An Equation of State for Methane in the Gas and Liquid Phases

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An equation of state was developed which represented experimental methane P-V-T data over the temperature range of 130 to 625°K. for pressures to 10,000 lb./sq. in. obs. with densities to 0.36 g./cc. For 598 experimental points the mean square percent deviation in the predicted pressures was 0.07% with only 10 points having deviations above 0.2%. The low density limit of the equation predicted second virial coefficients within 1 cc./mole of the accepted values for temperatures above 200°K.

The equation was developed by first analyzing isochoric data from the saturation point to the high temperature or pressure limit. An expression was then obtained, reflecting qualitative behavior of the isochores, that reproduced experimental data along each isochore with an average pressure error of 0.02% and a maximum error of 0.08%. This expression had the form $P = A + BT + C \exp [E (T - T_0)] + D \exp (k - F/T)$ where k and T_0 were normalizing constants and A through F were functions of density. From the density dependence of these parameters a single expression was obtained which fit the entire range of experimental data.

No attempt is made in this section to describe all of the equations of state that have been proposed. Literally hundreds of equations have appeared. Attention is restricted to those equations which have been most useful in describing the behavior of nonpolar gases. A few historical equations are also mentioned to emphasize the changes in the basic nature of the equation with time.

Soon after it was discovered that real gases did not obey the perfect gas law, attempts were made to explain the deviations by simple modifications of the perfect gas expression. Modifications were proposed by van der Waals (*32*) in 1873, by Clausius (*7*) in 1880, by Berthelot (*5*) in 1889, by Dieterici (*9*) in 1899, and by Wohl (*33*) in 1914. These equations had two points in common; the number of constants were limited to two or three and the equations were inaccurate over any extended temperature range.

With the advent of modern calculating machines, Beattie and Bridgeman (*1*) in 1928 proposed an equation of state having five adjustable constants. This was one of the first equations of state that did not demand that the isochores be linear. The pressure-temperature variation along a line of constant density was expressed as

$$P = A + BT + C/T^2$$

A, B, and C were then expressed as functions of density. The Beattie-Bridgeman equation fits experimental data for most gases at temperatures above the critical temperature but becomes unreliable in the region of the critical point or the saturation curve.

Because the Beattie-Bridgeman equation was unable to represent phase behavior, Benedict and associates (*2, 3, 4*) developed a refinement to this equation. The new equation, referred to as *the* BWR *equation*, retained the same isochoric expression as proposed by Beattie and Bridgeman, but utilized eight constants in expressing the density dependence of *A, B,* and *C*. This equation described the volumetric behavior of pure substances and mixtures in the gas phase down to molal volumes on the order of the critical volume. When the coefficients were evaluated correctly, the equation predicted the molal volume at the bubble point but was not useful in describing the volumetric behavior of liquids. Nevertheless, the equation possessed many useful characteristics and it was the first expression which was successful in predicting the vapor pressure and thermodynamic properties of the coexisting phases of pure fluids.

The precision with which the BWR equation fitted experimental data depended on the range of the data. Benedict, et al. (*4*) reportedly fit the methane data of Kvalnes and Gaddy (*17*), and Michels and Nederbragt (*21*) between −50 and 200°C. with an average error of 0.34% in the predicted pressure. Douslin, et al. (*10*) fit the BWR equation to their data on methane. Although no overall deviation was reported, deviations for individual isochores had average values of less than 0.25% at densities below the critical density. Above the critical density, errors in predicting pressure were as great as 2%.

After the publication of the BWR equation, no significant new equations of state appeared until 1955. This coincided with the emergence of digital computers as commercial calculating machines. Previous to this time the investigations had become as complex as was feasible with the computing tools available. With electronic digital computers it was possible to develop more complex equations of state which applied over wider temperature ranges and which fit the data with increased accuracy.

The first of these equations was proposed by Martin and Hou (*19*) and contained ten adjustable parameters. Martin, Kapoor, and Nevers (*20*) later increased the number of parameters to thirteen. In choosing a form for the isochoric pressure-temperature variation, Martin and Hou selected

$$P = A + BT + C \exp(-kT/T_c)$$

Utilizing *k* as constant number one, the other nine (or twelve) constants were specified in the density fit for *A, B,* and *C*. This equation was fit by Martin and Hou to seven gases. At densities less than 1.5 times the critical density, the maximum error was stated to be 1% and the average error was less than 0.5%. However, in the second paper by the same authors it was claimed that at 1.4 times the critical density, the modification reduced the maximum error from a *previous* high value of 5.98% to a new maximum value of 1.68%. The average deviation in the critical region was not discussed.

