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On the Extrapolation Behavior of Empirical Equations of State

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Generally, the extrapolation behavior of empirical equations of state is regarded as poor, but it can be shown that state-of-the-art equations of state yield reliable results well beyond the range where they were fitted to experimental data. During the past years a new generation of highly accurate equations of state which yield reasonable results even up to the limits of chemical stability of the considered substances has been developed. In this paper, the positive influence of recent methods for the development of equations of state on their extrapolation behavior is discussed. The influence of the mathematical structure on the extrapolation characteristics is analyzed and requirements for a reasonable behavior up to extreme temperatures and pressures are formulated. As possible ways for assessment of the extrapolation behavior of an equation of state, comparisons with experimental data at very high pressures and temperatures and with theoretically predicted features of the so-called "ideal curves" of a fluid are discussed. Finally, the current status of our knowledge of the extrapolation behavior of empirical equations of state is summarized and its shortcomings are pointed out.

KEY WORDS: empirical equations of state; high pressures; high temperatures; Hugoniot curve; argon; carbon dioxide; ethane; helium; methane; nitrogen; oxygen; water.

1. INTRODUCTION

Over the years, considerable interest in thermodynamic properties of fluids at very high pressures and temperatures has resulted mainly from applications in geology, petrology, and geophysics. Several simple equations of state have been developed especially for these applications. Usually, these equations are valid only in restricted ranges of temperature and pressure and they fail to represent properly accurate experimental data at lower

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temperatures and pressures. On the other hand, empirical multiparameter equations of state are able to represent thermodynamic data under fluid conditions for which there exist accurate experimental equipment, but they have often failed with respect to extrapolation beyond the range of temperatures and pressures of the data to which the equations were fitted. Instead of developing special equations of state for very high temperatures and pressures, it would be desirable to improve the extrapolation behavior of these accurate equations of state in order to describe the entire range of thermodynamic properties of a fluid as accurately as possible with a single equation of state. With this in mind, the extrapolation behavior of empirical equations of state was one of the main topics in the discussion sessions of the Fifth International Workshop on Equations of State, which took place at the Ruhr-Universität Bochum in 1990. De Reuck [1] summarized the results of this discussion, which focused mainly on the so-called "ideal curves" (see Section 5 and the Appendix) of pure fluids.

Based on this discussion, we investigated the representation of data outside the range of primary data, the influence of the mathematical structure of the equation on the extrapolation behavior, and the course of the ideal curves in more detail during our work on a new equation of state for carbon dioxide [2, 3]. The relevance of these investigations became obvious at the Twelfth Symposium on Thermodynamic Properties in 1994, when Pitzer and Sterner [4] presented their concept of an equation of state valid from zero to extreme pressures, which coincided with the first international presentation of our results [5]. With parameter sets for carbon dioxide and water, the equation of Pitzer and Sterner was subsequently published in different journals [6–8], whereas we hesitated to generalize the results found for the extrapolation behavior of empirical equations of state during our work on carbon dioxide. For the fluid state of pure carbon dioxide the temperature and pressure range covered by data measured with static apparatuses reaches up to 1076 K and 800 MPa, while the accuracy of the data already deteriorates at pressures above 316 MPa. Due to the relatively high critical temperature ($T_c \approx 304$ K) and the high critical pressure ($p_c \approx 7.38$ MPa) of carbon dioxide, these limits correspond to a reduced temperature of only $T/T_c = 3.54$ and a reduced pressure of $p/p_c = 108.4$ and $p/p_c = 42.8$ for the accurate data sets, respectively. In terms of reduced temperature and pressure, the range covered by reliable data is significantly larger for other reference substances.

In the meantime, the results we obtained for the extrapolation behavior of our equation of state for carbon dioxide have been confirmed by the more recent equations of state for water [9, 10], argon [11, 12], and nitrogen [13] and the investigation of ideal curves has additionally been extended to helium, oxygen, methane, and ethane. As long as other substances are chemically stable under the considered conditions, no reason became obvious why the results should not be transferable.

Following this introduction, three short examples are given for the representation of primary data at high pressures and temperatures in Section 2. In Section 3, comparisons with experimental data at pressures and temperatures beyond the range covered by primary data are discussed as a widely used opportunity to test the extrapolation behavior of equations of state. Starting from observations in Section 3, the influence of the mathematical form of an empirical equation of state on its extrapolation behavior is analyzed in Section 4. Finally, the question whether predictions for universal features of the ideal curves are suitable for an assessment of the extrapolation behavior of an equation of state is discussed in Section 5. The Appendix gives examples for the plots of the well-known zeroth- and first-order ideal curves of the compression factor calculated from accurate empirical equations of state.

Since this paper is not intended as a final report on the extrapolation behavior of empirical equations of state but as a summary of current developments of this topic, shortcomings are pointed out and some proposals for further investigations are made.

2. REPRESENTATION OF DATA AT HIGH PRESSURES AND HIGH TEMPERATURES

Among the accurate thermodynamic data available for pure fluids, experimental investigations of the (pressure, density, temperature) relation ($p\rho T$ data) usually cover the largest temperature and pressure range. Since empirical multiparameter equations of state are generally valid only in the range where they were fitted to data, the range where $p\rho T$ data are available determines the range of validity of reference equations of state.[3] Though this fact is widely known, only a few people are aware that this range usually reaches up to temperatures of more than 1000 K and pressures of more than 1000 MPa for well measured substances.

As an example, Fig. 1 shows the representation of accurate $p\rho T$ data for argon at high pressures and ambient temperatures. While the functional form of the equation of Gosman et al. [21] from 1969 was determined by trial and error, optimization algorithms [22–24] were used to establish the

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[3] The expression "reference equation of state" is used for empirical equations of state which are able to represent all (or nearly all) data available for the thermodynamic properties of a fluid to within their experimental uncertainty; based on the knowledge available at the time they were established, such formulations aim to yield the best possible description of the thermodynamic properties of the corresponding substance.

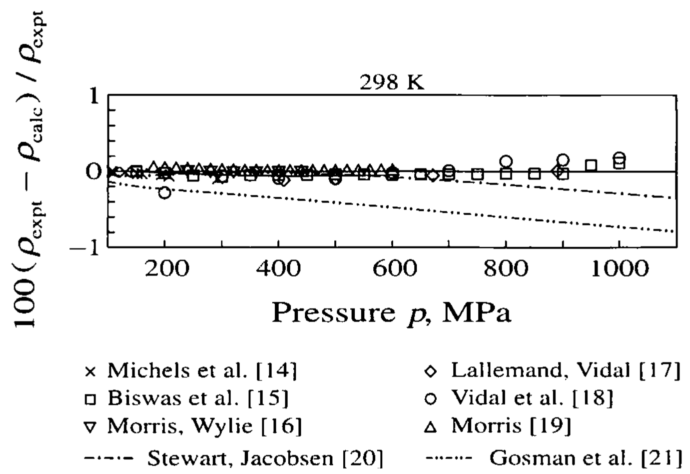

Fig. 1. Percentage deviations of selected $p\rho T$ data from values calculated from the equation of Tegeler et al. [11, 12] for argon. Values calculated from the equations of Stewart and Jacobsen [20] and Gosman et al [21] are plotted for comparison.

functional form of the later equations. The use of such algorithms has essentially improved the capabilities of empirical equations of state at high pressures and high temperatures.

Besides representing $p\rho T$ data, equations of state are also expected to yield reliable results for derived properties such as heat capacities or the speed of sound. Since these properties are related to derivatives of the $p\rho T$ surface and since their relation to the dependent variable of the equation of state is nonlinear in most cases, their representation is more sensitive to small inaccuracies of the equation and experimental data of these properties cannot be used directly in the common linear optimization algorithms. Over the last 10 years, improved strategies for the use of nonlinear data in the optimization process have been developed (see, e.g., Ref. 25), and very recently the first nonlinear optimization algorithm was presented [11, 26]. If one of these techniques is used, empirical equations of state are able to represent even caloric properties up to very high pressures. For nitrogen, for example, Fig. 2 shows deviations between speed-of-sound data at high pressures and values calculated from the equation of state of Jacobsen and Stewart [30], which is the origin of the so-called MBWR form, from the equation of Jacobsen et al. [29], which was the first equation with a functional form optimized for nitrogen, and the new reference equation [13], which was finalized using the nonlinear optimization algorithm developed by Tegeler et al. [11, 26].

