An Equation of State: Its Development from Argon Data and Its Application to Other Substances

Using PVT measurements available in the literature for argon, the following equation of state involving the excess properties π and τ was developed:

$$\pi = \alpha\tau + \beta\left[\psi + \frac{\tau}{\tau+1}\right]\frac{\tau}{\tau+1}$$

where α, β, and ψ are density-dependent functions. The results of this relationship for argon have been compared with those obtained using the BWR and the Stewart et al. (1981) equations of state. The present expression was applied in a generalized manner to nitrogen, methane, carbon dioxide, and ammonia. In addition, comparisons have been made using these four substances with three generalized relationships: a truncated virial, a modified Redlich-Kwong, and the Hirschfelder-Buehler-McGee-Sutton equations of state.

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SCOPE

Equations of state for single-component systems available in the literature can be classified as either accurate relationships specific to a particular substance or generalized expressions applicable to a variety of substances. For example, the equation of state proposed by Stewart et al. (1981) accurately reproduces the experimental PVT data of fluid argon for temperatures between the triple point and $T_R = 8.0$ and for densities up to $\rho_R = 3.5$. However, the use of 34 constants, specific to argon, hampers any attempt to formulate a generalized treatment based on this equation of state. On the other hand, the three expressions reported by Hirschfelder et al. (1958) constitute a generalized approach wherein each relationship is valid over a particular region of the PVT surface. Altogether these three expressions represent a generalized equation of state for the prediction of PVT behavior. The current investigation presents a new equation of state that was formulated specifically for fluid argon and applied to nitrogen, methane, carbon dioxide, and ammonia, in a generalized manner, with good results.

CONCLUSIONS AND SIGNIFICANCE

A comprehensive literature search for PVT measurements of fluid argon yielded 100 sources of information that provided a total in excess of 4,400 unscreened values. These values were compiled and were used to define the entire fluid region ranging from the dilute gaseous state up to the freezing curve. This compilation accommodates the saturated vapor, liquid, and solid states, the triple point ($T_t = 83.79$ K, $P_t = 68.82$ kPa, $\rho_t^v = 4.1167$ kg/m^3, $\rho_t^\ell = 1{,}416.0$ kg/m^3, $\rho_t^s = 1{,}622.7$ kg/m^3), and the critical point ($T_c = 150.65$ K, $P_c = 4.866$ MPa, $\rho_c = 529.1$ kg/m^3).

The experimental data were utilized to formulate the equation of state for argon

$$\pi = \alpha\tau + \beta\left[\psi + \frac{\tau}{\tau+1}\right]\frac{\tau}{\tau+1}$$

where the excess pressure $\pi = P_R - P_R^0$ and the excess temperature $\tau = T_R - T_R^0$. In these excess quantities, P_R^0 and T_R^0 refer to saturated vapor and liquid states associated with density isometrics or their extrapolations. For this equation, the density-dependent functions, α, β, and ψ, were established and are valid over the entire fluid region up to $\rho_R = 3.5$, which includes the dilute and dense fluid states for argon. For 2,601 selected values, this equation of state reproduces pressures and densities with average deviations of 0.97% and 0.48%, respectively. These deviations represent considerable improvement over corresponding values obtained from the BWR equation of state and compare favorably with those resulting from the model proposed by Stewart et al. (1981). The equation presented in this investigation is qualitatively correct and quantitatively exact and offers the most complete representation for the PVT behavior of fluid argon available.

Although the development of the equation of state presented in this study has been based only on data for argon, its application has been extended to include the PVT behavior of nitrogen ($z_c = 0.291$), methane ($z_c = 0.289$), carbon dioxide ($z_c = 0.275$), and ammonia ($z_c = 0.242$). This extension required information relating to the saturated vapor and liquid states for these four substances. This information was extracted from generalized correlations available in the literature. The average density deviations were found to be 1.17% (233 points) for nitrogen, 0.50% (792 points) for methane, 2.86% (495 points) for carbon dioxide, and 3.90% (517 points) for ammonia. For comparison, three generalized equations of state were applied to these four substances with the Hirschfelder-Buehler-McGee-

Sutton equation of state yielding the best overall results. For nitrogen and carbon dioxide, this expression produced average density deviations of 0.78% (233 points) and 1.64% (495 points), respectively, which are lower than those obtained from the equation of state of this study; however, this situation is reversed for methane and ammonia.

The compilation and empirical presentation for the PVT behavior of fluid argon are not novel, and many exacting studies are available in the literature (Angus and Armstrong, 1972; Costolnick and Thodos, 1963; Din, 1956; Gosman et al., 1969; Roder et al., 1968; Stewart et al., 1981). However, as with most scientific endeavors, work of this type quickly becomes outdated. Once a compilation is published, it becomes apparent to experimenters which regions on the PVT surface should be more carefully scrutinized. Consequently, new data are generated that fill in regions where such data were absent or that yield more precision in regions where unreliable data exist. Since empirical correlations are only as accurate as the experimental data that were used in the regressions, mathematical models must be updated whenever the experimental basis is changed. Therefore, the current attempt to compile and represent the PVT behavior of argon is a direct consequence of the abundance of reliable experimental data that have been published recently and that delineate the PVT behavior of argon more exactly than has been possible in the past.

The decision to study argon rather than any other of the myriad substances possible was not arbitrary. The simplicity and inertness of the argon molecule have nurtured a tremendous amount of theoretical and experimental interest in this monatomic substance. In the gaseous state, argon exhibits only a translational degree of freedom, being devoid of the rotational and vibrational degrees of freedom inherent in polyatomic molecules. Also, the lack of quantum contributions adds to the simplicity intrinsic to this spherical molecule. While both krypton and xenon also possess these characteristics, argon is less difficult to obtain in large quantities and hence has been more thoroughly studied experimentally and more thoroughly exploited industrially.

VAPOR-LIQUID EQUILIBRIUM PRESSURE

The vapor pressure function of argon was established over the entire domain from the triple point [$T_t = 83.79$ K, $P_t = 68.82$ kPa (516.17 mm Hg)] to the critical point [$T_c = 150.65$ K, $P_c = 4.866$ MPa (48.02 atm)]. The triple point and critical point values resulted from 29 and 9 sources of data, respectively. It should be noted that these temperatures and all that follow are based on the IPTS-68. Temperature scale conversions are discussed elsewhere (Wilsak, 1982). Using 263 internally consistent experimental values available from 24 literature sources, the following reduced vapor pressure expression was obtained:

$$\ln P_R = 4.6334 - \frac{4.5397}{T_R} - \frac{0.22715}{T_R^2} + 0.13114 T_R^{5.7406} \qquad (1)$$

Equation 1 reproduces corresponding experimental values with an average pressure deviation of 0.043% (263 points) and with a maximum deviation of 0.363%. Equation 1 has been adopted in this study, but is no better than three other five-parameter models examined. A normal boiling point, $T_b = 87.29$ K, results from 12 references and compares well with the value calculated from Eq. 1, $T_b = 87.297$ K. All details pertaining to this comprehensive vapor pressure relationship for argon can be found elsewhere (Wilsak and Thodos, 1984a).

VAPOR-LIQUID SATURATED DENSITIES

For establishing the saturated liquid density of argon, 17 sources of data were available and yielded 107 reliable points. These screened measurements were utilized to produce the relationship

$$\ln \rho_R = 1.24738(1 - T_R)^{0.291439} \qquad (2)$$

where $\rho_c = 529.1$ kg/m^3. Equation 2 is applicable from the triple point ($T_t = 83.79$ K, $\rho_t = 1416.0$ kg/m^3) to the critical point and reproduces experimental measurements with an average deviation of 0.16%. The hypothetical liquid density, as predicted by Eq. 2, at absolute zero becomes $(\rho_R)_{T=0} = 3.4812$ (1,841.9 kg/m^3).

The experimental information available for the saturated vapor densities of argon was limited to three sources, which yielded 13 reasonable values. Using Eq. 1 in conjunction with these 13 points, the compressibility factor, $z = z_c P_R / \rho_R T_R$, for the saturated vapor can be expressed as

$$z = 1 + (0.99769 z_c - 1) T_R^4 \exp[-0.6161(1 - T_R)^{0.2809}] \qquad (3)$$

where $z_c = 0.2933$. At $T_R = 1.00$, Eq. 1 yields a value $P_R = 0.99769$ rather than unity and therefore in order to maintain internal consistency between Eqs. 1, 2, and 3, this value of 0.99769 was incorporated into Eq. 3 instead of unity for the coefficient of z_c. Equation 3 coupled with Eq. 1 is capable of reproducing the experimental saturated vapor density measurements with an average deviation of 0.83%. Details associated with the development of Eqs. 2 and 3 can be found elsewhere (Wilsak and Thodos, 1984b), where the vapor-solid and liquid-solid coexistence behavior of argon is also reported.

