

A scaled fundamental equation for the thermodynamic properties of carbon dioxide in the critical region

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A scaled fundamental equation is presented for the thermodynamic properties of carbon dioxide in the critical region. The equation is constructed by combining earlier experimental pressure data of Michels and co-workers with new specific heat data obtained by one of the authors and represents the thermodynamic properties of carbon dioxide in the critical region at temperatures from 301.15 to 323 K and at densities from 290 to 595 kg/m³.

I. INTRODUCTION

The singular asymptotic behavior of the thermodynamic properties of fluids near the critical point satisfies scaling laws with universal critical exponents and scaling functions. Several attempts have been made to formulate representative equations for the thermodynamic properties of carbon dioxide in the critical region that incorporate the scaling laws.¹⁻⁶ However, the previous equations contained effective critical exponent values that differed from the universal critical exponent values predicted by theory.⁷ This deficiency can be repaired by extending the asymptotic equations so as to include at least one correction-to-scaling term as predicted by the renormalization-group theory of critical phenomena and by incorporating scaling fields that are combinations of the physical field variables in accordance with the revised scaling of the decorated lattice gas.⁸⁻¹⁰

Our interest in formulating an accurate scaled fundamental equation for carbon dioxide in the critical region was motivated by the fact that new precise experimental data for the isochoric specific heat of CO₂ have become available as measured by one of the authors.¹¹ These new specific-heat data replace the specific-heat data earlier reported by Lipa *et al.*¹²

There exists an increased interest in the thermodynamic properties of CO₂, in part because of the use of CO₂ as a solvent for supercritical extraction and in enhanced oil-recovery programs. To meet the demand for representative equations that yield the thermodynamic properties of CO₂, Ely *et al.* have recently developed a global fundamental equation for CO₂ valid in a large range of temperatures and densities.¹³ Like most fundamental equations in the literature, the global equation of Ely *et al.* remains analytic at the critical point and, therefore, fails to accommodate the divergent critical behavior of the isochoric specific heat. The re-

sults presented in this paper complement the work of Ely *et al.* by providing a fundamental equation which is accurate in the close vicinity of the critical point.

II. REVISED AND EXTENDED LINEAR MODEL

Fluids near the vapor-liquid critical point are expected to belong to the universality class of three-dimensional Ising-like systems.^{14,15} The renormalization-group theory of critical phenomena predicts that near the critical point the thermodynamic potential F of a spin system represented by a Landau-Ginzburg-Wilson Hamiltonian can be represented by an expansion of the form¹⁶

$$F = F_0 + |\tau|^{\beta(\delta+1)} f_0 \left(\frac{h}{|\tau|^{\beta\delta}} \right) + u_1 |\tau|^{\beta(\delta+1) + \Delta_1} f_1 \left(\frac{h}{|\tau|^{\beta\delta}} \right) + \dots \quad (2.1)$$

Here β and δ are the exponents of the critical power laws that characterize the asymptotic behavior of the order parameter along the coexistence boundary and of the ordering field along the critical isotherm, while the exponent Δ_1 accounts for the nonanalytic behavior of the first correction to the asymptotic power-law behavior. The variables τ and h are relevant scaling fields that vanish at the critical point, and u_1 is the first irrelevant scaling field that approaches a finite value at the critical point. For spin systems, the thermodynamic potential F can be identified with the Gibbs free energy divided by $k_B T$, where k_B is Boltzmann's constant and T the temperature. The scaling fields τ , h , and u_1 and the background function F_0 are assumed to be analytic functions of the physical fields, temperature T , and magnetic field H , or, equivalently, $1/k_B T$ and $H/k_B T$.

To apply the theory to fluid systems, it is assumed that the potential F can be identified with the pressure P and the magnetic field H with the chemical potential μ as is the case for the analogy between Ising model and lattice gas.¹⁸ Specifically, we consider the potential P/T as a function of $1/T$

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and μ/T and write the expansion (2.1) in the form

$$\begin{aligned} \tilde{P} = & \tilde{P}_0(\tilde{T}, \tilde{\mu}) + |\tau|^{\beta(\delta+1)} f_0 \left(\frac{h}{|\tau|^{\beta\delta}} \right) \\ & + u_1 |\tau|^{\beta(\delta+1) + \Delta_1} f_1 \left(\frac{h}{|\tau|^{\beta\delta}} \right), \end{aligned} \quad (2.2)$$

truncating the expansion after the first correction-to-scaling term. Here we introduce the reduced quantities

$$\begin{aligned} \tilde{P} = & \frac{P}{T} \frac{T_c}{P_c}, \quad \tilde{T} = -\frac{T_c}{T}, \quad \tilde{\mu} = \frac{\mu}{T} \frac{\rho_c T_c}{P_c}, \\ \tilde{\rho} = & \frac{\rho}{\rho_c}, \quad \tilde{U} = \frac{U}{P_c V}, \end{aligned} \quad (2.3)$$

where ρ is the density, V the volume, and U the internal energy, while T_c , P_c , and ρ_c are the values of T , P , and ρ at the critical point. In addition, we define the variables

$$\Delta\tilde{T} = \tilde{T} + 1, \quad \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}), \quad (2.4)$$

chosen such that $\Delta\tilde{T} = 0$ and $\Delta\tilde{\mu} = 0$ at the critical point. The functions $\tilde{\mu}_0(\tilde{T})$ and $\tilde{P}_0(\tilde{T}, \tilde{\mu})$ are analytic functions which we represent by truncated Taylor expansions in powers of $\Delta\tilde{T}$ and of $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$, respectively:

$$\tilde{\mu}_0(\tilde{T}) = \tilde{\mu}_c + \sum_{i=1}^4 \tilde{\mu}_i (\Delta\tilde{T})^i, \quad (2.5)$$

$$\tilde{P}_0(\tilde{T}, \tilde{\mu}) = 1 + \sum_{i=1}^3 \tilde{P}_i (\Delta\tilde{T})^i + \Delta\tilde{\mu} + \tilde{P}_{11} \Delta\tilde{T} \Delta\tilde{\mu}. \quad (2.6)$$

The scaling fields τ , h , and u_1 are analytic functions of $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$. To first order

$$h = \Delta\tilde{\mu} - \tilde{\mu} - \tilde{\mu}_0(\tilde{T}), \quad (2.7)$$

$$\tau = \Delta\tilde{T} + c \Delta\tilde{\mu}, \quad (2.8)$$

while u_1 can be approximated by a constant. In the approximation considered here, $h = 0$ at coexistence and $\tilde{\mu}_0(\tilde{T})$ is to be interpreted as the saturation chemical potential for $\Delta\tilde{T} < 0$ or its analytic extension for $\Delta\tilde{T} > 0$. The system-dependent constant c in Eq. (2.8) accounts for the mixing of the $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$ variables in the effective scaling field τ for nonsymmetric systems. The potential \tilde{P} satisfies the differential relation

$$d\tilde{P} = \tilde{U} d\tilde{T} + \tilde{\rho} d\tilde{\mu} = \left(\tilde{U} + \tilde{\rho} \frac{d\tilde{\mu}_0}{d\tilde{T}} \right) d(\Delta\tilde{T}) + \tilde{\rho} d(\Delta\tilde{\mu}). \quad (2.9)$$

This relation enables one to obtain expressions for the various thermodynamic properties from the potential \tilde{P} .

