and released from it, and that a single charging yields several data points. In essence, the high pressure and manifold system are evacuated, the vessel immersed in liquid nitrogen, the sample measured at low pressure and passed into the vessel and condensed. Alternately for noncondensables, a high pressure buret is used to measure the sample into the vessel. To conduct a run, the vessel is warmed, the contents stirred, the vessel placed in the thermostat bath, the temperature stabilized and the pressure measured. Then, stabilizations are made at other temperatures and the pressures measured. Since the high pressure capillary system to the pressure gauge separator is also filled with sample, a mass balance must be made to calculate the density of the material in the vessel for each temperature. Then a fraction of the sample is bled into the low pressure buret system and measured, and runs made for the same temperatures as before. As a check on the run series, the mass



Institute of Gas Technology's P-V-T apparatus diagrammed in Figure 13.

charged must equal the sum of the masses bled out of the vessel. Careful work with this relatively unsophisticated system yields densities with errors of less than 1:1,000. Michels, *et al.* (17) quote results accurate to 1:10,000 for a very refined apparatus.

A further variation of the basic method which has been widely used industrially for temperatures near ambient is that evolved by Bean (18, 19), Figure 3. The high pressure vessel A and the expansion volume B are immersed in the same thermostat bath. The expansion volume is relatively small so that numerous expansions (hence data points) are obtained to reduce the vessel pressure to near atmospheric. The industrial unit has been shown to yield densities with errors of less than 1:1,000 (19).

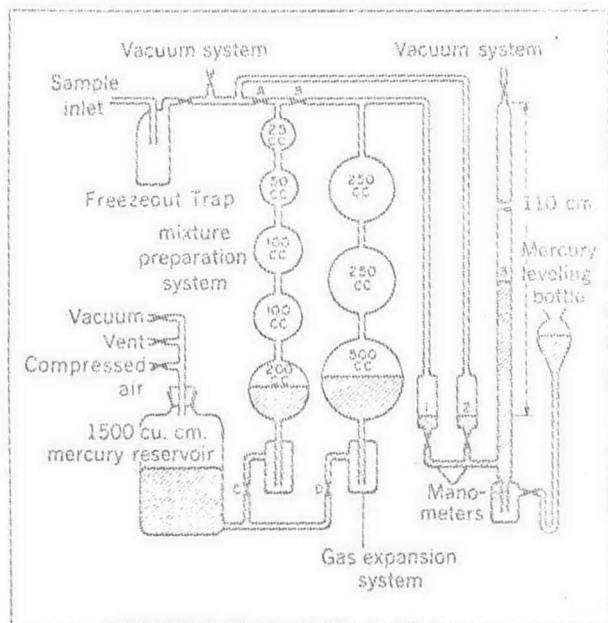


Figure 13. Schematic diagram of low pressure variable-volume apparatus (14).

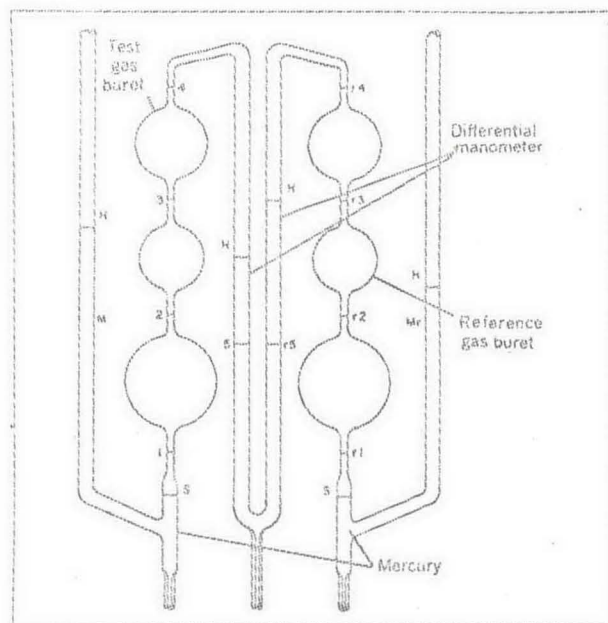


Figure 14. Differential P-V-T apparatus for obtaining second virial coefficients (35).

