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Accurate Effective Potentials of Real Substances from Acoustic Virial Coefficients

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Accurate second acoustic virial coefficients have been employed to determine parameters of an effective intermolecular potential for nine pure substances: argon, nitrogen, carbon dioxide, carbon tetrafluoride, and the first five alkanes (methane, ethane, propane, butane, and pentane). The values used for the second acoustic virial coefficients were taken from data reported in the literature. To obtain the form and parameters of the effective potential, we employed an inversion method recently introduced for volumetric second virial coefficients of nonconformal potentials. The potential parameters determined in this way are useful in predicting various gas properties. The model reproduces the experimental second virial data within their uncertainty, including volumetric second virial coefficients that were not used in the potential determination.

KEY WORDS: acoustic virial coefficients; intermolecular potentials; second virial coefficients.

1. INTRODUCTION

It is well known that thermodynamic properties of fluids can be obtained from a knowledge of the interactions between molecules. Nevertheless, there is no direct way to measure the latter. Hence, it is common to measure the thermodynamic properties and then infer from them the particular features of the molecular interactions. This approach is known in the literature as the inversion problem and some progress has been made in the past [1, 2]. Since the connection between the thermodynamic properties of a fluid and the interaction potential between its molecules is

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firmly established at low densities, i.e., for the gas phase, most of the work on the inversion problem has been on dilute gases. This restriction has the further advantage that only pair interactions are needed.

Some of the properties used in the inversion problem in gases are the shear viscosity, thermal conductivity, Joule–Thomson coefficients, volumetric virial coefficients, $B(T)$ [3, 4], and more recently, acoustic virial coefficients, $\beta_a(T)$ [5].

From the above list, $B(T)$ and $\beta_a(T)$ have been the most useful, since they have a simple relationship with the binary intermolecular potential energy. Several types of methods have been developed to obtain the intermolecular potential from these virial coefficients, and their limitations have been critically assessed by Knobler [2].

The most common methods assume a particular functional form for the intermolecular potential with few adjustable parameters, which are then fitted by minimizing the deviations between the predicted $B(T)$ or $\beta_a(T)$ and their experimental values over the measured temperature range. These methods have as advantages their easy implementation and that they provide an explicit function for the potential. Their principal disadvantage is that the accuracy of the result depends on they functional form proposed. An alternative approach was developed by Smith and co-workers [6, 7] for spherical molecules and extended by Ewing et al. [8] for nonspherical molecules. In this method no potential form is preassumed, but its implementation is rather difficult, since it requires a great amount of quality experimental data. For this reason, its application has been limited to a few substances [6–8].

This paper deals with a method recently proposed [9–11] in which the potential form is not completely predetermined, is easy to implement, and can be used for substances for which there is not much experimental information. The method is based on an exact extension of the principle of corresponding states to certain pairs of nonconformal potentials. It has been shown that the volumetric second virial coefficients $B(T)$ and $B_0(T)$ of two nonconformal intermolecular potentials $U(r)$ and $U_0(r)$ which differ in their slopes by a constant factor S are related to each other by a simple linear relationship [10]. It has also been shown that for many gases of interest, the above extension provides an excellent approximation [11]. Besides a simple expression for virial coefficients, the theory provides a reliable inversion method.

However, the application of the theory to $B(T)$ is limited by the accuracy of pVT data, which are usually not very good at low temperatures, mainly because of adsorption problems. This limitation also prevents the test of the constant-slope approximation and, hence, of the applicability of the theory. An alternative to overcome these limitations is the use of second acoustic virial coefficients β_a, which are normally more precise and accurate than the determinations of B at essentially any temperature.

In this paper, we extend the theory to acoustic virial coefficients and apply it to several substances with different molecular shapes. In Section 2 we describe the basic results of the theory and extend it to deal with the second acoustic virial coefficient. The results of this work are presented and discussed in Section 3. And finally, the main conclusions are presented in Section 4.