A number of other equations have appeared since 1955. In 1957, Pings and Sage (*24*) fit the volumetric data for propane. They utilized a 27 to 29 term orthogonal series to express the compressibility factor as a function of temperature and reciprocal molal volume. This was later increased to 34 terms (*23*). The arithmetic average of the absolute values of the errors in predicting pressures was

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0.51% when all the data points were included. Relative errors in the liquid phase near the bubble-point boundary were as large as 18%. In 1961, Bukacek and Peck (*6*) published a 13 constant equation of state for liquid and gaseous nitrogen. Although the equation was explicit in pressure, the authors chose to present the error in terms of deviations in the predicted density. This tended to minimize error indications in the liquid phase where small density differences account for large pressure changes. The root mean square error in density prediction was 0.7% and maximum errors were less than 1.5% except in the vicinity of the critical point where no quantitative estimate of the error was provided.

Recently, Strobridge (*26*) presented a 16 constant modification of the BWR equation for extension to the low temperature region. Crain and Sonntag (*8*) utilized this equation to fit nitrogen and argon data between 143 and 273°K. The average error in the predicted pressure was listed as 0.23% with no indication as to the maximum deviations. In 1964, Hansen (*12*) proposed a 16 constant generalized equation of state. No figure was given of the accuracy afforded by this equation.

The above discussion has been concerned with emphasizing the marked increase in the complexity of equations of state with the increase in the number of conditions imposed upon the predictions. When it was only desired to qualitatively represent the deviations of a gas from ideality, two constant equations sufficed. Quantitative representation of nonideal gas behavior required five to eight constants. Including the liquid phase and the critical region within the realm of prediction of the equation of state has increased the required number of constants to 20 or 30. It must be emphasized that even with this many constants, it is necessary to begin with a description of the fluid behavior which is qualitatively correct.

EXPERIMENTAL DATA

The experimental methane data selected for use in the equation of state development were those of Douslin, Harrison, Moore, and McCullough (*10*) covering temperatures from 273 to 625°K, and pressures to 6,000 lb./sq. in. abs. and the recent measurements by Vennix (*27, 30*) at temperatures of 273°K. and below. Data from from the two sources agreed to within 0.02% at the common temperatures of 273.15°K.

Details of the data measurements are available elsewhere (*27, 29*). In brief, a constant volume technique was utilized with resultant experimental determinations of the pressure-temperature behavior. A sample of 99.99% pure methane was charged into a spherical chamber of known volume. The amount of charge was determined by a differential weighing of the charging cylinder. The sphere was immersed in a constant temperature bath and the pressure was measured with an oil dead-weight gauge. The sphere temperature was measured with an imbedded platinum resistance thermometer. The pressure-temperature measurements were repeated for temperatures between the maximum temperature and the saturation temperature for the density of the sample under investigation. Measurements were usually continued to temperatures below the saturation temperature for a pseudo-isochore to obtain points on the vapor pressure curve. This procedure was repeated for methane samples at sixteen different densities having nominal values between 0.04 and 0.36 g./cc.

A critical comparison with previously published data showed serious discrepancies in the low temperature data of Kvalnes and Gaddy (*17*), Mueller (*22*), and van Itterbeek, Verbeke, and Staes (*15*). The latter investigators have since remeasured the data for liquid methane but it has not yet appeared in the public literature (*31*). The low density data measured by Hoover (*13*) is extremely precise but suffers from having 0.3% impurity in the methane. The virial coefficients calculated by Hoover were corrected for the impurities but the compressibility data were not. At temperatures above 273°K. there is excellent agreement among three sets of investigators, Douslin, et al. (*10*), Michels and Nederbragt (*21*), and Schamp, et al. (25). To avoid a plurality of high temperature data, only the more comprehensive data of Douslin, et al. were used in that region.

