Gas Compressibilities with the Burnett Apparatus

Methods and Apparatus

I. HAROLD SILBERBERG,[1] KENNETH A. KOBE,[2] and
JOHN J. McKETTA
University of Texas, Austin, Tex.

A one-page article presenting the highlights of this and the following two articles appears on page 1325 of the October 1959 issue of *Industrial and Engineering Chemistry*.

The compressibility or volumetric behavior of a gas may be described in terms of the dependence of the compressibility factor z upon any two of the variables pressure, volume, and temperature. The compressibility factor is defined by the relation,

$$z = \frac{pV}{nRT} \qquad (1)$$

Conventional methods for measuring gas compressibility require the simultaneous determination or knowledge of the pressure, temperature, volume, and mass of the gas. In the Burnett method, only pressure and temperature are measured. Neither volume nor mass measurements are required. Compressibility factors are determined directly from the experimental pressures by either graphical or analytical means. The composition of the experimental gas need not be known accurately; in fact, it is not even necessary to know the identity of it. The disadvantage of the method is that it is not suitable for use in the liquid or two-phase regions.

THE BURNETT METHOD

The Burnett method (*3, 4*), introduced in 1936 has not found widespread use, but has been used for comprehensive studies by Miller and others (*8, 9, 13, 20–22, 27*) and Schneider and coworkers (*15, 16, 18, 23, 24, 29, 30, 32*). Less extensive investigations have been carried out (*1, 2, 6, 7, 14, 25, 28, 33*) and commercial models of the Burnett apparatus are available from at least two instrument manufacturers.

The basic element of the apparatus is a compressibility cell comprised of two separate chambers, the volumes of which are essentially independent of the internal pressure. The two chambers, I and II, are interconnected through an expansion valve. The compressibility cell is enclosed in a constant temperature bath.

The experimental routine is begun by filling chamber I with the gas to an initial pressure p_0. Chamber II is then evacuated and the expansion valve opened, permitting pressure equalization between chambers I and II. When thermal equilibrium has been restored, the expansion valve is closed and a new pressure p_1 is measured. The evacuation, expansion, and pressure measurement is repeated until pressures too low for accurate measurement are attained. In this manner, a series of isothermally measured pressures p_0, p_1, p_2, . . . , p_{r-1}, p_r . . . is obtained. Such a series of pressures may be called a single run for that gas at the designated temperature. Generally the procedure is repeated, starting with a different initial pressure, p_0, until a sufficient number of runs has been made to establish the isotherm.

Pressure-Ratio Relations. If V_{I} and V_{II} are the respective volumes of chambers I and II, the ratio expressed in the following equation is a true apparatus constant.

$$n = \frac{V_{\mathrm{I}} + V_{\mathrm{II}}}{V_{\mathrm{I}}} \qquad (2)$$

The number of moles of gas involved in the rth expansion may be expressed by the following equation:

$$n = \frac{p_{r-1}V_{\mathrm{I}}}{z_{r-1}RT} = \frac{p_r(V_{\mathrm{I}} + V_{\mathrm{II}})}{z_rRT} \qquad (3)$$

Utilizing Equation 2, Equation 3 may be written as follows:

$$\frac{p_{r-1}}{p_r} = N\frac{z_{r-1}}{z_r} \qquad (4)$$

There is strong experimental and theoretical evidence to support the assertion that $\lim\limits_{p\to 0} z = 1$. This limit applied to Equation 4 leads to the relations

$$\lim_{p_r\to 0}\frac{p_{r-1}}{p_r} = \lim_{p_{r-1}\to 0}\frac{p_{r-1}}{p_r} = N \qquad (5)$$

$$\lim_{p_r\to 0}\frac{p_r}{p_{r-1}} = \lim_{p_{r-1}\to 0}\frac{p_r}{p_{r-1}} = \frac{1}{N} \qquad (6)$$

Equations 5 and 6 show that N may be evaluated from any of four different extrapolations of experimental pressure-ratio data on a given gas. If the compressibility factor isotherm is linear with pressure, both p_{r-1}/p_r *vs.* p_{r-1} and p_r/p_{r-1} *vs.* p_r will give linear graphs, considerably facilitating an accurate extrapolation.

Compressibility Factor Relations. If Equation 4 is applied repetitively to the first, second, . . . , rth expansions, the resulting equations may be combined to produce the relation:

$$p_rN^r = \frac{p_0}{z_0}\,z_r \qquad (7)$$

It is apparent from Equation 7 that

$$\lim_{p_r\to 0} p_rN^r = \frac{p_0}{z_0} \qquad (8)$$

Contrary to the case with the pressure-ratio relations, Equations 7 and 8 apply only to the pressure measurements in the same run. The limiting value of p_rN^r, p_0/z_0, is a run constant which depends only upon the initial pressure p_0 and the compressibility of the experimental gas.

In a graphical evaluation of the data, p_rN^r is plotted against the pressure p_r and the zero-pressure ordinate p_0/z_0 obtained by extrapolation. The compressibility factor z_r at pressure p_r may then be calculated from Equation 7. The shape of the p_rN^r isotherm for each run is similar to the shape of the compressibility factor isotherm. If the latter approaches linearity at low pressures, which is generally the case, extrapolation can be made with considerable accuracy. Because any error in p_0/z_0 is introduced directly into each z_r, accurate low pressure measurements are essential unless the isotherm exhibits linearity to relatively high pressures.

Because N is raised to the power r in Equation 7, the effect of errors in N is considerably magnified. As a first approximation, the error in p_rN^r from an error in N is r times that error in N. Accurate knowledge of the apparatus constant N is the key to accurate compressibility determinations with the Burnett apparatus.

At higher pressures the data points generally fall rather far apart in a given run, whereas they group much more closely at the lower pressures. After a few runs, an isotherm may be well

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[1] Present address, Magnolia Petroleum Co., Field Research Laboratories, Dallas, Tex.

[2] Deceased.

established at lower pressures, but additional points may still be needed at higher pressures. In such a case, it is necessary to continue the expansions in each subsequent run only until a pressure is obtained in the region in which the isotherm is already established. If the run is terminated at a pressure p_k at which the compressibility factor z_k is known accurately, the following relation may be used to calculate the values of z_r:

$$z_r = z_k \frac{p_r N^r}{p_k N^k} \tag{9}$$

Of course, any error in z_k is introduced directly into the z_r.

ANALYTICAL TREATMENT OF DATA

The graphical methods are rigorously applicable to any gas, and with sufficient care, may produce results that compare favorably with those of any other method of compressibility measurement. Analytical methods of data treatment, however, possess advantages such as the following:

Much of the subjectivity is eliminated in the treatment of the data.

The coefficients which result may, under certain conditions, be considered as virial coefficients or may be used to calculate virial coefficients.

The correlation of data on mixtures is facilitated.

Interpolation into the data with respect to pressure, and perhaps with respect to temperature, is facilitated.

On the other hand, an analytical treatment of the data requires a mathematical expression capable of representing the experimental data within the limits of their precision. For isotherms of moderate curvature, such functions are easily obtained. For isotherms of considerable curvature, the determination of a satisfactory function may be difficult. In fact, for many systems, this limitation precludes the use of analytical methods.

The methods described here are simply those which correspond to conventional analytical expressions for volumetric behavior or which have been used by others with the Burnett method. Other expressions may in some cases be equally satisfactory, or perhaps superior. The techniques of analysis may be useful in developing other such methods.