PVT DATA OF ARGON IN THE FLUID STATE

Experimental measurements available in the literature are not ordinarily presented in a form convenient for a self-consistency evaluation. Along these lines, such measurements have been presented as isotherms, isobars, and/or isochors. In order to develop a criterion for comparison, independent of an equation of state, the experimental information was used to produce isobaric relationships of reduced density versus reduced temperature. This procedure entailed a meticulous examination of information available from each source by first plotting the reported experimental measurements on large-scale graphs from which the isobaric information was extracted. This comprehensive survey was quite exhaustive and involved 27 sources of data, each of which was subjected to this outlined plotting and cross-plotting procedure. The isobaric values obtained from this graphical treatment offered a means for comparison between sources of information. Acceptance or rejection of these smoothed data was based on their internal consistency and their comparison with the smoothed data of other investigators. This screening procedure eliminated from further consideration the measurements reported by Bridgman (1935), Lippold (1969), Polyakov and Tsiklis (1967), Rabinovich et al. (1970), Ramsay and Travers (1901), and Sorokin and Blagoi (1970). The smoothed data of the 21 remaining sources are presented in Figures 1 and 2. Figure 1 expresses, on rectilinear coordinates, isobaric relationships that span the range of $0.20 < P_R < 260$ and $T_R < 3.00$. On the other hand, Figure 2 highlights the isobaric relationships for the less dense region by virtue of the logarithmic scales. In this figure, the smallest isobar is $P_R = 0.007$, while the temperature and density extend to $T_R = 8.0$ and $\rho_R = 0.0010$, respectively. The isobars of Figures 1 and 2 properly intersect the coexistence curves. The isobars above the critical pressure intersect only the freezing curve, while isobars below the

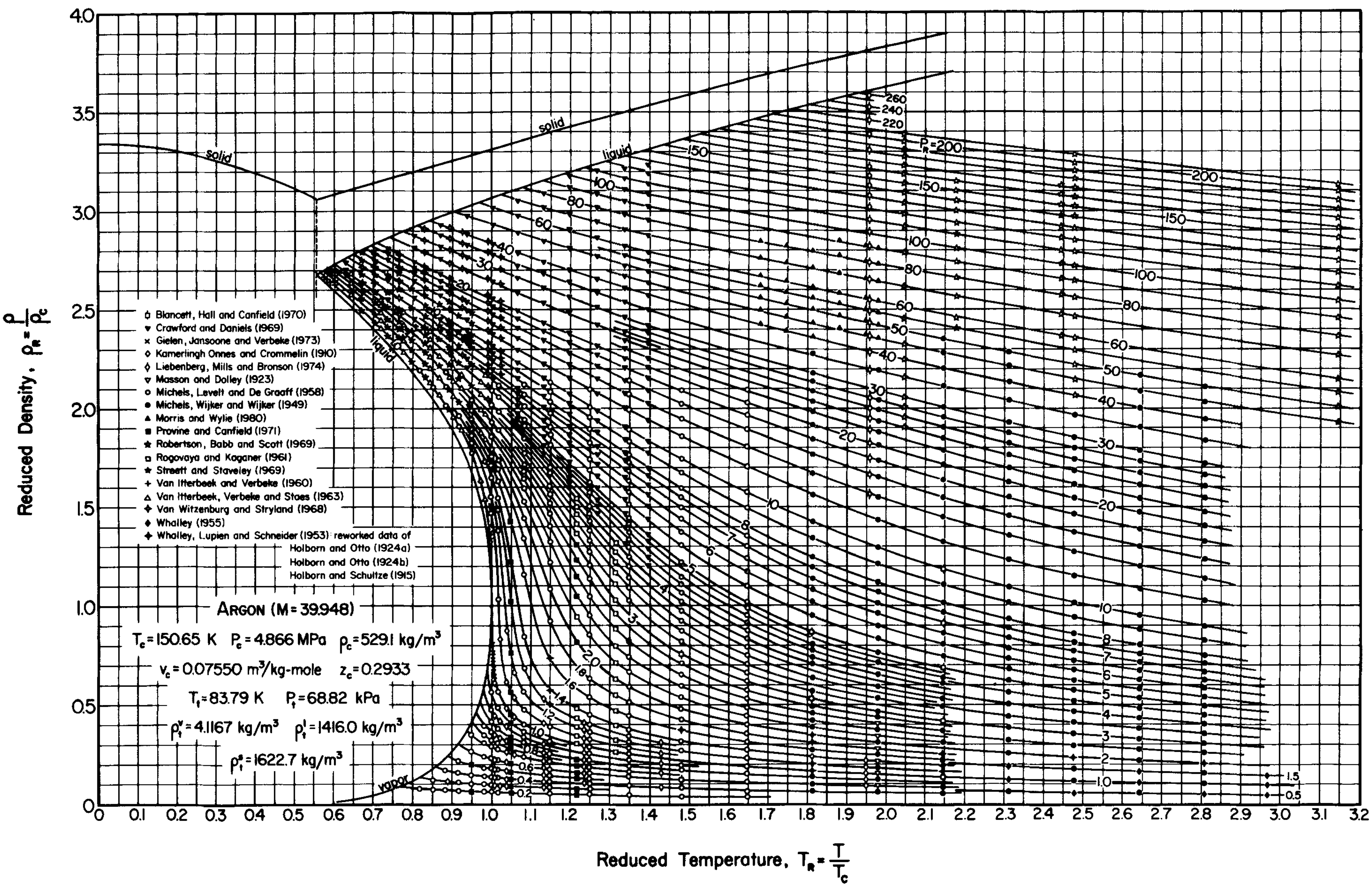

Figure 1. Isobaric behavior for argon obtained from cross-plotted experimental data (rectilinear coordinates).

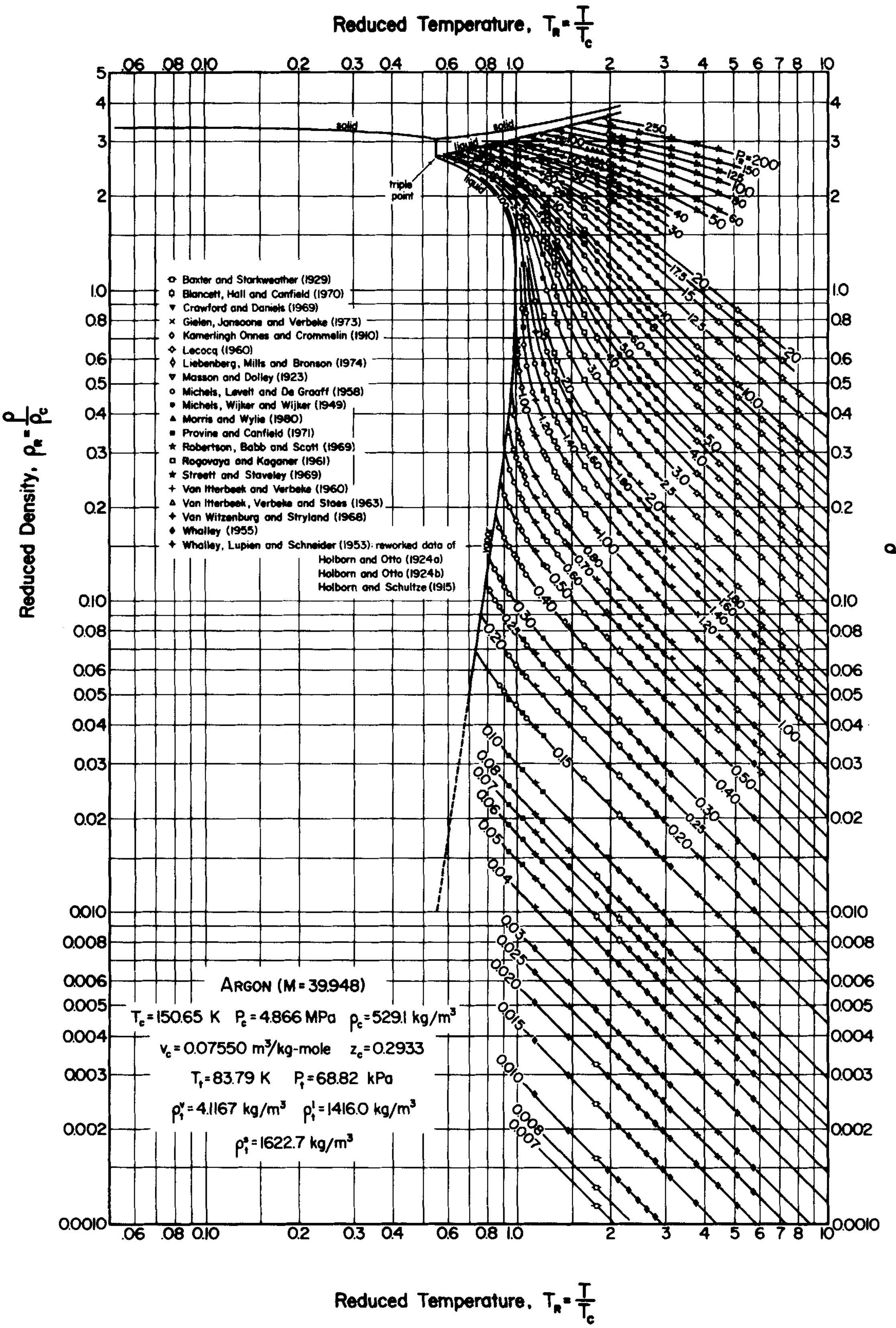

Figure 2. Isobaric behavior for argon obtained from cross-plotted experimental data (logarithmic coordinates).

critical pressure and above the triple point pressure intersect the vapor-liquid coexistence curves as well.