### 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

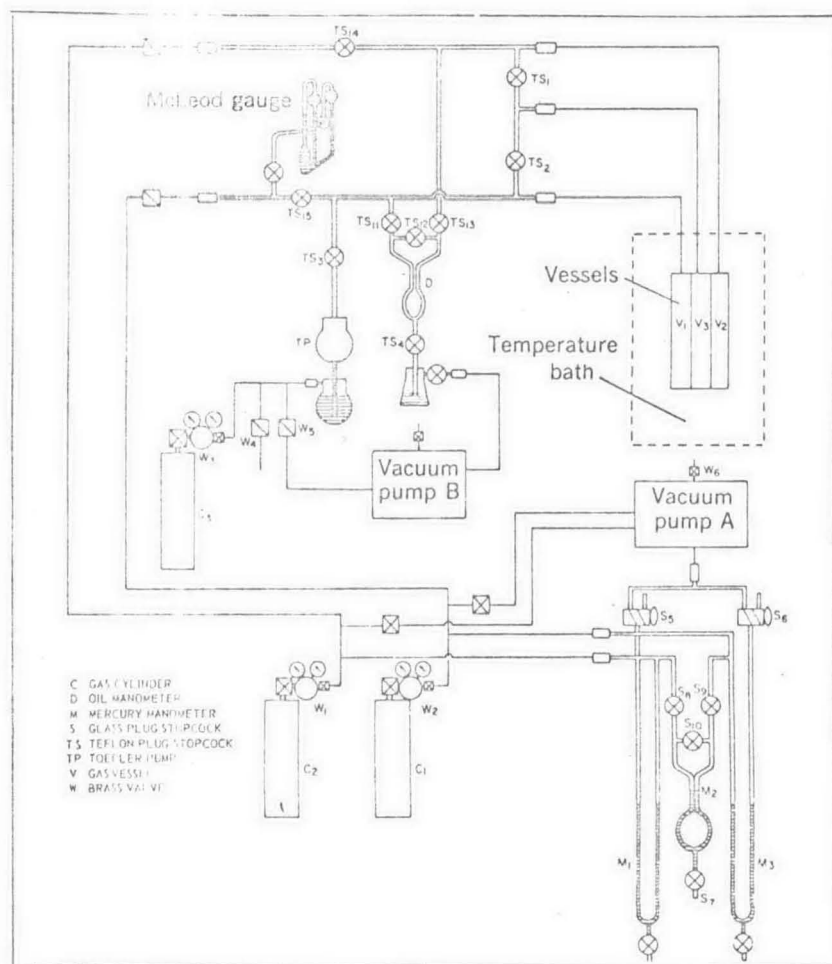


Figure 15. Differential apparatus for determining interaction of second virial coefficients directly (6).

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-

tures. 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,  $V_1$ , 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  $V_1$  and then in both vessels, one obtains:

$$P_0 V_1 = Z_0 n_0 RT \quad (10)$$

$$P_1 (V_1 + V_2) = Z_1 n_0 RT \quad (11)$$

This can be rearranged to give

$$\left(\frac{P_1}{P_0}\right) N = \left(\frac{P_1}{P_0}\right) (V_1 + V_2) / V_1 \cdot \frac{Z_0}{Z_1} \quad (12)$$

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

$$\left(\frac{P_j}{P_0}\right) N^j = Z_j / Z_0 \quad (13)$$

$$P_j N^j = P_0 Z_j / Z_0 \quad (13a)$$

The limit of the ratio  $P_j / P_0$  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  $P_0/Z_0$  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 compressibilities 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.*,

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

The data for several expansions were fitted to:

$$PV = (PV)_0 (1+\beta P) \quad (15)$$

Then  $\beta$  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

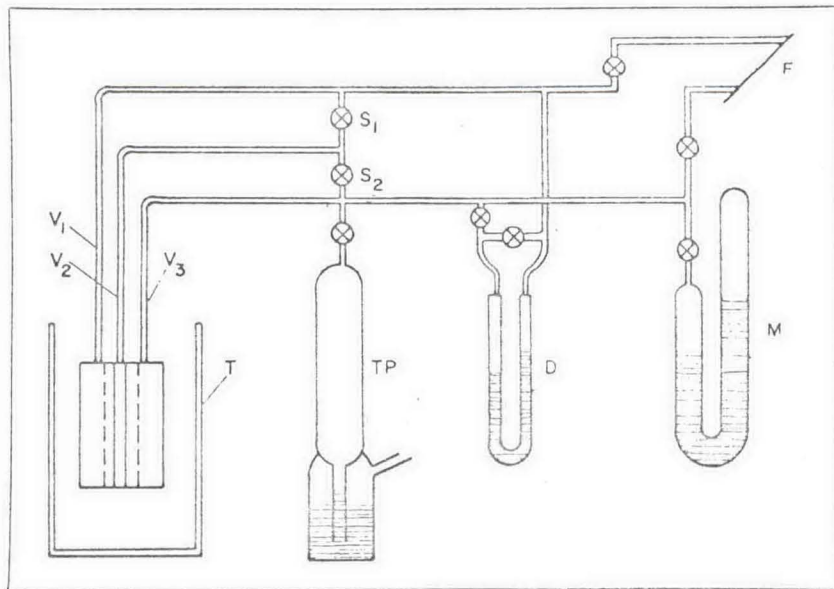


Figure 16. Details of a differential P-V-T apparatus (6).