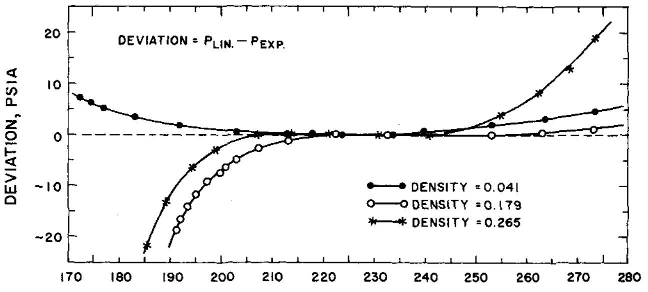

Fig. 1. Deviations from linearity for three selected isochores.

The total amount of experimental data involved 598 distinct points well distributed over the entire region and with a significant number of points in the critical region.

DEVELOPMENT OF THE EQUATION OF STATE

The data reported elsewhere (*27*)[*] are not true isochoric data since the sample mass remained constant during a run but the container volume varied slightly over the temperature range of the measurements. In fact, the spherical cell design was employed so that an accurate calculation could be made of the volume changes due to pressure. It is possible to calculate pressure corrections to obtain data along true isochores and this has been done (*30*). However, in the derivation of an overall equation of state these corrections are not necessary and the fitting was to the original experimental data in order to retain as much accuracy as possible. The actual experimental data will be referred to as *pseudo-isochoric data.*

The first step in the development of the equation of state was the preparation of large scale plots of pressure vs. temperature from which it was observed that the pseudo-isochores were nearly straight, deviating from linearity as saturation was approached. To obtain a quantitative estimate of this deviation, a straight line was passed analytically through two points in the higher temperature region. Deviations of the individual points from the straight line were calculated and plotted vs. temperature. Low temperature deviations from linearity were observed to occur for all the experimental pseudo-isochores. Also noticed was a smaller but consistent deviation in the higher temperature region. To ascertain whether this upper deviation was real or whether it was a product of the measurement method, the high temperature data of Douslin, et al. was treated in an analogous fashion. Depending upon the density involved, the upper deviation began around 250°K. and continued to increase throughout the range of data available. Deviations from linearity for the low temperature data are illustrated in Figure 1 for three pseudo-isochores corresponding to nominal densities of 0.04, 0.18, and 0.26 g./cc. It can be observed that the upper deviations were all in the same direction while the direction of the lower deviations depended upon the density.

In order to determine the qualitative nature of the low temperature nonlinearity, a number of different graphs of the deviation vs. temperature were prepared. It was found that the logarithm of the deviation was a linear function of temperature for all of the pseudo-isochores. A similar investigation was made of the upper deviation. The data of Douslin, et al. was included for this study. A linear relation was observed between the logarithm of the upper

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[*] Available from University Microfilms, Ann Arbor, Michigan

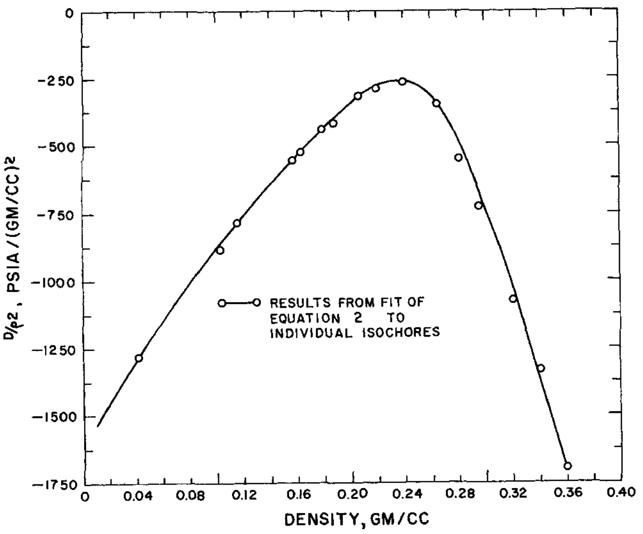

Fig. 2. Variation of D/ρ^2 with density.

