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GUIDELINES FOR PUBLICATION OF EQUATIONS OF STATE—I. PURE FLUIDS

(Technical Report)

Prepared for publication by

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Guidelines for publication of equations of state—I. Pure fluids (Technical Report)

1 INTRODUCTION

1.1 Objective

During recent decades equations of state have become a major tool for the correlation and prediction of thermodynamic properties of fluids. Equations of state can be applied to pure substances as well as to mixtures, and therefore a very large number of publications deal with the development or improvement of equations of state.

In order to give authors, editors, and reviewers of publications on new equations of state some guidelines and to ensure that future publications will be more profitable for the reader, some criteria for pure fluids are given that ought to be fulfilled by a good manuscript. There are three major objectives that should be dealt with in a publication on equations of state:

1. The publication should constitute an advancement in concept or in quantitative performance. The latter should be demonstrated.
2. The publication should enable readers to decide whether they want to use it or not.
3. The publication should help readers to program and use the equation of state.

1.2 Equation of state

The term *equation of state* in the strict sense refers to

- either the thermal equation of state, $p(V_m, T)$
- or the caloric equation of state, $U_m(V_m, T)$.

Both are linked by rigid thermodynamic relationships to the *fundamental equation*, $A_m(V_m, T)$. Of these three, the fundamental equation is the most complete. The thermal equation of state lacks the ideal gas terms which contribute to heat capacity, but not to pressure; the caloric equation of state lacks the ideal gas pressure term. But the ideal gas terms are not equally important for all applications, and the choice of the most appropriate functional form therefore depends on the intended application. In the following text, *equation of state* usually refers to the thermal equation of state, because this is the most common of the three. But these guidelines apply just as well to caloric or fundamental equations.

1.3 Types of Equations of State

Generally, the following kinds of equations of state can be distinguished:

- *Empirical* equations usually contain a large number of substance-specific parameters. The parameters have little physical meaning, but are fitted to experimental data. These equations are typically designed for one fluid only, or at most for a small group of fluids. They are very accurate for their target fluids within the range of thermodynamic conditions for which their parameters were fitted, but may be unreliable outside this range, or for other fluids.

> *Theoretical* equations are based on statistical thermodynamic insight. They have fewer substance-dependent parameters, and these parameters have physical meanings. Due to the present limitations of theory, such equations tend to be less accurate, but may represent property trends correctly even far away from their fitting range.

This distinction is, to some extent, arbitrary. For instance, the well-known virial equation of state may be regarded as an empirical equation (i.e., as a power series in density, with coefficients to be fitted to experimental data) as well as a theoretical equation (if the coefficients are calculated from the appropriate integrals over Boltzmann factors). Furthermore, there are *semiempirical* equations, which combine features of theoretical and empirical equations. The so-called cubic equations of state are usually semiempirical.

1.4 Usage

When applying an equation of state to the calculation or tabulation of thermodynamic properties, authors should distinguish between *correlation* and *prediction* of data:

1. The term *correlation* should be used for calculations, where a set of parameters is obtained by regression techniques from experimental data, and then data of the same type are generated.
2. The term *prediction* should be used for calculations, where a set of parameters obtained otherwise (by theory, data base, or regression of a different property) is used.

The distinction is of course not sharp. But the goal of scientific work on equations of state should be the calculation of all thermodynamic properties with a single parameter set for each chemical compound, rather than working with different parameter sets for each property.

2 GENERAL CONSIDERATIONS

Because of the wide spectrum of modern equations of state, it is difficult to set up a general set of guidelines which will be applicable to all types of equations. Some of the thermodynamic criteria discussed below may be automatically satisfied by some equations of state, but difficult to fulfill or even inapplicable for others. For instance, it is to be expected that wide-range empirical equations which accurately represent all the critically assessed data will meet all criteria, whereas theoretical equations will usually trade compliance to some criteria for applicability to a wider range of substances.

Since these criteria are of importance to many of the scientific community, those discussed in this section should therefore be considered by authors.

Where accurate data are available, authors should always show how well these are represented by the equation of state.

Authors of equations of state should investigate the behaviour of their functions in the limits of high pressure, high temperature, and low temperature. Several points to be checked are listed below.

Some of these points may seem irrelevant to some readers; e.g., the author of an equation of state for natural gas compounds may deem it pointless to discuss the behaviour of the equation at temperatures exceeding twice the critical temperature. But experience shows that, once published, equations of state are frequently applied to other compounds or other thermodynamic conditions than those for which they had been designed.

