

the maximum temperature deviation is 0.0174 deg, while the mean of the absolute values of the temperature deviations is 0.0109 deg. The deviations of Clark et al. [14] (experiments by Michels) appear to oscillate slightly about the zero axis except at the lower temperatures where the maximum temperature deviation occurs. For the data of Clark et al. [14], the maximum temperature deviation is 0.0339 deg, while the mean of the absolute values of the temperature deviations is 0.00925 deg. The data of Michels et al. [1] also exhibit a small oscillation with a maximum temperature deviation of 0.0309 deg and a mean of 0.0158 deg. For the data of van Itterbeek et al. [16], the maximum temperature deviation is 0.156 deg, while the mean is 0.0484 deg.

The summary of the deviations between the temperature predicted by the vapor pressure equation (14) and the experimental temperature is given in table 5.

TABLE 5. Summary of vapor pressure deviations

Max. temp. deviation	Mean abs. temp. deviation	Source
0.0339	0.00925	Clark et al. [14]. ^a
.108	.0290	Clark et al. [14].
.0309	.0158	Michels et al. [1].
.0174	.0109	Flubacher et al. [15].
.156	.0484	van Itterbeek et al. [16].

^a Experiments by Michels.

By independent means, Ziegler et al. [2] obtained "best" values for the normal boiling point tempera-

ture and triple point temperature. It is important to note the deviations between the temperatures given by Ziegler et al. [2] and the temperatures predicted by the vapor pressure equation (14). The normal boiling point temperature given by Ziegler is 87.280 ± 0.015 K, while the normal boiling point temperature predicted by equation (14) is 87.2838 K. The triple point temperature recommended by Ziegler is 83.80 K, while the triple point temperature predicted by eq (14) is 83.8038 K, which corresponds to a temperature deviation of 0.0045 percent.

TABLE 6. Least squares estimates of coefficients for vapor pressure eq (14)^a

Coefficient	Least squares estimate	Standard deviation of coefficient	Significance level ^b
A	-1.062454904×10^3	4.993×10^1	99.5%+
B	-4.271440691	1.056	99.5%+
C	$1.524254979 \times 10^{-2}$	5.670×10^{-3}	99 %
D	2.992927939×10^1	4.796	99.5%+
E	$2.465760638 \times 10^{-3}$	5.049×10^{-4}	99.5%+

^a Where P is in atm and T is in K.

^b These parameters are significant at the level indicated when applying the standard F test.

Table 6 lists the five coefficients for eq (14). Also tabulated in table 6 are the standard deviations and a significance level of these parameters. The significance level indicates these parameters are significant at least to the level indicated when applying the standard F test.

7. The P - V - T Surface

Many equations of state have been proposed to represent the P - V - T surface. Some of these equations represent the experimental data adequately in limited regions of the thermodynamic surface but are quite inadequate in other regions. Other equations, taking the form of polynomials along isotherms or isochores, are well suited to represent a single source of highly precise experimental data. However, the use of these polynomial expressions becomes very difficult in a complete correlation of the P - V - T surface with multiple sets of experimental data with odd spacings of temperature and density.

In this analysis the P - V - T surface was basically represented by an equation of state proposed by Benedict, Webb, and Rubin [23] with modifications by Bloomer and Rao [24] and further modified and extended by Strobridge [25].

The Benedict-Webb-Rubin equation was developed by defining and utilizing a quantity \bar{A} , called the residual work content. The residual work content was defined as the difference between the Helmholtz function for a real substance and the Helmholtz function for an ideal gas.

The Helmholtz function

$$A = U - TS \quad (33)$$

may be combined with the first and second laws of thermodynamics,

$$dU = TdS - PdV. \quad (34)$$

The resulting relationship is

$$d\bar{A} = -PdV - SdT. \quad (35)$$

From eq (35),

$$\left(\frac{\partial \bar{A}}{\partial \rho}\right)_T \rho^2 = \bar{P} \quad (36)$$

where \bar{P} is the difference in pressure between the real and ideal gas. Then

$$P = \rho RT + \rho^2 \left(\frac{\partial \bar{A}}{\partial \rho}\right)_T \quad (37)$$

where the first term on the right side of eq (37) is the ideal gas pressure and the second term is the difference between the real and ideal gas pressure. Benedict et al. [23] proposed an expression for the residual work content which was actually an extension of the Beattie and Bridgeman equation. The extension to the Beattie-Bridgeman equation was

necessary in order to represent more accurately the real fluid properties at densities which were higher than the Beattie-Bridgeman equation could adequately represent. Beattie noted that isometrics could be expressed by an equation of the form

$$(P - \rho RT) / \rho^2 = RTF_1(\rho) - F_2(\rho) - F_3(\rho) / T^2. \quad (38)$$

Equations for the functions F_1 , F_2 , and F_3 were then empirically developed to fit experimental data and, at the same time, remain consistent with the residual work content. By these means, Benedict et al. developed an eight adjustable parameter equation of state for hydrocarbons.