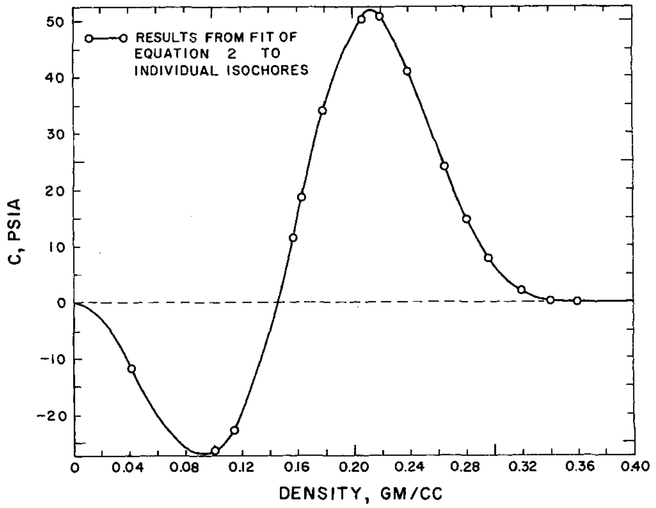

Fig. 3. Variation of C with density.

deviation and the reciprocal of the absolute temperature. Expressing these observations analytically, the pressure-temperature variation at pseudo-constant density could be represented by

$$P = A + BT + C\ e^{ET} + D\ e^{F/T} \tag{1}$$

Martin suggested earlier (*19*) that the isochores had exponential nonlinearity, but the exponential constant was considered to be invariant with density.

It was not possible to fit the pseudo-isochore with polynomial expressions for the deviations. The reciprocal temperature expression used by Beattie and Bridgeman (*1*) and by Benedict, et al. (*2*) was also unsatisfactory. It should be noted here that the deviations from linearity being considered are an order of magnitude greater than the adjustments applied to generate true isochoric data. The same deviations were present in the adjusted data.

Equation (1) was then fitted to the data for each pseudo-isochore. In fitting the data at densities of 0.20 g./cc. and below, the interpolated data of Douslin, et al. were included in order to better define the upper deviation. Interpolation was performed using a four-point formula on $(Z-1)/\rho$ at each of the experimental temperatures reported by Douslin, et al. For ease in numerical computation, Equation (1) was rewritten as

$$P = A + BT + C\ e^{E(T-T_0)} + D\ e^{(k-F/T)} \tag{2}$$

The constants T_0 and k were included in order that the exponentials would be more nearly unity. In the nonlinear least square fit of Equation (2) to the data, the minimization was with respect to the square of the relative error in pressure since the pressure varied by two orders of magnitude over the range of investigation.

The results of the individual pseudo-isochore fits are indicated in Table 1. All of the measured data were included in each fit. The table reflects the ability of Equation (2) to fit pseudo-isochores in the high and low density ranges and in the vicinity of the critical density. The data at a density of 0.36 g./cc. contain seven points which were qualitatively in the liquid region; that is, at a temperature below the critical temperature. Although the other six points for this density were above the critical temperature, the experimental density was 2.2 times the critical density and the entire pseudo-isochore can be considered to behave as a liquid. The pseudo-isochore having a nominal density of 0.164 g./cc. was only 1.008 times the critical density and contained 8 points that were within 5 deg. of the critical temperature. The average absolute deviation in the pressure predicted for these 8 points was 0.013%.

To ascertain the density dependence of the parameters A through F, Equation (2) was rewritten in terms of the residual quantity $(Z-1)/\rho$.

$$\frac{Z-1}{\rho} = \frac{\dfrac{P}{\rho RT} - 1}{\rho}$$

$$= \frac{A}{\rho^2 RT} + \frac{1}{\rho}\left(\frac{B}{\rho R} - 1\right)$$

$$+ \frac{C}{\rho^2 RT}\ e^{E(T-T_0)} + \frac{D}{\rho^2 RT}\ e^{(k-F/T)} \tag{3}$$

For the compressibility factor to approach 1 at zero density and for the residual quantity to remain finite, the following conditions must hold:

$$A/\rho \rightarrow 0 \text{ with } A/\rho^2 \text{ finite}$$

$$B/\rho \rightarrow R$$

$$C/\rho \rightarrow 0 \text{ with } C/\rho^2 \text{ finite}$$

$$D/\rho \rightarrow 0 \text{ with } D/\rho^2 \text{ finite} \tag{4}$$

In the set of units employed in the present investigation, R was specific for methane and had the value