If an equation of state becomes unreliable or even physically unreasonable above or below certain values of (reduced) density and temperature, these values should be given.

Authors should warn their readers against mathematical problems, such as divergent behaviour, if these exist. Piecewise defined functions should be avoided, unless required by special physical reasons, because their derivatives can become discontinuous.

Example: The parameters a_c and b of the Peng-Robinson equation of state [1]

$$p = \frac{RT}{V_m - b} - \frac{a_c \alpha(T)}{V_m(V_m + b) - b(V_m - b)} \tag{1}$$

can readily be obtained from critical data:

$$a_c = 0.45724 \frac{R^2 T_c^2}{p_c} \qquad b = 0.07780 \frac{RT_c}{p_c} \tag{2}$$

It has been suggested that effective critical data should be used for hydrogen [2]:

$$\begin{aligned} (T_{c,\text{eff}}/\text{K}) &= \begin{cases} 31.85 + 0.0679(T/\text{K}) & T \le 173\,\text{K} \\ 43.6 & T > 173\,\text{K} \end{cases} \\ (p_{c,\text{eff}}/\text{MPa}) &= \begin{cases} 1.109 + 0.00544(T/\text{K}) & T \le 173\,\text{K} \\ 2.05 & T > 173\,\text{K} \end{cases} \end{aligned} \tag{3}$$

with temperatures given in K and pressures in MPa. These functions are continuous, but not their derivatives. As a consequence, the enthalpy of hydrogen or hydrogen-containing mixtures, calculated with the Peng-Robinson equation using these functions, would become discontinuous, and the heat capacity divergent for all densities at 173 K.

In some equations of state the transition from one functional form to another takes place at the critical temperature (e.g., generalized van der Waals model by Nguyen Van Nhu et al. [3]), thus creating nonanalytic behaviour at this temperature. It should be noted, however, that critical anomalies are known to occur in a narrow density range only, not at all densities. Furthermore, the discontinuities at the critical point cause problems in calculations of mixture properties, where the true critical point is no longer given by the criteria of mechanical stability.

2.1 Parameters

It should be clearly indicated in the manuscript which variables are considered as substance-specific and adjustable, and which are universal constants.

In many applications the parameters of an equation of state will be calculated, or at least estimated, from the critical properties. In this case the authors should give the relationship between the critical properties (p_c, T_c, V_{mc}) and these parameters. They should state which of the critical properties are reproduced exactly with their parameters. In the case of many-parameter equations, it may be difficult to obtain simple relationships, but then at least physically meaningful ranges of these parameters can be indicated.

It should also be explained which physical properties have been used, or should best be used, to calculate the substance-dependent parameters. The objective functions used for the estimation of these parameters should be specified.

If parameters are temperature-dependent, the authors should choose a functional form which allows extrapolation to high temperatures (compare Sections 3.3 and 3.5).

Unless special physical reasons demand so, pressure-dependent parameters in an equation of state $p(V_m, T)$ are undesirable.

2.2 The Critical Point

It is well known that analytical equations of state will have difficulties in the vicinity of critical points. Nevertheless, it is possible to construct equations that give the correct critical compressibility factor Z_c as defined by the experimental values of pressure, temperature, and density. It is necessary that the authors of equations of state indicate their value or range of Z_c, because this tells whether it is possible to use this property for parameter fitting. Furthermore, readers who are especially interested in the prediction of pVT data will be grateful for having Z_c, because this gives information about systematic deviations of the equation of state. Of course, the correct representation of Z_c alone does not guarantee that the equation of state will perform well in the critical region.

2.3 The Two-Phase Region

The calculation of vapour-liquid phase equilibria usually involves the calculation of densities at given pressure and temperature. Authors of noncubic equations should state how many minima and maxima a $p(V_m)$ isotherm can have, or indicate, how initial values for the calculation of orthobaric densities can be estimated.

An expression for the Helmholtz energy or for the fugacity should be given in order to facilitate the calculation of the vapour pressure curve. If for some reason it is impossible to give explicit equations for $f(V_m, T)$ or $A_m(V_m, T)$, an algorithm for the calculation of vapour pressures should be outlined.