GENERAL TRENDS AND LIMITING CONDITIONS

For the development of an equation of state, it is more convenient to describe the general behavior of density isometrics rather than that of isobars or isotherms. Figures 1 and 2 were used to obtain the reduced pressure dependence on reduced temperature for density isometrics that range from $\rho_R = 0.0015$ up to $\rho_R = 3.5$. To establish the $P_R - T_R$ projection of the PVT surface of argon, 1,499 smoothed values were extracted from Figures 1 and 2 and were graphed on large scale plots. Figures 3 and 4 present the density isometric behavior of argon. Figure 3 shows this behavior for moderate temperatures and pressures where the density isometrics

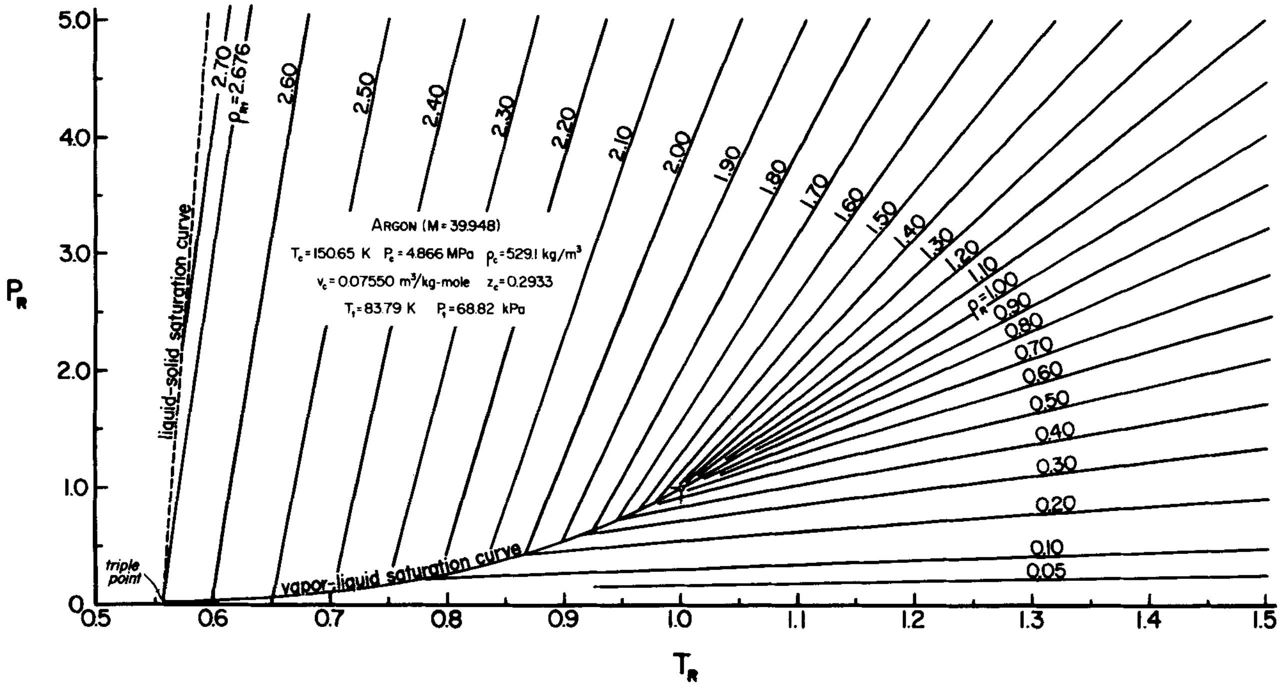

Figure 3. Density isometrics for the fluid region of argon in the vicinity of the triple and critical points.

are shown to intersect the vapor-liquid saturation curve. In this figure, the vapor pressure curve properly extends into the fluid region along the critical density isometric (ρ_R = 1.00). The critical isometric reverses in curvature somewhat above the critical point at T_R = 1.28.

The isometrics below the critical ($\rho_R < 1.00$) and above the triple point vapor density ($\rho_R > 0.0078$) intersect the vapor pressure curve, while those at lower densities meet the sublimation curve. An inflection point exists for each isometric in the immediate vicinity of the critical isometric. However, for lower isometrics, no inflection points exist. These isometrics become increasingly flatter with decreasing density.

The density isometrics above the critical ($\rho_R > 1.00$) and below the triple point liquid density ($\rho_R < 2.676$) intersect the vapor pressure curve from the liquid side, while for higher isometrics ($\rho_R > 2.676$) the intersection occurs with the saturated pressure curve in the liquid-solid coexistence region. Again, the presence of an inflection point was noted for each isometric in the vicinity of the critical isometric. However, for higher isometrics, no inflection points were found to exist. These isometrics become increasingly steeper with increasing density.

The density isometrics of Figure 4 extend to temperatures of T_R = 10 and pressures in excess of P_R = 200. In this figure, high density isometrics ($\rho_R > 2.676$) are shown to intersect the liquid-solid saturation curve for densities up to ρ_R = 3.50.

Two limiting conditions are borne out from the development of the isometric relationships of this investigation. At very low densities, ideal gas behavior is approached and at higher temperatures all isometrics become increasingly linear.

DEVELOPMENT AND QUALITATIVE ANALYSIS OF A NEW EQUATION OF STATE

As shown in Figures 3 and 4, each isometric intersects one of the three saturated pressure curves at a unique point. These saturated pressure curves are associated with the vapor-solid, vapor-liquid and liquid-solid coexistence regions. The points of intersection can be used as reference points. In order to simplify the approach, the presence of the vapor-solid and liquid-solid coexistence regions will be ignored while the vapor pressure curve of the vapor-liquid coexistence region will be retained and extrapolated past the triple point to the origin. Therefore, the isometrics that intersect the vapor-solid and liquid-solid coexistence curves are extrapolated to meet the extension of the vapor pressure curve. With this arrangement, all the isometrics of fluid argon will intersect the vapor pressure curve and its extension. These points of intersection will be used as reference points.

The proposed equation of state involves the pressure and temperature in the excess quantities, $\pi = P_R - P_R^0$ and $\tau = T_R - T_R^0$, where P_R^0 and T_R^0 represent the reference point for an isometric. This value is obtained at the intersection of the isometric with the vapor pressure curve. If the density of the isometric is $\rho_R > 1.00$, then Eq. 2 yields T_R^0, while Eq. 3 accommodates the subcritical isometrics. The pressure, P_R^0, corresponding to T_R^0 is then calculated from Eq. 1. With the definitions of the excess pressure $\pi = P_R - P_R^0$ and the excess temperature $\tau = T_R - T_R^0$, the entire vapor-liquid coexistence region reduces to the point $\pi = 0$ and $\tau = 0$.

The formulation of a functional form for an equation of state that is explicit in π and τ and implicit in density entailed the examination of a number of preliminary models. All these models were fitted to the 1,499 smoothed values extracted from the enlarged plots corresponding to Figures 1 and 2. The final model was required to predict the qualitative trends of isometric fluid behavior and to satisfy the limiting conditions at high temperatures. This final model was determined to be

$$\pi = \alpha\tau + \beta\left[\psi + \frac{\tau}{\tau + 1}\right]\frac{\tau}{\tau + 1} \tag{4}$$

where α, β, and ψ are only functions of density. For the limiting condition of high temperatures, Eq. 4 degenerates to the linear form:

$$\pi = \alpha\tau + \beta[\psi + 1] \tag{5}$$

The first partial derivative of Eq. 4 along an isometric becomes

$$\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho R} = \left(\frac{\partial \pi}{\partial \tau}\right)_{\rho R} = \alpha + \frac{\beta}{(\tau + 1)^2}\left[\psi + \frac{2\tau}{\tau + 1}\right] \tag{6}$$

which is positive if α, β, ψ, and τ are greater than zero. Since π and τ are positive by definition, and the values of α, β, and ψ turn out to be positive, it then follows that $(\partial\pi/\partial\tau)_{\rho_R} > 0$, a condition consistent with real fluid behavior. When the second partial derivative of Eq. 4 is equal to zero, the inflection point of an isometric is established. Thus

$$\left(\frac{\partial^2 P_R}{\partial T_R^2}\right)_{\rho R} = \left(\frac{\partial^2 \pi}{\partial \tau^2}\right)_{\rho R} = \frac{2\beta}{(\tau + 1)^3}\left[\frac{1 - 2\tau}{\tau + 1} - \psi\right] \tag{7}$$