2. THEORY

According to del Río et al. [9–11] the second virial coefficient $B(T)$ of a gas of interest can be expressed in terms of a reference $B_0(T)$. In terms of reduced second virial coefficients B^*, this relationship is

$$\begin{aligned} B^*(T^*) &= \frac{3B(T^*)}{2\pi L r_m^3} \\ &= 1 - S + SB_0^*(T^*) \qquad (1) \end{aligned}$$

where L is Avogadro's constant, $T^* = kT/\varepsilon$ is the reduced temperature, k is Boltzmann's constant, r_m, ε, and S are parameters characterizing the potential of interest U, and B_0^* is the reduced virial coefficient derived from a reference spherical potential $U_0(r)$. When U_0 is chosen suitably, Eq. (1) is a good approximation for a wide class of gases and is exact when the slopes of U and U_0 against r^3 differ by a constant factor S. The parameters r_m and ε determine, respectively, the distance and energy scales of U, and S is a shape parameter. Of course, when $S = 1$, U and U_0 are conformal, and from Eq. (1), $B^*(T^*)$ and $B_0^*(T^*)$ become identical.

Here we choose the Kihara-type reference potential:

$$\frac{U_0(z)}{\varepsilon_0} = \left[\frac{1-a}{z-a}\right]^{12} - 2\left[\frac{1-a}{z-a}\right]^{6}$$

where $z = r/r_{m0}$ is a dimensionless distance, r is the intermolecular distance, r_{m0} is the position of the minimum, and $a = 0.0957389$ is the hard-core diameter of U_0 measured in units of r_{m0}. This choice has proven suitable for a large number of real gases [12]. Since the reference B_0^* is used only in reduced units, the values of ε_0 and r_{m0} are irrelevant.

Further, it has also been shown [10] that the following spherical potential, none conformal with respect to U_0, has the required slope ratio S

$$\frac{U_{\rm ef}(z;\,S)}{\varepsilon}=\left[\frac{1-a}{\{(z^3-1)/S+1\}^{1/3}-a}\right]^{12}-2\left[\frac{1-a}{\{(z^3-1)/S+1\}^{1/3}-a}\right]^{6} \tag{2}$$

and, hence, its virial coefficient $B^*_{\rm ef}(T^*)$ satisfies Eq. (1) exactly. This means that $B^*_{\rm ef}(T^*)=B^*(T^*)$ and thus $U_{\rm ef}(z,\,S)$ is an appropriate effective potential for the gas of interest. In Eq. (2), $z=r/r_{\rm m}$, $r_{\rm m}$ is the position of the minimum of $U_{\rm ef}$, and ε is its depth. In order to invert the $B(T)$ data and determine the potential parameters $r_{\rm m}$, ε, and S, we use Eq. (1). $B^*_0(T^*)$ is expressed in terms of the collision diameters σ_0 and R_0 by

$$B^*_0(T^*)=\sigma_0^3 e^{1/T^*}-R_0^3(e^{1/T^*}-1) \tag{3}$$

where

$$\sigma_0^3(T^*)=\sum_{m=0}^{4} c_m(\ln T^*)^m \tag{4}$$

and

$$R_0^3(T^*)=\sigma_0^3\sum_{m=0}^{10} l_m(\ln T^*)^m \tag{5}$$

The coefficients in Eqs. (4) and (5) were determined numerically and are given in Table I. In this work, instead of using values of $B(T)$ directly we want to use the more precise values of the acoustic virial $\beta_{\rm a}(T)$; these two coefficients are related by [5]

$$\tfrac{1}{2}\beta_{\rm a}(T)=B+P_{\rm a}T(dB/dT)+Q_{\rm a}T^2(d^2B/dT^2) \tag{6}$$