To specify the fundamental equation, we need explicit expressions for the scaling functions f_0 and f_1 in Eq. (2.2). In practice, empirical closed-form expressions are used that conform to the asymptotic behavior and the symmetry of the Ising model; they require a transformation to parametric variables r and θ , where r measures a distance from the critical point and θ a location on a contour of constant r .^{7,19,20} A transformation commonly used is

$$h = ar^{\beta\delta}\theta(1 - \theta^2), \quad (2.10a)$$

$$\tau = r(1 - b^2\theta^2), \quad (2.10b)$$

where a and b are constants. At coexistence $h = 0$ and the values $\theta = \pm 1$ correspond to the two branches of the coex-

istence curve. The transformation (2.10) implies that the singular part $\Delta\tilde{P} = \tilde{P} - \tilde{P}_0(\tilde{T}, \tilde{\mu})$ of the potential \tilde{P} must depend on r and θ in such a way that

$$\left(\frac{\partial \Delta\tilde{P}}{\partial h} \right)_\tau = r^\beta [m_0(\theta) + r^\Delta m_1(\theta)]. \quad (2.11)$$

Since f_0 and f_1 in Eq. (2.1) are even in h , and hence even in θ , it follows that $m_0(\theta)$ and $m_1(\theta)$ must be odd in θ . The simplest assumption is to assume that $m_0(\theta)$ and $m_1(\theta)$ are proportional to θ :

$$m_0(\theta) = k_0\theta, \quad (2.12)$$

$$m_1(\theta) = k_1\theta. \quad (2.13)$$

The linear approximation (2.12) for $m_0(\theta)$ was originally introduced by Schofield *et al.*²¹ and defines the so-called linear model.⁷ The generalization Eq. (2.13) of the linear-model approximation to the first correction-to-scaling term was introduced by Balfour *et al.*^{8,22} With the equations (2.12) and (2.13) for $m_0(\theta)$ and $m_1(\theta)$ the scaled fundamental equation for the potential \tilde{P} becomes

$$\tilde{P} = \tilde{P}_0(\tilde{T}, \tilde{\mu}) + ar^{\beta(\delta+1)} [k_0 p_0(\theta) + k_1 r^\Delta p_1(\theta)], \quad (2.14)$$

where $p_0(\theta)$ and $p_1(\theta)$ are polynomials of the form

$$p_0(\theta) = p_{00} + p_{20}\theta^2 + p_{40}\theta^4, \quad (2.15)$$

$$p_1(\theta) = p_{01} + p_{21}\theta^2 + p_{41}\theta^4. \quad (2.16)$$

The coefficients p_{ji} are functions of the critical exponents β , δ , and Δ_1 and of the constant b^2 as presented in Table III of the Appendix. Equations for various thermodynamic properties derived from this potential are also presented in the Appendix.

For the universal critical exponents β , δ , and Δ_1 we have adopted the values

$$\beta = 0.325, \quad \delta = 4.82, \quad \Delta_1 = 0.50 \quad (2.17)$$

in good agreement with the theoretical values for these exponents.²³ The system-dependent constants that determine the scales of the fields h , τ , and u_1 are represented by the coefficients a , k_0 , and k_1 . However, universality of the scaling functions implies that the constant b^2 be universal. The renormalization-group theory indicates that the linear-model approximation (2.12) for $m_0(\theta)$ is not exact, but only correct up to order ϵ^2 , where $\epsilon = 4 - d$ with d the dimensionality of the system.²⁴⁻²⁷ However, with the choice

$$b^2 = 1.3757 \quad (2.18)$$

the linear model reproduces the ratios of the asymptotic power laws to within the numerical accuracy that these ratios are known theoretically.¹⁰ The linear model thus yields an adequate approximant for the asymptotic scaling behavior of the thermodynamic potential. The universal values used here for β , δ , Δ_1 , and b^2 are the same as previously adopted in the application of the revised and extended linear model to light steam,¹⁰ heavy steam,²⁸ isobutane,²⁹ and ethylene.^{30,31} Universality of the scaling function f_1 in Eq. (2.1) implies universal ratios for the amplitudes in the first correction term to the asymptotic power laws which also have been estimated from theory.^{23,27,32-35} As pointed out elsewhere, the extended linear-model approximation (2.13) for $m_1(\theta)$

implies ratios for these correction-to-scaling amplitudes that differ from the current theoretical predictions.²³ Hence, the extended linear model, while incorporating the asymptotic scaling behavior with considerable accuracy, only yields an order of magnitude estimate for the correction-to-scaling terms. A more complete treatment of the leading corrections to scaling would require the addition of a term of the form $h_1(\theta)r^{\Delta_1}$ in the expression (2.10a) for the scaling field h .³⁶

III. APPLICATION TO CARBON DIOXIDE

The scaled fundamental equation as defined in the preceding section contains the following system-dependent parameters: the critical parameters T_c , ρ_c , and P_c , the parameters a , k_0 , k_1 , and c which determine the relationship between the scaling fields and the physical variables, the parameters \tilde{P}_1 , \tilde{P}_2 , \tilde{P}_3 , and \tilde{P}_{11} which determine the analytic background in the pressure and the parameters $\tilde{\mu}_c$, $\tilde{\mu}_1$, $\tilde{\mu}_2$, $\tilde{\mu}_3$, and $\tilde{\mu}_4$ which determine the analytic background in the chemical potential. The values of these parameters obtained for CO₂ are presented in Table IV of the Appendix. The resulting fundamental equation represents the thermodynamic surface of CO₂ in the range of temperatures and pressures bounded by

$$\begin{aligned} 301.15 < T < 323 \text{ K}, \\ 290 < \rho < 595 \text{ kg/m}^3. \end{aligned} \quad (3.1)$$