Linearization of Functions. In such analytical methods, it is customary to employ a least squares routine, or some other curve-fitting procedure, to evaluate the constants of the selected function; first, however, the function must be linearized with respect to the undetermined constants. A Taylor's series expansion is useful for this purpose.

In general, if a function of the variables x_i contains the coefficients K_j, the function $F(x_i, K_j)$ may be expanded in a Taylor's series about the approximate solution (x_i, K_{j_0}). If the following definition is made:

$$\Delta K_j = K_j - K_{j_0} \tag{10}$$

and if second and higher order derivatives are neglected, the following relation is valid:

$$F(x_i,K_j) = F(x_i,K_{j_0}) + \sum_j \frac{\partial F}{\partial K_j}\bigg|_{\substack{x_i = x_i \\ K_j = K_{j_0}}} \Delta K_j \tag{11a}$$

$$F(x_i,K_j) = F^0 (x_i,K_{j_0}) + \sum_j \frac{\partial F^0}{\partial K_{j_0}} \Delta K_j \tag{11b}$$

The set of unknown constants K_j is transformed into a new set of unknown constants ΔK_j. Derivatives higher than the first have been neglected in Equation 11, so an iterative procedure is always required in the solution of such an equation.

Leiden Expansion of z. The Leiden expansion of the compressibility factor z is represented by the following equation:

$$z = 1 + \frac{B'}{V} + \frac{C'}{V^2} + \ldots \tag{12}$$

For a particular gas, the second virial coefficient B', the third virial coefficient C', etc., are all functions of temperature only. For convenience of notation, Equation (12) may be rewritten as:

$$z = 1 + \sum_{j=1} a_j' \left(\frac{RT}{V}\right)^j = 1 + \sum_{j=1} a_j' \left(\frac{p}{z}\right)^j \tag{13}$$

from which it follows that

$$B' = a_1' \, RT, \; C' = a_2' \, (RT)^2, \text{ etc.} \tag{14}$$

If the run constant A is defined by the equation

$$A = z_0/p_0 \tag{15}$$

Equation 7 may be written as

$$z_r = A p_r N^r \tag{16}$$

or as

$$p_r/z_r = (AN^r)^{-1} \tag{17}$$

Equation 13 may then be written as

$$p_r = F_r(r,N,A,a_j') = (AN^r)^{-1} + \sum_{j=1} a_j'(AN^r)^{-(j+1)} \tag{18}$$

Equation 18 relates all pressure measurements obtained in a particular run.

When Equation 18 is expanded in a Taylor's series and all derivatives of order higher than the first are neglected, there results the equation

$$F_r(r,N,A,a_j') = F_r^0(r,N_0,A_0,a_{j_0}') + \frac{\partial F_r^0}{\partial N_0}\Delta N + \frac{\partial F_r^0}{\partial A_0}\Delta A + \sum_{j=1} \frac{\partial F_r^0}{\partial a_{j_0}'} \Delta a_{j_0} \tag{19}$$

where

$$\frac{\partial F_r^0}{\partial N_0} = -\frac{r}{N_0}\left[(A_0N_0^r)^{-1} + \sum_{j=1} (j+1)\, a_{j_0}' (A_0N_0^r)^{-(j+1)}\right] \tag{20}$$

$$\frac{\partial F_r^0}{\partial A_0} = -\frac{1}{A_0}\left[(A_0N_0^r)^{-1} + \sum_{j=1} (j+1)\, a_{j_0}' (A_0N_0^r)^{-(j+1)}\right] \tag{21}$$

$$\frac{\partial F_r^0}{\partial a_{j_0}'} = (A_0N_0^r)^{-(j+1)} \tag{22}$$

The linearized coefficients ΔN, ΔA, and Δa_j are as defined by Equation 10.

Berlin Expansion of z. The following equation represents the Berlin expansion of the compressibility factor z:

$$z = 1 + Bp + Cp^2 + \ldots . \tag{23}$$

For convenience of notation, the coefficients may be expressed in a more general form.

$$z = 1 + \sum_{j=1} a_j p^j \tag{24}$$

For a particular gas, the coefficients a_j are functions of temperature only. The corresponding coefficients of Equations 13 and

24 may be exactly interrelated, provided that the two expressions are both infinite series, by inversion of the series.

Pressure-Ratio Method. If Equation 24 is applied to Equation 4, there results the following general expression for the pressure-ratio:

$$\frac{p_{r-1}}{p_r} = N + \sum_{j=1} a_j p_{r-1}^j \left[N - \left(\frac{p_r}{p_{r-1}}\right)^{j-1}\right] \quad (25)$$

For simplification of notation, the following definition may be made:

$$y = \frac{p_r}{p_{r-1}} \quad (26)$$

Equation 25 may then be written as

$$\frac{p_{r-1}}{p_r} = f_{r-1}\,(p_{r-1}, y, N, a_j) = N + \sum_{j=1} a_j p_{r-1}^j \left[N - y^{j-1}\right] \quad (27)$$

When Equation 27 is expanded in a Taylor's series and all derivatives of order higher than the first are neglected, there results the equation:

$$f_{r-1}\,(p_{r-1}, y, N, a_j) = f_{r-1}^0\,(p_{r-1}, y, N_0, a_{j_0}) + \frac{\partial f_{r-1}^0}{\partial N_0}\Delta N + \sum_{j=1} \frac{\partial f_{r-1}^0}{\partial a_{j_0}}\Delta a_j \quad (28)$$

where

$$\frac{\partial f_{r-1}^0}{\partial N_0} = 1 + \sum_{j=1} a_{j_0} p_{r-1}^j \quad (29)$$

$$\frac{\partial f_{r-1}^0}{\partial a_{j_0}} = \sum_{j=1} p_{r-1}^j \left[N_0 - y^{j-1}\right] \quad (30)$$

The linearized coefficients ΔN and Δa_j are as defined by Equation 10.

When Equation 4 is inverted and Equation 24 applied to it,

$$\frac{p_r}{p_{r-1}} = \frac{1}{N} + \sum_{j=1} a_j p_r^j \left[\frac{1}{N} - \left(\frac{p_{r-1}}{p_r}\right)^{j-1}\right] \quad (31)$$

or, as before,

$$\frac{p_r}{p_{r-1}} = g_r\,(p_r, y, N, a_j) = \frac{1}{N} + \sum_{j=1} a_j p_r^j \times \left[\frac{1}{N} - \left(\frac{1}{y}\right)^{j-1}\right] \quad (32)$$

When Equation 32 is expanded in a Taylor's series and all derivatives of order higher than the first are neglected, there results the equation:

$$g_r\,(p_r, y, N, a_j) = g_r^0\,(p_r, y, N_0, a_{j_0}) + \frac{\partial g_r^0}{\partial N_0}\Delta N + \sum_{j=1} \frac{\partial g_r^0}{\partial a_{j_0}}\Delta a_j \quad (33)$$

where

$$\frac{\partial g_r^0}{\partial N_0} = -\frac{1}{N_0^2}\left[1 + \sum_{j=1} a_{j_0} p_r^j\right] \quad (34)$$

$$\frac{\partial g_r^0}{\partial a_{j_0}} = \sum_{j=1} p_r^j \left[\frac{1}{N_0} - \left(\frac{1}{y}\right)^{j-1}\right] \quad (35)$$

The linearized coefficients ΔN and Δa_j are as defined by Equation 10.