Table I. Coefficients in Eqs. (4) and (5) for the Reference System

m	c_m	l_m	m	l_m
0	7.663231×10^{-1}	2.679787	5	-8.736313×10^{-3}
1	-7.247002×10^{-2}	6.843878×10^{-1}	6	1.682856×10^{-3}
2	-5.656659×10^{-3}	-7.144487×10^{-2}	7	5.884160×10^{-4}
3	6.161109×10^{-4}	7.788582×10^{-3}	8	-4.426439×10^{-4}
4	7.577864×10^{-5}	1.644212×10^{-2}	9	8.633161×10^{-5}
			10	-4.761344×10^{-6}

where $P_a = (\gamma^{pg} - 1)$, $Q_a = (P_a)^2/2\gamma^{pg}$, and γ^{pg} is the ratio C_p^{pg}/C_V^{pg}; the superscript pg denotes the ideal-gas property. Values of γ^{pg} can be obtained by extrapolating measurements of the speed of sound u in the zero-pressure limit by means of [5]

$$\lim_{p \to 0} u^2(p, T) = \frac{RT\gamma^{pg}}{M} \tag{7}$$

where M is the molar mass of the particular gas of interest.

When substituting Eq. (1) in Eq. (6) we need the derivatives of B_0^* with respect to T. These were calculated both numerically and analytically from Eqs. (4) and (5) yielding essentially the same results, so that Eqs. (4) and (5) can be used reliably to express β_a in terms of P_a, Q_a, S, and B_0^*. By combining Eqs. (1) and (3)–(6), we obtain the values β_a^{cal} calculated from the model as a function of T, ε, r_m, and S. The desired values of the intermolecular parameters are those that minimize the mean square deviation Q, defined by

$$Q^2(\varepsilon, r_m, S) = \sum [\beta_a^{exp}(T) - \beta_a^{cal}(T)]^2/N \tag{8}$$

where β_a^{exp} denotes the experimental data and N is the number of experimental points. We minimized Q^2 in Eq. (8) using a simplex method [13]. Once ε, r_m, and S are determined in this way, the effective potential $U(z, S)$ is simply obtained by substitution into Eq. (2). It is important to mention that when the theory is applied to nonspherical potentials, these parameters include the effects of the nonspherical geometry as angle averages. This means that in these cases the potential $U(z, S)$ obtained has to be considered as an angle–averaged or spherical effective potential.

3. RESULTS

We studied substances for which reliable experimental information for both B and β_a have been reported [14–23]. These include real substances made of spherical, quasi-spherical, and short linear molecules. Nine substances were studied: argon (spherical), methane, carbon tetrafluoride (quasi-spherical), nitrogen, carbon dioxide, ethane, propane, butane, and pentane (linear). For each of these substances we determined the parameters of the model from the corresponding set of β_a^{exp}, and their values are reported in Table II together with the value of Q. The first point to note is that the model is able to reproduce the acoustic second virial coefficients quite well. Typical deviations $\Delta\beta_a = \beta_a^{exp} - \beta_a^{cal}$ are shown in

Table II. Intermolecular Potential Parameters ε, r_m, and S Obtained from the Second Acoustic Virial Coefficients[a]

Substance	N	(ε/k) (K)	r_m (nm)	S	Q ($cm^3 \cdot mol^{-1}$)	$[T_l, T_h]$[b] (K)
Ar	21	148.671	0.364350	0.98990	0.12	[110, 450]
CH_4	11	197.862	0.400254	0.949610	0.12	[125, 375]
CF_4	6	331.434	0.446153	0.64816	0.12	[174, 301]
N_2	9	132.480	0.388341	0.91934	0.27	[80,373]
CO_2	6	467.605	0.385869	0.62514	0.20	[250, 450]
C_2H_6	17	384.923	0.452940	0.77589	0.22	[220, 450]
C_3H_8	7	520.820	0.495147	0.70059	0.41	[225, 375]
C_4H_{10}	8	751.639	0.422850	0.87218	0.50	[250, 320]
C_5H_{12}	7	825.192	0.518317	0.65747	1.60	[270, 330]

[a] In order to reproduce the values of Q, ε, r_m, and S they are given to more significant figures than strictly justified by their estimated uncertanties.