To determine the values of the system-dependent parameters we have considered the accurate P - ρ - T measurements of Michels and co-workers^{37,38} and the new specific-heat data of Edwards.¹¹ The P - ρ - T data are comprised of data from two different experiments. In the critical region the major part of the pressure data are provided by the measurements of Michels *et al.*³⁸; these data are grouped in isotherms ranging from 276 to 313 K with densities ranging from about 168 to about 913 kg/m³ and pressures ranging from about 3.8 to about 10 MPa. Within the range specified by Eq. (3.1), there are also two isotherms, at 313 and 323 K measured by Michels *et al.* with a different experimental technique.³⁷ In the interpretation of P - ρ - T data of both experiments attention must be made to the temperature scale as discussed by Levelt Sengers *et al.*^{4,39} The thermometers of Michels *et al.* were purportedly calibrated by the P. T. R. in Berlin; the relationship of this calibration to the current international practical temperature scale (IPTS 68), T_{68} , can be represented by a constant temperature shift in the limited temperature range of validity of the scaled equation. We determined this temperature shift by requiring that the vapor-pressure measurements of Michels *et al.* agree with the vapor-pressure measurements obtained by Levelt Sengers and Chen³⁹ in 1972. This procedure yielded a shift of

$$T_{68} = T_{\text{Michels}} - 0.035 \text{ K}. \quad (3.2)$$

In addition, we determined the temperature shift necessary to make the pressures of Michels *et al.* at the critical isochore coincide with the pressure measurements of Levelt Sengers and Chen above the critical temperature. Within statistical

uncertainty the latter procedure yielded the same temperature shift.

Pressure data alone do not accurately determine the location of the critical point.^{10,40} We therefore first determined the critical temperature T_c from an analysis of the C_v data of Edwards with the result¹¹

$$T_c = 304.107 \text{ K}. \quad (3.3)$$

This value of T_c , from the C_v and thermal time constant data of Edwards, is 0.02 K lower than the value $T_c = 304.127$ K determined by Moldover from a visual observation of the temperature of meniscus disappearance.⁴¹ We do not know which of the two values for T_c is more accurate on an absolute basis. A case can be made that the C_v data yield an estimate for T_c averaged over a finite albeit small volume, while the value reported by Moldover is based on a local observation. Generally, the value of T_c is also known to be very sensitive to impurities.

The parameters ρ_c , P_c , a , k_0 , k_1 , c , \tilde{P}_1 , \tilde{P}_2 , \tilde{P}_3 , and \tilde{P}_{11} were determined by fitting the equation for the pressure to the experimental pressure data of Michels *et al.* In performing the analysis we assumed $\sigma_p = 0.0001$ MPa, $\sigma_T = 0.005$ K, $\sigma_\rho = 10^{-4}\rho$ for the errors in the experimental pressures, temperatures, and densities, estimated from the description of the experimental procedure and the degree of consistency between the two sets of data of Michels *et al.*^{37,38} The equation for the pressure with

$$P_c = 7.3721 \text{ MPa}, \quad \rho_c = 467.69 \text{ kg/m}^3, \quad (3.4)$$

reproduces the experimental pressure data in the range specified by Eq. (3.1) with a standard chi square of 1.96.

In Figures 1 and 2 we represent a comparison between the experimental pressure data of Michels and co-workers^{37,38} and the pressures calculated from the scaled fundamental equation presented in this paper. In the same figures we have included a comparison with the pressures calculated from the analytic equation of Ely *et al.*¹³ The differences $\Delta = (P_{\text{exp}} - P_{\text{calc}})/P_{\text{exp}}$ between the pressures cal-

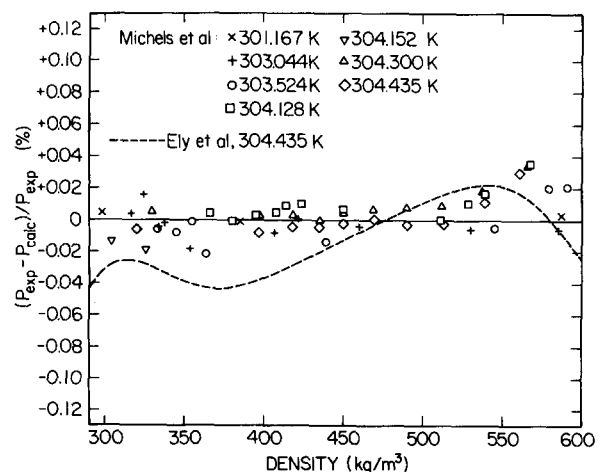


FIG. 1. Percentage differences between the experimental pressure data of Michels *et al.* and the values calculated from the scaled fundamental equation at room temperatures between 301.167 and 304.435 K. The dashed curve corresponds to pressures calculated from the analytic equation of Ely *et al.*

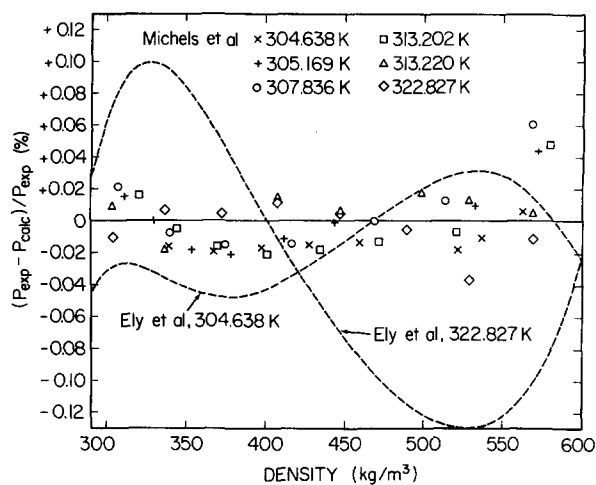


FIG. 2. Percentage differences between the experimental pressure data of Michels *et al.* and the values calculated from the scaled fundamental equation at temperatures between 304.638 and 322.827 K. The dashed curves correspond to pressures calculated from the analytic equation of Ely *et al.*

culated from our fundamental equation and the experimental pressures of Michels *et al.* have an average magnitude $\langle |\Delta| \rangle = 0.012\%$ in the range specified by Eq. (3.1). In the same range of densities and temperatures the analytic equation of Ely *et al.* shows deviations with an average magnitude $\langle |\Delta| \rangle = 0.026\%$. The global equation of Ely *et al.* does not reproduce the pressures of Michels *et al.* in the critical region within experimental precision. However, the deviations are still small if one considers the fact that Ely *et al.* did not use the experimental pressure data of Michels *et al.* in determining the values of the parameters in their global equation.