A special case of the pressure-ratio method arises when the isothermal variation of the compressibility factor with pressure may be considered to be linear.

$$z = 1 + Bp \quad (36)$$

In such a case, Equation 4 leads directly to two expressions which are already linearized with respect to their coefficients.

$$\frac{p_{r-1}}{p_r} = N + B\,(N-1)\,p_{r-1} \quad (37)$$

$$\frac{p_r}{p_{r-1}} = \frac{1}{N} + \frac{B\,(1-N)}{N}p_r \quad (38)$$

Equations 37 and 38 are useful for treating data from gases such as hydrogen and helium, which possess linear isotherms to relatively high pressures.

These pressure-ratio relations may be applied to all data taken on a given gas at a constant temperature in a particular Burnett apparatus. This feature is the chief advantage of the pressure-ratio methods.

Method Using Run Constant. When Equations 16 and 24 are combined, there results the following equation:

$$Ap_r N^r = 1 + \sum_{j=1} a_j p_r^j \quad (39)$$

Equation (39) may be rewritten as

$$p_r = F_r(r, A, N, a_j, p_r) = \frac{1}{AN^r - \sum_{j=1} a_j p_r^{j-1}} \quad (40)$$

Equation 40 relates all pressure measurements obtained in a particular run.

When Equation 40 is expanded in a Taylor's series and derivatives of order higher than the first are neglected,

$$F_r(r, A, N, a_j, p_r) = F_r^0(r, A_0, N_0, a_{j_0}, p_r) + \frac{\partial F_r^0}{\partial A_0}\Delta A + \frac{\partial F_r^0}{\partial N_0}\Delta N + \sum_{j=1} \frac{\partial F_r^0}{\partial a_{j_0}}\Delta a_j \quad (41)$$

where

$$\frac{\partial F_r^0}{\partial A_0} = -N_0^r (F_r^0)^2 \quad (42)$$

$$\frac{\partial F_r^0}{\partial N_0} = -rA_0 N_0^{r-1} (F_r^0)^2 \quad (43)$$

$$\frac{\partial F_r^0}{\partial a_{j_0}} = p_r^{j-1} (F_r^0)^2 \quad (44)$$

The linearized coefficients ΔA, ΔN, and Δa_j are as defined by Equation 10.

Pfefferle (*20–22*) has employed a method in which Equation 39 is algebraically linearized with respect to the constants. Because certain approximations are involved in the development, an iterative procedure is required for the solution, just as for Equation 41. A disadvantage of the method lies in the fact that, in the least squares routine, residuals of a function of pressure rather than of pressure itself are treated, making interpretation of the significance of the residuals somewhat more difficult. The results from Pfefferle's method were compared with those from Equation 41 for the helium calibration data at 100° C. (Table 1) and found to be identical well within the limits of precision of the data.

Method Using p_0. The run constant A may be eliminated from Equation 40 by means of Equations 15 and 24.

$$A = \frac{z_0}{p_0} = \frac{1}{p_0}\left[1 + \sum_{j=1} a_j p_0^j\right] \quad (45)$$

Equation 40 may then be written as

$$p_r = F_r(r, p_0, N, a_j, p_r) = \frac{1}{\frac{1}{p_0}\left[1 + \sum_{j=1} a_j p_0^j\right] N^r - \sum_{j=1} a_j p_r^{j-1}} \tag{46}$$

Equation 46 relates all pressure measurements obtained in a particular run.

When Equation 46 is expanded in a Taylor's series and derivatives of order higher than the first are neglected, there results the following expression:

$$F_f(r, p_0, N, a_j, p_r) = F_r^0(r, p_0, N_0, a_{j_0}, p_r) + \frac{\partial F_r^0}{\partial N_0} \Delta N + \sum_{j=1} \frac{\partial F_r^0}{\partial a_{j_0}} \Delta a_j \tag{47}$$

where

$$\frac{\partial F_r^0}{\partial N_0} = -(F_r^0)^2 \frac{r N_0^{r-1}}{p_0} \left[1 + \sum_{j=1} a_{j_0} p_0^j\right] \tag{48}$$

$$\frac{\partial F_r^0}{\partial a_{j_0}} = -(F_r^0)^2 \sum_{j=1} \left[N_0^r p_0^{j-1} - p_r^{j-1}\right] \tag{49}$$

The linearized coefficients ΔN and Δa_j are as defined by Equation 10.

The error in the initial pressure, p_0, of a run is a chance variable, so there is a possibility that an unusually large random error in p_0 might introduce appreciable bias in the results of Equation 47. To prevent it, several determinations of p_0 might be made at the beginning of a run and the average value of these determinations used in the solution.

Leiden Expansion of ln z. This analytical method of data treatment was developed by Pfefferle (20–22) when it was found that the 30° C. isotherms of carbon dioxide and mixtures rich in carbon dioxide could not be presented successfully by Equation 24 with a reasonable number of terms. The equation used to represent the data was as follows:

$$z = \exp\left[b'\left(\frac{RT}{V}\right) + c'\left(\frac{RT}{V}\right)^2 + d'\left(\frac{RT}{V}\right)^3 + \ldots\right] \tag{50}$$

which may also be written as

$$\ln z = b'\left(\frac{p}{z}\right) + c'\left(\frac{p}{z}\right)^2 + d'\left(\frac{p}{z}\right)^3 + \ldots \tag{51}$$

Equation 50 is unusual in that, regardless of the number of terms in the polynominal exponent, it generates an infinite series for the compressibility factor z.

Equations 16, 17, and 51 may be combined into the following equation:

$$\ln p_r = -\ln A - r \ln N + b'(AN^r)^{-1} + c'(AN^r)^{-2} + d'(AN^r)^{-3} + \ldots \tag{52}$$

Equation 52 relates all pressures measured in a particular run. If $\ln p_r$ is expanded in a Taylor's series according to Equation 52, and the function G_r is defined as follows:

$$G_r = -\ln(A_0 N_0^r p_r) + b_0'(A_0 N_0^r)^{-1} + c_0'(A_0 N_0^r)^{-2} + d_0'(A_0 N_0^r)^{-3} + \ldots \tag{53}$$

neglecting all derivatives of order higher than the first, the result may be expressed as follows:

$$G_r = \frac{1}{A_0}\left[1 + b_0'(A_0 N_0^r)^{-1} + 2c_0'(A_0 N_0^r)^{-2} + 3d_0'(A_0 N_0^r)^{-3} + \ldots\right]\Delta A + \frac{r}{N_0}\left[1 + b_0'(A_0 N_0^r)^{-1} + 2c_0'(A_0 N_0^r)^{-2} + 3d_0'(A_0 N_0^r)^{-3} + \ldots\right]\Delta N - (A_0 N_0^r)^{-1}\Delta b' - (A_0 N_0^r)^{-2}\Delta c' - (A_0 N_0^r)^{-3}\Delta d' - \ldots \tag{54}$$

The linearized coefficients ΔA, ΔN, $\Delta b'$, $\Delta c'$, etc., are as defined by Equation 10.

Berlin Expansion of ln z. This analytical method of data treatment was introduced by Harper (*8*, *9*) as a counterpart of the Leiden expansion method just described. The equation to represent the data was as follows:

$$z = \exp\left[bp + cp^2 + dp^3 + \ldots\right] \tag{55}$$

which may also be written as

$$\ln z = bp + cp^2 + dp^3 + \ldots \tag{56}$$

Equation 56 also generates an infinite series for the compressibility factor z, regardless of the number of terms in the polynominal exponent.