which yields

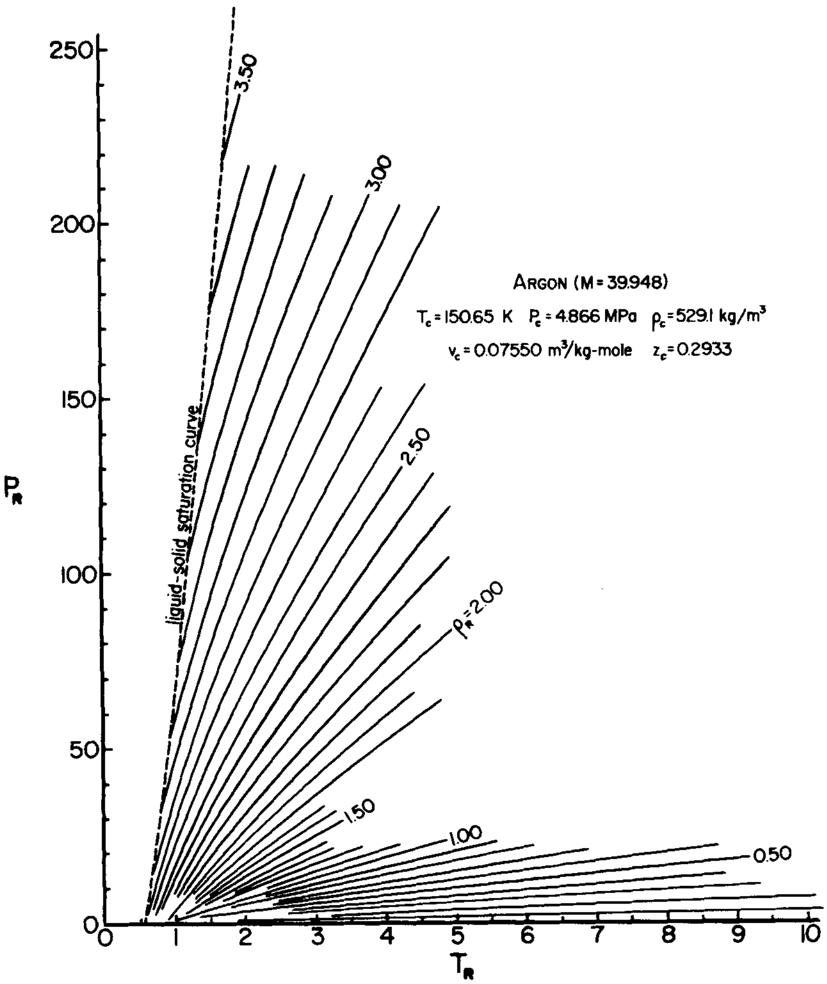

Figure 4. Density isometrics for the complete fluid region of argon.

$$\tau_i = \frac{1 - \psi}{2 + \psi} \tag{8}$$

when Eq. 7 is set equal to zero. Equation 8 requires that ψ range between −2 and +1 for τ_i to be positive. For other values of ψ, τ_i becomes negative, and therefore the inflection point does not lie in the fluid phase plane.

To satisfy the limiting condition of ideal gas behavior, Eq. 4 must reduce to the form

$$\lim_{\rho_R \to 0} \pi = \frac{\rho_R}{z_c} \tau \tag{9}$$

where $z_c = P_c v_c / RT_c$. Since an ideal gas lacks a vapor-liquid coexistence region, π and τ in Eq. 9 are synonymous with P_R and T_R, respectively. A comparison between Eqs. 4 and 9 indicates that the conditions

$$\lim_{\rho_R \to 0} \alpha = \frac{\rho_R}{z_c} \tag{10}$$

$$\lim_{\alpha \to \rho_R / z_c} \beta = 0 \tag{11}$$

and

$$\lim_{\alpha \to \rho_R / z_c} \beta \psi = 0 \tag{12}$$

are sufficient to ensure the proper limiting behavior of Eq. 9 at low densities.

After developing several functional forms consistent with Eqs. 10 to 12, the density dependencies of the parameters in Eq. 4 were established to be

$$\alpha = \frac{1}{z_c} \frac{\rho_R}{\rho_R + 1} \left[1 + \frac{3}{2} \frac{\rho_R}{\rho_R + 1} (1 + \rho_R + \rho_R^2) \right] \tag{13}$$

$$\beta = \rho_R^3 \tag{14}$$

$$\psi = \frac{1}{\rho_R^{3/2}} \frac{1 + \rho_R^8}{1 + a \rho_R^8} + (\rho_R - 1)^2 [b + c(\rho_R - 1)^2] \tag{15}$$

where $a = 4.4096$, $b = 0.73813$, and $c = -0.021664$. Equations 13 to 15 are valid for densities up to $\rho_R = 3.45$, which is considerably above the liquid triple point density ($\rho_R = 2.676$).

The equation of state presented by the relationship of Eq. 4, coupled with the density-dependent parameters α, β, and ψ given by Eqs. 13, 14, and 15, is capable of generating the PVT surface for fluid argon. Since this equation of state satisfies Eqs. 5 and 9, extrapolations to high temperatures and/or low densities are justified.

DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL VALUES

The equation of state expressed by Eq. 4 has been applied to calculate values that were compared with corresponding experimental measurements. In this comparison all available sources of experimental information for argon were consulted. This entailed 27 references that date from 1901 and extend to the present. Table 1 presents the sources of information that yielded 2,955 experimental measurements, of which 2,601 were considered reliable.

The calculation of pressure, given temperature and density, follows directly from Eqs. 1 to 3, which determine P_R^0 and T_R^0, and Eqs. 13 to 15, which establish α, β, and ψ for Eq. 4. Deviations between experimental and calculated pressures are summarized for each source in Table 1. The average pressure deviation was 0.97% (2,601 points). It should be noted that the average deviations of 2.99% (Streett and Staveley, 1969), 2.60% (Van Itterbeek and Verbeke, 1960), and 2.53% (Van Itterbeek et al., 1963) result from

TABLE 1. SUMMARY OF PERCENT DEVIATIONS FOR PRESSURE AND DENSITY RESULTING FROM CALCULATED AND CORRESPONDING EXPERIMENTAL VALUES FOR ARGON

		This Investigation				Stewart et al. (1981)			
		Pressure		Density		Pressure		Density	
Reference	Points	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Baxter and Starkweather (1929)	3	0.08	0.09	0.08	0.09	0.01	0.01	0.01	0.01
Blancett et al. (1970)	72	0.31	5.36	0.27	3.09	0.12	5.68	0.08	3.26
Bridgman (1935)*	78	16.0	35.6	4.19	9.91	16.4	35.1	4.29	10.0
Crawford and Daniels (1969)	270	1.03	4.97	0.16	0.59	1.36	3.24	0.24	0.72
Gielen et al. (1973)	141	0.18	0.80	2.66	11.2	0.12	0.35	3.69	27.7
Kamerlingh Onnes and Crommelin (1910)	125	0.75	2.90	1.63	10.4	0.44	2.50	1.05	9.83
Lecocq (1960)	126	0.61	1.69	0.52	1.23	0.12	0.45	0.10	0.34
Liebenberg et al. (1974)	22	0.92	1.56	0.22	0.35	1.19	2.58	0.27	0.54
Lippold (1969)*	68	7.59	28.9	0.60	2.12	5.76	27.1	0.45	1.84
Masson and Dolley (1923)	25	0.31	0.66	0.31	0.67	0.14	0.27	0.14	0.27
Michels et al. (1958)	296	0.47	8.72	0.48	5.42	0.10	1.49	0.12	4.79
Michels et al. (1949)	355	0.34	0.93	0.28	0.90	0.04	0.16	0.02	0.05
Morris and Wylie (1980)	43	1.03	1.38	0.25	0.30	0.34	0.45	0.08	0.10
Polyakov and Tsiklis (1967)*	64	2.78	8.18	0.92	2.69	3.74	8.23	1.27	2.66
Provine and Canfield (1971)	62	0.43	1.68	0.49	1.86	0.12	1.19	0.09	0.29
Rabinovich et al. (1970)*	61	1.36	6.20	1.18	6.09	1.07	6.17	0.94	6.11
Ramsay and Travers (1901)*	35	1.83	10.9	1.83	9.77	1.75	10.5	1.76	9.38
Robertson et al. (1969)	287	0.66	2.45	0.21	1.12	0.19	1.00	0.06	0.26
Rogovaya and Kaganer (1961)	74	3.12	72.2	0.38	3.01	3.05	72.4	0.21	2.55
Sorokin and Blagoi (1970)*	48	31.7	883.0	0.30	0.58	35.5	892.0	0.38	0.76
Streett and Staveley (1969)	139	2.99	90.9	0.08	0.65	5.23	141.0	0.13	0.66
Tanner and Masson (1930)	5	0.28	0.62	0.28	0.60	0.07	0.15	0.07	0.14
Van Itterbeek and Verbeke (1960)	50	2.60	9.54	0.04	0.10	2.12	8.95	0.03	0.11
Van Itterbeek et al. (1963)	116	2.53	19.1	0.15	0.47	2.55	29.8	0.14	0.55
Van Witzenburg and Stryland (1968)	114	2.71	18.3	0.32	3.85	1.18	17.9	0.31	20.1
Whalley (1955)	180	0.29	2.33	0.32	4.71	0.09	2.30	0.12	4.17
Whalley et al. (1953)	96	0.37	3.84	0.40	4.18	0.13	3.48	0.15	3.91
All data	2,955	2.07		0.62		1.99		0.51	
Selected data	2,601	0.97		0.48		0.82		0.36	

* Sources not selected.

the higher sensitivity of pressure for the dense fluid state in the vicinity of the triple point. On the other hand, the small deviation of 0.18% (Gielen et al., 1973) results from the relatively low sensitivity of pressure in the immediate vicinity of the critical point.