Prediction of vapour pressure curves should always be attempted and the deviations from experimental vapour pressures and orthobaric volumes reported. As the vapour pressure and the vapour molar volume may cover several orders of magnitude, relative deviations should be reported.

2.4 Single-Phase Properties

2.4.1 Volumetric Properties

The ability of an equation of state to predict pVT data should also be demonstrated. In most cases it may not be practical to present extensive tabulations or contour maps, but it should always be possible to give a few indications of performance.

Often pressure deviations at specified density and temperature convey more information than volume deviations at specified pressure and temperature. In the dense liquid it is useful to give both. Also for accurate many-parameter equations pressure deviations should be given for the critical region.

A sufficient number of pVT data should be located far away from the perfect gas conditions. Finally, comments on the range of validity of the equation and the reliability of extrapolations should be given.

2.4.2 *Caloric Properties*

The estimation of caloric data, such as residual specific heat capacities (isochoric or isobaric) or speed of sound is also of general interest as well as industrial importance. Authors are urged to report predictions of such data.

In this context it is perhaps noteworthy that for equations of the van der Waals type, i.e. equations consisting of a hard-body repulsion and an attraction term, the contribution of the repulsion term to the heat capacity is zero, unless the molecular volume parameter is temperature-dependent.

Example: The van der Waals repulsion term

$$p_{\mathrm{rep}} = \frac{RT}{V_{\mathrm{m}} - b} \tag{4}$$

around which so many equations of state have been built, is associated with the following Helmholtz energy (The superscript "id" indicates an ideal gas reference state):

$$A_{\mathrm{m}} = A_{\mathrm{m}}^{\mathrm{id}} - RT \ln \frac{V_{\mathrm{m}} - b}{V_{\mathrm{m}}^{\mathrm{id}}} \tag{5}$$

and this yields the internal energy:

$$U_{\mathrm{m}} = -T^2 \left(\frac{\partial A_{\mathrm{m}}/T}{\partial T} \right)_{V_{\mathrm{m}}} = U_{\mathrm{m}}^{\mathrm{id}} + 0 \tag{6}$$

Since real molecules do not have hard repulsion potentials, usage of a hard-body term can be expected to be disadvantageous for caloric properties, unless the molecular volume parameter is made temperature-dependent or the attractive term of the equation of state is given a temperature dependence that compensates that of the repulsion term.

3 FURTHER CONSIDERATIONS

The criteria discussed in this section may not be applicable to all equations of state, but authors who report on the extent to which their equations are able to meet them will provide information which may be of help to many readers and users.

Brown [4] has described several "characteristic curves", along which certain thermodynamic properties of the fluid agree with those of the perfect gas. His considerations were extended by Angus [5] and Rowlinson [6]. De Reuck [7] has discussed the usefulness of these characteristic curves for extrapolating equations of state. The following characteristic curves are of special interest in this context.

It must be stressed that some of these curves involve rather extreme conditions of temperatures and pressures, and some authors may feel that these curves are irrelevant for their work. Nevertheless, part of these curves is eventually accessible to experiments. Furthermore, these curves establish limiting conditions which may be useful for extrapolations.

3.1 The Joule Inversion Curve: Curve A

This curve has also been called the Amagat curve by Brown. It is characterized by any of the following equations:

$$\begin{aligned} \left(\frac{\partial Z}{\partial T}\right)_V &= 0 \qquad & \left(\frac{\partial U}{\partial V}\right)_T &= 0 \\ \left(\frac{\partial Z}{\partial p}\right)_V &= 0 \qquad & \left(\frac{\partial p}{\partial T}\right)_V &= \frac{p}{T} \end{aligned} \tag{7}$$

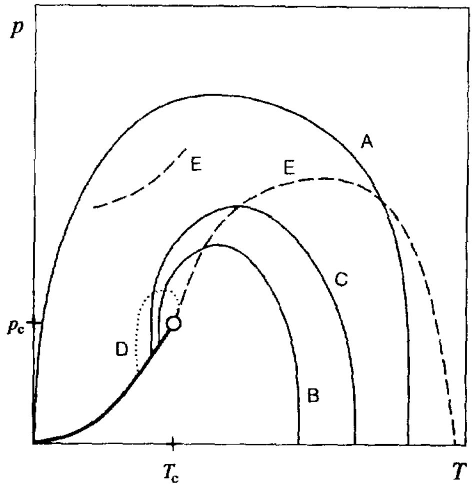


Fig. 1 Schematic representation of Brown's characteristic curves. A: Joule inversion curve, B: Boyle curve, C: Joule–Thomson inversion curve, D: isochore inflection curve, E: isobar inflection curve.