Method Using Run Constant. In the method developed by Harper (*8*, *9*), Equation 56 applied to the rth pressure measurement and Equation 16 are combined with the following result:

$$\ln p_r = -\ln A - r \ln N + bp_r + cp_r^2 + dp_r^3 + \ldots \tag{57}$$

Equation 57 relates all pressures measured in a particular run, and it is linear in the constants ln A, ln N, b, c, d, etc. No approximations are involved in developing Equation 57, so an iterative procedure is not required in the solution. This advantage could be outweighed by Harper's discovery that the value of the second virial coefficient (b in this equation) is highly dependent upon the degree of the polynomial.

Method Using p_0. It is possible to improve on the method just described in a manner which reduces the amount of computational work involved in a solution. According to the definition of A in Equation 15 and to Equation 56, the following equation may be written:

$$\ln A = \ln z_0 - \ln p_0 = bp_0 + cp_0^2 + dp_0^3 + \ldots - \ln p_0 \tag{58}$$

If Equations 57 and 58 are combined, there results the equation

$$\ln \frac{p_r}{p_0} = -r \ln N + bp_0\left[\frac{p_r}{p_0} - 1\right] + cp_0^2\left[\frac{p_r^2}{p_0^2} - 1\right] + dp_0^3\left[\frac{p_r^3}{p_0^3} - 1\right] + \ldots \tag{59}$$

Equation 59 relates all pressures measured in a particular run.

In Equation 59, the ratio p_r/p_0 is treated as the variable rather than p_r. To minimize the error introduced by random errors in p_0, several determinations of p_0 might be made at the beginning of each run.

Pressure-Ratio Method. If Equation 4 is written in logarithmic form, the following equation results:

$$\ln \frac{p_{r-1}}{p_r} = \ln N + \ln z_{r-1} - \ln z_r \tag{60}$$

If Equations 56 and 60 are combined, the resulting equation will be

$$\ln \frac{p_{r-1}}{p_r} = \ln N + bp_r\left[\frac{p_{r-1}}{p_r} - 1\right] + cp_r^2\left[\frac{p_{r-1}^2}{p_r^2} - 1\right] + dp_r^3\left[\frac{p_{r-1}^3}{p_r^3} - 1\right] + \ldots \tag{61}$$

Equation 61 applies to all measurements made on a given gas at a constant temperature in a particular Burnett apparatus. A similar development can be made for the ratio p_r/p_{r-1}. Equation 61 is linear in the constants ln $\mathcal{N}$, b, c, d, etc., and so may be solved directly without necessity for an iterative procedure.

EXPERIMENTAL APPARATUS

Compressibility Cell. The details of construction of the compressibility cell are shown in Figure 1. The body, heads, cap screw rings, and caps were machined from cold rolled steel. The overall length of the assembled cell, excluding thermocouple gland nuts, is 19-1/4 inches. The two chambers were bored to a 2-1/2 inch-diameter to within approximately 3/4 inch of each other. The outside diameter of the body is 4 inches and the caps are 5-1/2 inches in diameter. Iron-constantan thermocouples extend through packing assemblies to approximately the geometric center of each chamber. There are five ports for 1/4 inch high-pressure tubing, three entering chamber I and two entering chamber II, not shown in Figure 1.

The cell closures are conventional. A bead was machined on the flange of the head and a matching groove on the opposing face of the cell. A soft steel gasket is compressed between the head and the end of the cell by eight cap screws bearing on a cap screw ring. The thermocouple packing assembly is incorporated in the head at each end of the cell.

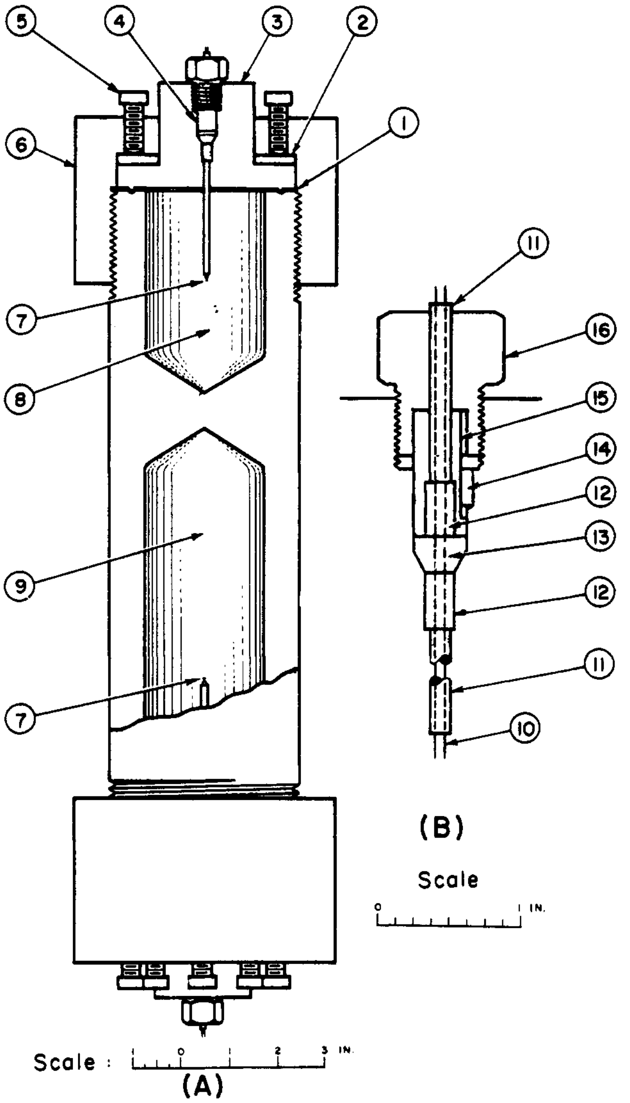

Figure 1. A is the Compressibility Cell, B is the Thermocouple packing assembly

1. Head gasket
2. Cap screw ring
3. Head
4. Thermocouple packing assembly
5. Cap screw
6. Cap
7. Thermocouple junctions
8. Chamber II
9. Chamber I.
10. Thermocouple wires
11. Ceramic insulators
12. Ceramic insulators
13. Teflon packing
14. Follower key
15. Follower
16. Packing nut

The volumes of the two chambers plus tubing and other components associated with them are approximately 745 ml. and 310 ml. respectively. The effect of internal pressure on the volume of either chamber or the two chambers combined has been calculated according to relations given by Comings for thick-walled cylinders (*5*). At room temperature, the change in volume is approximately 0.013% per 1000 p.s.i. internal pressure. At 200° C., this figure will be somewhat increased, perhaps to as great as 0.015%.

The arrangement of the valves associated with the compressibility cell is shown schematically in Figure 2. Valve 1 is the filling valve for chamber I. Valve 2 connects chamber I with the differential pressure indicator and the pressure measuring system. Valve 3 is the expansion valve connecting chambers I and II. Valve 4 is the dumping valve for chamber II. These valves are attached directly to the cell by mounting brackets. With the exception of valve 2, a commercially available high-pressure stainless steel needle valve, these valves were especially developed to provide positive bubble-tight closing with each operation. As shown in Figure 3, the valve seat is a copper plug pressed into place in a Type 416 stainless steel bar-stock body. The valve stem is of heat-treated Type 420 stainless steel. Teflon packing is employed.