New P - ρ - T data for CO_2 have recently been obtained by Haynes.⁴² Two of the isotherms measured by Haynes include data points inside the range of validity of the scaled equation, namely at 310 and at 320 K. A comparison of the calculated pressure values with the experimental pressures of Haynes is presented in Fig. 3. The deviations of these experimental pressures of Haynes from our scaled funda-

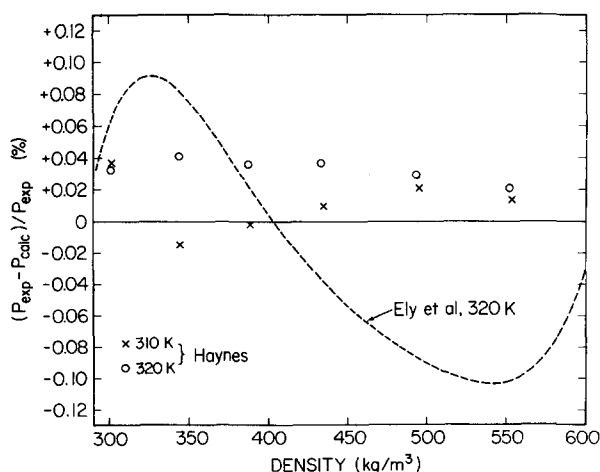


FIG. 3. Percentage differences between the experimental pressure data of Haynes and the values calculated from the scaled fundamental equation. The dashed curve corresponds to pressures calculated from the analytic equation of Ely *et al.*

mental equation have an average magnitude $\langle |\Delta| \rangle = 0.03\%$, to be compared with the average $\langle |\Delta| \rangle = 0.05\%$ for the equation of Ely *et al.*

The coefficients μ_2 , μ_3 , and μ_4 in Eq. (2.5) specify an analytic background contribution to the specific heat and are, therefore, determined from a fit to the experimental C_v data. Edwards has obtained almost 6000 measurements¹¹ in the critical region at two isochores with $\rho = 467.8$ and 434.39 kg/m^3 at temperatures ranging from 287 to 313 K. Magee and Ely⁴³ have also recently reported an extensive set of C_v data of compressed CO_2 . The data of Magee and Ely do not approach the critical point sufficiently close to specify the critical behavior of the specific heat, but they yield detailed information on the magnitude of C_v for CO_2 outside the critical region. The specific-heat data, as originally reported by Edwards, do not reduce to the specific-heat data found by Magee and Ely outside the critical region. The latter data are consistent with the C_v values earlier reported by Michels and de Groot⁴⁴ and by Michels and Strijland.⁴⁵ The difficulty with the work of Edwards is that the heat capacity of the empty calorimeter was never measured. Instead, the heat capacity of the empty calorimeter was estimated from its known composition. We assumed that the discrepancy between the data of Edwards and the other literature data outside the critical region is due to insufficient accuracy in the knowledge of the heat capacity of the empty calorimeter. We therefore redetermined the heat capacity of the empty calorimeter by requiring that the specific heat data of Edwards should coincide with those of Magee and Ely outside the critical region. Since the C_v data of Edwards and of Magee and Ely were obtained at substantially different densities, this goal cannot be easily accomplished by comparing the experimental data directly. Since the equation of Ely was developed with the C_v data of Magee and Ely as input, we demanded instead that the specific heat calculated from the scaled equation agree with the specific heat calculated from the analytic equation of Ely at a matchpoint at the boundary of the region (3.1) of the validity of the scaled equation. The matchpoint chosen for this purpose corresponds to a temperature T_0 and a density ρ_0 such that

$$T_0 = 322.827 \text{ K}, \quad \rho_0 = 404.5 \text{ kg/m}^3, \quad (3.5)$$

where both equations yield an identical pressure $P_0 = 10.1136 \text{ MPa}$. This procedure implied that a constant value of 9.64 J/mol K had to be subtracted from the data as reported originally by Edwards.

In determining $\tilde{\mu}_2$, $\tilde{\mu}_3$, and $\tilde{\mu}_4$ from the corrected C_v data of Edwards, we used the error estimates $\sigma_T = 0.005 \text{ K}$ and $\sigma_\rho = 0.05 \text{ kg/m}^3$ for temperature and density; for σ_{C_v} we used the standard deviations found by Edwards from spline fits to the various experimental runs,¹¹ except that we adopted a minimum error of 0.25%. With the values thus found for $\tilde{\mu}_2$, $\tilde{\mu}_3$, and $\tilde{\mu}_4$, the scaled equation reproduces the experimental C_v data of Edwards with a standard chi square of 3.8. The actual experimental and calculated C_v data are shown in Figs. 4 and 5, while a plot of the deviations between experimental and calculated C_v values relative to the estimated error is shown in Fig. 6. As can be seen from Fig. 6, the deviations are not completely random, although most data

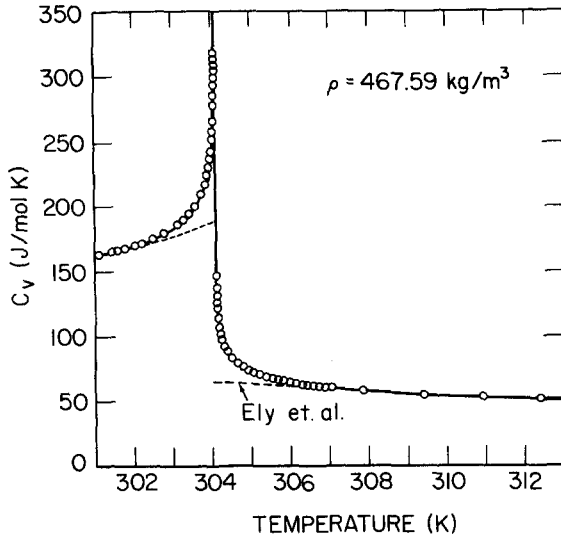


FIG. 4. Specific heat C_v as a function of temperature at $\rho = 467.59 \text{ kg/m}^3$. The data points are experimental values of Edwards, the solid curve represents C_v values calculated from the scaled fundamental equation, and the dashed curve indicates C_v values calculated from the analytic equation of Ely *et al.*

points are within three standard deviations. In particular, we think that the systematic trends noticeable at temperatures below the critical temperature indicate a limitation of our linear model in its capability of fully accounting for corrections to scaling and lack of vapor liquid symmetry. While our linear model has been demonstrated to reproduce the thermodynamic properties of fluids in the supercritical region,^{23,46} it has always been difficult to cover a significant range below the critical temperature.^{10,28-31}