It encloses all the other curves discussed below except for the high temperature end of the isobar inflection curve (see Section 3.5). A large part of the Joule inversion curve may be beyond the melting line or outside the experimentally accessible range.

Its intersection with the temperature axis (the zero-pressure limit) marks a state where the second virial coefficient has a maximum ($\mathrm{d}B/\mathrm{d}T = 0$). This maximum is a consequence of soft repulsion, which results in a temperature-dependent effective collision diameter. Again, the temperature of this maximum may be too high for many substances, but not for all. Authors are advised to state whether their equation of state can describe this maximum, or at least a part of the Joule inversion curve.

Example: For the van der Waals equation [8]

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} \tag{8}$$

the resulting 2nd virial coefficient is $B = b - a/RT$, hence there is no maximum possible. Similarly, the Redlich-Kwong equation [9]

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} \quad \text{with} \quad a(T) = \frac{a_0}{\sqrt{T}} \tag{9}$$

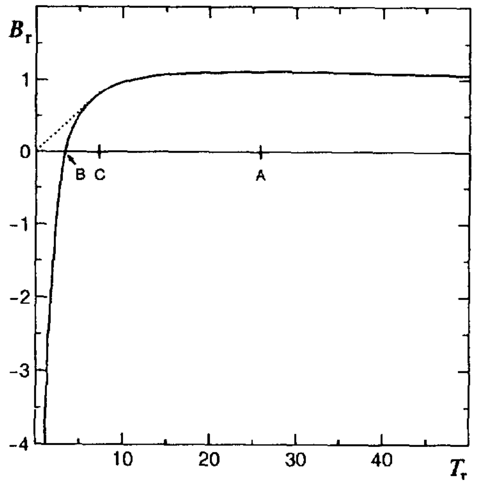
leads to $B = b - a/\left(RT^{1.5}\right)$, again ruling out a maximum. As soon as the covolume parameter b is made temperature dependent, however, a maximum becomes possible.

It is interesting to discuss the second condition of the Joule inversion curve, $(\partial U/\partial V)_T = 0$, for van der Waals type equations, i.e. equations consisting of a repulsion and an attraction term, $p = p_\mathrm{rep} + p_\mathrm{att}$. The condition describes a balance between a repulsive contribution to internal energy (overlap of molecules) and an attractive one (more molecules within range of attractive potential well), caused by compression of a fluid. An equation with a true hard-body term (temperature-independent size parameter, repulsion term proportional to T) cannot have solutions for the Joule inversion curve, unless the contribution of the attraction term to U is able to change sign.

Example: The Deiters equation [10, 11]

$$p = \frac{RT}{V_\mathrm{m}}\left(1 + cc_0\frac{4\xi - 2\xi^2}{(1-\xi)^3}\right) - \frac{RT^*bc^2}{V_\mathrm{m}^2}\tilde{T}_\mathrm{eff}\left(\mathrm{e}^{1/\tilde{T}_\mathrm{eff}} - 1\right)I_1(\xi, c) \tag{10}$$

Fig. 2 Reduced second virial coefficient $B_r = B/(N_A\sigma^3)$ of the Lennard–Jones 12/6 fluid, as a function of the reduced temperature $T_r = k_BT/\varepsilon$. A: Joule inversion temperature, B: Boyle temperature, C: Joule–Thomson inversion temperature. ·······: tangent at Joule–Thomson inversion temperature.



with reduced density ξ and effective reduced temperature $\tilde{T}_{\text{eff}}(\xi, c)$ has a temperature-independent size parameter, but allows the polynomial $I_1(\xi, c)$ to change sign at high densities. The equation will yield Joule inversion points only for very high densities; it fails, especially, to reproduce the maximum of the virial coefficient curve.

This consideration applies to rather extreme conditions of pressure and temperature, however. Usually, isochores begin at the vapour pressure curve with negative curvature, but become almost straight lines at higher temperatures (except for a small range near to the critical point, indicated by curve D in Fig. 1; see Section ?). At temperatures and pressures where overlap of molecules is still insignificant, i.e. sufficiently far below the Joule inversion point, the extrapolation of these straight lines to zero temperature passes the ordinate at negative pressure, namely at the attractive pressure p_{att} (see Fig. 3). Authors should be aware that high temperatures (below the Joule inversion temperature) may randomize fluid structure, but do not turn off the intermolecular potentials, hence $p_{\text{att}} < 0$ must hold.