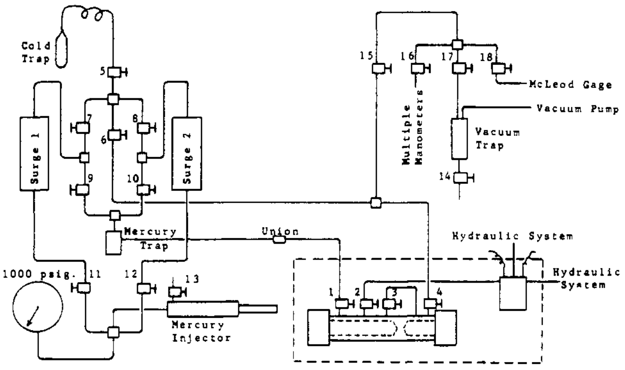

Figure 2. Vacuum and charging system

The compressibility cell is mounted in a constant temperature oil bath with a capacity of approximately 18 gallons. The bath oil is circulated by two 5-inch marine-type propellers located in diagonally opposite corners of the rectangular bath and heated by two pairs of tubular immersion heaters. The heat output of one pair is controlled manually by a variable autotransformer, while that of the other pair is varied by an E. H. Sargent and Co. Model S Thermonitor, a thermistor-actuated proportional controller. With this arrangement, it is possible to control the bath temperature to within ±0.02° C. in the temperature range of 50° to 200° C.

Vacuum System. The vacuum requirements of the Burnett apparatus are not so rigorous as those of certain other types of compressibility apparatus. The vacuum system shown schematically in Figure 2 can reduce the pressure in chamber II to below 50 microns in about 10 minutes and, for outgassing purposes, can reduce the pressure in the entire compressibility cell to below 5 microns.

Standard high-pressure needle valves and 1/4 inch high-pressure tubing are used in the vacuum system. Vacuums are measured by a McLeod gage connected through Valve 18. In parallel with the McLeod gage is a mercury U-tube manometer (enclosed in the multiple manometers' constant temperature air bath) which serves as the barometer for the apparatus. Valve 16 connects to the multiple manometer system.

Charging System. For compounds having low vapor pressures at room temperature, the compound in the liquid state

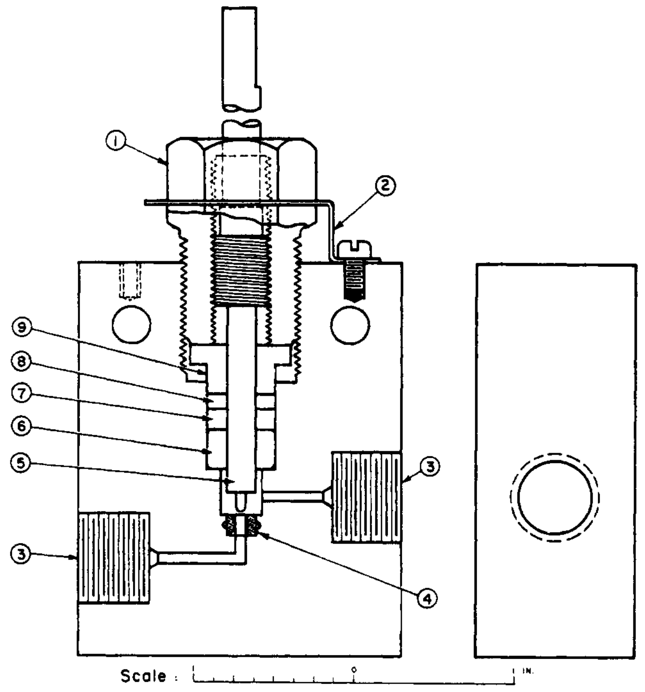

Figure 3. Copper seat high pressure valve

1. Packing nut
2. Lock ring
3. 1/4 inch high pressure tubing ports
4. Copper seat
5. Valve stem
6. Spacer ring
7. Packing ring
8. Teflon packing
9. Packing follower

must be charged to the compressibility cell by positive displacement. With the charging system, shown schematically in Figure 2, the liquid is displaced by mercury into the compressibility cell. Two 800-ml. surges are used. One receives the experimental compound as it is discharged from chamber II. The receiver surge also serves as a source of mercury for the injector, a piston displacement pump which transfers the mercury to the other surge, from which the charges to chamber I are made. When the supply of hydrocarbon in the charging surge is exhausted, the roles of the two surges are reversed. Because the receiving surge can reduce the pressure in chamber II only to the vapor pressure at room temperature, recovery of the remaining gas may generally be accomplished with a cold trap (Figure 2).

The stainless steel charging surges are each equipped with two electrical probes to indicate when the mercury levels reach the maximum and minimum positions within the surges. As an additional precaution, a mercury trap is included in the charging line. An electrical probe in the bottom of the trap indicates the presence of even a very small amount of mercury. Standard high-pressure stainless steel tubing and valves are used throughout the charging system.

For gases available in high-pressure cylinders, the charging system is not necessary. For such work, the charging system connection to the union shown in Figure 2 is broken and the cylinder is connected directly to this union.

Temperature Measurement. Temperatures are measured by iron-constantan thermocouples and a Leeds and Northrup Model No. 8662 potentiometer. The temperature of the reference junction is measured to ±0.01° C. with a mercury thermometer. Two of the thermocouple measuring junctions enter the compressibility cell. A third junction is employed to indicate the temperature of the oil in the constant temperature bath. By means of a selector switch, each of these three junctions may be placed separately in series with the reference junction and the resulting electromotive force measured by the potentiometer. Precautions are taken to prevent erroneous thermo-electric effects in the thermocouple circuits.

Prior to the calibration of the thermocouples, the potentiometer was calibrated, and its standard cell voltage measured by comparison with standards. The thermocouples were calibrated against mercury thermometers in the range from 35° to 100° C. and against a platinum resistance thermometer in the ranges from -33° to +40° C. and from 100° to 245° C. Agreement of the two scales at their overlapping points was within the limits of experimental precision. The thermocouple calibration is believed to contain systematic errors no greater than ±0.05° at -30° C. increasing with temperature to ±0.12° at 245° C., or about ±0.02% of the absolute temperature. The precision of the temperature measurement is ±0.03° C.

Pressure Measurement. Experimental pressures up to 65 p.s.i.a. are measured with the multiple manometers, a set of three mercury manometers in series, each of which is capable of measuring a pressure difference of approximately 17 p.s.i. Pressures above 65 p.s.i.a. are measured with the piston gage which has a range up to 2000 p.s.i.g. The heart of the pressure-measuring system, however, is the mercury differential pressure indicator, an instrument which indicates when the gas pressure in chamber I is exactly balanced by the hydraulic pressure generated by either the multiple manometers or the piston gage. These three instruments, along with suitable oil injectors and Bourdon tube pressure gages, are all inter-connected with high-pressure steel tubing and valves in a hydraulic system filled with crystal oil. This system is shown in Figure 4.

The differential pressure indicator (Figure 5) is essentially a mercury U-tube manometer with electrical probes to locate by contact the surfaces of the mercury in the oil and gas sides. When a balance exists between the gas and hydraulic pressures and when the mercury interfaces are exactly at the points of contact with the probe ends, then a previously determined pressure difference exists between the gas pressure and the hydraulic pressure at some reference point in the measuring system. Balances are always obtained after both interfaces have been moved upward as a result of injection of oil into the center tube of the instrument.