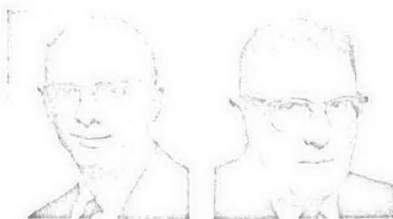
eliminate first- and even some second-order effects directly. Addingley and Whytlaw-Gray (35) were apparently the first to compare directly the gas under investigation with an approximately equimolar quantity of a well-investigated reference gas. They measured the small differences in volume when the gases were at identical pressures. Haman and Pearse (36) and later McGlashen and Potter (37), Figure 14, measured the small difference in pressure when the two gases were confined as nearly as possible at the same temperature and equal volumes. The apparatus is as nearly symmetrical as possible. The test gas is charged to the left buret and the reference gas to the right through the manometer tubes M, with the mercury withdrawn. The mercury levels were then raised to the first buret mark to confine the gases in the same volume and the amount of one adjusted to give the same pressure. Then, the two were successively compressed to fill only two and only one bulb each and the pressure difference measured. The pressures are related directly to the second virial coefficient. To yield an accuracy of 2:1,000 in the second virial, the initial total pressure need only be known to 1:1,000. The need for maximum possible accuracy is concentrated on measurements of the pressure differences.

Interaction second virial coefficients have been measured directly by Knobler, *et al.* (38), and by Magasanik and Ellington (5, 6), Figure 15 and 16. In this case, three vessels of equal volume are held at the same temperature. Two vessels,  $V_1$  and  $V_2$ , are filled with one gas, Figure 16, the third,  $V_3$ , with the second gas, all at precisely the same pressure. Then the contents of vessel  $V_2$  of the first component are mixed with those of the second component in  $V_3$  by repeated flushing into and out of the expansion vessel TP. The mixture is then compressed back to the initial volumes in  $V_2$  and  $V_3$  and the difference in pressure between the mixture and that of the reference volume,  $V_1$ , measured directly with the differential manometer D. This difference can be related directly to the interaction second virial coefficient. Thus, first-order total pressure and second-order pure component second virial effects are screened out to give more accurate interaction coefficients directly.

### Recommendations

If recommendations were to be made on the basis of this review, they would be:

1. That more of the experimental efforts for obtaining new  $P$ - $V$ - $T$



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data be directed at obtaining values accurate to 1:5,000 or better.

2. That more efforts be directed toward obtaining data near phase boundaries, and for the dense fluid.
3. That effort be made to extend each new work to existing data and reconcile discrepancies so that larger internally consistent sets will result.
4. That new efforts include relatively extensive ranges of more than one independent variable to obtain full advantage of the smoothing effects obtainable with analytical fits.
5. That effort be made to develop more special methods that will yield data directly on second order effects.

It is recognized that these recommendations are in the direction of increased cost for new efforts, but the added value of them to other investigators and engineers should more than make it worthwhile. #