Example: For the Redlich-Kwong equation (9), the attraction term converges toward zero:

$$\lim_{T\to\infty} p_{\text{att}} = \lim_{T\to\infty} \frac{a}{\sqrt{T}V_{\text{m}}(V_{\text{m}} + b)} = 0 \tag{11}$$

The attraction term drops too rapidly at high temperatures. For the van der Waals equation (8), p_{att} along an isochore is constant. The attractive pressure term of the SPHCT [12] equation (12) converges against a negative limit:

$$p = \frac{RT}{V_{\text{m}}}\left(1 + c\frac{4\xi - 2\xi^2}{(1-\xi)^3} - \frac{\frac{z}{\tau}\xi Y}{1 + \frac{1}{\tau}\xi Y}\right) \qquad \text{with} \quad Y = \exp\left(\frac{\epsilon q}{2ck_{\text{B}}T}\right) - 1$$

$$\lim_{T\to\infty} p_{\text{att}} = \lim_{T\to\infty}\left(-\frac{RT\frac{z}{\tau}\xi Y}{V_{\text{m}}\left(1 + \frac{1}{\tau}\xi Y\right)}\right) = -\frac{N_{\text{A}}\frac{z}{\tau}\xi\epsilon q}{2V_{\text{m}}c} \tag{12}$$

The Deiters [10] equation (10) behaves similarly.

The Redlich-Kwong-Soave [13] equation of state, which has the same density dependence as the original Redlich-Kwong equation, but a different temperature dependence, yields a maximum at too low temperatures ($T_{\max}/T_c \approx 2\ldots3$, depending on the value of m. This is due to the physically unreasonable increase of the attraction term $|p_{\text{att}}|$ with temperature above T_c.

$$\begin{aligned} a(T) &= a_c\left(1+m\left(1-\sqrt{\frac{T}{T_c}}\right)\right)^2 \\ \frac{\mathrm{d}B}{\mathrm{d}T} = 0 \quad &\Rightarrow \quad T_{\max} = T_c\left(1+\frac{1}{m}\right)^2 \end{aligned} \tag{13}$$

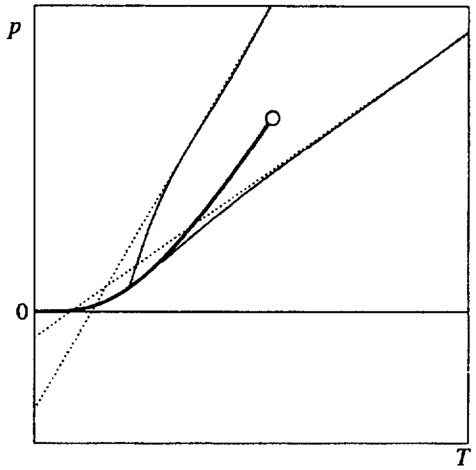


Fig. 3 Behaviour of isochores (schematic) solid: isochores, bold: vapour pressure curve, dotted: extrapolation of high-temperature part of isochores.

In some publications the undesirable high-temperature behaviour of $a(T)$ has been avoided by setting $a(T) = a_c = \text{const}$ for temperatures above the critical. But this creates discontinuities in some derivatives, as discussed above (see Chapter 2). The Peng-Robinson equation (1) behaves similarly.

3.2 The Joule-Thomson Inversion Curve: Curve C

This curve is also called the Charles curve by Brown. It is characterized by any of the following equations:

$$\left(\frac{\partial Z}{\partial T}\right)_p = 0 \qquad \left(\frac{\partial Z}{\partial V}\right)_p = 0 \qquad \left(\frac{\partial T}{\partial p}\right)_H = 0 \qquad \left(\frac{\partial H}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T} \tag{14}$$

The Joule-Thomson inversion curve lies completely inside the Joule inversion curve. It passes through one maximum — according to corresponding states correlations at about 11.75 p_c and 2.25 T_c — and should have no further extrema or inflection points.