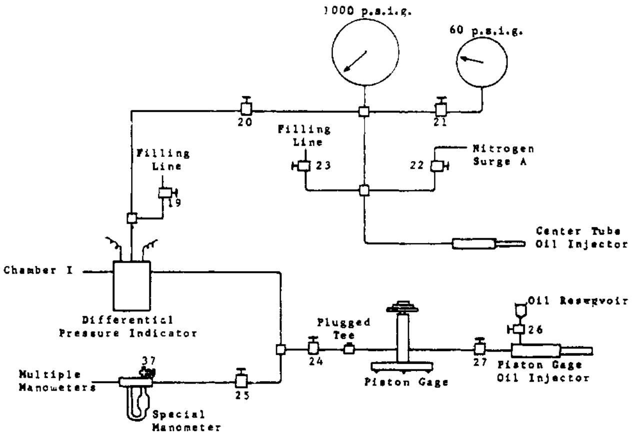

Figure 4. Hydraulic system

The differential pressure indicator was machined from Type 416 stainless steel bar stock. Ports for 1/4-inch high-pressure tubing permit connections to each of the three tubes. Electrical probes enter both the gas and oil-side tubes through packing assemblies at the top of the instrument. Contact of the mercury with a probe is indicated by a neon lamp in series with the probe. A valve in the differential pressure indicator permits the gas-side tube to be shut off from both the center and oil-side tubes. The instrument is mounted in the constant temperature oil bath containing the compressibility cell.

The differential pressure indicator and its associated hydraulic system constitute a two-fluid manometer which is further complicated by one portion being at the oil bath temperature and the remainder at room temperature. The effect of the oil bath temperature on the hydraulic head correction was determined by calibration against the multiple manometers at pressures below 65 p.s.i.a. at 100° and 200° C. The corrections for the considerably lesser effect of variation in room temperature were easily calculated.

At pressures up to 65 p.s.i.a., hydraulic pressures are generated and measured by the mutliple manometers apparatus. In this apparatus, a nitrogen gas pressure is transmitted to the oil by means of a special mercury U-tube manometer (Figure 6) and is measured by one or more of a group of three mercury U-tube manometers in series. The manometers are interconnected through surges which may be filled independently from a gas cylinder. Each surge is also provided with a bleed, and two are provided with connections to the vacuum system (Figure 7).

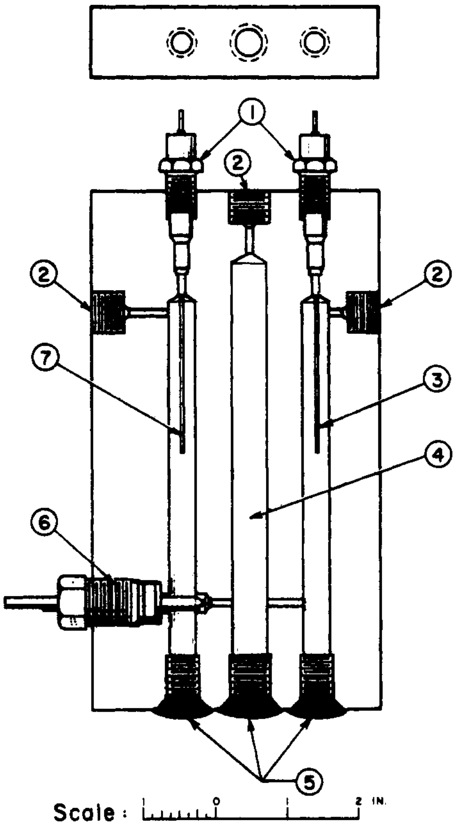

Figure 5. Differential pressure indicator

1. Probe packing assemblies
2. 1/4 in. high pressure tubing ports
3. Oil-side probe
4. Center tube
5. Welded plugs
6. Valve
7. Gas-side probe

The special Manometer is a borosilicate glass U-tube manometer with the glass tubes sealed into the head with neoprene O-rings. The portion of the manometer containing the oil-mercury interface is made of 1-inch heavy-wall borosilicate glass tubing and the remainder is made of 1/2-inch heavy-wall tubing. Capillary depression of the oil-mercury interface, which might otherwise be difficult to evaluate, is minimized by this large diameter. Lucite plates with matched etched reference lines provide a fixed point in the manometer which permits reference to the rest of the hydraulic system.

All surges and manometers, as well as the manometer used in connection with the vacuum system, are mounted on a rack and enclosed in a constant temperature air bath maintained at either 45° or 50° C. The manometers are observed through the glass door of the air bath by means of a precision cathetometer divided to 0.05 mm. The observed heights of the mercury columns, corrected for capillary depression, are reduced to 0° C. and a gravity of 980.665 cm. per sec.^{2}

Pressures above 65 p.s.i.a. are measured with a simple piston type gage manufactured by the Ruska Instrument Corp. The piston diameter was measured by the manufacturer by comparison with end standards and reported to be 0.40695 inch at 25° C. with a radial clearance between piston and cylinder of 0.00002 in. This diameter was confirmed by micrometer caliper measurement which agreed to closer than 0.0001 inch. The effective piston diameter was taken to be 0.40697 inch at 25° C. The effect of temperature on the piston area was taken to be 2×10^{-5} per °C.

The weights supplied with the piston gage were calibrated on analytical-type balances against a set of Class S weights which had been calibrated by the U. S. Bureau of Standards. For actual use, the in vacuo masses so obtained were corrected for the mass of displaced air. The acceleration of gravity in the laboratory was taken to be 979.289 cm. per sec.^{2} (*10*). The pressure generated by the piston gage when unloaded was determined by comparison with the multiple manometers at pressures below 65 p.s.i.a.

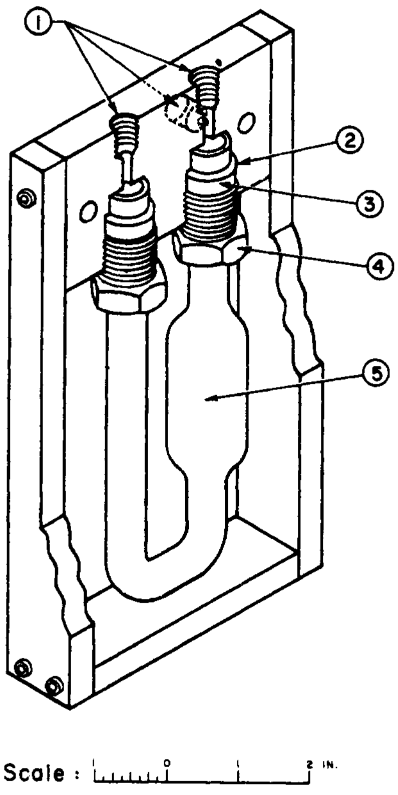

Figure 6. Special manometer

1. 1/8 in. N.P.T. connections
2. Neoprene O-ring
3. O-ring follower
4. Packing nut
5. Borosilicate glass manometer

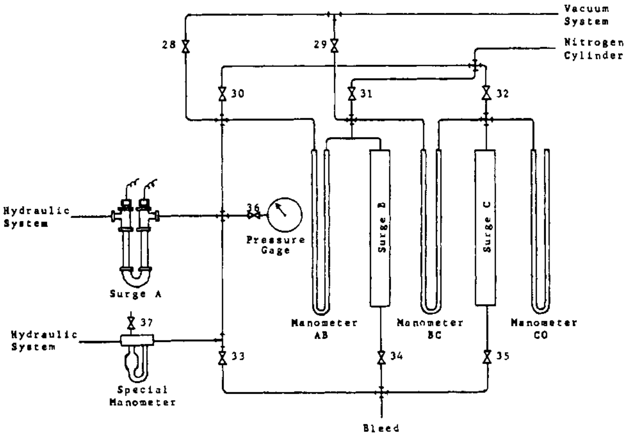

Figure 7. Multiple manometer apparatus

In order that a fixed hydraulic head be associated with all measurements with the piston gage, a pointer is used to indicate the correct position for the piston at the time of the measurement. By means of the cathetometer, it is possible to relate the hydraulic head corrections for the multiple manometers and the piston gage on the basis of a common reference plane in the hydraulic system.