### LITERATURE CITED

1. White, C. E., *Research/Development*, 14, p. 40-43 (March, 1963).
2. Starling, K. E., and R. T. Ellington, "Viscosity correlations for non-polar dense fluids," paper presented at the New Orleans Meeting of A.I.Ch.E. (February, 1963), to be published in *A.I.Ch.E. Journal*.
3. Eakin, B. E., and R. T. Ellington, *J. Petrol. Technol.*, 14, p. 210-214 (February, 1963).
4. Edmister, W. G., "Ideas from Europe for research on vapor and liquid properties at high pressures and at low temperatures," paper presented at the Southwest Regional Meeting of the Am. Chem. Soc., Oklahoma City, Okla. (December, 1960).
5. Magasanik, D., and R. T. Ellington, "Unlike-molecule interactions from second virial coefficients." (In preparation.)
6. Magasanik, D., "Unlike-molecule interactions from second virial and Joule-Thomson coefficients," Ph.D. thesis, Inst. of Gas Technology, Chicago, Ill. (January, 1963).
7. Schneider, W. G., *Can. J. Research*, 27B, p. 339-53 (1949).
8. Owens, E. J., and G. Thodos, *A.I.Ch.E. Journal*, 3, p. 451-61 (1957).
9. Lee, A. L., K. E. Starling, J. P. Dolan, and R. T. Ellington, "Liquid, gas and dense fluid viscosity of methane-*n*-butane system." (In preparation.)
10. Bauer, N., and S. Z. Lewin, "Determination of density," Chapter IV, p. 132-190, in Weissberger, A., ed., "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York (1959).
11. Silberberg, I. H., "Compressibility factors of light paraffin hydrocarbons at low pressures," Masters thesis, University of Texas, Austin, Texas (1951).
12. Silberberg, I. H., P. K. Kuo and J. J. McKetta, *Pet. Eng.*, 24, p. C7-C20 (1952).
13. Comings, E. W., "High Pressure Technology," p. 115-202, McGraw Hill, New York (1956).
14. Mason, D. McA., and B. E. Eakin, *Inst. of Gas Technology, Research Bulletin No. 32* (December, 1961).
15. Bennett, C. O., and B. F. Dodge, *Ind. Eng. Chem.*, 44, p. 180-85 (January, 1952).
16. Solbrig, C. W. and R. T. Ellington, *Chem. Eng. Progr. Symp. Series*, 59, No. 44, p. 127-36, (1963).
17. Michels, A., T. Wassenaar, and T. N. Zwiering, *Physica*, 18, p. 67-74 (January, 1952).
18. Bean, H. S., *J. Res. Nat. Bur. Standards*, 4, p. 645-61 (1930).
19. Bloomer, O. T., *Inst. of Gas Technology, Research Bulletin No. 13*, (May, 1952).
20. Michels, A., and R. O. Gibson, *Ann. Physik*, 87, p. 850-76 (1928).
21. Schamp, H. W., E. A. Mason, A. C. B. Richardson, and A. Altman, *Phys. Fluids*, 1, p. 329-37 (August, 1958).
22. Hagenbach, W. P., and E. W. Comings, *Ind. Eng. Chem.*, 45, p. 606-09 (March, 1953).
23. Connolly, J. F., and G. A. Kandalic, *Phys. Fluids*, 3, p. 463-67 (May-June, 1960).
24. Dousin, D. R., R. T. Moore, J. P. Dawson, and G. Waddington, *J. Am. Chem. Soc.*, 80, p. 2031-38 (May 9, 1958).
25. Doolittle, A. K., I. Simon, and M. Cornish, *A.I.Ch.E. Journal*, 6, p. 150-62 (March, 1960).
26. Sage, B. H., and W. N. Lacey, "Apparatus for determination of volumetric behavior of fluids," in *Am. Petro. Inst. "Report of progress-Fundamental research on occurrence and recovery of petroleum, 1946-47,"* p. 36-48, *Am. Petro. Inst.* (1949).
27. Bridgeman, P. W., "The physics of high pressure," G. Bell and Sons, Ltd., London (1949).
28. Burnett, E. S., *J. Appl. Mech.*, 3, p. A-136-A-140 (1936).
29. Mueller, W. H., T. W. Leland, Jr., and R. Kobayashi, *A.I.Ch.E. Journal*, 7, p. 267-72 (June, 1961).
30. Pfeferle, W. C., Jr., J. A. Goff, and J. G. Miller, *Chem. Phys.*, 23, p. 509-13 (March, 1955).
31. Schneider, W. G., and J. A. H. Duffie, *J. Chem. Phys.*, 17, p. 751-54 (September, 1949).
32. Silberberg, I. H., K. A. Kobe, and J. J. McKetta, *J. Chem. Eng. Data*, 4, p. 314-23 (October, 1959).
33. Canfield, F. B., "The compressibility factors and second virial coefficients for helium-nitrogen mixtures at low temperatures and high pressures," Ph.D. thesis, Rice University, Houston, Texas (1962).
34. Burnett, E. S., "Application of the Burnett method of compressibility determinations to multiphase fluid mixtures," U.S. Bureau of Mines, RM6267, Pittsburgh (1963).
35. Addingley, C. G. and R. Whytlaw-Gray, *Trans. Faraday Soc.*, 24, p. 378-87 (1928).
36. Hamann, S. D., and J. F. Pearse, *Trans. Faraday Soc.*, 48, p. 101-106 (1952).
37. McGlashen, M. L., and D. J. B. Potter, *Proc. Roy. Soc. (London)*, 267A, p. 478-500 (1962).
38. Knobler, C. M., J. J. M. Beenakker, and J. F. P. Knapp, *Physica*, 25, p. 909-916 (1959).