The calculation of density, given pressure and temperature, is not as straightforward. A value for density is assumed that establishes parameters α, β, and ψ. For this assumed density, a corresponding value for T_R^0 is calculated from Eq. 2 or Eq. 3. Equation 1 then yields the corresponding vapor pressure P_R^0. With the given pressure and temperature and these calculated values of P_R^0 and T_R^0, π and τ are established. If Eq. 4 is satisfied, the assumed density is correct; otherwise, the process is repeated. Densities calculated in this manner have been compared with corresponding experimental measurements to yield the deviations summarized in Table 1. The average density deviation was 0.48% (2,601 points). For the dense fluid state in the vicinity of the triple point, density deviations become insensitive, while at the critical point the sensitivity is high. This behavior is contrary to that observed for pressure deviations. Therefore, both measures of uncertainty are included for a comprehensive comparison between calculated and experimental values. The calculation of temperature, given density and pressure, did not yield any additional significant information (Wilsak, 1982), and therefore only pressure and density deviations are reported.

COMPARISON WITH THE BENEDICT-WEBB-RUBIN EQUATION OF STATE

Zudkevitch and Kaufmann (1966) applied the BWR equation of state to argon and established the eight constants associated with this equation. The conditions of their studies ranged in temperature from 160 K (T_R = 1.062) to 600 K (T_R = 3.983) and in pressure from 101 kPa (P_R = 0.0208) to 51.68 MPa (P_R = 10.621). Using the constants presented by Zudkevitch and Kaufmann, values were calculated and compared with corresponding experimental measurements involved in the present study. For these comparisons, the ranges of temperature and pressure were restricted to the conditions stipulated by them. In addition, these ranges were further restricted to densities of less than ρ_R = 1.3, since higher density values yielded progressively increasing deviations. Experimental measurements in the region bounded by these conditions were compared with corresponding values calculated by the BWR equation of state and also by Eq. 4 of this study. For 739 points considered reliable, the BWR equation generated average deviations of 0.44% and 0.48% for pressure and density, respectively. On the other hand, Eq. 4 produced average deviations of 0.35% and 0.38% for pressure and density, respectively. These comparisons are summarized in Table 2.

Outside of the fitting region, the deviations associated with the BWR equation became excessive. These deviations were found to be particularly large near the critical point and also in the vicinity of the triple point for the dense fluid state where negative calculated pressures were encountered. Near the critical point, the experimental measurements of Kamerlingh Onnes and Crommelin (1910), when compared with values calculated using the BWR equation, resulted in average deviations of 2.46% and 9.11% with maximum deviations of 9.17% and 107% for pressure and density, respectively. The excessive deviations in the vicinity of the triple point are exemplified from the work of Van Itterbeek et al. (1963), who report measurements for this region. Their experimental values, when compared with values calculated from the BWR equation, yielded average deviations of 108 and 1.90% for pressure and density, respectively, with corresponding maximum deviations of 3,040% and 7.55%.

COMPARISON WITH THE STEWART-JACOBSEN-BECKER-TENG-MUI EQUATION OF STATE

The most recent and quantitatively exacting model representing the fluid behavior of argon was presented in a paper at the Eighth Symposium on Thermophysical Properties by Stewart et al. (1981).

TABLE 2. SUMMARY OF PERCENT DEVIATIONS FOR PRESSURE AND DENSITY RESULTING FROM CALCULATED AND CORRESPONDING EXPERIMENTAL VALUES FOR ARGON[*]

		This Investigation				Zudkevitch and Kaufmann (1966)			
		Pressure		Density		Pressure		Density	
Reference	Points	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Blancett et al. (1970)	66	0.24	0.84	0.24	0.85	0.20	1.04	0.19	0.82
Crawford and Daniels (1969)	1	0.33	0.33	0.24	0.24	0.94	0.94	0.69	0.69
Kamerlingh Onnes and Crommelin (1910)	40	0.59	1.50	0.75	1.94	0.82	1.98	1.02	3.75
Lecocq (1960)	20	0.33	0.76	0.30	0.61	1.04	1.35	0.95	1.26
Masson and Dolley (1923)	25	0.31	0.66	0.31	0.67	0.27	0.58	0.28	0.59
Michels et al. (1958)	88	0.30	1.15	0.33	1.22	0.41	1.95	0.48	3.20
Michels et al. (1949)	246	0.37	0.93	0.34	0.90	0.37	1.10	0.35	1.07
Provine and Canfield (1971)	21	0.30	0.86	0.37	1.17	0.36	1.38	0.45	1.30
Rabinovich et al. (1970)[†]	48	1.00	6.20	0.90	6.09	0.45	7.27	0.44	7.26
Ramsay and Travers (1901)[†]	35	1.83	10.9	1.83	9.77	1.52	9.78	1.56	8.87
Rogovaya and Kaganer (1961)	32	0.37	1.23	0.44	1.32	0.46	1.89	0.58	3.43
Tanner and Masson (1930)	5	0.28	0.62	0.28	0.60	0.41	0.65	0.42	0.65
Whalley (1955)	120	0.35	2.33	0.41	4.71	0.43	3.81	0.52	7.53
Whalley et al. (1953)	75	0.39	3.84	0.44	4.18	0.63	3.72	0.71	4.52
All data	822	0.46		0.47		0.49		0.52	
Selected data	739	0.35		0.38		0.44		0.48	

[*] Restricted to the BWR fitting range: $\rho_R < 1.3$, $1.1 < T_R < 4.0$, and $0.021 < P_R < 10.6$.

[†] Sources not selected.

The equation of state proposed by them defines P_R in terms of T_R and ρ_R for argon and utilizes 34 adjustable parameters. These parameters were established using the experimental data of nine sources involving 1,328 values. The range of temperature, pressure, and density of these values is comparable to that involved in the present investigation.

Using 2,955 experimental values compiled in the current study and corresponding values calculated using their equation of state for argon, the deviations summarized for each source are presented in Table 1. The overall average of these deviations for the 2,601 selected values is 0.82% for pressure and 0.36% for density. These average deviations can be compared to 0.97% for pressure and 0.48% for density that resulted from the use of Eq. 4. A careful examination of the deviations reported in Table 1 indicates that Eq. 4 is capable of predicting values slightly better near the critical point and for the dense fluid state in the vicinity of the triple point.

APPLICATION OF EQUATION OF STATE OF THIS STUDY WITH OTHER SUBSTANCES

Because of the generalized nature of Eq. 4, it may be of interest to apply it to substances other than argon. In this context, PVT data for nitrogen, methane, carbon dioxide, and ammonia were obtained from the comprehensive compilations of Byrne and Thodos (1961), Dingrani (1970), Kennedy and Thodos (1960), and Groenier and Thodos (1960), respectively. For these comparisons, the critical point values reported in each of these sources were utilized. For their vapor pressure behavior, the generalized treatment of Gómez-Nieto and Thodos (1977) was consulted. For the densities associated with the vapor-liquid coexistence region, the generalized correlation for the saturated vapor state of Edwards and Thodos (1974) was employed, while the correlation of Campbell (1983) was used for the saturated liquid state.

Densities were calculated and compared with corresponding values from the literature. The range of temperature, pressure, and density considered for each substance is indicated in Table 3. This table categorizes the data into six regions. The critical point region (CP) has been confined to the conditions: $1.07 > T_R > 0.998$, $1.5 \geqslant P_R \geqslant 1.0$, and $1.4 \geqslant \rho_R \geqslant 0.8$. The compressed fluid region (CF) has been designated to be between the saturated liquid state and the isobar $P_R = 2.00$ with $\rho_R \geqslant 2.0$ and the temperature ranging from the triple point to the critical point. All other points were segregated into the following four density ranges: $\rho_R < 0.1$, $0.1 \leqslant \rho_R < 1.0$, $1.0 \leqslant \rho_R < 2.0$, and $\rho_R \geqslant 2.0$. The use of these six categories presents a simplified histogram of average deviations.