A detailed examination was made of the uncertainties in pressure measurements by the two methods, and it was concluded that the systematic error in pressure measurement for this apparatus does not exceed 0.04% in the range from atmospheric pressure to 1000 p.s.i.a. Random errors are more difficult to evaluate, because they are a matter of probability. However, it is believed that errors larger than 0.03% with the multiple manometers and 0.02% with the piston gage are rare.

CALIBRATION WITH HELIUM

The graphical determination of the apparatus constant $\mathcal{N}$ is made most easily and accurately by using a gas with a linear compressibility factor isotherm. In such a case, as is shown by Equations 37 and 38, linear relationships apply to the pressure ratios. Analytical determination of $\mathcal{N}$ is most accurately made with a gas having a linear isotherm, because representation of the compressibility behavior is easily accomplished by Equation 36. Helium possesses linear isotherms up to moderately high pressures, so is well suited as the calibrating gas for the Burnett apparatus.

The helium was designated by the Bureau of Mines as Grade A Helium, indicating a purity of 99.99+%, the impurity being hydrogen. No further purification of this helium was deemed necessary. To investigate the effect of temperature on $\mathcal{N}$, compressibility measurements were made at 100° and 200° C. Several runs were made at each temperature. The data from each run are presented in Table I.

The helium calibration data were treated analytically in three different ways. The compressibility factor isotherm was assumed to be linear with pressure, as represented by Equation 36, an assumption which was subsequently supported by the excellence of the fit. The least squares criterion of fit to the data was employed. There was considerable evidence that the percentage precision of the pressure measurements is essentially independent of the pressure, so the residuals in the least squares routine were weighted accordingly. The three Berlin expansion methods employed were the pressure-ratio method represented by Equation 38, the method using the run constant represented by Equation 40, and the method using p_0 represented by Equation 46. In the latter methods, $a_1 = B$, and a_2, a_3, etc., all are zero.

The pressure-ratio method was applied to the complete set of data taken at each of the two temperatures. The resulting values of $\mathcal{N}$ and B are included in Table IV. A statistical evaluation of the confidence limits (*12*) of these values of $\mathcal{N}$ indicates a 95% probability that $\mathcal{N}$ differs from 1.415078 at 100° C. by no more than 0.0098% and from 1.415057 at 200° C. by no more than 0.0133%.

Table I. Helium Calibration Data

Temp., °C.	Run No.	r	p_r, Atm.	$\frac{p_r}{p_{r-1}}$
100	8	0	60.9122	----
		1	42.7591	0.70198
		2	30.0757	0.70337
		3	21.1854	0.70440
		4	14.9382	0.70512
		5	10.5386	0.70548
		6	7.4379	0.70578
		7	5.2522	0.70614
100	9	0	68.4999	----
		1	48.0573	0.70157
		2	33.7793	0.70290
		3	23.7854	0.70414
		4	16.7679	0.70497
		5	11.8285	0.70543
		6	8.3477	0.70573
		7	5.8926	0.70590
		8	4.1622	0.70633
		9	2.9392	0.70616
		10	2.0778	0.70693
100	10	0	53.8347	----
		1	37.8242	0.70260
		2	26.6193	0.70376
		3	18.7573	0.70465
		4	13.2282	0.70523
		5	9.3332	0.70555
		6	6.5899	0.70607
		7	4.6545	0.70630
		8	3.2874	0.70630
		9	2.3223	0.70643
		10	1.6402	0.70626
100	11	0	6.1955	----
		1	4.3747	0.70610
		2	3.0902	0.70638
		3	2.1828	0.70638
		4	1.5419	0.70638
100	12	0	4.0327	----
		1	2.8497	0.70664
		2	2.0127	0.70630
200	14	0	67.1662	----
		1	47.2084	0.70286
		2	33.2351	0.70401
		3	23.4222	0.70474
		4	16.5225	0.70542
		5	11.6656	0.70604
		6	8.2305	0.70553
		7	5.8140	0.70640
		8	4.1056	0.70616
		9	2.9011	0.70661
		10	2.0499	0.70662
200	16	0	54.8903	----
		1	38.6172	0.70353
		2	27.2064	0.70451
		3	19.1822	0.70506
		4	13.5358	0.70564
		5	9.5544	0.70586
		6	6.7444	0.70589
		7	4.7617	0.70603
		8	3.3657	0.70682
		9	2.3773	0.70634
		10	1.6800	0.70667
200	17	0	62.1479	----
		1	43.7001	0.70316
		2	30.7734	0.70420
		3	21.6900	0.70483
		4	15.3010	0.70544
		5	10.7991	0.70578
		6	7.6249	0.70607
		7	5.3843	0.70614
		8	3.8031	0.70634
		9	2.6868	0.70646
		10	1.8985	0.70662
		11	1.3417	0.70668
200	18	0	4.4775	----
		1	3.1628	0.70639
		2	2.2349	0.70661
		3	1.5792	0.70661
		4	1.1157	0.70648

The two Berlin expansion methods were applied to three high-pressure runs at each temperature. The results are summarized in Tables II and III. Comparison of the results of the two methods for individual runs shows that effect on $\mathcal{N}$ of random errors in p_0 was in no case as great as 0.001%. The effect on B was greater, particularly at 200° C. In Table IV, the weighted means of the results in Tables II and III are compared with the results from the pressure-ratio method. These weighted means were determined by weighting the results from each run by the number of pressure measurements in that run.

The second virial coefficients of helium at 100° and 200° C. are compared with the values reported by others in Table V. The two values from this work are those resulting from the pressure-ratio method, primarily because that method permits simultaneous treatment of all data taken at a given temperature. Agreement at 100° C. is good; however, because Keesom's values (11) appear to be generally low, there is a possibility that the value for B at 200° C. determined in this work is also low. This is perhaps a consequence of the presence in the system of the mercury vapors from the differential pressure indicator. It can be both theoretically and experimentally demonstrated that, because of the geometry of the apparatus and the slow diffusion rate of mercury vapors, the addition of mercury to the system during a run is negligible. However, the concentration of mercury vapor, although far from the saturation value, may nonetheless have been sufficiently great as to cause the second virial coefficient of the mixture to depart significantly from that of pure helium.