Its intersection with the temperature axis (the low-pressure limit at high temperatures) marks a point where the tangent to the virial coefficient curve passes through the origin:

$$\frac{\mathrm{d}B}{\mathrm{d}T} = \frac{B}{T} \tag{15}$$

3.3 The Boyle Curve: Curve B

Along this curve, the compressibility factor is pressure- or density-independent:

$$\begin{aligned} &\left(\frac{\partial Z}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{p}{V} \\ &\left(\frac{\partial Z}{\partial V}\right)_T = 0 \end{aligned} \tag{16}$$

This curve lies completely inside the Joule–Thomson inversion curve. At its intersection with the temperature axis, the second virial coefficient is zero. Most realistic equations of state will yield this intersection at reasonable values of the Boyle temperature, but the overall temperature dependence of the second virial coefficient should be discussed in more detail.

Example: It has been shown in 3.1 that a temperature-dependent size parameter will allow even a simple equation of state such as the van der Waals equation to reproduce maxima of the second virial coefficient. It should be noted, however, that a linear function for the covolume, $b = b_0 - b_1 T$, eventually leads to negative virial coefficients at high temperatures again, thus creating a second (physically unreasonable) Boyle temperature. Further restrictions on the temperature dependence of the covolume will be discussed in Section 3.5.

Example: The Soave temperature function (13) discussed in 3.1 may cause the second virial coefficient curve to pass through a second Boyle point to a negative limiting value at high temperatures.

The third virial coefficient has a more complicated temperature dependence. At least for nonpolar molecules, however, it should be negative at very low temperatures, and positive (slightly declining) at very high temperatures, assuming that three-body contributions to the intermolecular potential are negligible.

Example: The van der Waals equation (8) yields a constant positive third virial coefficient $C = b^2$. For the Redlich-Kwong (9) and SPHCT (12) equations, C is always positive and increases with decreasing temperature.

3.4 The Isochore Inflection Curve: Curve D

Isochores with near-critical densities are usually found to have an inflection point. The locus of inflection points, represented by curve D in Fig. 1, originates at the critical point and runs back to the vapour pressure curve on the liquid side. It is defined by either of the following equations:

$$\begin{aligned} &\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0 \\ &\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \end{aligned} \tag{17}$$

The curvature of isochores is positive within the isochore inflection curve, and negative outside.

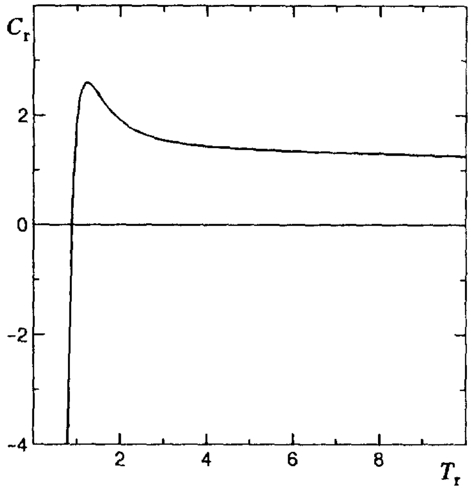


Fig. 4 Reduced third virial coefficient of the Lennard–Jones 12/6 fluid $C_r = C/(N_A\sigma^3)^2$ as a function of the reduced temperature $T_r = k_BT/\varepsilon$.

In the vicinity of the critical point, the isochoric heat capacity increases due to fluctuations. Consequently, C_V isotherms exhibit a maximum close to, and a weak divergence exactly at the critical point. The latter, however, cannot be expressed with analytical equations of state. Further away from the critical point, C_V isotherms exhibit minima.

Authors may assist their readers by stating whether their equation can describe extrema of the isochoric heat capacity or inflection points of isochores.

Example: The Redlich-Kwong equation of state cannot reproduce isochoric inflection points and is therefore unable to correlate heat capacities near to the critical point.

3.5 The Isobar Inflection Curve: Curve E

The high compressibility of a fluid near to its critical point gives rise to maxima of the isobaric heat capacity. These are also associated with inflection points in molar volume isobars:

$$\begin{gathered}\left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0 \\ \left(\frac{\partial C_p}{\partial p}\right)_T = 0\end{gathered} \tag{18}$$

Most equations of state have no difficulty in reproducing this behaviour, at least qualitatively. There is, however, a second curve fulfilling these criteria: At high pressures, the C_p vs. p diagrams for nonpolar components exhibit shallow minima, which move away to higher pressure with increasing temperature. These minima are due to details of molecular packing (explained by the statistical thermodynamics of rigid body fluids) as well as soft repulsion between molecules. The authors of equations of state should state whether their equation is able to generate these C_p minima.