It is possible to reduce the standard chi square to 1.9 by fitting the experimental C_v data to our scaled fundamental equation with all parameters left free. However, the resulting

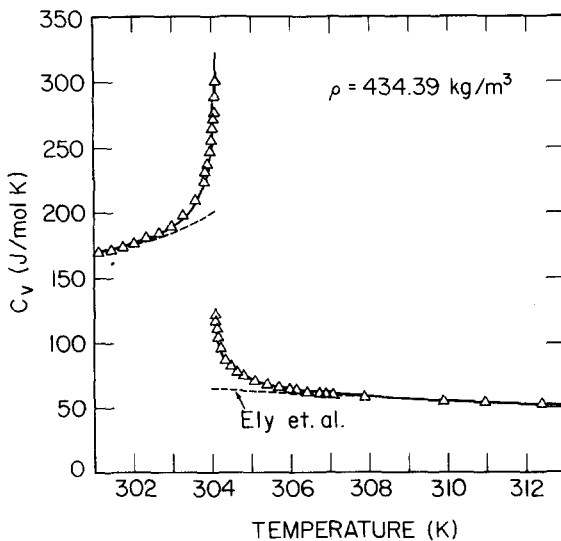


FIG. 5. Specific heat C_v as a function of temperature at $\rho = 434.39 \text{ kg/m}^3$. The data points are experimental values of Edwards, the solid curve represents C_v values calculated from the scaled fundamental equation, and the dashed curve indicates C_v values calculated from the analytic equation of Ely *et al.*

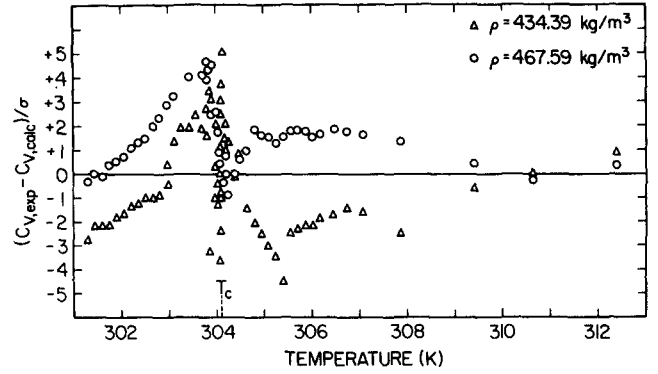


FIG. 6. Deviations of the experimental C_v values of Edwards from the C_v values calculated with our scaled equation relative to the estimated error σ .

fundamental equation does not yield a satisfactory representation of the experimental pressure data. The reason is that the C_v data of Edwards are limited to two densities close to ρ_c and therefore do not specify the density dependence of the thermodynamic properties reliably. The equation, presented in this paper, is the best we can obtain if we want to maintain consistency between the C_v data and the available pressure data. The deviations $\Delta = (C_{v,\text{expt}} - C_{v,\text{calc}}) / C_{v,\text{expt}}$ of the experimental C_v data from those calculated with the scaled equation have an average magnitude $\langle |\Delta| \rangle = 1.5\%$. In Figs. 4 and 5 we also indicate the C_v values calculated from the equation of Ely *et al.*¹³ As any analytic equation, the equation of Ely *et al.* does not reproduce the actual divergent behavior of the specific heat near the critical point. Away from the critical point, scaled and analytic equations represent the experimental C_v data with comparable quality.

As mentioned earlier, the new C_v data of Magee and Ely⁴³ were primarily obtained at temperatures and densities outside the critical region. A comparison with the few experimental C_v data of Magee and Ely inside the region of validity (3.1) of our scaled equation is presented in Fig. 7. Our scaled equation and the equation of Ely *et al.* yield a similar representation of these data.

Finally, the coefficients $\tilde{\mu}_c$ and $\tilde{\mu}_1$ determine the zero-point values of enthalpy and entropy. Specifically, the enthalpy zero fixes $\tilde{\mu}_1$ and the entropy zero fixes $\tilde{\mu}_c + \tilde{\mu}_1$ and hence $\tilde{\mu}_c$. We determined these parameters by requiring that the enthalpy and entropy calculated from the scaled equation agree with those of the global equation of Ely *et al.* at the matchpoint specified by Eq. (3.5).

The linear model implies the following asymptotic power laws along the critical isochore $\rho = \rho_c$, the coexistence curve $\rho = \rho_{\text{cxc}}$ and the critical isotherm $T = T_c$:

$$\tilde{C}_v / \tilde{T}^2 = A + |\Delta \tilde{T}|^{-\alpha} \quad \text{for } \rho = \rho_c, \quad T > T_c, \quad (3.6a)$$

$$C_v / \tilde{T}^2 = A - |\Delta \tilde{T}|^{-\alpha} \quad \text{for } \rho = \rho_c, \quad T < T_c, \quad (3.6b)$$

$$\tilde{\rho} - 1 = \pm B |\Delta \tilde{T}|^\beta \quad \text{for } \rho = \rho_{\text{cxc}}, \quad T < T_c, \quad (3.7)$$

$$\tilde{\chi} = \Gamma^+ |\Delta \tilde{T}|^{-\gamma} \quad \text{for } \rho = \rho_c, \quad T > T_c, \quad (3.8a)$$

$$\tilde{\chi} = \Gamma^- |\Delta \tilde{T}|^{-\gamma} \quad \text{for } \rho = \rho_{\text{cxc}}, \quad T < T_c, \quad (3.8b)$$

$$\Delta \tilde{\mu} = \pm D |\tilde{\rho} - 1|^\delta \quad \text{for } T = T_c, \quad (3.9)$$