[b] The experimental temperature range.

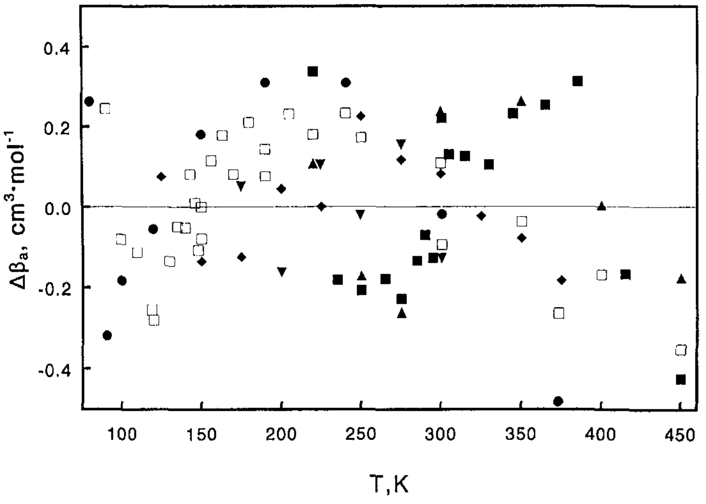

Fig. 1. Absolute deviations $\Delta\beta_a$ for the following substances: □, argon [15, 18]; ◆, methane [16]; ▼, carbon tetrafluoride [17]; ●, nitrogen [18]; ▲, carbon dioxide [19]; ■, ethane [20].

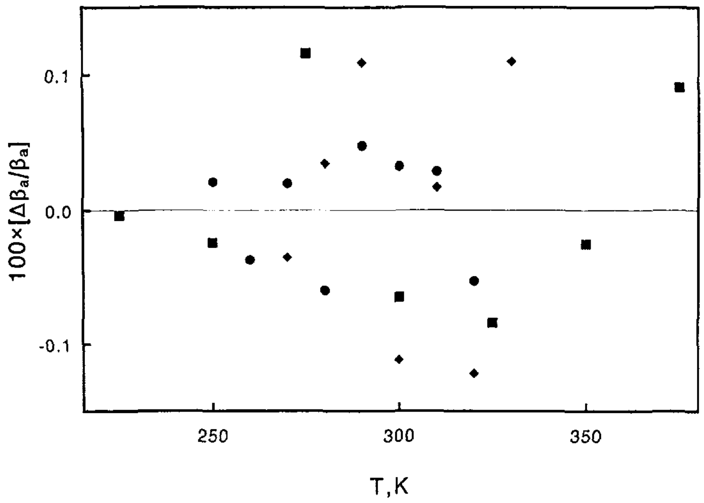

Fig. 2. Relative deviations $\Delta\beta_a$ for medium-size alkanes: ■, propane [21]; ●, butane [22]; ◆, petane [23].

Figs. 1 and 2. By and large, β_a^{cal} disagrees with β_a^{exp} by at most about $\pm 0.4\ cm^3 \cdot mol^{-1}$ for the first six substances (see Fig. 1), but for the longer alkanes considered (propane, butane, and pentane), the absolute deviations are larger. The deviations are of the same order of magnitude as the estimated errors in β_a^{exp}. It is worth mentioning that for the longer alkanes β_a is quite large in the temperature range studied (typically β_a has a magnitude around $1000\ cm^3 \cdot mol^{-1}$), so that the relative deviations are quite small, at most $\pm 0.1\%$ (see Fig. 2).