Example: The van der Waals (8) and Redlich-Kwong (9) equations of state cannot reproduce high-pressure isobaric inflection points: At high pressures the van der Waals repulsion term outweighs the attraction term, yielding $p \approx p_{\text{rep}} = RT/(V_m - b)$, hence $V_m \approx RT/p_{\text{rep}} + b$. This function evidently cannot have inflection points.

If the repulsion term of these equations is replaced by a true hard-sphere term (Carnahan-Starling term [14]), isobaric inflection points at high pressures can be predicted qualitatively.

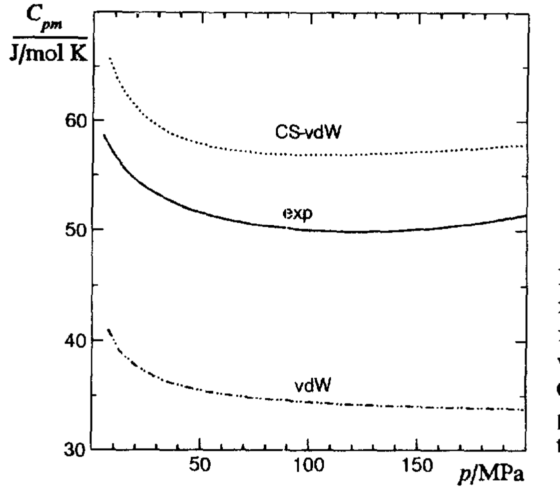


Fig. 5 Isobaric heat capacity of methane at 200 K as a function of pressure. Comparison of heat capacities from an IUPAC correlation of experimental data [15] with predictions from the van der Waals and the Carnahan–Starling–van der Waals equations (with parameters calculated from critical pressure and temperature).

A feature closely related to the isobaric inflection point is the temperature dependence of the cubic expansion coefficient $\alpha = V^{-1}(\partial V/\partial T)_p$. Because of

$$\frac{\partial \alpha}{\partial T} = -\alpha^2 + \frac{1}{V}\frac{\partial^2 V}{\partial T^2} = -\alpha^2 - \frac{1}{TV}\frac{\partial C_p}{\partial p} \qquad (19)$$

the existence of a minimum of C_p at some pressure implies $\partial\alpha/\partial T = 0$ at a lower pressure, i.e. the cubic expansion coefficient becomes temperature-independent. It has been observed for many nonpolar substances that isotherms in an α vs. p diagram, over a rather large temperature range, pass through a common intersection point [16].

It has been shown above (see Section 3.3) that a temperature-dependent covolume may add desirable features to an equation of state. The functional form of the temperature dependence must be chosen with great care.

Example: Consider again the high pressure limit of a cubic equation of state such as the van der Waals equation (8) or the Redlich-Kwong equation (9):

$$p \approx p_{\mathrm{rep}} = RT/(V_{\mathrm{m}} - b) \qquad (20)$$

Salim and Trebble [17] have pointed out that in this case the isobaric heat capacity is given by

$$C_p = C_p^{\mathrm{id}} - pT\frac{\mathrm{d}^2 b}{\mathrm{d}T^2} \qquad (21)$$

If the temperature dependence of the covolume is convex ($\mathrm{d}^2b/\mathrm{d}T^2 > 0$), a negative heat capacity can result.

On the other hand, physical insight demands $b > 0$ and $\mathrm{d}b/\mathrm{d}T < 0$. From this one can conclude that the covolume of a cubic equation of state, plotted against temperature, must have a negative curvature at low temperatures and a positive curvature at high temperatures.

This argument does not apply to noncubic equations, and it should be noted that theoretical studies of softly repulsive systems indicate $\mathrm{d}^2b/\mathrm{d}T^2 > 0$ at all temperatures. This illustrates that the choice of the repulsion term and the temperature dependence of the covolume parameter are interrelated.

4 SUBSTANCES

It is difficult to give recommendations as to which substances should be used to test an equation of state. The proper choice depends on the theoretical background of the equation or on the application for which it was designed. Authors of empirical wide-range equations of state for specific substances will base their work on extensive, critically assessed sets of experimental data. Otherwise the authors should be urged to apply their equations of state to substances for which IUPAC International Tables of the Fluid State or compilations of similar quality exist.

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