with

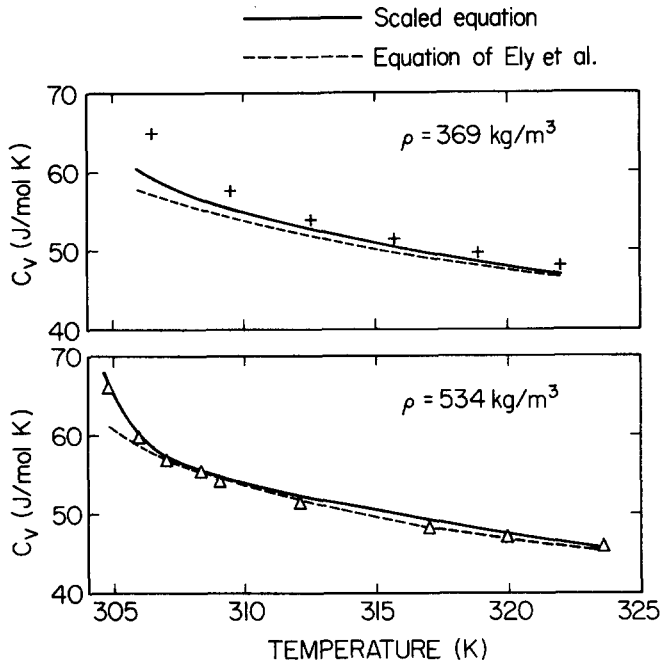


FIG. 7. Specific heat C_v as a function of temperature at two isochores corresponding to $\rho = 369 \text{ kg/m}^3$ and $\rho = 534 \text{ kg/m}^3$. The data points are experimental values of Magee and Ely, the solid curves represent C_v values calculated from the scaled fundamental equation, and the dashed curves indicate C_v values calculated from the analytic equation of Ely *et al.*

$$\alpha = 2 - \beta(\delta + 1) = 0.1085, \quad \gamma = \beta(\delta - 1) = 1.2415 \quad (3.10)$$

and with^{7,47,48}

$$A^+ = ak_0 \beta(\delta + 1)(\beta\delta + 1 - \beta)(2 - \beta\delta - \beta)p_{00} = 3.06, \quad (3.11a)$$

$$A^- = A^+ (p_{00} + p_{20} + p_{40})/p_{00}(b^2 - 1)^{\beta(\delta + 1)} = 5.75, \quad (3.11b)$$

$$B = k_0/(b^2 - 1)^\beta = 1.68, \quad (3.12)$$

$$\Gamma^+ = k_0/a = 0.052, \quad (3.13a)$$

$$\Gamma^- = \Gamma^+(b^2 - 1)^{\beta\delta - \beta - 1} [1 - b^2(1 - 2\beta)]/2 = 0.0106, \quad (3.13b)$$

$$D = a(b^2 - 1)b^{\delta - 3}/k_0^\delta = 4.51. \quad (3.14)$$

The values $B = 1.68$ and $\Gamma^+ = 0.052$ may be compared with the values $B = 1.59 \pm 0.03$ and $\Gamma^+ = 0.046 \pm 0.002$ earlier determined by Sengers and Moldover from an analysis of interferometric compressibility-profile data.⁴⁹ The differences reflect the limited accuracy with which these critical amplitudes can be determined from P - ρ - T data. The correlation length ξ diverges as

$$\xi = \xi_0 |\Delta \tilde{T}|^{-\nu} \quad \text{for } \rho = \rho_c, \quad T > T_c, \quad (3.15)$$

with

$$\nu = \beta(\delta + 1)/3 = 0.63. \quad (3.16)$$

Two-scale-factor universality predicts that the correlation-length amplitude ξ_0 is related to the specific heat amplitude A^+ by^{27,50}

$$\xi_0 (A^+ P_c / k_B T_c)^{1/3} = 0.27. \quad (3.17)$$

The validity of two-scale-factor universality for gases near the critical point was verified by Sengers and Moldover.⁴⁹ Substitution of Eq. (3.11a) into Eq. (3.17) yields $\xi_0 = 0.154 \text{ nm}$ in agreement with the experimental value $\xi_0 = (0.150 \pm 0.009)$ determined by Lunacek and Cannell.⁵¹

IV. DISCUSSION

The scaled fundamental equation, presented in this paper supplements the global analytic fundamental equation of Ely *et al.*¹³ for CO_2 by providing an accurate representation of the thermodynamic properties in the near vicinity of the critical point. Specifically, use of a scaled equation is necessary to accommodate the experimentally observed divergent behavior of the specific heat.

The disadvantage of the scaled fundamental equation is that its validity is restricted to a small range [Eq. (3.1)] around the critical point. In fact, the agreement with experimental data deteriorates very rapidly as soon as the scaled fundamental equation is extrapolated outside this range. The problem is that the scaled equation used here does not extrapolate properly to any known limit far away from the critical point, neither at low or high densities nor at low or high temperatures. In formulating the scaled fundamental equation the potential is separated into a singular critical contribution and an analytic background contribution. Renormalization-group analysis has demonstrated the existence in the critical region of analytic terms driven by the critical fluctuations that vanish in the classical limit as discussed by Nicoll *et al.*^{17,52-54} Hence, our analytic background is an effective background combining critical and classical analytic contributions. Attempts to formulate a global fundamental equation that incorporates the crossover from singular behavior near the critical point to the proper classical behavior far away from the critical point are currently in progress.⁵⁵

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APPENDIX: EQUATIONS FOR REVISED AND EXTENDED LINEAR MODEL

The reduced thermodynamic quantities are defined as follows:

TABLE I. Parametric equations for singular terms.

$$\begin{aligned}
\Delta\tilde{\mu} &= ar^{\beta\delta}\theta(1-\theta^2) \\
\Delta\tilde{T} &= r(1-b^2\theta^2) - c\Delta\mu \\
\Delta\tilde{P} &= ar^{\beta(\delta+1)}[k_0p_0(\theta) + r^\Lambda k_1p_1(\theta)] \\
\left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{T}}\right)_{\Delta\tilde{\mu}} &= ar^{\beta(\delta+1)-1}[k_0s_0(\theta) + r^\Lambda k_1s_1(\theta)] \\
\left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{\mu}}\right)_{\Delta\tilde{T}} &= r^\beta[k_0 + r^\Lambda k_1]\theta + c\left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{T}}\right)_{\Delta\tilde{\mu}} \\
\left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}^2}\right)_{\Delta\tilde{\mu}} &= ar^{\beta(\delta+1)-2}[k_0w_0(\theta) + r^\Lambda k_1w_1(\theta)] \\
\left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{\mu}^2}\right)_{\Delta\tilde{T}} &= a^{-1}r^{-\beta(\delta-1)}[k_0u_0(\theta) + r^\Lambda k_1u_1(\theta)] \\
&\quad + 2cr^{\beta-1}[k_0v_0(\theta) + r^\Lambda k_1v_1(\theta)] + c^2\left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}^2}\right)_{\Delta\tilde{\mu}} \\
\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}\partial\Delta\tilde{\mu}} &= r^{\beta-1}[k_0v_0(\theta) + r^\Lambda k_1v_1(\theta)] + c\left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}^2}\right)_{\Delta\tilde{\mu}}
\end{aligned}$$