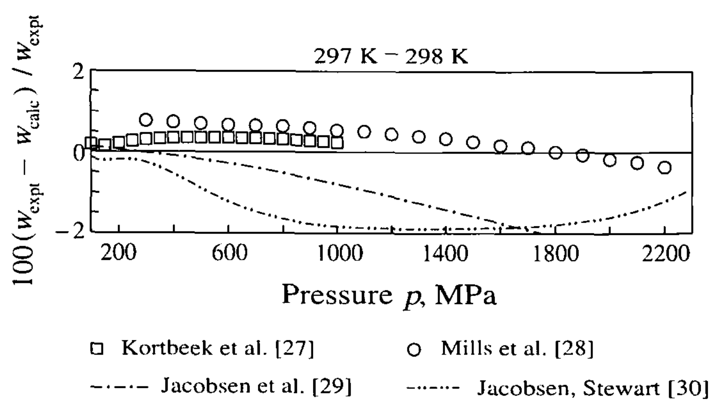

Fig. 2. Percentage deviations of selected high-pressure speed-of-sound data from values calculated from the equation of Span et al. [13] for nitrogen. Values calculated from the equations of Jacobsen et al. [29] and of Jacobsen and Stewart [30] are plotted for comparison.

Though the representation of data at high pressures is an important feature for many applications, it is more important for the extrapolation discussion to point out that state-of-the-art equations of state are not flexible enough to follow systematically wrong courses of single data sets in the high-pressure region. During the optimization of the mathematical form strongly correlated pairs of terms are automatically replaced by single terms with a similar contribution and steps for the optimization of the length of the equation are implied. To achieve a very high accuracy, recent reference equations usually contain 30 to 42 terms with one fitted parameter each, but only very view of these terms contribute significantly to the behavior in the high-pressure region and the flexibility of the equations in this region is therefore very restricted. The other terms are needed for the highly accurate description of properties at lower pressures and in the critical region[4] (see Section 4). Figure 3 shows a comparison between experimental data for carbon dioxide and results from our new reference equation of state [3], which is used for the baseline, and from the high-pressure equation of Pitzer and Sterner [7]. With 42 fitted coefficients, the empirical reference equation represents the accurate data at pressures up to 60 MPa clearly better than the equation of Pitzer and Sterner with 28 fitted coefficients, but at pressures above 100 MPa it yields results similar to

[4] Such a mathematical structure is not always advantageous since it implies a high flexibility in the low-pressure region; especially in the critical region an extensive set of accurate date is needed to avoid misbehavior.

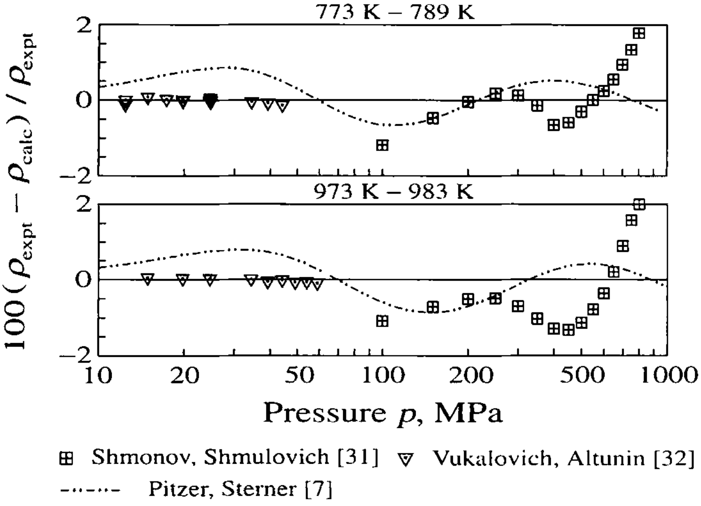

Fig. 3. Percentage deviations of selected $p\rho T$ data from values calculated from the equation of Span and Wagner [3] for carbon dioxide. Values calculated from the equation of Pitzer and Sterner [7] are plotted for comparison.

those of the high-pressure equation and does not follow the faulty course of the data.[5]

In contradiction to common teachings, empirical equations with a carefully optimized mathematical structure are not flexible enough to follow incorrect courses of data sets in the high-pressure and -temperature region even if these data are the only experimental information which is available in this region. Thus, it can be concluded that they will also be stable enough to yield a reasonable extrapolation behavior in regions not covered by data. Qualitatively this statement agrees with experience made during the establishment of several reference equations of state (e.g., Refs. 3, 10, 11, 13, and 25) but it has not been quantified up to now. It is clear that the limits of the range in which an extrapolation is useful depend on the considered property, on the demanded accuracy, on features of the data set used to establish the equation, and finally, on features of the equation itself. Thus, a simple answer cannot be expected; systematic studies on this topic are still lacking.

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[5] For a more detailed discussion on the shortcomings of the date sets of Shmonov and Shmulovich [31], see Sterner and Pitzer [6].

3. COMPARISONS WITH DATA BEYOND THE RANGE OF PRIMARY DATA

At pressures and temperatures beyond the range covered by $p\rho T$ data, additional experimental information on fugacities is available, particularly for substances of geological interest. The origin of these data is measurements of chemical equilibria and their evaluation depends on sets of thermodynamic data of the other components involved in the chemical equilibrium. The resulting fugacities vary significantly depending on the assumptions made for the other components. Geologists are familiar with the internally consistent sets of thermodynamic data needed for the evaluation of the measured equilibria, but scientists working on reference equations of state are usually not. Thus, it would be valuable to set up a pure-component database by calculating the corresponding fugacities from the equilibrium data published mainly in geological literature.

For carbon dioxide, only Haselton et al. [33] have published pure-component fugacities which are derived from the evaluation of their experimental results for the decarbonation of magnesite and calcite. Figure 4 compares these data with results calculated from the equations of state of Span and Wagner [3] and of Pitzer and Sterner [7]. While Pitzer

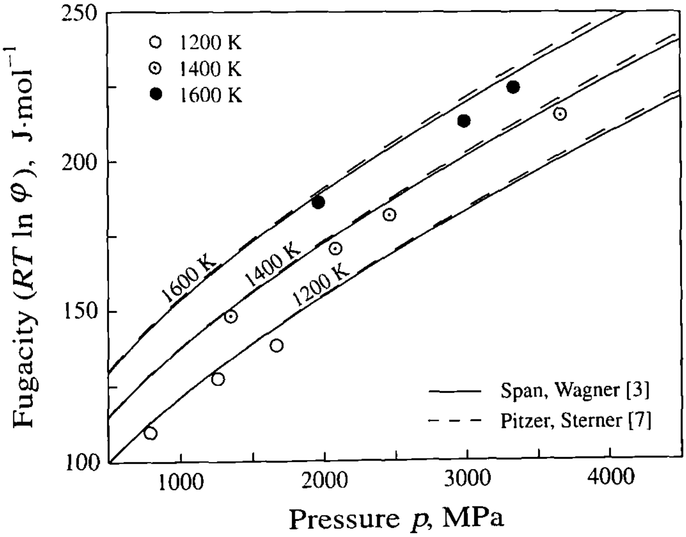

Fig. 4. Fugacities calculated from the equations of Span and Wagner [3] and of Pitzer and Sterner [7] at high temperatures. The corresponding experimental results of Haselton et al. [33] are given as symbols indicating the isotherm to which they belong.

and Sterner fitted their equation to an extensive set of fugacities calculated from published equilibria data by themselves, the data of Haselton et al. were used only for an assessment of the extrapolation behavior during the development of our equation. Nevertheless, the empirical reference equation, which is fitted to data only up to pressures of 800 MPa and temperatures of 1073 K, yields a slightly better representation of these data up to 1600 K and more than 3600 MPa.

At even higher pressures and temperatures shock-wave measurements of the Hugoniot curve are available for some substances. The evaluation of the Hugoniot relation

$$h_{\mathrm{h}} - h_0 = \tfrac{1}{2}(p_{\mathrm{h}} - p_0)(\rho_0^{-1} + \rho_{\mathrm{h}}^{-1}) \tag{1}$$

or

$$u_{\mathrm{h}} - u_0 = \tfrac{1}{2}(p_{\mathrm{h}} + p_0)(\rho_0^{-1} - \rho_{\mathrm{h}}^{-1}) \tag{2}$$

yields data for the enthalpy h_{h} or the internal energy u_{h} as a function of pressure p_{h} and density ρ_{h} at shock-wave pressures up to 0.1 GPa and temperatures of several thousand Kelvin; the index 0 corresponds to the initial state prior to release of the shock wave. Consideration of these data in the development of reference equations of state, which are usually formulated as a function of temperature and density, results in nonlinear relations involving iterative solutions for temperature. Any attempt to use these data in linear optimization algorithms requires a precorrelation of the temperatures belonging to the Hugoniot data. Since no $p\rho T$ data, which could verify the precorrelated temperatures are available under these extreme conditions, this approach implies the risk of distorting the experimental information.