For any given substance, the values of the potential parameters in Table II are close to those obtained directly by inversion of $B(T)$. The errors in these parameters have two sources: first, the error introduced by the assumption of a constant S in the inversion method and, second, that introduced by the experimental data. Tests performed with model potentials show that the first type of error is larger for smaller values of S and is estimated as 5% in ε and about 10% in r_m for CO_2, which has the smallest S. For the other substances, this error should be smaller. Because β_a^{exp} has errors of $\pm 0.1\ cm^3 \cdot mol^{-1}$, the second type of error is about 0.1% for all the parameters and is therefore negligible compared to the first.

Since the volumetric $B(T)$ are determined with considerably less accuracy than β_a^{exp}, the parameters obtained from the latter should be more reliable than those derived from the former. Hence, we have tested the capability of predicting $B(T)$ from the model and the parameters in

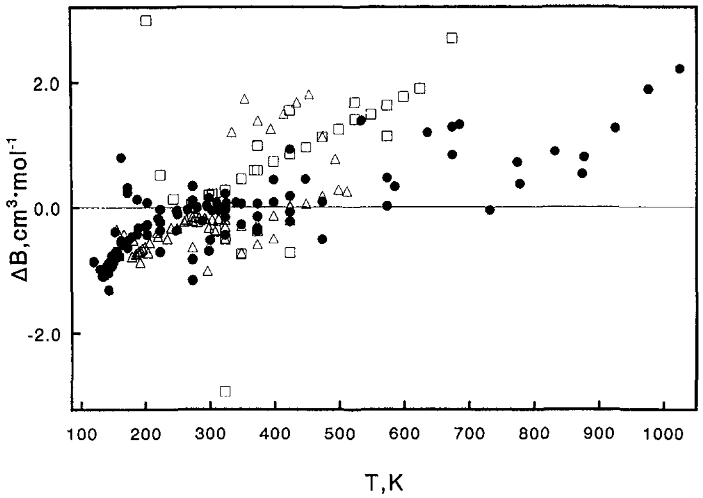

Fig. 3. Deviations ΔB of selected B data taken from the literature with respect to the values predicted with the model. ●, Argon [14, 24]; △, methane [14, 25, 26]; □, carbon tetrafluoride [14].

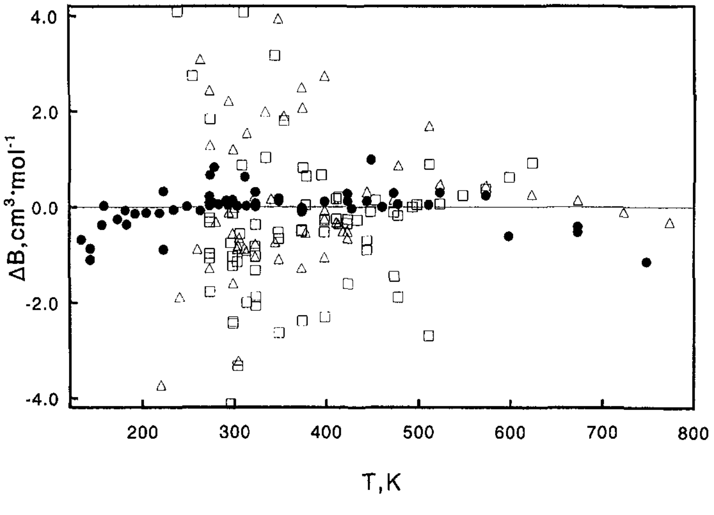

Fig. 4. Deviations ΔB of selected B data taken from the literature with respect to the values predicted with the model. ●, Nitrogen [14, 27, 28]; △, carbon dioxide [14, 29]; □, ethane [14].