Table II. Results from Helium Runs with Berlin Expansion Using Run Constant

Temp., °C.	Run No.	$10^2 A$, Atm.$^{-1}$	$10^4 B$, Atm.$^{-1}$	$\mathcal{N}$
100	8	1.678756	3.6994	1.415100
	9	1.496817	3.7022	1.415047
	10	1.894529	3.6997	1.415070
200	14	1.516236	2.7365	1.415076
	16	1.849412	2.7962	1.415125
	17	1.636993	2.8050	1.415068

Table III. Results from Helium Runs with Berlin Expansion Using p_0

Temp., °C.	Run No.	$10^4 B$, Atm.$^{-1}$	$\mathcal{N}$
100	8	3.7151	1.415089
	9	3.6893	1.415054
	10	3.6985	1.415070
200	14	2.7423	1.415073
	16	2.7490	1.415134
	17	2.7808	1.415078

Because the use of a single value of $\mathcal{N}$ at all experimental temperatures was desirable as a convenience and appeared to be warranted by the calibration results, the value of 1.41507 was selected as the apparatus constant. It is believed that the error in this value does not exceed 0.01%.

NOMENCLATURE

A = Run constant, $\frac{z_0}{p_0}$
a_j = Coefficient of p^j in Berlin expansion of z
a_j' = Coefficient of $\left(\frac{RT}{V}\right)^j$ in Leiden expansion of z
B = Second virial coefficient in Berlin expansion of z
B' = Second virial coefficient in Leiden expansion of z
b = Coefficient of p in Berlin expansion of ln z
b' = Coefficient of $\frac{RT}{V}$ in Leiden expansion of ln z

Table IV. Summary of Results of Analytical Treatment of Helium Calibration Data

Temp., °C.	Method	$\mathcal{N}$	$10^4 B$, Atm.$^{-1}$
100	Pressure ratio	1.415078	3.694
	Using run constant	1.415070	3.701
	Using p_0	1.415069	3.700
200	Pressure ratio	1.415057	2.774
	Using run constant	1.415089	2.771
	Using p_0	1.415094	2.758

Table V. Comparison of Second Virial Coefficients of Helium

	Source	$10^4 B$, Atm.$^{-1}$		Source	$10^4 B$, Atm.$^{-1}$
100° C.	This work	3.694	200° C.	This work	2.774
	(11)	3.52		*(11)*	2.60
	(17)	3.706		*(19)*	2.851
	(19)	3.718		*(24)*	2.853
	(24)	3.728		*(31)*	2.758
	(26)	3.64			
	(31)	3.692			

C = Coefficient of p^2 in Berlin expansion of z
C' = Third virial coefficient
c = Coefficient of p^2 in Berlin expansion of ln z
c' = Coefficient of $\left(\frac{RT}{V}\right)^2$ in Leiden expansion of ln z
d = Coefficient of p^3 in Berlin expansion of ln z
d' = Coefficient of $\left(\frac{RT}{V}\right)^3$ in Leiden expansion of ln z
j = Index identifying term in virial-type expansions
ln = Logarithm to the base 2.718 . . .
$\mathcal{N}$ = Burnett apparatus constant
n = Number of moles
p = Absolute pressure
p_0 = Initial pressure of a run
R = Gas constant
r = The number of an expansion in a run
T = Absolute temperature
V = Molal volume (total volume wherever n appears in conjunction)
V_{I} = Volume of chamber I
V_{II} = Volume of chamber II
z = Compressibility factor, pV/nRT
z_0 = Compressibility factor at pressure p_0

Subscripts:

0 = Approximate value (except in the case of p_0 and z_0)
r = Pertaining to the state after the r-th expansion
$r-1$ = Pertaining to the state after the $(r-1)$st expansion

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Leo J. Hirth assisted in the design and construction of the apparatus. H. R. Heichelheim aided in processing the calibration data and in operating the computer.

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Compressibility of Isopentane with the Burnett Apparatus

I. HAROLD SILBERBERG,[1] JOHN J. McKETTA, and KENNETH A. KOBE[2]
University of Texas, Austin 12, Tex.

For the range in which modern compressibility data on isopentane at temperatures of interest are lacking, the Burnett method (*5*) is ideally suited. For complete and accurate establishment of the isotherms, the relatively low vapor pressures require an apparatus capable of accurate measurements at low as well as high pressures.

The Burnett apparatus constant, N, was determined by helium calibration to be 1.41507, and compressibility factor isotherms of gaseous isopentane, from 50° to 200° C. and at pressures up to 65 atm., were determined as described in the preceding article (*17*). Vapor pressures, saturated vapor densities, and second virial coefficients were also determined.

EXPERIMENTAL

Isopentane Purity. The research grade isopentane was obtained from the Phillips Petroleum Co. The purity of this isopentane, based on a determination of the melting point, was stated to be 100%. Dissolved air was removed from the hydrocarbon by two condensations under vacuum conditions at dry ice temperatures. The high purity of the isopentane was confirmed by a traverse of the two-phase region at 175° C. The vapor pressure from 90% vapor to 10% vapor (by volume) did not vary by more than 0.01 atm.

RESULTS

Vapor Pressures. Vapor pressures of isopentane were measured from 50° to 175° C. at 25° C. intervals, at least two measurements at each temperature. Separate charges of isopentane were used for each measurement. The observed vapor pressures were correlated and smoothed graphically by a residual technique and compared (Table I) with those values reported by Isaac, Li, and Canjar (*6*) and with values similarly smoothed from Young's data (*20*). The total maximum uncertainty in these vapor pressures including that portion corresponding to the temperature uncertainty, is estimated not to exceed 0.25%.

Table I. Comparison of Vapor Pressure Data

Temp., ° C.	Vapor Pressure, Atm. Isaac, others (*6*)	Young (*20*)	This Work
50	. . .	2.022	2.025
75	. . .	3.954	3.983
100	. . .	7.031	7.106
125	11.881	11.621	11.787
150	18.474	18.171	18.449
175	27.590	27.171	27.556

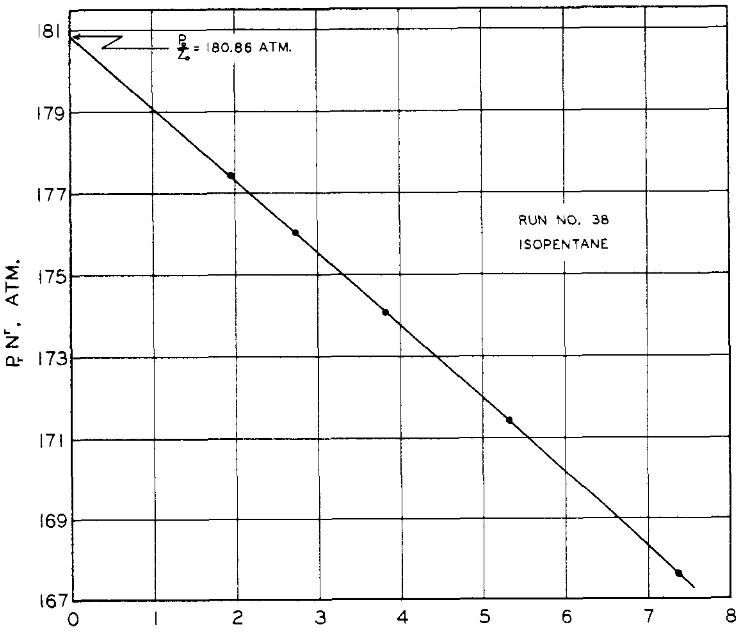

Figure 1. Graphical method to obtain p_0/z_0

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[1] Present address, Field Research Laboratory, Magnolia Petroleum Co., Dallas 21, Tex.
[2] Deceased.