Figure 5 shows plots of the Hugoniot curve of carbon dioxide calculated from the recent equations of Span and Wagner [3] and of Pitzer and Sterner [7] and from the older equations of Ely et al. [34] and Ely [35, 36]. The relevant experimental data for carbon dioxide reach up to pressures of 28550 MPa and temperatures of approximately 4150 K; at higher pressures spontaneous disintegration is observed [37]. Iteration of the Hugoniot condition from the equation of Ely et al. [34] yields far too high pressures and the equation of Ely [35, 36] results in pressures which are far too low. Our new equation of state yields pressures which are also clearly too low, if the scatter of the data is identified with their uncertainty. However, bearing in mind the extreme conditions during a shock-wave experiment, we consider this result at least as reasonable. The equation of Pitzer and Sterner yields the best representation of the Hugoniot data, but again, there is a major difference in the way these data are considered.

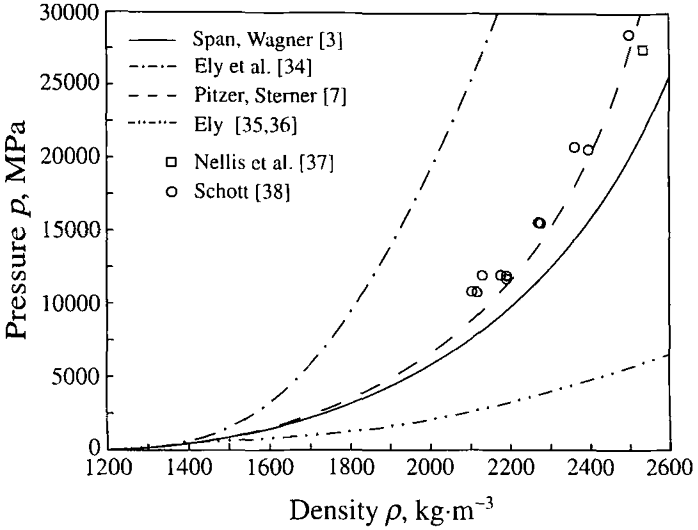

Fig. 5. Plots of the Hugoniot curve of carbon dioxide calculated from the equations of Span and Wagner [3], Pitzer and Sterner [7], Ely et al. [34], and Ely [35, 36]. The corresponding experimental results of Nellis et al. [37] and Schott [38] are given as symbols.

$p\rho T$ data derived from the Hugoniot data were used with high weights in fitting the coefficients of the equation of Pitzer and Sterner, whereas we used the Hugoniot data only for an assessment of the extrapolation behavior of our equation.

Figure 6 shows the plot of isotherms calculated from the equations of Ely [35, 36] and Ely et al. [34] in the pressure, temperature, and density range relevant for the representation of the Hugoniot data. The Hugoniot data at the lowest pressures correspond to temperatures of approximately 1500 K and the data at the highest pressures to temperatures of approximately 4150 K. The equation of Ely, which resulted in too low pressures on the Hugoniot curve (see Fig. 5), yields a much too steep plot of the $p\rho T$ isotherms and, correspondingly, too high pressures. For the equation of Ely et al., too high pressures could be expected from the plot of the Hugoniot curve, but Fig. 6 shows an unreasonable plot with intersecting $p\rho T$ isotherms and negative pressures. Obviously, the typical plot of the Hugoniot curve given in Fig. 5 is not sufficient for an assessment of the extrapolation behavior and has to be supplemented by other criteria, whereby conditions regarding the functional form of the equations turned out to be very useful (see Section 4). Both the equation of Pitzer and Sterner and our new equation yield reasonable plots of the same isotherms,

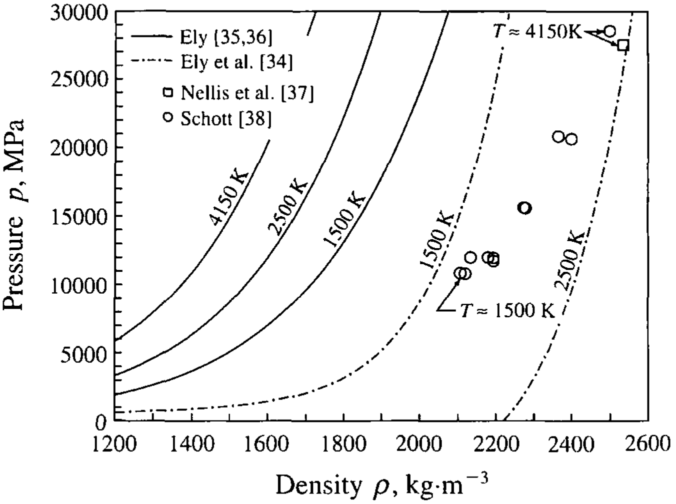

Fig. 6. Pressures calculated from the equations of Ely et al. [34] and Ely [35, 36] on three isotherms at very high temperatures. For comparison the experimental Hugoniot data of Nellis et al. [37] and Schott [38] are given together with approximate values of the temperature at the lowest and highest shock pressures.

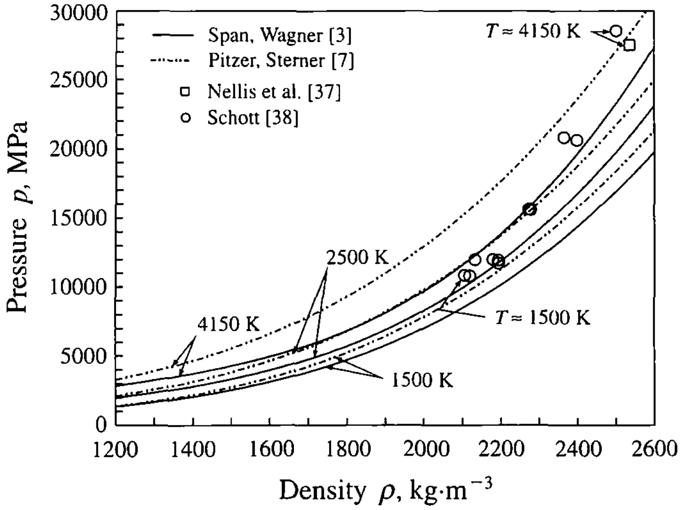

Fig. 7. Pressures calculated from the equations of Span and Wagner [3] and Pitzer and Sterner [7] on three isotherms at very high temperatures. For comparison the experimental Hugoniot data of Nellis et al. [37] and Schott [38] are given together with approximate values of the temperature at the lowest and highest shock pressures.

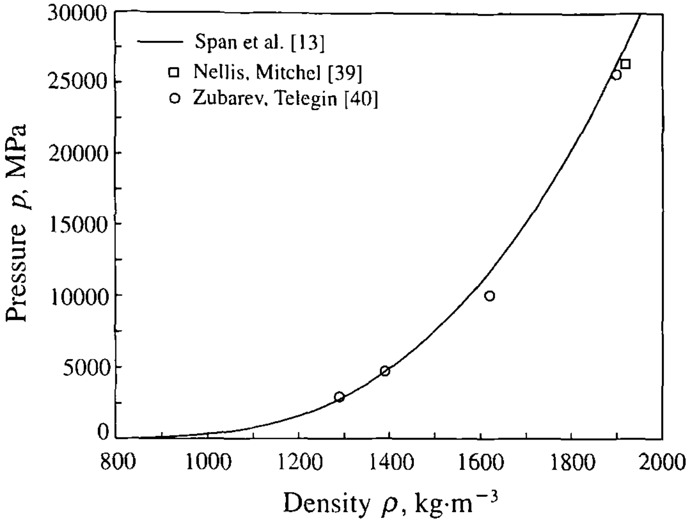

Fig. 8. Plot of the Hugoniot curve of nitrogen calculated from the equation of Span et al. [13]. The corresponding experimental results of Nellis and Mitchel [39] and Zubarev and Telegin [40] are given as symbols.

though the predicted pressures differ considerably especially for the 4150 K isotherm (see Fig. 7).