After further modifications, Strobridge [25] extended the Benedict-Webb-Rubin equation to represent more accurately the properties of nitrogen. The Strobridge modifications resulted in an equation with sixteen adjustable parameters.

The form of the equation expressed by Strobridge was the one adopted for the determination of the argon P - V - T surface. This form of equation appeared justified because corresponding states theory indicated that there should be reasonable correspondence between nitrogen and argon [18]. The equation of state then used is

$$\begin{aligned} P = & \rho RT + \rho^2(n_1 T + n_2 + n_3/T + n_4/T^2 + n_5/T^4) \\ & + \rho^3(n_6 T + n_7) + \rho^4 n_8 T \\ & + \rho^3(n_9/T^2 + n_{10}/T^3 + n_{11}/T^4) \exp(-n_{16}\rho^2) \\ & + \rho^5(n_{12}/T^2 + n_{13}/T^3 + n_{14}/T^4) \exp(-n_{16}\rho^2) \\ & + \rho^6 n_{15}. \end{aligned} \quad (39)$$

As a matter of convenience, eq (39) was solved for $Z - 1$, and the resulting expression was then fitted to the data by least squares. This expression is

$$\begin{aligned} Z - 1 = & \frac{\rho}{R} (n_1 + n_2/T + n_3/T^2 + n_4/T^3 + n_5/T^5) \\ & + \frac{\rho^2}{R} (n_6 + n_7/T) + \frac{\rho^3}{R} n_8 \\ & + \frac{\rho^2}{R} (n_9/T^3 + n_{10}/T^4 + n_{11}/T^5) \exp(-n_{16}\rho^2) \\ & + \frac{\rho^4}{R} (n_{12}/T^3 + n_{13}/T^4 + n_{14}/T^5) \exp(-n_{16}\rho^2) \\ & + \frac{\rho^5}{R} n_{15}/T. \end{aligned} \quad (40)$$

A preliminary least squares fit of eq (40) to the selected P - V - T data indicated possible round-off discrepancies due to the very large number of arithmetic operations involved with the solution of the normal equations. Therefore, the computer program for the least squares fitting routine was written for double precision arithmetic which carried 20 decimal figures throughout the calculations. This

procedure essentially doubled the number of significant figures carried by the computer, so that round-off error due to the large number of arithmetic operations would be minimized.

In addition, an effort was made to check the results of the least squares solution to see if round-off error, due to operating on an ill-conditioned matrix, was present. The method used to perform this check is outlined as follows: The set of normal equations was obtained by standard techniques. The second normal equation in the set was multiplied by a constant and added to the first normal equation. This sum then replaced the original second normal equation. The third normal equation was then multiplied by a different constant and added to the new second normal equation, and so forth. Each of the constant multipliers was, in general, different. The constants were selected so that each of the diagonal elements of the matrix formed by the resulting set of normal equations was larger than the elements to its right. This criterion was used since appreciable loss of accuracy may occur if a diagonal is smaller than elements to its right. The entire check procedure is then equivalent to the rotation of each of the normal equations relative to the others. The solution to the matrix with rotated vectors could then be obtained. If the solution was the same as that for the original matrix, then it was considered likely that a sufficient number of significant figures was carried in the double precision computer solution to make round-off errors insignificant. For the preliminary least squares fit mentioned above, the solution to the matrix with rotated vectors was the same as the original matrix, to eight significant figures. Although eight significant figures is not indicative of the precision of the original P - V - T data, the agreement of the two solutions indicated that numerical round-off errors were probably insignificant.

The preliminary least squares fit showed that the data of Walker [11] deviated substantially from those of Michels et al. [1] and Rogovaya et al. [7]. Therefore, the data of Walker were not used in the subsequent fits to eq (40). (Further mention of Walker's data will be made later.)

In the subsequent fits it was found desirable to satisfy the standard least squares criteria and, in addition, to simultaneously constrain eq (40) to exactly satisfy three specific requirements at the critical point. The specific constraints which were used are:

1. The critical isotherm of the equation of state (40) has zero slope at the critical point.

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad (\text{critical point})$$

2. The critical isotherm of the equation of state (40) has a point of inflection at the critical point.

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \quad (\text{critical point})$$