Case I

This case assumes that nitrogen, methane, carbon dioxide, and ammonia have the same vapor-liquid equilibrium behavior and critical compressibility factor as argon. Therefore, all the relationships presented for argon were applied without any modifications. This approach assumes that the law of corresponding states is equally valid for these four substances, despite the fact that their z_c values vary from 0.291 for nitrogen to 0.242 for ammonia. The results of this treatment are summarized in Table 3, where the overall average deviations are 1.30% (233 points) for nitrogen, 1.16% (792 points) for methane, 6.38% (495 points) for carbon dioxide, and 13.37% (517 points) for ammonia. As the substances depart in behavior from argon, as indicated by their z_c values, the average deviations increase.

Case II

For this case, all the conditions postulated in Case I are retained except that the actual value of z_c for each substance is substituted into Eq. 13. This treatment utilizes the concept of the third correlating parameter first suggested by Meissner and Seferian (1951) and later used extensively by Lydersen et al. (1955). The results of this approach are summarized in Table 3. The average deviations of this analysis were found to be 1.17% (233 points) for nitrogen, 0.54% (792 points) for methane, 3.24% (495 points) for carbon dioxide, and 7.94% (517 points) for ammonia. As expected, the introduction of the actual values of z_c produces a general overall improvement over Case I. However, as noted in Case I, these deviations continue to increase as these substances depart in behavior from argon.

Case III

In addition to the involvement of the actual value of z_c used in Eq. 13, the vapor-liquid coexistence behavior for each substance was obtained from the generalized correlations corresponding to vapor pressure, saturated vapor, and saturated liquid densities. These generalized correlations replace Eqs. 1, 2, and 3, which are needed to calculate P_R^0 and T_R^0, while Eqs. 4, 14, and 15 remain unchanged. The values of a, b, and c in Eq. 15 are still kept the same as given for argon. The results of this treatment produced

TABLE 3. PERCENT DEVIATIONS FOR DENSITY RESULTING FROM VALUES CALCULATED USING EQ. 4 AND CORRESPONDING VALUES FROM THE LITERATURE FOR NITROGEN, METHANE, CARBON DIOXIDE AND AMMONIA

		Case I		Case II		Case III		Case IV	
	Points	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Nitrogen ($z_c = 0.291$): $0.50 \le T_R \le 1.50$, $0.10 \le P_R \le 180$ and $0.020 \le \rho_R \le 3.495$									
$\rho_R \ge 2.00$	103	0.82		0.78		0.97			
$2 > \rho_R \ge 1$	39	1.44		1.30		1.28			
$1 > \rho_R \ge 0.1$	54	2.08		1.79		1.77			
$0.1 > \rho_R$	23	0.89		0.76		0.83			
CF	12	0.30		0.29		0.27			
CP	2	12.23		12.00		2.32			
Total	233	1.30	19.04	1.17	18.93	1.17	5.21		
No. Pts w/dev. >3%		17		13		11			
Methane ($z_c = 0.289$): $0.60 \le T_R \le 2.61$, $0.15 \le P_R \le 113$ and $0.074 \le \rho_R \le 2.80$									
$\rho_R \ge 2.00$	142	0.37		0.29		0.43			
$2 > \rho_R \ge 1$	125	1.03		0.58		0.42			
$1 > \rho_R \ge 0.1$	443	1.54		0.66		0.55			
$0.1 > \rho_R$	36	1.05		0.18		0.30			
CF	42	0.25		0.24		0.60			
CP	4	1.34		0.86		0.25			
Total	792	1.16	3.54	0.54	2.63	0.50	3.14		
No. Pts w/dev. >1%		514		77		41			
Carbon Dioxide ($z_c = 0.275$): $0.71 \le T_R \le 20.0$, $0.030 \le P_R \le 50.0$ and $0.010 \le \rho_R \le 2.96$									
$\rho_R \ge 2.00$	94	1.84		1.69		3.13		1.13	
$2 > \rho_R \ge 1$	64	6.38		4.46		4.87		2.04	
$1 > \rho_R \ge 0.1$	160	8.34		3.95		3.80		3.39	
$0.1 > \rho_R$	167	7.12		2.86		1.13		1.13	
CF	8	3.42		3.58		0.89		0.31	
CP	2	13.94		11.63		2.48		1.16	
Total	495	6.38	19.04	3.24	18.03	2.86	14.10	1.96	12.07
No. Pts w/dev. >10%		58		3		3		1	
No. Pts w/10% > dev. >5%		307		110		94		40	
Ammonia ($z_c = 0.242$): $0.70 \le T_R \le 10.0$, $0.030 \le P_R \le 40.0$ and $0.010 \le \rho_R \le 3.33$									
$\rho_R \ge 2.00$	160	5.78		7.44		2.88			
$2 > \rho_R \ge 1$	66	4.79		4.91		3.69			
$1 > \rho_R \ge 0.1$	132	18.03		9.07		7.64			
$0.1 > \rho_R$	151	21.28		8.78		1.97			
CF	6	7.64		8.25		1.17			
CP	2	15.66		8.65		0.27			
Total	517	13.37	29.69	7.94	16.95	3.90	17.59		
No. Pts w/dev. >10%		270		148		40			

CF Region: $T_R \le 1.0$, $P_R \le 2.0$ and $\rho_R \ge 2.00$

CP Region: $0.998 < T_R < 1.07$, $1.0 \le P_R \le 1.5$ and $0.80 \le \rho_R \le 1.4$

average deviations of 1.17% (233 points) for nitrogen, 0.50% (792 points) for methane, 2.86% (495 points) for carbon dioxide, and 3.90% (517 points) for ammonia, as presented in Table 3. These deviations represent an improvement over Cases I and II and still retain the same trend with departure from argon as noted before.

Case IV

This case was limited to carbon dioxide, which involved the conditions outlined in Case III plus an estimation of the parameters a, b, and c specific for carbon dioxide needed in Eq. 15. It would prove of interest if further improvement would be realized with a reevaluation of these constants. Because of the similar nature to argon, no significant improvement for nitrogen and methane was expected and consequently no attempt was made to reevaluate parameters for these substances. On the other hand, if an improvement is found for carbon dioxide, an improvement should follow for ammonia if parameters a, b, and c are evaluated specifically for this substance. The parameters $a = 0.83690$, $b = 1.0097$, and $c = -0.054784$ yielded for carbon dioxide the average deviation 1.96% (495 points), as reported in Table 3, which can be compared with the corresponding deviation of 2.86% from Case III.

COMPARISON WITH OTHER GENERALIZED EQUATIONS OF STATE

In order to compare the capability of Eq. 4 to predict densities for substances other than argon with other generalized equations of state already presented in the literature, the compounds nitrogen, methane, carbon dioxide, and ammonia were once again utilized as test substances. These substances possess a diversity in their critical compressibility factors ranging from $z_c = 0.291$ to 0.242 and represent both polar and nonpolar molecules. For these substances, the conditions of Case III were applied to Eq. 4, as discussed previously.

The virial equation of state, first suggested by Kamerlingh Onnes (1901), has received considerable attention and can be developed through theoretical arguments if the potential functions for intermolecular interactions are known (Hirschfelder et al., 1954). Since information is available only for the evaluation of second and third virial coefficients, the virial equation of state was truncated to the third term. In this treatment, the generalized methods of Tsonopoulos (1974) and of Orbey and Vera (1983) were used for determining the second and third virial coefficients, respectively. When applied to nitrogen, methane, carbon dioxide, and ammonia for $\rho_R < 0.75$, the average *density deviations* were found to be 1.07% (73 points), 0.26% (411 points), 0.99% (307 points), and 2.36% (267 points), respectively. Application of the truncated virial

TABLE 4. PERCENT DEVIATIONS FOR DENSITY RESULTING FROM VALUES CALCULATED USING VARIOUS GENERALIZED EQUATIONS OF STATE AND CORRESPONDING VALUES FROM THE LITERATURE FOR NITROGEN, METHANE, CARBON DIOXIDE AND AMMONIA