Table II. By means of Eq. (1), we calculated the values of B in a temperature range, including temperatures higher than those at which $\beta_a^{\rm exp}$ has been reported, and compared the results with selected experimental data of class 1 according to the classification suggested by Dymond and Smith [14]. The deviations $\Delta B = B^{\rm exp} - B^{\rm cal}$ are shown in Figs. 3 to 5. It can be seen clearly that the bulk of the data is within a band of ± 2.0 $\rm cm^{-3} \cdot mol^{-1}$ (see Figs. 3 and 4). Considering that the uncertainty in $B^{\rm exp}$ is either ± 1.0 $\rm cm^{-3} \cdot mol^{-1}$ or $0.02B$ (whichever is greater) for these substances, the agreement is quite good. The case of argon is the most remarkable: $\beta_a^{\rm exp}$ data cover the temperature range $90 \leqslant T \leqslant 450$ K, whereas $B^{\rm cal}$ shows good agreement with $B^{\rm exp}$ at $90 \leqslant T \leqslant 1000$ K. Once again, the predictions of $B(T)$ for the longer alkanes, whose relative deviations are shown in Fig. 5, are not as good, although most points are within $\pm 4\%$, which is close to the errors in $B^{\rm exp}$ for these substances. The r.m.s. deviations (Q_B) in B obtained for each substance are given in Table III.

Hence, the potential parameters obtained from $\beta_a^{\rm exp}$ reproduce the values of $B(T)$ over wide temperature ranges quite well. However, the inverse is not true; using the values of ε, $r_{\rm m}$, and S obtained directly from $B^{\rm exp}(T)$ in Eq. (1), we were unable to predict β_a within its experimental uncertainty and deviations larger than ± 2.0 $\rm cm^3 \cdot mol^{-1}$ were obtained. This corresponds to a deviation of about 20 times the typical uncertainty of the acoustic coefficients.

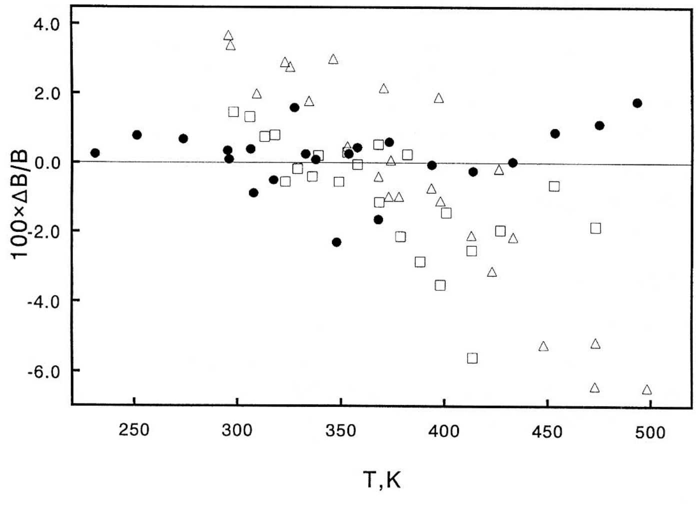

Fig. 5. Relative deviations $\Delta B/B$ of selected B data taken from the literature [14] with respect to the values predicted with the model. ●, Propane; △, butane; □, pentane.

Table III. Comparison of N_B Experimental Data of B with the Model Potential Using Parameters in Table II

Substance	N_B	Q_B ($\mathrm{cm^3 \cdot mol^{-1}}$)	$[T_l, T_h]^a$ (K)
Ar	103	0.68	[120, 1020]
CH_4	58	0.72	[155, 511]
CF_4	38	1.20	[203, 673]
N_2	56	0.40	[133, 748]
CO_2	53	1.48	[220, 774]
C_2H_6	68	1.68	[238, 623]
C_3H_8	22	2.6	[230, 474]
C_4H_{10}	25	13.2	[296, 498]
C_5H_{12}	23	11.6	[298, 473]

[a] The temperature range for the comparisons.

4. CONCLUSIONS

The model, based on a three-parameter nonconformal approach to volumetric virial coefficients, has been shown to work in the case of the second acoustic virial coefficient β_a^{exp}. The model is able to represent β_a^{exp} within the experimental error for several spherical and nonspherical molecules, although some residual systematic deviations are still apparent. The approach provides the parameters and functional form of an effective potential from which the volumetric $B(T)$ can be derived over a temperature range wider than that of the initial data. Since the values of β_a^{exp} are considerably more accurate and precise than those of $B^{\mathrm{exp}}(T)$, the error in determining the effective potential is small but mostly due to the model itself. Hence, it would be worth considering more refined versions of the model, e.g, using different shape parameters for the attractive and repulsive parts of the potential.