TABLE 1. RESULT OF FITS TO INDIVIDUAL PSEUDO-ISOCHORES
Nonlinear equation used was of form

$$P = A + B\,T + C \exp\,[E(T - 190.7)] + D \exp\,(6.0 - F/T)$$

Nominal Density (g./cc.)	Number of points	Avg. Pressure Deviation (%)	Max. Pressure Deviation (%)
0.041	14	0.02	0.03
0.103	10	0.01	0.03
0.116	19	0.02	0.04
0.158	13	0.01	0.04
0.164	18	0.02	0.04
0.179	19	0.01	0.03
0.188	20	0.01	0.02
0.206	14	0.02	0.03
0.220	27	0.02	0.03
0.240	16	0.01	0.01
0.265	15	0.02	0.05
0.280	15	0.03	0.08
0.296	20	0.01	0.03
0.320	16	0.03	0.08
0.340	12	0.02	0.05
0.360	13	0.03	0.07

$$R = \left(82.06 \frac{\text{cc. atm.}}{\text{mole °K.}}\right) \left(14.696 \frac{\text{lb./sq.in.abs.}}{\text{atm.}}\right) \Big/ (16.042 \text{ g./mole}) = 75.175 \frac{\text{lb./sq.in.abs./°K.}}{\text{g./cc.}}$$

The functional dependencies of A and B upon density were as expected since these constants represent the intercept and slope of the linear sections of the isochores. In the formulation of the overall equation of state, A/ρ^2 was represented as a fourth-order polynomial in density and B/ρ as a fifth-order polynomial with the first term having a value equal to R, 75.175. As indicated in Figure 2, D/ρ^2 was also regular with density and could also be represented as a fourth-order polynomial. The orders of the polynomials were arrived at by adding and deleting terms in the overall fit to ascertain whether higher order terms were significant. In this manner, it was also determined that F was a linear function of density while E varied slightly from linearity.

The representation of C as a function of density was more complicated as can be understood from an inspection of Figures 3 and 4 representing the density dependence of C and C/ρ^2, respectively. It is evident that a simple polynomial dependence will not conform to the observed behavior. After considerable investigation it was determined that C could be represented by the product of a polynomial with repeated roots and an exponential in density. The polynomial provided the sinusoidal variation and the exponential product assured the limiting zero behavior at high densities.

At this point, consideration was given to the problem of calculating thermodynamic properties from the resulting equation of state. This involves differentiations with respect to temperature followed by an integration with respect to density. Since it was desirable that the integration would be analytic and it involved exponential factors in the kernel, certain restrictions were placed upon permissable forms for the density dependence of the C term. The form chosen for C/ρ^2 was

$$C/\rho^2 = (\rho + \rho_0)^{n-1} [(\rho + \rho_0)^n - (\alpha + \rho_0)^n] [(\beta + \rho_0)^n - (\rho + \rho_0)^n]\, e^{a + b\,(\rho + \rho_0)^n} \quad (5)$$

where ρ_0 was a negative root to insure that the polynomial remained finite for positive values of ρ, α was the root close to a value of 0.14 and β was a root which returned the polynomial to zero at high density. This expression restricted the polynomial from having additional roots which would have allowed it to oscillate at high densities or at values between the experimental points. The powers imposed upon the roots and in the exponential assure that the resulting thermodynamic expressions can be evaluated analytically. By trial it was determined that a value of n equal to 3 provided the best fit.

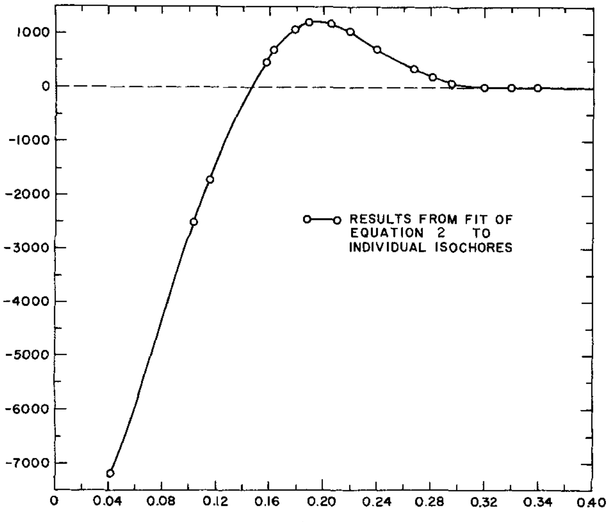

Fig. 4. Variation of C/ρ^2 with density.