During the development of the new reference equation of state for nitrogen [13], Hugoniot data were directly used according to Eq. (2.1) as $\Delta h = h(p_{\mathrm{h}}, \rho_{\mathrm{h}}) - h(p_0, \rho_0)$ in combination with the new nonlinear optimization algorithm of Tegeler et al. [11, 26]. This procedure resulted in a good representation of the Hugoniot curve, although the Hugoniot data were used only with low weights; their contribution to the sum of squares was less than 1% of the total sum of squares. Figure 8 shows the plot of the Hugoniot curve calculated from the new equation of state for nitrogen. Obviously, reference equations of state are not necessarily inferior to special high-pressure equations with regard to the representation of Hugoniot data, but it remains questionable whether this very good representation is a kind of overfitting or not, since little is known about the accuracy of the data.

4. THE INFLUENCE OF THE FUNCTIONAL FORM

Today reference equations of state are usually formulated as empirical descriptions of the fundamental equation

$$f = f(T, \rho), \tag{3}$$

where the specific Helmholtz free energy f is usually split into a part representing the contribution of the hypothetical ideal gas, $f^0(T, \rho)$, at the given values of temperature T and density ρ and a residual part, $f^r(T, \rho)$. Thermal properties of a pure fluid can be described by derivatives of the residual part alone; the ideal-gas part is needed only for the description of caloric properties and can theoretically be derived at a high accuracy from spectroscopic data. Thus, the main problem in the development of reference equations of state is the formulation of a suitable empirical description of the residual part of the Helmholtz free energy. For this purpose, equations of the general form

$$\frac{f^r(T, \rho)}{RT} = \phi^r(\tau, \delta) = \underbrace{\sum_{i=1}^{I_{\text{Pol}}} n_i \, \delta^{d_i} \tau^{t_i}}_{\text{polynomial terms}} + \underbrace{\sum_{j=1}^{J_{\text{Exp}}} n_j \, \delta^{d_j} \tau^{t_j} \exp(-\delta^{p_j})}_{\text{exponential terms}} + \underbrace{\sum_{k=1}^{K_{\text{crit}}} n_k \, f_{\text{crit}}(\delta, \tau)}_{\text{critical region terms}} \tag{4}$$

have been developed from the classical BWR equation of state [41], where R is the gas constant, δ the reduced density ρ/ρ_n and τ the inverse reduced temperature T_n/T. Depending on the accuracy of the available data sets and the distribution of the data, the number of terms in Eq. (4), with one adjustable parameter n_i, n_j, or n_k each, varies between 20 and more than 50. Exponential terms can be found with density powers p_j ranging from 1 to 8; according to the value of p_j these terms are called E_1 to E_8 terms here. The critical-region terms in Eq. (4) correspond to different expressions which have been developed in order to improve the description of properties in the critical region (see, e.g., Refs. 3, 25, and 42), but since these terms have no influence on the extrapolation behavior, they are not discussed here. In state-of-the-art equations the values of the exponents d_i, t_i, d_j, t_j, and p_j, the total number of terms and their distribution between the different types of terms are determined by optimization strategies [11, 22–24, 26, 43], while the coefficients n_i, n_j, and n_k are determined by nonlinear multiproperty fits.

Older equations of state, e. g., the well-known MBWR-type equation [30], are usually formulated for the compression factor $z(T, \rho) = p(T, \rho)/(\rho RT)$ using polynomial terms and E_2 terms as functional forms. Since the exponents d_i and t_i of the polynomial terms do not change when the equation for z is integrated to yield ϕ^r, the results discussed here are valid for formulations in both z and ϕ^r.

Generally the terms in Eq. (4) are highly intercorrelated and it is assumed that the behavior of an empirical equation of state cannot be associated with the behavior of single terms in the equation. This conclusion is true in most cases, but not for the extrapolation to very high temperatures and very high pressures, which also correspond to high densities. For high densities the behavior of the equation is influenced only by polynomial terms and by E_1 terms, if the E_1 terms are combined with high density powers ($d_j \geqslant \approx 5$). For high temperatures, which correspond to small values of τ, terms with high temperature exponents t_i or t_j fade away, too. Under these conditions, which are typical, for example, for the region covered by Hugoniot data, one or a small number of leading terms can be identified which determine the behavior of the whole equation.

For the equations of Ely [35, 36], Ely et al. [34], and Span and Wagner [3], Table I lists the number of polynomial terms I_{Pol}, the values of their exponents d_i and t_i, and rounded values of their coefficients n_i according to the general form given in Eq. (4); the MBWR-type equation of Ely et al. [34] was integrated and expressed in reduced variables to match with the form of Eq. (4). The pressure calculated from an equation for ϕ^{r} corresponds to

$$p = p^0 + p^{\mathrm{r}} = RT\rho + RT\,\frac{\rho^2}{\rho_n}\left(\frac{\partial \phi^{\mathrm{r}}}{\partial \delta}\right)_\tau \tag{5}$$

where p^0 is the pressure of the hypothetical ideal gas and p^{r} is the residual contribution to the pressure. Thus, along an isotherm the contribution of a polynomial term i in Eq. (4) to the residual pressure grows proportional to ρ^{d_i+1}.

At high densities and moderate temperatures, the behavior of the MBWR-type equation [34] is dominated by the polynomial term with $I = 19$ and $d_{19} = 8$. The high-density power of this term is responsible for the sharp increase in pressure on low-temperature isotherms, which is still visible for the 1500 K isotherm in Fig. 6. At higher temperatures, the influence of this term decreases due to the inverse temperature exponent $t_{19} = 3.0$ and the term with $I = 10$, $d_{10} = 3$, and $t_{10} = 0.0$ becomes dominant. Since n_{10} is negative, the whole equation yields intersecting isotherms and negative pressures for high temperatures. This example is typical for an empirical equation of state which describes the available data at high densities with many highly intercorrelated polynomial terms; equations like this yield an unpredictable and, in most cases, unreasonable extrapolation behavior.

At high temperatures and densities the behavior of the equation of Ely [35, 36], which uses the functional form developed by Schmidt and

Table I. Parameters of the Polynomial Terms in the Equations of State for Carbon Dioxide of Ely [35, 36], Ely et al. [34], and Span and Wagner [3]

	Ely et al.[a] [34]			Ely [35, 36]			Span and Wagner [3]		
T_n[b]	1 K			304.130 K			304.1282 K		
ρ_n	$44.0098\ \mathrm{kg \cdot m^{-3}}$			$467.824\ \mathrm{kg \cdot m^{-3}}$			$467.6\ \mathrm{kg \cdot m^{-3}}$		
I_{Pol}	19			13			7		
i	n_i	d_i	t_i	n_i	d_i	t_i	n_i	d_i	t_i
1	$-0.197 \cdot 10^{+0}$	1	0.0	$0.485 \cdot 10^{+0}$	1	0.0	$0.389 \cdot 10^{+0}$	1	0.00
2	$0.176 \cdot 10^{+2}$	1	0.5	$-0.192 \cdot 10^{+1}$	1	1.5	$0.294 \cdot 10^{+1}$	1	0.75
3	$-0.388 \cdot 10^{+3}$	1	1.0	$0.452 \cdot 10^{+0}$	1	2.5	$-0.559 \cdot 10^{+1}$	1	1.00
4	$0.506 \cdot 10^{+5}$	1	2.0	$0.838 \cdot 10^{+2}$	2	−0.5	$-0.768 \cdot 10^{+0}$	1	2.00
5	$-0.553 \cdot 10^{+7}$	1	3.0	$0.311 \cdot 10^{+0}$	2	1.5	$0.317 \cdot 10^{+0}$	2	0.75
6	$0.265 \cdot 10^{-2}$	2	0.0	$-0.184 \cdot 10^{+0}$	2	2.0	$0.548 \cdot 10^{+0}$	2	2.00
7	$-0.214 \cdot 10^{+1}$	2	1.0	$0.449 \cdot 10^{-1}$	3	0.0	$0.123 \cdot 10^{+0}$	3	0.75
8	$0.105 \cdot 10^{+3}$	2	2.0	$-0.362 \cdot 10^{-1}$	3	1.0			
9	$-0.410 \cdot 10^{+7}$	2	3.0	$-0.170 \cdot 10^{-1}$	3	2.5			
10	$-0.127 \cdot 10^{-3}$	3	0.0	$0.804 \cdot 10^{-3}$	6	0.0			
11	$0.140 \cdot 10^{+0}$	3	1.0	$0.320 \cdot 10^{-3}$	7	2.0			
12	$0.206 \cdot 10^{+1}$	3	2.0	$-0.659 \cdot 10^{-5}$	7	5.0			
13	$0.120 \cdot 10^{-2}$	4	1.0	$-0.462 \cdot 10^{-4}$	8	2.0			
14	$-0.162 \cdot 10^{+0}$	5	2.0						
15	$0.217 \cdot 10^{+3}$	5	3.0						
16	$0.522 \cdot 10^{-2}$	6	2.0						
17	$-0.478 \cdot 10^{-4}$	7	2.0						
18	$-0.255 \cdot 10^{+0}$	7	3.0						
19	$0.383 \cdot 10^{-2}$	8	3.0						

[a] The equation of Ely et al. was integrated to match with Eq. (4); the high numbers of the coefficients of this equation are due mainly to the reduction with $T_n = 1$ K.