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REFERENCES

1. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces. Their Origin and Determination* (Clarendon Press, Oxford, 1981).

2. C. M. Knobler, *Pure Appl. Chem.* **55**:455, (1983).
3. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Mol. Phys.* **35**:1443 (1978).
4. T. Kihara, *Intermolecular Forces* (John Wiley, New York, 1978).
5. J. P. M. Trusler, *Physical Acoustics and Metrology of Fluids* (Adam Hilger, Bristol, 1991), pp. 4–9.
6. H. E. Cox, F. W. Crawford, E. B. Smith, and A. R. Tindell, *Mol. Phys.* **40**:705 (1980).
7. E. B. Smith, A. R. Tindell, B. H. Wells, and F. W. Crawford, *Mol. Phys.* **42**:937 (1981).
8. M. B. Ewing, M. L. McGlashan, and J. P. M. Trusler, *Mol. Phys.* **60**:681 (1987).
9. F. del Río, J. E. Ramos, A. Gil-Villegas, and I. A. McLure, *J. Phys. Chem.* **100**:9104 (1996).
10. F. del Río, J. E. Ramos, and I. A. McLure, *J. Phys. Chem.* **102**:10568 (1998).
11. J. E. Ramos, F. del Río, and I. A. McLure, *J. Phys Chem.* **102**:10576 (1998).
12. J. E. Ramos, M.Sc. thesis (Universidad Autónoma Metropolitana, México, 1998).
13. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
14. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon Press, Oxford, 1980).
15. A. F. Estrada-Alexanders and J. P. M. Trusler, *J. Chem. Thermodyn.* **27**:1075 (1995).
16. J. P. M. Trusler and M. Zarari, *J. Chem. Thermodyn.* **24**:973 (1992).
17. M. B. Ewing and J. P. M. Trusler, *J. Chem. Phys.* **29**:991 (1989).
18. M. B. Ewing and J. P. M. Trusler, *Physica A* **184**:415 (1992).
19. A. F. Estrada-Alexanders and J. P. M. Trusler, *J. Chem. Thermodyn.* **30**:1589 (1998).
20. A. F. Estrada-Alexanders and J. P. M. Trusler, *J. Chem. Thermodyn.* **90**:1075 (1997).
21. J. P. M. Trusler and M. Zarari, *J. Chem. Thermodyn.* **28**:329 (1996).
22. M. B. Ewing, A. R. H. Goodwin, M. L. McGlashan, and J. P. M. Trusler, *J. Chem. Thermodyn.* **20**:243 (1988).
23. M. B. Ewing, A. R. H. Goodwin, and J. P. M. Trusler, *J. Chem. Thermodyn.* **21**:867 (1989).
24. C. Tegeler, R. Span, and W. Wagner, *Eine neue Fundamentalgleichung für das fluide Zustandsgebiet von Argon für Temperaturen von der Schmelzlinie bis 700 K und Drücke bis 1000 Mpa, Fortschr.-Ber. VDI Reihe 3 Nr. 480* (VDI Verlag, Düsseldorf, 1997).
25. R. Kleinrahm, W. Duschek, W. Wagner, and M. Jaeschke, *J. Chem. Thermodynamics* **20**:621 (1988).
26. G. Händel, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* **24**:685 (1992).
27. P. Nowak, R. Kleinrahm, and W. Wagner, *J Chem. Thermodyn.* **29**:1137 (1997).
28. W. Duschek, R. Kleinrahm, W. Wagner, and M. Jaeschke, *J. Chem. Thermodyn.* **20**:1069 (1988).
29. W. Duschek, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* **22**:827 (1990).