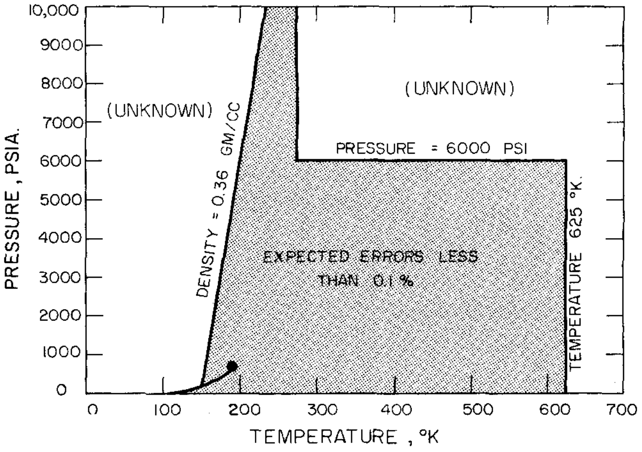

Fig. 5. Region of applicability of equation of state.

The equation was now ready to be assembled in a form where it could be fit to the entire range of experimental data available for methane. In this final form, the exponential in Equation (5) was combined with the first exponential in Equation (2) to provide the final expression, with units the same as given for R; P in lb./sq.in.abs., ρ in g./cc., and T in °K.

$$\begin{aligned} P = {} & \rho^2 [A_1 + A_2\rho + A_3\rho^2 + A_4\rho^3 + A_5\rho^4] \\ & + \rho T [R + B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + B_5\rho^5] \\ & + \rho^2 (\rho + \rho_0)^2 [(\rho + \rho_0^3) - (\alpha + \rho_0)^3] \\ & [(\beta + \rho_0)^3 - (\rho + \rho_0)^3]\, e^{G - [E_1 + E_2(\rho + \rho_0)^3](T - T_0)} \\ & + \rho^2 [D_1 + D_2\rho + D_3\rho^2 + D_4\rho^3 + D_5\rho^4]\, e^{k - (F_1 + F_2\rho)/T} \end{aligned} \quad (6)$$

It should be noted that in this form G is a parameter which has to be determined with the other parameters since there is no pure multiplier in front of the first exponential, while k is a constant which can be assigned any convenient value since it only changes the values of the D_i by a constant amount. For convenience, k was selected as equal to 6.0. It should be noted that these parameters are not all independent.

DETERMINATION OF THE CONSTANTS IN THE EQUATION OF STATE

The values of the constants in Equation (6) were determined by a simultaneous fit to all 598 data points. This involved an iterative procedure in which the sum of squares of the relative error in the predicted pressure was minimized. From an analysis of the density dependence of C, E, and F, suitable initial values for all the nonlinear parameters in Equation (6) were selected. With these terms fixed, a linear least squares curve fit was programmed to determine initial values for the remainder of the constants. Utilizing these initial values, the iteration proceeded to apply corrections to all the parameters as determined from the derivative functions which minimized the squared error sum. Fifty to seventy-five iterations were usually necessary to arrive at a minimum. It was possible to overrelax the corrections by a factor of 25. A number of iterative searches were made utilizing different initial parameter values to assure that the optimum was not merely a local minimum.

RESULTS AND CONCLUSIONS

The constants for the equation of state determined as outlined in the previous section are given in Table 2. The number of significant figures is necessary for precision and does not indicate variance. Also given in the Table are values of the coefficients for the compressibility equation as a function of reduced temperature and density using critical constants equal to 190.77°K., 671.0 lb./sq.in.abs. and 0.1625 g./cc. (*27*). The compressibility equation has the form

$$\begin{aligned} Z = 1 &+ B_1\rho_R + B_2\rho_R^2 + B_3\rho_R^3 + B_4\rho_R^4 + B_5\rho_R^5 \\ &+ \rho_R\,[A_1 + A_2\rho_R + A_3\rho_R^2 + A_4\rho_R^3 + A_5\rho_R^4]\,(1/T_R) \\ &+ \rho_R(\rho_R + \rho_0)^2\,[(\rho_R + \rho_0)^3 - (\alpha + \rho_0)^3] \\ &\quad [(\beta + \rho_0)^3 - (\rho_R + \rho_0)^3] \\ &\quad \left(\frac{1}{T_R}\right) e^{G - [E_1 + E_2\,(\rho_R + \rho_0)^3]\,(T_R - T_0)} \\ &+ \rho_R\,[D_1 + D_2\rho_R + D_3\rho_R^2 + D_4\rho_R^3 + D_5\rho_R^4] \\ &\quad \left(\frac{1}{T_R}\right) e^{k - (F_1 + F_2\,\rho_R)/T_R} \end{aligned} \tag{7}$$

These parameters do not necessarily have physical significance. The hole theory of Fukuda (*11*) may eventually lead to some significance.