[b] The equations of Ely and Ely et al. are valid for temperatures according to IPTS-68 [44], while our new equation is valid for temperatures according to ITS-90 [45]. However, the difference between the temperature scales is negligible for the extrapolation discussion.

Wagner [46] for oxygen, is dominated by the term with $I = 10$, $d_{10} = 6$, and $t_{10} = 0.0$. The polynomial terms with higher density powers are theoretically dominant in the high-density limit, but since they are combined with higher values of t_i, this influence becomes visible only at low temperatures, where carbon dioxide is already in the solid state for the corresponding densities. Though for this equation intersections of isotherms are avoided in the fluid region, extrapolation of the oxygen-type equation does not yield reasonable results. Figure 6 shows that the exponent $d_{10} = 6$ results in a very sharp increase in pressure.

Based on these and similar observations for other equations of state, an attempt was made to formulate demands on the mathematical form of an empirical equation of state in order to ensure a more reasonable extrapolation behavior. These demands can be summarized in the following way:

- The number of polynomial terms in the equation should be small; if possible, less than 10.

Intercorrelations between the polynomial terms affecting the extrapolation to high densities cannot be avoided completely this way, but they are reduced considerably. At the same time an increased number of E_1 terms has to be used to guarantee the necessary flexibility of the equation in the range of intermediate densities. For functional forms like this, usually only one or two terms determine the behavior of the equation in the range of very high temperatures and densities. The term which is dominant at high densities (high values of δ) and high temperatures (small values of τ) is the polynomial term with the smallest temperature exponent t_i among the terms with the highest density exponents d_i. For this term the following requirements can be formulated:

- The coefficient n_i has to be positive to yield a positive contribution to the residual pressure.
- The temperature exponent should fulfill the condition $0 < t_i < 1$ since the pressure should increase on an isochore with increasing temperature but the compression factor should decrease.
- The density exponent d_i has to be an integer value and should be equal to three or four.

These conditions were considered during the development of the new reference equations of state for carbon dioxide [3], water [9, 10], argon [11, 12], and nitrogen [13]. For our new equation of state for carbon dioxide, Fig. 9 shows the relative contributions of all polynomial terms, of all E_1 terms, and of the leading polynomial term to the residual pressure p^r; the plotted lines correspond to isotherms. In the region where the available Hugoniot data indicate that carbon dioxide is still chemically stable roughly for reduced densities $4.5 < \rho/\rho_c < 5.5$ and reduced temperatures $5 < T/T_c < 15$, the polynomial term with $d_7 = 3$ and $t_7 = 0.75$ dominates the behavior of the equation with a contribution of more than 70% of the total residual pressure. Since this dominant term fulfills the requirements given above, the whole equation behaves reasonably in the high-density limit. The negative contribution of the E_1 terms in the range of intermediate densities was not desired with respect to extrapolation but unavoidable for the representation of accurate data at lower temperatures;

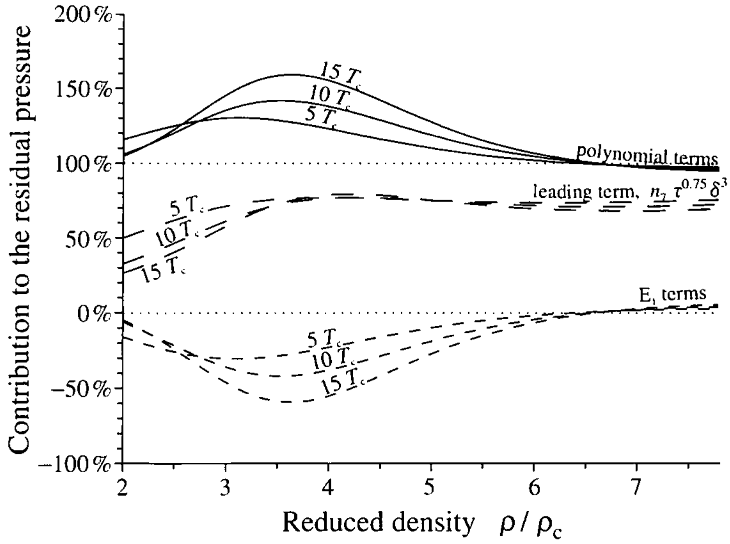

Fig. 9. Contribution to the residual pressure p^r according to Eq. (5) of all polynomial terms, all E_1 terms, and the leading polynomial term of the equation of Span and Wagner [3] for carbon dioxide.

at least with respect to basic properties such as pressure, enthalpy, and fugacity, it does not affect the extrapolation up to the limits where spontaneous disintegration occurs.

Similar to carbon dioxide, the mathematical form has finally been a compromise between requirements for representing the data set and the extrapolation behavior for the other reference equations [9–13] as well. But nevertheless, the extrapolation behavior of an empirical equation of state becomes predictable from its mathematical structure by such investigations and unreasonable behavior can be avoided. The new equations of state for carbon dioxide, water, argon, and nitrogen yield reasonable results up to extreme temperatures and pressures.

The condition given for the density power of the leading term, $3 \leqslant d_i \leqslant 4$, results from experiences with the slope of isotherms calculated from different preliminary equations and is completely empirical. This condition seems to be inconsistent with the results of Pitzer and Sterner [4, 6–8], who claim that the isothermal slope of the residual part of the Helmholtz free energy becomes linear for high temperatures and pressures. Based on these theoretical considerations it seems incomprehensible why the equation of Pitzer and Sterner and our new equation of state for carbon dioxide yield at least similar results up to the limits of the chemically stable region (see Figs. 4, 5, and 7). A more detailed investigation of the numerical behavior of the formulation of Pitzer and Sterner shows that its behavior at high densities is determined by a strong intercorrelation between the positive contribution of the polynomial term, which is linear in density, and the negative contribution of the fractional terms in the equation. The leading linear term becomes dominant only for densities far beyond the densities accessible by shock-wave measurements, which reach up to $\rho/\rho_c \approx 5.5$ for nondisintegrated carbon dioxide. In the region covered by Hugoniot data the equation of Pitzer and Sterner mimics a slope of ϕ^r, which implies a density dependence with exponents between 2.6 for 4150 K and 2.9 for 1500 K. Thus, the results of Pitzer and Sterner indeed support leading density powers of $d_i = 3$ for the polynomial terms in an empirical equation of state.

5. THE REPRESENTATION OF IDEAL CURVES AS A CRITERION FOR REASONABLE EXTRAPOLATION BEHAVIOR

Ideal curves are curves along which one property of a real fluid is equal to the corresponding property of the hypothetical ideal gas at the same temperature and density. Based on this very general definition, ideal curves can be defined for almost every property, but usually the discussion is focused on the ideal curves of the compression factor and its first derivatives; these curves are given in Table II together with their definitions. In the 1960s, there was an intensive investigation of ideal curves in

Table II. The Zeroth- and First-Order Ideal Curves of the Compression Factor and Their Definition in Terms of the Compression Factor, $z(T, \rho)$, and of the Residual Part of the Reduced Helmholtz Energy, $\phi^r(\tau, \delta)$