$$\begin{aligned}
\tilde{T} &= -\frac{T_c}{T}, \quad \tilde{\mu} = \frac{\mu}{T} \frac{\rho_c T_c}{P_c}, \quad \tilde{P} = \frac{P}{T} \frac{T_c}{P_c}, \\
\tilde{\rho} &= \frac{\rho}{\rho_c}, \quad \tilde{U} = \frac{U}{V} \frac{1}{P_c}, \quad \tilde{A} = \frac{A}{VT} \frac{T_c}{P_c}, \\
\tilde{H} &= \frac{H}{VT} \frac{T_c}{P_c}, \quad \tilde{S} = \frac{S}{V} \frac{T_c}{P_c}, \quad \tilde{\chi} = \rho T \left(\frac{\partial\rho}{\partial P}\right)_T \frac{P_c}{\rho_c^2 T_c}, \\
\tilde{C}_v &= \frac{C_v}{V} \frac{T_c}{P_c}, \quad \tilde{C}_p = \frac{C_p}{V} \frac{T_c}{P_c}, \\
\tilde{w} &= \frac{w}{T^{1/2}} \left(\frac{\rho_c T_c}{P_c}\right)^{1/2}. \tag{A1}
\end{aligned}$$

In the above, T is the temperature, μ the chemical potential, P the pressure, ρ the density, V the volume, U the internal energy, A the Helmholtz free energy, S the entropy, C_v the heat capacity at constant volume, C_p the heat capacity at constant pressure, and w the thermodynamic sound velocity. The corresponding thermodynamic differential relations are

TABLE II. Auxiliary functions for parametric equations.

$$\begin{aligned}
p_i(\theta) &= p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4 \quad (i=0,1) \\
s_i(\theta) &= s_{0i} + s_{2i}\theta^2, s'_i(\theta) = 2s_{2i}\theta \quad (i=0,1) \\
q(\theta) &= 1 + [b^2(2\beta\delta - 1) - 3]\theta^2 - b^2(2\beta\delta - 3)\theta^4 \\
u_0(\theta) &= [1 - b^2(1 - 2\beta)\theta^2]/q(\theta) \\
u_1(\theta) &= [1 - b^2(1 - 2\beta - 2\Delta_1)\theta^2]/q(\theta) \\
v_0(\theta) &= [\beta(1 - 3\theta^2)\theta - \beta\delta(1 - \theta^2)\theta]/q(\theta) \\
v_1(\theta) &= [(\beta + \Delta_1)(1 - 3\theta^2)\theta - \beta\delta(1 - \theta^2)\theta]/q(\theta) \\
w_0(\theta) &= [(\beta\delta + \beta - 1)(1 - 3\theta^2)s_0(\theta) - \beta\delta(1 - \theta^2)\theta s'_0(\theta)]/q(\theta) \\
w_1(\theta) &= [\beta\delta + \beta - 1 + \Delta_1)(1 - 3\theta^2)s_1(\theta) - \beta\delta(1 - \theta^2)\theta s'_1(\theta)]/q(\theta)
\end{aligned}$$

$$\begin{aligned}
d\tilde{P} &= \tilde{U}d\tilde{T} + \tilde{\rho}d\tilde{\mu}, \\
d\tilde{A} &= -\tilde{U}d\tilde{T} + \tilde{\mu}d\tilde{\rho}, \\
d\tilde{H} &= -\tilde{T}d\tilde{U} + \tilde{\rho}d\tilde{\mu}, \\
d\tilde{S} &= \tilde{T}d\tilde{U} - \tilde{\mu}d\tilde{\rho}. \tag{A2}
\end{aligned}$$

The fundamental equation for the potential \tilde{P} has the form

$$\tilde{P} = 1 + \sum_{i=1}^3 \tilde{P}_i(\Delta\tilde{T})^i + \Delta\tilde{\mu}(1 + \tilde{P}_{11}\Delta\tilde{T}) + \Delta\tilde{P}, \tag{A3a}$$

with

$$\Delta\tilde{T} = \tilde{T} + 1, \tag{A3b}$$

$$\Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_c - \sum_{i=1}^4 \tilde{\mu}_i(\Delta\tilde{T})^i. \tag{A3c}$$

The parametric equations for $\Delta\tilde{\mu}$, $\Delta\tilde{T}$, $\Delta\tilde{P}$, and the derivatives of $\Delta\tilde{P}$ with respect to $\Delta\tilde{\mu}$ and $\Delta\tilde{T}$ are presented in Table I in terms of auxiliary functions listed in Table II. From the fundamental equation (A3) one can calculate the other thermodynamic properties by using the following thermodynamic relationships^{9,10}:

$$\tilde{\rho} = 1 + \tilde{P}_{11}\Delta\tilde{T} + \left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{\mu}}\right)_{\Delta\tilde{T}}, \tag{A4}$$

TABLE III. Values of universal constants in the revised and extended linear model.

$$\begin{aligned}
\beta &= 0.325 \quad \delta = 4.82 \quad \Delta_1 = 0.50 \\
b^2 &= 1.3757 \\
P_{00} &= + \frac{\beta(\delta-3) - b^2\beta(\delta-1)(2-\beta\delta-\beta)}{2b^4\beta(\delta+1)(\beta\delta+\beta-1)(2-\beta\delta-\beta)} = 0.586\ 535 \\
P_{20} &= - \frac{\beta(\delta-3) - b^2(2\beta\delta-1)(2-\beta\delta-\beta)}{2b^2(\beta\delta+\beta-1)(2-\beta\delta-\beta)} = -1.026\ 243 \\
P_{40} &= + \frac{2\beta\delta-3}{2(2-\beta\delta-\beta)} = 0.612\ 903 \\
P_{01} &= + \frac{\beta(\delta-3) - 3\Delta_1 - b^2(\beta\delta-\beta-\Delta_1)(2-\beta\delta-\beta-\Delta_1)}{2b^4(\beta\delta+\beta+\Delta_1)(\beta\delta+\beta-1+\Delta_1)(2-\beta\delta-\beta-\Delta_1)} = 0.103\ 25 \\
P_{21} &= - \frac{\beta(\delta-3) - 3\Delta_1 - b^2(2\beta\delta-1)(2-\beta\delta-\beta-\Delta_1)}{2b^2(\beta\delta+\beta-1+\Delta_1)(2-\beta\delta-\beta-\Delta_1)} = 0.160\ 32 \\
P_{41} &= + \frac{2\beta\delta-3}{2(2-\beta\delta-\beta-\Delta_1)} = -0.169\ 86 \\
s_{00} &= (\beta\delta+\beta)p_{00} = 1.109\ 430 \\
s_{20} &= - \frac{\beta(\delta-3)}{2b^2(2-\beta\delta-\beta)} = -1.981\ 395 \\
s_{01} &= (\beta\delta+\beta+\Delta_1)p_{01} = 0.246\ 92 \\
s_{21} &= - \frac{\beta(\delta-3) - 3\Delta_1}{2b^2(2-\beta\delta-\beta-\Delta_1)} = -0.843\ 41
\end{aligned}$$