	Nitrogen ($z_c = 0.291$)			Methane ($z_c = 0.289$)			Carbon Dioxide ($z_c = 0.275$)			Ammonia ($z_c = 0.242$)		
	Points	Avg.	Max.	Points	Avg.	Max.	Points	Avg.	Max.	Points	Avg.	Max.
Truncated Virial Equation of State												
$\rho_R \geq 2.00$	103	75.94		142	104.1		94	35.78		160	33.50	
$2 > \rho_R \geq 1$	39	6.83		125	6.11		64	10.30		66	16.10	
$1 > \rho_R \geq 0.75$	4	2.56		68	0.83		20	2.34		16	12.03	
$0.75 > \rho_R \geq 0.10$	50	1.30		375	0.28		140	1.26		116	4.50	
$0.10 > \rho_R$	23	0.59		36	0.10		167	0.76		151	0.71	
CF	12	110.3		42	150.6		8	121.4		6	78.07	
CP	2	22.34		4	5.16		2	17.79		2	29.68	
Total	233	40.96	273.5	792	27.85	633.9	495	10.87	413.6	517	15.04	262.0
Total for $\rho_R < 0.75$	73	1.07	7.29	411	0.26	6.40	307	0.99	3.87	267	2.36	21.82
Modified Redlich-Kwong Equation of State												
$\rho_R \geq 2.00$	103	3.18		142	1.14		94	2.09		160	17.59	
$2 > \rho_R \geq 1$	39	1.64		125	2.09		64	2.69		66	16.04	
$1 > \rho_R \geq 0.10$	54	1.19		443	0.40		160	6.98		132	6.71	
$0.10 > \rho_R$	23	0.59		36	0.14		167	0.88		151	0.81	
CF	12	2.25		42	1.26		8	3.28		6	12.82	
CP	2	1.10		4	6.16		2	3.71		2	13.66	
Total	233	2.14	9.90	792	0.86	9.36	495	3.36	383.2	517	9.65	28.95
Hirschfelder-Buehler-McGee-Sutton Equation of State												
$\rho_R \geq 2.00$	103	0.60		142	0.94		94	1.21		160	3.94	
$2 > \rho_R \geq 1$	39	0.91		125	1.50		64	2.45		66	9.86	
$1 > \rho_R \geq 0.10$	54	1.14		443	0.78		160	2.53		132	5.58	
$0.10 > \rho_R$	23	0.48		36	0.41		167	0.78		151	0.89	
CF	12	0.57		42	0.92		8	0.29		6	1.84	
CP	2	2.51		4	2.53		2	0.43		2	3.90	
Total	233	0.78	5.03	792	0.92	3.89	495	1.64	7.71	517	4.20	152.8
Equation 4 Case III (see Table 3)												
Total	233	1.17	5.21	792	0.50	3.14	495	2.86	14.10	517	3.90	17.59

CF Region: $T_R \leq 1.0$, $P_R \leq 2.0$ and $\rho_R \geq 2.00$

CP Region: $0.998 < T_R < 1.07$, $1.0 \leq P_R \leq 1.5$ and $0.80 \leq \rho_R \leq 1.4$

equation of state above $\rho_R = 0.75$ is not recommended, because higher order terms should be included. However, in order to obtain a basis for comparison, the application of this truncated virial equation of state was extended to higher densities. The average deviations obtained from this extended approach increase dramatically and are presented for each substance in Table 4.

Reid and Sherwood (1966) present a modification of the Redlich-Kwong equation of state, which, in its modified form, is applicable over wide conditions of temperature and pressure. This equation contains 25 constants and is of a generalized form. When applied to nitrogen, methane, carbon dioxide, and ammonia, average density deviations of 2.14% (233 points), 0.86% (792 points), 3.36% (495 points), and 9.65% (517 points) were obtained, respectively. Table 4 summarizes the deviations resulting from this modified Redlich-Kwong equation of state.

The equation of state proposed by Hirschfelder et al. (1958) has also been included in these comparisons. Their method requires the division of the PVT surface into three regions, where different relationships are associated with each region. For the development of the parameters of this equation of state, they utilized PVT data for nitrogen, carbon dioxide, and ammonia, which represent three of the four test substances included in the current study. Using the approach outlined by Hirschfelder et al. (1958), the average density deviations were found to be 0.78% (233 points) for nitrogen, 0.92% (792 points) for methane, 1.64% (495 points) for carbon dioxide, and 4.20% (517 points) for ammonia. These deviations are summarized in Table 4.

An overall examination of density deviations shows that the Hirschfelder-Buehler-McGee-Sutton equation of state represents an improvement over the truncated virial relationship and the modified Redlich-Kwong expression. However, the results indicate that Eq. 4, in its present form, performs better for the prediction of densities for methane and ammonia and falls somewhat short for the prediction of values for nitrogen and carbon dioxide, when compared with the equation proposed by Hirschfelder et al. (1958).

SUMMARY AND CONCLUSIONS

PVT data available in the literature for argon ($z_c = 0.2933$) have been thoroughly examined and used to develop an equation of state of the form

$$\pi = \alpha\tau + \beta\left[\psi + \frac{\tau}{\tau + 1}\right]\frac{\tau}{\tau + 1}$$

where π and τ are dimensionless excess pressure and temperature variables and parameters α, β, and ψ are only functions of density. This relationship satisfies the limiting conditions at high temperatures and at low densities. For 2,601 selected measurements of argon this equation of state reproduces pressures and densities with average deviations of 0.97% and 0.48%, respectively. The BWR equation of state has been included by testing it within its fitting domain, which involved 739 experimental points yielding average deviations of 0.44% and 0.48% for pressure and density, respectively, compared to 0.35% and 0.38% obtained from the equation of state presented in this investigation. In addition, the equation of Stewart et al. (1981), which contains 34 adjustable parameters, has also been used to calculate values for the 2,601 selected measurements, which produced average deviations of 0.82% and 0.36% for pressure and density, respectively.

The equation of state resulting from this study was applied in a generalized manner to calculate densities for nitrogen ($z_c = 0.291$), methane ($z_c = 0.289$), carbon dioxide ($z_c = 0.275$), and ammonia ($z_c = 0.242$). Using generalized correlations available in the literature for vapor pressures and saturated vapor and liquid densities, this equation reproduces corresponding experimental measurements with average density deviations of 1.17% (233 points) for nitrogen, 0.50% (792 points) for methane, 2.86% (495 points) for carbon dioxide, and 3.90% (517 points) for ammonia. Additional comparisons were made using three generalized PVT relationships available in the literature. A three-term truncated virial equation of state and the modified Redlich-Kwong equation of state yielded overall average deviations higher than those obtained from the generalized expression of Hirschfelder et al. (1958) and Eq. 4. The generalized approach of Hirschfelder et al. proves somewhat better in predicting densities for nitrogen and carbon dioxide, while Eq. 4 yields slightly better results for methane and ammonia. These comparisons indicate that Eq. 4 is adaptable to the generalized prediction of the PVT behavior for single component systems.

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NOTATION

a,b,c = constants for Eq. 15
P = pressure, kPa
P_c = critical pressure, kPa
P_R = reduced pressure, P/P_c
P_R^0 = reduced vapor pressure associated with density isometric
P_t = triple point pressure, kPa
R = gas constant
T = temperature, K
T_b = normal boiling point, K
T_c = critical temperature, K
T_R = reduced temperature, T/T_c
T_R^0 = reduced saturated temperature associated with density isometric
T_t = triple point temperature, K
v = molar volume, m^3/kg·mol
v_c = critical molar volume, m^3/kg·mol
z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α,β,ψ = density-dependent functions, Eq. 4
π = excess pressure, $P_R - P_R^0$
ρ = density, kg/m^3
ρ_c = critical density, kg/m^3
ρ_R = reduced density, ρ/ρ_c
ρ_t^ℓ = liquid density at triple point, kg/m^3
ρ_t^s = solid density at triple point, kg/m^3
ρ_t^v = vapor density at triple point, kg/m^3
τ = excess temperature, $T_R - T_R^0$
τ_i = excess temperature at inflection point, Eq. 8

LITERATURE CITED

Angus, S., and B. Armstrong, eds., *International Thermodynamic Tables of the Fluid State, Argon, 1971*, Butterworth & Co., London (1972).

Baxter, G. P., and H. W. Starkweather, "The Density, Compressibility and Atomic Weight of Argon. II.," *Proc. Natl. Acad. Sci. U.S.*, **15**, 441 (1929).

Blancett, A. L., K. R. Hall, and F. B. Canfield, "Isotherms for the He-Ar System at 50°C, 0°C, and −50°C up to 700 Atm," *Physica*, **47**, 75 (1970).

Bridgman, P. W., "The Melting Curves and Compressibilities of Nitrogen and Argon," *Proc. Am. Acad. Arts and Sci.*, **70**, 1 (1935).

Byrne, R., and G. Thodos, "The P.V.T.-Behavior of Diatomic Substances in Their Gaseous and Liquid States," *AIChE J.*, **7**, 185 (1961).

Campbell, S. W., "The Saturated Liquid Densities of Polar and Nonpolar Substances," M.S. Thesis, Northwestern Univ., Evanston, IL (1983).

Costolnick, J. J., and G. Thodos, "A Reduced Equation of State for Gaseous and Liquid Substances," *AIChE J.*, **9**, 269 (1963).

Crawford, R. K., and W. B. Daniels, "Equation-of-State Measurements in Compressed Argon," *J. Chem. Phys.*, **50**, 3171 (1969).

Din, F., ed., *Thermodynamic Functions of Gases*, Butterworths Scientific Publications, London (1956).