Designation	Definition in terms of the	
	Compression factor	Residual Helmholtz energy
(Classical) ideal curve	$z = 1$	$\left(\frac{\partial\phi^r}{\partial\delta}\right)_\tau = 0$
Boyle curve	$\left(\frac{\partial z}{\partial\rho}\right)_T = 0$	$\left(\frac{\partial\phi^r}{\partial\delta}\right)_\tau + \delta\left(\frac{\partial^2\phi^r}{\partial\delta^2}\right)_\tau = 0$
Joule–Thomson inversion curve	$\left(\frac{\partial z}{\partial T}\right)_p = 0$	$\left(\frac{\partial\phi^r}{\partial\delta}\right)_\tau + \delta\left(\frac{\partial^2\phi^r}{\partial\delta^2}\right)_\tau + \tau\left(\frac{\partial^2\phi^r}{\partial\delta\,\partial\tau}\right) = 0$
Joule inversion curve	$\left(\frac{\partial z}{\partial T}\right)_\rho = 0$	$\left(\frac{\partial^2\phi^r}{\partial\delta\,\partial\tau}\right) = 0$

order to specify criteria for a generalized behavior of pure fluids. Well-known results are those of Brown [47], which were summarized by Rowlinson [48], and the results of Gunn et al. [49] and Miller [50], especially on the Joule–Thomson inversion curve. Less well-known are the very detailed studies by Morsy [51], Straub [52], and Schaber [53], which have been published only in German. More recently, Angus [54] and de Reuck [1] gave short summaries of the known characteristics of ideal curves. Although various authors have stated that the representation of ideal curves is a sensitive test for the extrapolation behavior of equations of state, systematic investigations have always dealt with results for simple model fluids, with simple equations of state, or with values derived directly from experimental data or from compression factors tabulated for corresponding states approaches. In order to see whether ideal curves are really useful for an assessment of the extrapolation behavior of empirical equations of state, we compared the ideal curves calculated from equations of state for argon [11, 12], nitrogen [13, 29, 30], oxygen [46], methane [25], ethane [55], carbon dioxide [3, 7], water [9, 10], and helium [56] with each other and with the "theoretical" predictions.

Figure 10 shows a typical plot of the ideal curves discussed here in a reduced (pressure, temperature) diagram with logarithmic axes. The dashed lines indicate the limits of the regions, where primary data (usually $p\rho T$ data) are available for the corresponding substance. For reference substances with low critical temperatures and pressures such as nitrogen and argon, the Boyle, the ideal, and the Joule–Thomson inversion curve lie completely within the range covered by primary data; for helium even the Joule inversion curve lies within this range. The situation changes if substances with higher values for the critical temperature and the critical pressure or with a more restricted data set are investigated. For carbon dioxide and methane the Joule–Thomson inversion curve reaches into the extrapolation region; for water, oxygen, and ethane the Boyle and the ideal curve exceed the temperature range and the Joule inversion curve also exceeds the pressure range covered by data.

When considering results of earlier investigations, certain features of the ideal curves should be universal at least for simple substances [49, 50, 53]. Table III summarizes the results of a comparison of these "theoretical predictions" with the corresponding values calculated from the equations of state considered here. For nitrogen and carbon dioxide, the results of different equations are given for comparison.

The best agreement among the results calculated from the different equations of state can be found for the densities on the ideal and the Boyle curve at $T = T_c$. Since simple corresponding-states approaches yield good results in the extended critical region of simple fluids, this good agreement

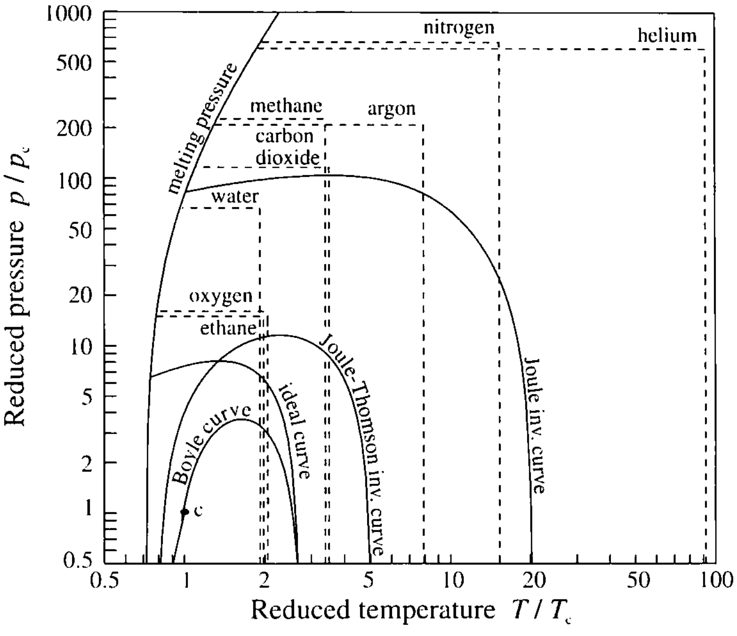

Fig. 10. A typical plot of the zeroth- and first-order ideal curves of the compression factor in a reduced double-logarithmic (pressure, temperature) diagram. The dashed lines indicate the regions where primary data are available for the substances considered in this paper.

could be expected. The results for carbon dioxide, water, and helium differ considerably.

For argon, methane, oxygen, and nitrogen the position of the pressure maximum of the Joule–Thomson inversion curve varies only within ±2% in terms of reduced pressure and reduced temperature. Due to its location at reasonably high pressures and more than twice the critical temperature, the position of this maximum could be an interesting extrapolation criterion, for example, for equations of state for refrigerants, but unfortunately the results differ significantly from the expected values for more complex fluids. The same is true for the reduced temperatures at the end points of the Boyle, the ideal, and the Joule–Thomson inversion curve, which agree within ±4% for argon, methane, oxygen, and nitrogen, while significantly different results were found for the other substances.

Thus, the numerical results for the characteristic points of the different ideal curves are useful as criteria for an assessment of the extrapolation behavior only for simple substances with limited data sets. A comparison between the different equations of state for nitrogen and carbon dioxide

Table III. Characteristic Values of the Ideal Curves of Helium, Argon, Methane, Oxygen, Nitrogen, Ethane, Carbon Dioxide, and Water Calculated from Accurate Equations of State in Comparison with "Theoretically" Predicted Values

Substance	Equation	ω	θ_B, θ_I[a]	θ_{JT}[b]	θ_J[c]	$\delta_B\|_{T=T_c}$[d]	$\delta_I\|_{T=T_c}$[e]	$\pi_{max,JT}$	θ[f]
Predicted values		0.00	2.66	5.00	19.5	1.435	2.235	11.8	2.25
Helium	Sychev et al. [56]	−0.39	4.67	9.03	29.9	1.407	2.201	17.5	4.48
Argon	Tegeler et al. [11, 12]	0.00	2.71	5.07	20.3	1.425	2.201	11.6	2.30
Methane	Setzmann & Wagner [25]	0.01	2.67	5.14	[g]	1.428	2.203	11.8	2.28
Oxygen	Schmidt & Wagner [46]	0.02	2.62	4.90	[g]	1.425	2.201	11.7	2.25
Nitrogen	Span et al. [13]	0.04	2.59	4.82	17.4	1.425	2.193	11.6	2.20
	Jacobsen et al. [29]	0.04	2.60	4.83	16.6	1.423	2.191	11.6	2.20
	Jacobsen & Stewart [30]	0.04	2.58	4.76	16.1	1.429	2.195	11.6	2.21
Ethane	Friend et al. [55]	0.10	2.45	4.57	[g]	1.428	2.196	12.1	2.14
Carbon dioxide	Span & Wagner [3]	0.23[h]	2.37	4.45	26.9	1.441	2.232	12.5	1.94
	Pitzer & Sterner [7]	0.23[h]	2.36	4.29	23.8	1.448	2.242	13.4	1.90
Water	Pruß & Wagner [9, 10]	0.34	2.35	3.93	7.7	1.540	2.638	18.7	1.96

[a] Reduced temperature $\theta = T/T_c$, at which the Boyle and the ideal curve end for $\rho = 0$; at this temperature the condition $B(T) = 0$ holds for the second virial coefficient.

[b] Reduced temperature $\theta = T/T_c$, at which the Joule–Thomson inversion curve ends for $\rho = 0$; at this temperature the condition $dB/dT = B/T$ holds for the second virial coefficient.

[c] Reduced temperature $\theta = T/T_c$, at which the Joule inversion curve ends for $\rho = 0$; at this temperature the condition $dB/dT = 0$ holds for the second virial coefficient.

[d] Reduced density $\delta = \rho/\rho_c$ on the Boyle curve for $T = T_c$.

[e] Reduced density $\delta = \rho/\rho_c$ on the ideal curve for $T = T_c$.

[f] Reduced pressure $\pi = p/p_c$ and temperature $\theta = T/T_c$ at the pressure maximum of the Joule Thomson inversion curve.