The constants given in Table 2 reproduce the experimental pressures including the saturation vapor pressures with an average absolute error of 0.04% and a root mean square error of 0.07%. The distribution of error for the 598 data points is given in Table 3. A total of only 10 points had errors in excess of 0.20%. Ninety-five percent of the errors were less than 0.1%, the estimated accuracy of the data, indicating that the equation was reproducing the data within the limits of error of the measurements.

TABLE 2. COEFFICIENT VALUES FOR THE EQUATION OF STATE

Coefficient	Pressure Equation (6)	Reduced Compressibility Equation* (7)
A_1	−168379.37	−1.9079137
A_2	100983.52	0.1859404
A_3	2074154.8	0.6206085
A_4	−12444994.0	−0.6050965
A_5	17600314.0	0.1390605
B_1	369.46526	0.7986446
B_2	554.53908	0.1947895
B_3	−8614.1411	−0.4916982
B_4	44316.430	0.4110596
B_5	−43179.188	−0.0650830
D_1	−741.18776	−0.8398430
D_2	−2806.7029	−0.5167966
D_3	80674.262	2.4138572
D_4	−345392.00	−1.6793539
D_5	382530.92	0.3022386
E_1	0.046002000	8.7758015
E_2	0.21177000	0.1733543
F_1	1378.7933	7.2275164
F_2	−1344.1846	−1.1449913
G	34.348141	8.423558
T_0	−147.71055	−0.774286
k	6.00000	1.394830
α	0.141199	0.868917
β	0.361788	2.226390
ρ_0	0.113318	0.697342

* *Critical parameters used for reduction were 190.77°K. and 0.1625 g./cc.*

TABLE 3. DISTRIBUTION OF PERCENT ERROR IN CALCULATED PRESSURE FOR THE 598 POINTS

Error Range %	Number of Points in Error Range
0.00-0.05	487
0.05-0.10	79
0.10-0.15	15
0.15-0.20	7
0.20-0.30	2
0.30-0.40	3
0.40-0.50	1
0.50-0.60	4

Large values of $(\partial P/\partial \rho)$ occur at high density where the expected error in ρ is less than 0.02%. A complete error analysis is available elsewhere (*27*).

Figure 5 is a graphic illustration of the region of applicability of the equation of state. Within the crosshatched region the expected errors in calculating pressures are less than 0.1%. Except for a region near the critical point where the isotherms become flat, densities can also be predicted within 0.1%. This involves substituting a pressure and temperature into Equation (6) and iterating for the corresponding density. At points removed from the critical the iteration converges rapidly to a value within 0.1% of the measured value. Although no data are available in the high temperature high pressure region, the form of the isochoric equation, Equation (1), should allow for reasonable extrapolations with no danger of sudden oscillations which are usually present when extrapolating high order polynomial expressions.

Virial coefficients calculated from Equation (6) can be expressed as the low density limits of $(Z - 1)/\rho$ and its derivative with respect to density. For the second virial coefficient the resulting expression is

$$\begin{aligned} B = \lim_{\rho\to 0}\left(\frac{Z-1}{\rho}\right) &= \frac{1}{RT}\,(A_1 + B_1T + D_1e^{k - F_1/T}) \\ &+ \rho_0^2\left(\frac{1}{RT}\right)[\rho_0^3 - (\alpha + \rho_0^3)] \\ &\quad [(\beta + \rho_0)^3 - \rho_0^3]\, e^{G - (E_1 + E_2\,\rho_0^3)\,(T - T_0)} \end{aligned} \tag{8}$$

The form of the third virial coefficient is given by

$$\begin{aligned} C = \lim_{\rho\to 0}\left\{\frac{\partial\left(\dfrac{Z-1}{\partial\rho}\right)}{\partial\rho}\right\} &= \frac{1}{RT}\left[A_2 + B_2T + \left(D_2 - \frac{D_1F_2}{T}\right) e^{k - F_1/T}\right] \\ &+ \rho_0^2\left(\frac{1}{RT}\right)(\rho_0^3 - \alpha_0^3)\,(\beta_0^3 - \rho_0^3)\left[\frac{2}{\rho_0}\right. \\ &\left. + \frac{3\rho_0^2}{(\rho_0^3 - \alpha_0^3)} - \frac{3\rho_0^2}{(\beta_0^3 - \rho_0^3)} - 3E_2\rho_0^2\,(T - T_0)\right] \\ &\quad e^{G - (E_1 + E_2\,\rho_0^3)\,(T - T_0)} \end{aligned} \tag{9}$$