Dingrani, J., "The PVT Behavior of Methane: Extension of van der Waals Equation of State in the Compressed Gaseous and Liquid Regions," M.S. Thesis, Northwestern Univ. (1970).

Edwards, M. N. B., and G. Thodos, "Prediction of Saturated Vapor Densities for Nonpolar Substances," *J. Chem. Eng. Data*, **19**, 14 (1974).

Gielen, H., V. Jansoone, and O. Verbeke, "Application of an Empirical Equation of State to the Critical Region of Methane and Argon," *J. Chem. Phys.*, **59**, 5763 (1973).

Gómez-Nieto, M., and G. Thodos, "Generalized Vapor Pressure Behavior of Substances Between Their Triple Points and Critical Points," *AIChE J.*, **23**, 904 (1977).

Gosman, A. L., R. D. McCarty, and J. G. Hust, "Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres," *Natl. Stand. Ref. Data Series—NBS 27* (1969).

Groenier, W. S., and G. Thodos, "Pressure-Volume-Temperature Behavior of Ammonia in the Gaseous and Liquid States," *J. Chem. Eng. Data*, **5**, 285 (1960).

Hirschfelder, J. O., R. J. Buehler, H. A. McGee, Jr., and J. R. Sutton, "Generalized Equation of State for Gases and Liquids," *Ind. Eng. Chem.*, **50**, 375 (1958); erratum, *Ind. Eng. Chem., Fund.*, **1**, 224 (1962).

Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).

Holborn, L., and J. Otto, "Concerning the Isotherms of Some Gases up to 400°C and Their Significance for the Gas Thermometer," *Z. Physik*, **23**, 77 (1924a).

———, "Concerning the Isotherms of Helium, Nitrogen and Argon Below 0°C," *Z. Physik*, **30**, 320 (1924b).

Holborn, L., and H. Schultze, "Concerning the Pressure Balance and the Isotherms of Air, Argon and Helium Between 0 and 200°C," *Ann. Physik*, **47**, 1089 (1915).

Kamerlingh Onnes, H., "Expression of the Equation of State of Gases and Liquids by Means of Series," *Commun. Phys. Lab. Univ. Leiden, No. 71*, 1 (1901).

Kamerlingh Onnes, H., and C. A. Crommelin, "Isotherms of Monatomic Gases and of Their Binary Mixtures. VII. Isotherms of Argon Between +20°C and −150°C," *Commun. Phys. Lab. Univ. Leiden, No. 118b*, 13 (1910).

Kennedy, J. T., and G. Thodos, "Reduced Density Correlation for Carbon Dioxide," *J. Chem. Eng. Data*, **5**, 293 (1960).

Lecocq, A., "Experimental Determination of the Equation of State of Argon up to 1000°C and 1000 kg/cm^2," *J. Rech. Centre Natl. Rech. Sci. Lab. Bellevue (Paris)*, **11**, 55 (1960).

Liebenberg, D. H., R. L. Mills, and J. C. Bronson, "High-Pressure Apparatus for Simultaneous Adiabatic and Isothermal Compressibility Measurements: Data on Argon to 13 Kbar," *J. Appl. Phys.*, **45**, 741 (1974).

Lippold, H., "Isothermal Compressibility and Density of Liquid Argon and Neon up to Pressures of 1000 kg/cm^2," *Cryogenics*, **9**, 112 (1969).

Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, "Generalized Thermodynamic Properties of Pure Fluids," *Univ. Wisconsin Eng. Exp. Sta. Rept. 4* (1955).

Masson, I., and L. G. F. Dolley, "The Pressures of Gaseous Mixtures," *Proc. Roy. Soc. London*, **A103**, 524 (1923).

Meissner, H. P., and R. Seferian, "P-V-T Relations of Gases," *Chem. Eng. Prog.*, **47**, 579 (1951).

Michels, A., J. M. Levelt, and W. de Graaff, "Compressibility Isotherms of Argon at Temperatures Between −25°C and −155°C, and at Densities up to 640 Amagat (Pressures up to 1050 Atmospheres)," *Physica*, **24**, 659 (1958).

Michels, A., Hub. Wijker, and Hk. Wijker, "Isotherms of Argon Between 0°C and 150°C and Pressures up to 2900 Atmospheres," *Physica*, **15**, 627 (1949).

Morris, E. C., and R. G. Wylie, "Accurate Method for High Pressure PVT Measurements and Results for Argon for $T = -20$ to $+35$°C and p in the Range 200–480 MPa," *J. Chem. Phys.*, **73**, 1359 (1980).

Orbey, H., and J. H. Vera, "Correlation for the Third Virial Coefficient Using T_c, P_c and ω as Parameters," *AIChE J.*, **29**, 107 (1983).

Polyakov, E. V., and T. S. Tsiklis, "Molar Volumes and Thermodynamic Properties of Argon at Pressures of 10,000 Atm and Temperatures up to 400°C," *Zh. Fiz. Khim.*, **41**, 2370 (1967).

Provine, J. A., and F. B. Canfield, "Isotherms for the He-Ar System at −130, −115, and −90°C up to 700 Atm," *Physica*, **52**, 79 (1971).

Rabinovich, V. A., L. A. Tokina, and V. M. Berezin, "Experimental Determination of the Compressibility of Neon and Argon at 300 to 720°K for Pressures up to 500 Bar," *Teplofiz. Vys. Temp.*, **8**, 789 (1970); English translation by the Consultants Bureau, a division of Plenum Publishing Corp., New York, 745 (1971).

Ramsay, W., and M. W. Travers, "II. Argon and Its Companions," *Phil. Trans. Roy. Soc. London*, **A197**, 47 (1901).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd ed., McGraw-Hill, New York, pp. 75–77 (1966).

Robertson, S. L., S. E. Babb, Jr., and G. J. Scott, "Isotherms of Argon to 10,000 Bars and 400°C," *J. Chem. Phys.*, **50**, 2160 (1969); erratum, *J. Chem. Phys.*, **51**, 3152 (1969).

Roder, H. M., R. D. McCarty, and V. J. Johnson, "Saturated Liquid Densities of Oxygen, Nitrogen, Argon, and Parahydrogen," *NBS Tech. Note 361* (1968).

Rogovaya, I. A., and M. G. Kaganer, "The Compressibility of Argon at Low Temperatures up to 200 Atmospheres," *Russ. J. Phys. Chem.*, **35**, 1049 (1961).

Sorokin, V. A., and Y. P. Blagoi, "Investigation of Isothermal Compressibility of Liquid Argon and Methane up to 500 Atm at Low Temperatures," *Termodinamicheskie i Termokimicheskie Konstanty*, 97 (1970).

Stewart, R. B., R. T. Jacobsen, J. H. Becker, C. J. Teng, and P. K. K. Mui, "Thermodynamic Properties of Argon from the Triple Point to 1200 K with Pressures to 1000 MPa," *Symp.*, Thermophysical Properties, NBS, Gaithersburg, MD (1981).

Streett, W. B., and L. A. K. Staveley, "Experimental Study of the Equation of State of Liquid Argon," *J. Chem. Phys.*, **50**, 2302 (1969).

Tanner, C. C., and I. Masson, "The Pressures of Gaseous Mixtures," *Proc. Roy. Soc. London*, **A126**, 268 (1930).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **20**, 263 (1974).

Van Itterbeek, A., and O. Verbeke, "Density of Liquid Nitrogen and Argon as a Function of Pressure and Temperature," *Physica*, **26**, 931 (1960).

Van Itterbeek, A., O. Verbeke, and K. Staes, "Measurements on the Equation of State of Liquid Argon and Methane up to 300 kg cm^{-2} at Low Temperatures," *Physica*, **29**, 742 (1963).

Van Witzenburg, W., and J. C. Stryland, "Density Measurements of Compressed Solid and Liquid Argon," *Can. J. Phys.*, **46**, 811 (1968).

Whalley, E., "Thermodynamic Properties of Argon in the Temperature Range −100 to +600°C and Pressure Range 0 to 80 Atmospheres," *Can. J. Tech.*, 33, 111 (1955).

Whalley, E., Y. Lupien, and W. G. Schneider, "The Compressibility of Gases," *Can. J. Chem.*, **31**, 722 (1953).

Wilsak, R. A., "The Complete PVT-Behavior of Fluid Argon: Graphical Representations and Empirical Models Culminating in a New Equation of State," M.S. Thesis, Northwestern Univ. (1982).

Wilsak, R. A., and G. Thodos, "Critical Assessment of Four Vapor Pressure Functions over the Complete Vapor-Liquid Coexistence Region," *Ind. Eng. Chem., Fund.*, **23**, 75 (1984a).

Wilsak, R. A., and G. Thodos, "The Coexistence Behavior of the Vapor-Liquid-Solid Equilibrium States for Argon," *J. Chem. Eng. Data*, **29**, 255 (1984b).

Zudkevitch, D., and T. G. Kaufmann, "Application of the Benedict-Webb-Rubin Equation of State to Argon," *AIChE J.*, **12**, 577 (1966).

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