[g] Equations without a maximum in $B(T)$ yield no intersection between the Joule inversion curve and the axis $\rho = 0$.

[h] Calculated from an extrapolation of the vapor pressure equation given in Ref. 3.

supports this thesis. Although the accuracy of reference equations of state for nitrogen in the high-temperature, high-pressure region has been improved substantially since 1973 [13, 29, 30], the three investigated equations yield very similar results for the characteristic points of the ideal curves; based on these results, no assessment of the equations is possible. For carbon dioxide, the differences between the equation of Span and Wagner [3] and that of Pitzer and Sterner [7] are larger, but since carbon dioxide does not belong to the group of simple substances, the differences are not yet significant enough for an assessment.

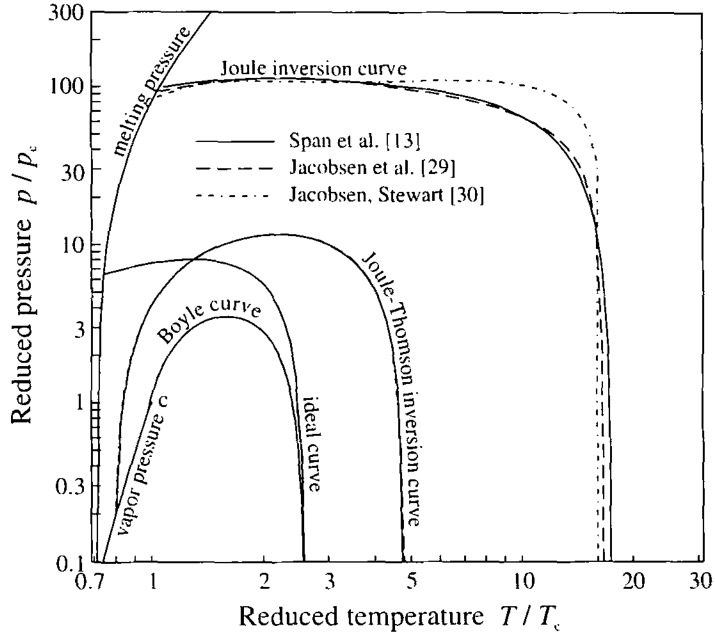

Fig. 11. Plots of the zeroth- and first-order ideal curves of the compression factor calculated from three reference equations of state for nitrogen [13, 29, 30].

Nevertheless, the plot of the ideal curves[6] contains important information on the behavior in the high-temperature, high-pressure region. To demonstrate the sensitivity of this graphical criterion, Fig. 11 shows the plot of the ideal curves of nitrogen calculated from three different equations of state. For the Boyle, the ideal, and the Joule–Thomson inversion curve all three equations yield very similar plots. Based on the level of accuracy achieved by empirical reference equations of state, no problems in the representation of ideal curves should occur in the range where accurate data are available. For the Joule inversion curve calculated from the equation of Jacobsen and Stewart [30], an inflection point can be seen at about $T/T_c \approx 3.5$ and $p/p_c \approx 100$. At this point the differences between densities calculated from the equations of Jacobsen and Stewart and Span et al. [13] are still within $\Delta p/p \approx \pm 0.1\%$ but with an increasing tendency toward higher temperatures and pressures where they exceed the limit of

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[6] Plots of the ideal curves, the Boyle curves, the Joule–Thomson inversion curves, and the Joule inversion curves of all considered substances are given in the Appendix. For helium, the results of a transformation by effective critical parameters [57] are also shown in the Appendix.

±1 %. Thus, the plot of the Joule inversion curve seems to be a reasonably sensitive indication for incorrect behavior of an equation of state at high temperatures and pressures.

The same can be shown from a comparison between the two equations [3, 7] for carbon dioxide. Figure 3 shows that the equation of Pitzer and Sterner [7] deviates from the data of Vukalovich and Altunin [32] by up to $\Delta p/p \approx 1\%$ for $T/T_c \leqslant 3.5$ and $p/p_c \leqslant 8$; in Fig. 12, these deviations result in visible deformations of the Boyle and the ideal curve. At higher temperatures stronger deformations of the Joule–Thomson and the Joule inversion curve occur.

Since the equation of Pitzer and Sterner was fitted to second virial coefficients resulting from a corresponding-states approach, the end temperatures for all ideal curves are constrained to values within the expected limits (see the footnotes to Table III). But obviously inconsistencies between the second virial coefficients and other data in the high-temperature region resulted in "overhanging" plots of all ideal curves. If corresponding-states approaches are used to improve the extrapolation behavior, a transformation of $p\rho T$ data seems to be advantageous (see, e.g., Ref. 58).

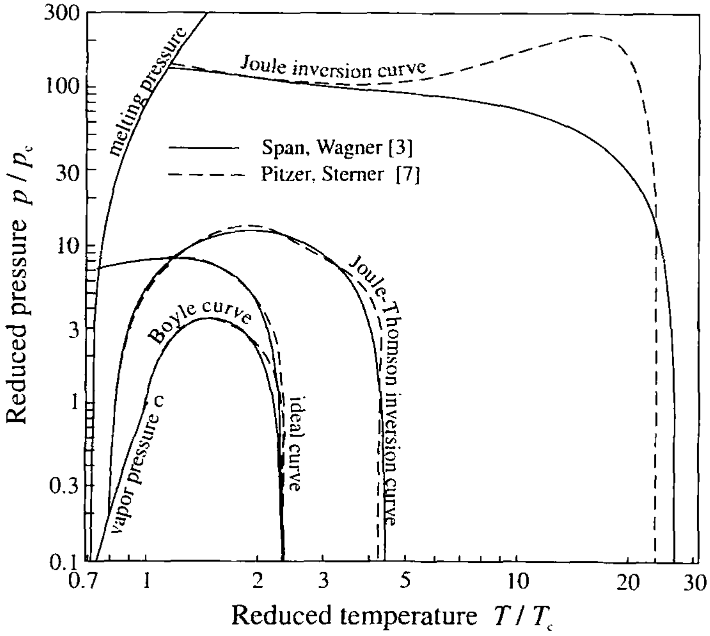

Fig. 12. Plots of the zeroth- and first-order ideal curves of the compression factor calculated from the equation of Span and Wagner [3] and Pitzer and Sterner [7] for carbon dioxide.

6. SUMMARY AND CONCLUSION

It has been shown that state-of-the-art multiparameter equations of state are able to represent thermal and caloric data up to very high pressures and temperatures and that they are nevertheless not flexible enough to follow systematically deviant plots of experimental data in this region. Comparisons with fugacities and Hugoniot data at very high pressures and temperatures have been shown as examples for an assessment of the extrapolation behavior.

At very high temperatures and pressures, the extrapolation behavior of an equation of state can be explained by certain features of its functional form. The investigation of these relations resulted in demands on the functional form of an empirical equation of state, which make it possible to achieve a reasonable extrapolation behavior up to extreme conditions of temperature and pressure.

Finally, ideal curves have been investigated as an extrapolation criterion for the region of high temperatures and high pressures. Numerical values for reduced variables at characteristic points of the ideal curves are sufficiently universal only for simple substances, but the plots given in the Appendix show common features for all investigated substances. Deformations of the ideal curves turned out to be a suitable criterion for the detection of faulty behavior.

Considering these results, empirical equations of state can be designed to behave reasonably far beyond the pressure and temperature range where accurate experimental data are available, if intended even up to the limits of chemical stability of the respective substance.

Though this statement is very encouraging, it also contains the major shortcoming of current findings on the extrapolation behavior of empirical equations of state. While different criteria can be used to test whether the extrapolation behavior of an equation of state is reasonable, only little is known about uncertainties beyond the range covered by reliable experimental data. A systematic investigation of this problem is lacking.

Furthermore, corresponding-states approaches (see e.g., Refs. 58 and 59) and molecular dynamics calculations (see e.g., Ref. 60) can be very useful both for tests regarding the extrapolation behavior of empirical equations of state and for establishing equations of state for substances with restricted data sets. Though several publications on these techniques exist, their potential for the development of reference equations of state has never been investigated to a level where clear rules for their use, their limitations, and the resulting uncertainties could be given.