These expressions using the coefficients from the first column of Table 2 yield virial coefficients in terms of (cc./g.) and have to be converted to (cc./mole) utilizing the molecular weight of 16.042. These expressions were evaluated over the appropriate temperature range and are compared with experimental values in Figures 6 and 7. Calculated second virial coefficients were in good agreement with the experimental values (*10, 14*). Although the calculated third virial coefficients did not give quantitatively good agreement, the qualitative agreement of the calculations is remarkable when it is remembered that the low density data of Hoover (*14*) were not included in the curve fit.

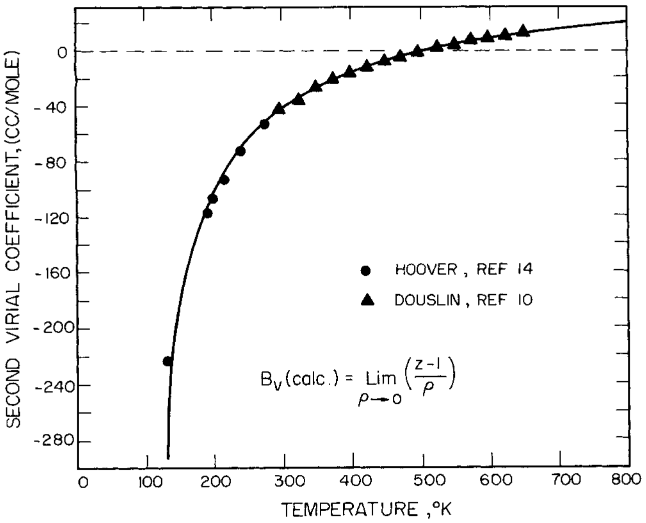

Fig. 6. Calculated and experimental second virial coefficients.

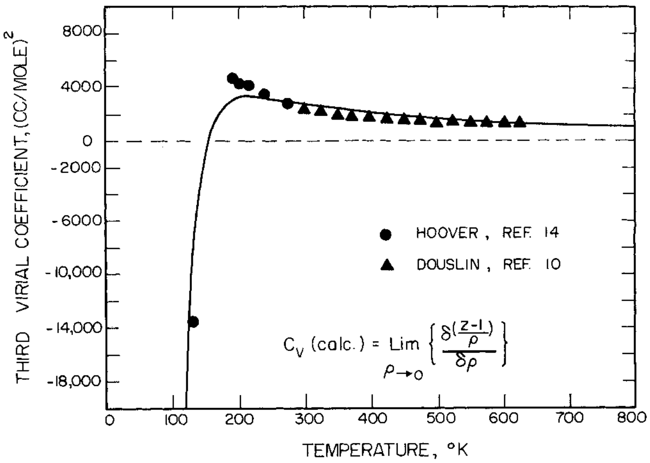

Fig. 7. Calculated and experimental third virial coefficients.

Had these data been in a form where they could be included in the fit it can be expected that the third virial calculations would be in better agreement.

As mentioned earlier, the equation of state is such as to allow analytical expressions to be derived for the thermodynamic properties for methane. Due to the lengthiness of these expressions they are not reproduced in the present paper. Calculations have been performed to evaluate these expressions and to compare them with available experimental thermodynamic data. With the agreement attained between experimental and predicted volumetric behavior, it can be expected that the calculated thermodynamic properties will also be highly accurate.

The calculations (*28*) showed excellent agreement with calorimetric enthalpy data (*16*). The use of a single equation of state for the entire range produces thermodynamic properties which are internally consistent. Where applicable, P-V-T techniques are less expensive than calorimetric.

Using the coefficients for the reduced equation of state should also provide accurate predictions for fluids such as argon and the other inert gases which have two parameter corresponding states agreement with methane.

The reduced equation of state also provides an excellent reference for corresponding states principle applications to pure components or to mixtures, provided that deviations from the simple two parameter corresponding states principle are considered (*18*).

In conclusion, this equation of state very closely represents a wide range of experimental P-V-T data for a large amount of highly accurate data for methane in a format suitable for extraction of thermodynamic properties as well as P-V-T behavior.

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