TABLE IV. Values of system-dependent constants in the revised and extended linear model for CO₂.

| Critical constants | |
|-------------------------------------|--|
| $T_c = 304.107$ K | |
| $\rho_c = 467.69$ kg/m ³ | |
| $P_c = 7.3721$ MPa | |
| Scaling-function constants | |
| $a = 23.364$ | |
| $k_0 = 1.2200$ | |
| $k_1 = 0.50407$ | |
| $c = -0.016207$ | |
| Pressure background constants | |
| $\tilde{P}_1 = +5.9939$ | |
| $\tilde{P}_2 = -27.759$ | |
| $\tilde{P}_3 = +5.5503$ | |
| $\tilde{P}_{11} = -0.13644$ | |
| Thermal background constants | |
| $\tilde{\mu}_0 = -28.215$ | |
| $\tilde{\mu}_1 = -33.213$ | |
| $\tilde{\mu}_2 = -17.373$ | |
| $\tilde{\mu}_3 = -23.442$ | |
| $\tilde{\mu}_4 = +118.01$ | |

$$\tilde{U} = \tilde{P}_1 + 2\tilde{P}_2\Delta\tilde{T} + 3\tilde{P}_3(\Delta\tilde{T})^2 + \tilde{\rho}[\tilde{\mu}_1 + 2\tilde{\mu}_2\Delta\tilde{T} + 3\tilde{\mu}_3(\Delta\tilde{T})^2 + 4\tilde{\mu}_4(\Delta\tilde{T})^3] + \tilde{P}_{11}\Delta\tilde{\mu} + \left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{T}}\right)_{\Delta\tilde{\mu}}, \quad (\text{A5})$$

$$\tilde{A} = \tilde{\rho}\tilde{\mu} - \tilde{P}, \quad (\text{A6})$$

$$\tilde{H} = \tilde{P} - \tilde{T}\tilde{U}, \quad (\text{A7})$$

$$\tilde{S} = \tilde{H} - \tilde{\rho}\tilde{\mu} = -\tilde{T}\tilde{U} - \tilde{A}, \quad (\text{A8})$$

$$\tilde{\chi} = \left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{\mu}^2}\right)_{\Delta\tilde{T}}, \quad (\text{A9})$$

$$\left(\frac{\partial\tilde{P}}{\partial\tilde{\rho}}\right)_{\tilde{T}} = \frac{\tilde{\rho}}{\tilde{\chi}}, \quad (\text{A10})$$

$$\left(\frac{\partial\tilde{P}}{\partial\tilde{T}}\right)_{\tilde{\rho}} = \tilde{P}_1 + 2\tilde{P}_2\Delta\tilde{T} + 3\tilde{P}_3(\Delta\tilde{T})^2 + \tilde{P}_{11}\left[\Delta\tilde{\mu} - \frac{\tilde{\rho}}{\tilde{\chi}}\right] + \left(\frac{\partial\Delta\tilde{P}}{\partial\Delta\tilde{T}}\right)_{\Delta\tilde{\mu}} - \frac{\tilde{\rho}}{\tilde{\chi}}\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}\partial\Delta\tilde{\mu}}, \quad (\text{A11})$$

$$\begin{aligned} \frac{\tilde{C}_v}{\tilde{T}^2} &= 2\tilde{P}_2 + 6\tilde{P}_3\Delta\tilde{T} - \tilde{\rho}[2\tilde{\mu}_2 + 6\tilde{\mu}_3\Delta\tilde{T} + 12\tilde{\mu}_4(\Delta\tilde{T})^2] \\ &\quad - \frac{\tilde{P}_{11}^2}{\tilde{\chi}} + \left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}^2}\right)_{\Delta\tilde{\mu}} - \frac{2\tilde{P}_{11}}{\tilde{\chi}}\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}\partial\Delta\tilde{\mu}} \\ &\quad - \frac{1}{\tilde{\chi}}\left(\frac{\partial^2\Delta\tilde{P}}{\partial\Delta\tilde{T}\partial\Delta\tilde{\mu}}\right)^2, \end{aligned} \quad (\text{A12})$$

$$\tilde{C}_p = \tilde{C}_v + \frac{\tilde{\chi}}{\tilde{\rho}^2}\left[\tilde{P} - \tilde{T}\left(\frac{\partial\tilde{P}}{\partial\tilde{T}}\right)_{\tilde{\rho}}\right]^2, \quad (\text{A13})$$

$$\tilde{w} = \left[\frac{\tilde{C}_p}{\tilde{C}_v}\left(\frac{\partial\tilde{P}}{\partial\tilde{\rho}}\right)_{\tilde{T}}\right]^{1/2}. \quad (\text{A14})$$

The values of these thermodynamic properties at the coexistence boundary are obtained⁹ by taking $\theta = \pm 1$.

The values of the universal constants β , δ , Δ_1 , b^2 , p_{ji} , and s_{ji} are presented in Table III. The values of the system-dependent constants a , k_0 , k_1 , c , \tilde{P}_1 , \tilde{P}_{11} , $\tilde{\mu}_c$, and $\tilde{\mu}_i$ for CO₂ are presented in Table IV.

The scaled fundamental equation presented here represents the thermodynamic surface of CO₂ in the range of temperatures and pressures bounded by

$$\begin{aligned} 301.15 < T < 323 \text{ K}, \\ 290 < \rho < 595 \text{ kg/m}^3. \end{aligned} \quad (\text{A15})$$

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