Finally, there is still no common agreement about the importance of the extrapolation behavior. While thermodynamic data at very high temperatures and pressures are regarded as important, for example, for substances such as argon, nitrogen, and carbon dioxide, they are probably of purely academic interest for refrigerants which disintegrate at temperatures below twice their critical temperature. Finally, since there is always a compromise among the complexity of an equation of state, the expenditure for its establishment, its quality in the regions where experimental data are available, its extrapolation behavior, and various other criteria, it is not useful to formulate extreme requirements on the extrapolation behavior under all circumstances. As long as there is no common agreement on this topic, the most important conclusion is that authors should indicate limitations of their equations of state.

APPENDIX

The plots of the Boyle curves, the classical ideal curves, the Joule–Thomson inversion curves, and the Joule inversion curves of all considered substances are given in Figs. A1 to A4. The general shape of the curves is very similar except for water and helium; conclusions drawn for the Joule inversion curve remain vague, since the plots of this curve reflect the extrapolation behavior of the equations of state rather than features of the considered substances. Only the Joule inversion curve of helium lies completely within the range covered by primary data, but the shape of the ideal curves of the quantum gas helium is too different to allow well-founded conclusions for other substances. The ideal and the Boyle curve of helium can be scaled to the corresponding curves of simple substances by the effective critical parameters proposed by Gunn et al. [57], but for the Joule–Thomson inversion and the Joule inversion curve this approach fails (see Fig. A5). Thus, the Joule inversion curves of argon and nitrogen are probably the best approximations of the general shape of the Joule inversion curve of simple fluids.

ACKNOWLEDGMENTS

The authors are indebted to the Deutsche Forschungsgemeinschaft for their financial support in connection with the development of the new equations of state for carbon dioxide [3] and nitrogen [13]. Furthermore, we are indebted to all participants of the fifth and sixth workshop on equations of state, whose contributions to the extrapolation discussion were inspiring and helpful, and, especially, to Mrs. K. M. de Reuck, whose summary of the discussion in 1990 [1] was the starting point of this work.

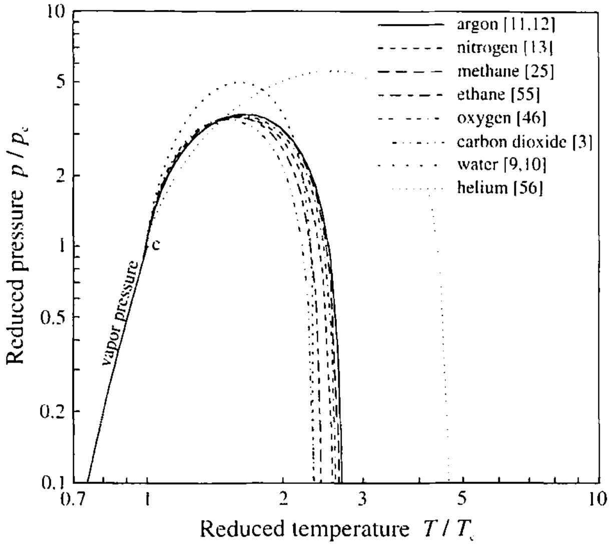

Fig. A1. Plots of the Boyle curves calculated from reference equations of state for all substances considered in this paper.

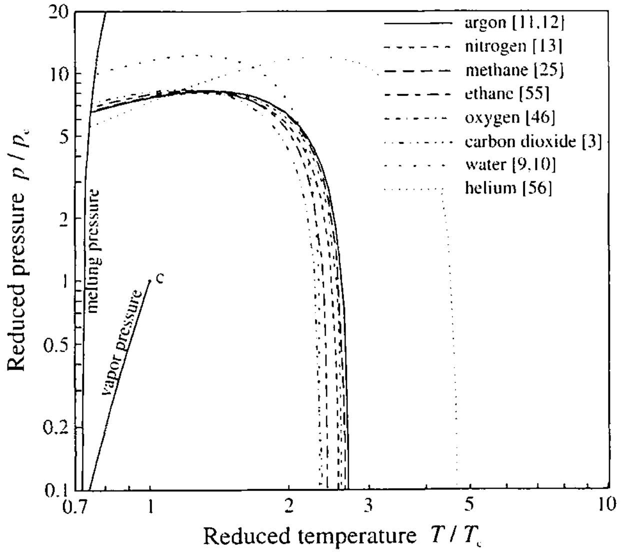

Fig. A2. Plots of the ideal curves calculated from reference equations of state for all substances considered in this paper.

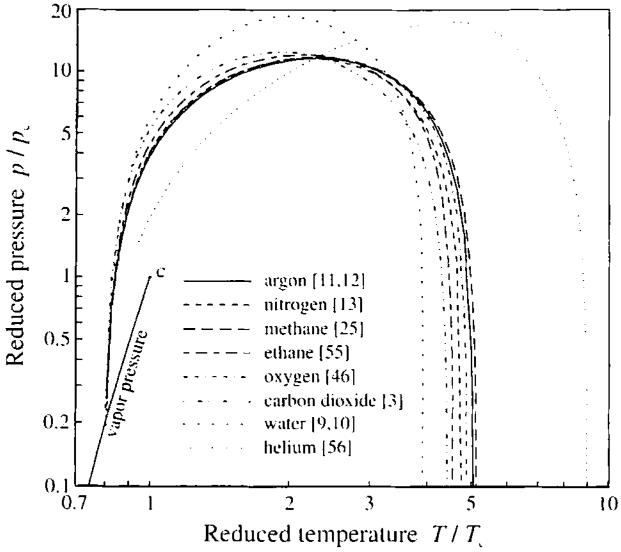

Fig. A3. Plots of the Joule-Thomson inversion curves calculated from reference equations of state for all substances considered in this paper.

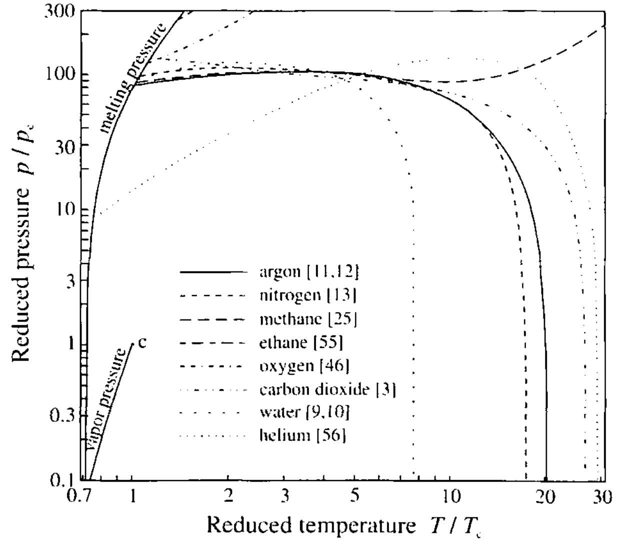

Fig. A4. Plots of the Joule inversion curves calculated from reference equations of state for all substances considered in this paper.

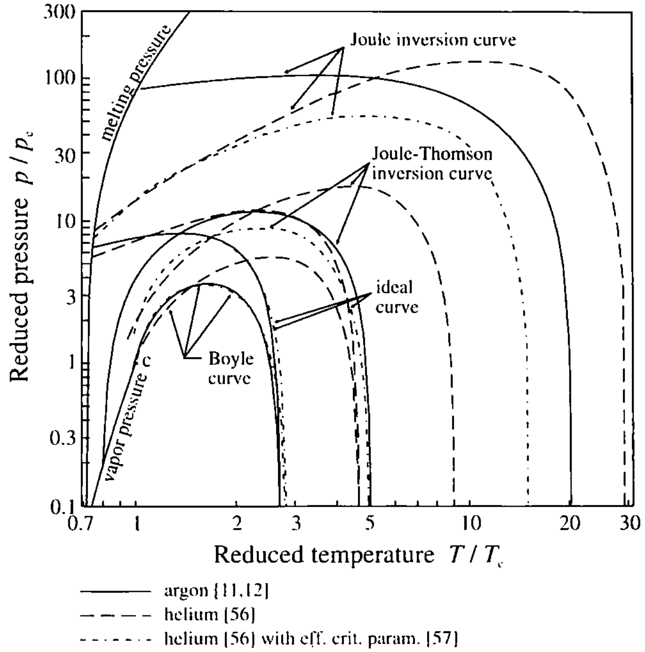

Fig. A5. Plots of the zeroth- and first-order ideal curves of the compression factor calculated from the equation of Sychev et al. [56] for helium and from the same equation after scaling with the effective critical parameters proposed by Gunn et al. [57]. The corresponding curves for argon [11, 12] are given for comparison. The plotted phase boundaries correspond to the phase boundaries of argon.

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