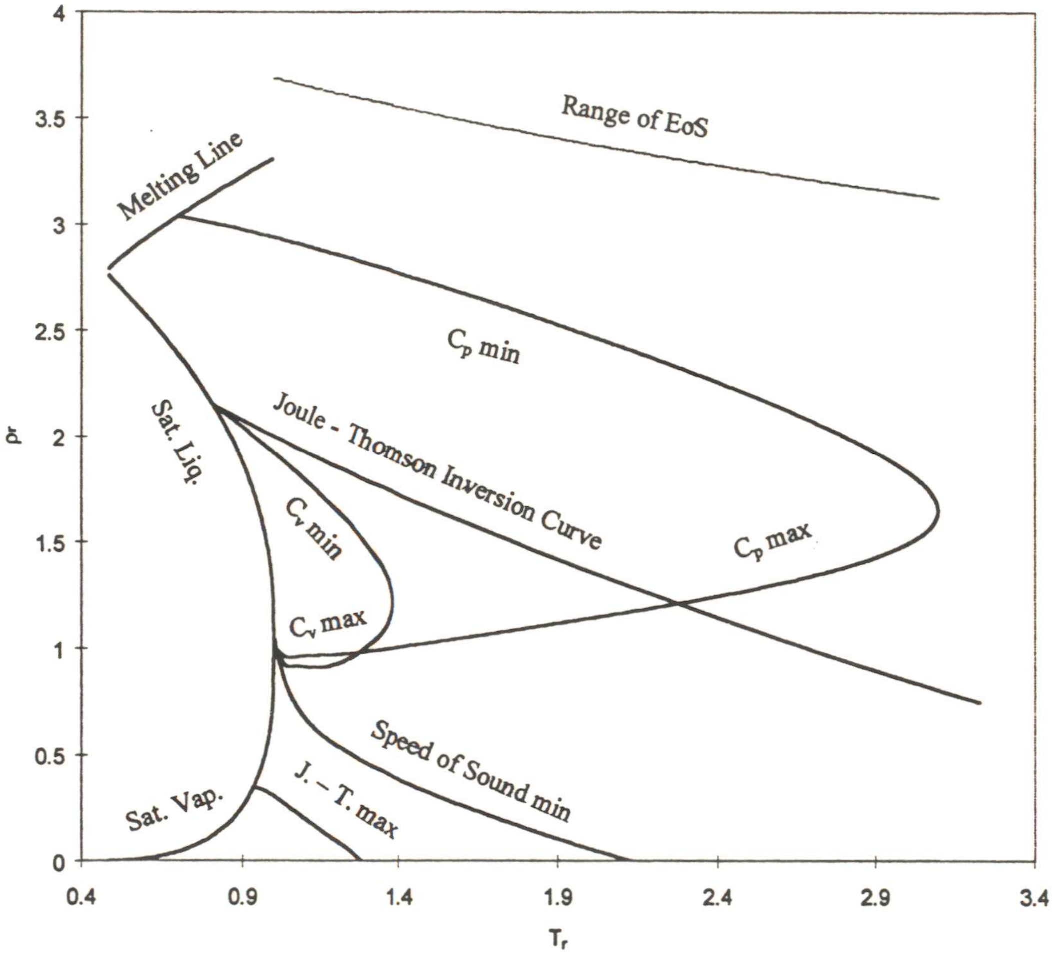
Derivative Properties from High Precision Equations of State



April 1998

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Derivative Properties from High Precision Equations of State

Literature Review

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Summary

In this literature study high accuracy equations of state for pure substances fitted to a large number of experimental data have been studied and compared on their ability to produce accurate values for derivative properties. The range and the complexity of the equations have also been compared. In order to limit the scope of the study 5 equations of state have been chosen :

- The Schmidt Wagner EOS (SWEOS)
- The Bender EOS (20-MBWR)
- The Jacobsen Stewart EOS (32-MBWR)
- The Hill EOS
- The Goodwin EOS

These equation have been compared on their ability to produce accurate reference data for the following derivative properties :

- Isochoric heat capacity
- Isobaric heat capacity
- Speed of sound
- Joule - Thomson coefficient

Two strategies for calculation of derivative properties have also been studied :

- The calculation of parameters in a multiparameter equation of state using mixing rules.
- The Extended Corresponding States principle (ECS).

The SWEOS and the 32MBWR equations were found to produce reference data of the highest quality. Being analytical, these equations are also easy to utilise. The SWEOS equation produced more accurate values than the 32MBWR equation in the critical region. The advantage of the 32MBWR equation is the large number of formulations available in the literature, and the fact that the functional form of the equation is not varying.

The only procedure for the calculation of derivative properties of mixtures that has been tested is the ECS procedure. The accuracy of derivative properties obtained with the ECS principle was found to be good. The complexity of the calculations was found to be the biggest weakness of the procedure.

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1. Introduction

In today's scientific literature there are a great number of equations of state (EOS) available. There are no universal equations that are able to cover all substances and their mixtures. For light or non polar substances the available equations of state can be divided into three main groups :

- Mechanical statistical based equations of state
- Cubic equations of state
- Empirical equations with a great number of adjustable parameters

The statistical mechanical based equations has so far mainly been of scientifical interest. The workers in the field of statistical mechanics are trying to link the microscopic structure of a compound to its macroscopic behavior.

The class of cubic equations of state is the most widely used one. The great simplicity of the equations has made them a natural choice for engineering purposes. The equations has from two to five adjustable parameters. The parameters can be correlated to the critical temperature, pressure and density as well as the acentricity factor. The numerical expense of evaluating the equations is relatively small. The equations are valid within a limited range, and are often not able to give qualitatively correct values for derivative properties such as isochoric and isobaric heat capacity.

The empirical equations in the third category are often used in tabulating thermodynamic properties of pure compounds. The equations are valid within a wide range. The precision is frequently within the experimental accuracy. However these equations are not thermodynamically consistent in the direct vicinity of the critical point. The numerical expense of evaluating the equations is high because of the great number of terms in the equations. The derivative properties shows quantitative correct behavior. The quality of the derivative properties are dependent on the functional form of the equation, the procedure used in fitting the parameters and the accuracy of the experimental data.

The aim of this review is to discuss the available wide range high precision equations that are available. The equations will be compared on the ability to represent the following derived properties in the homogenous region :

- The isochoric heat capacity
- The isobaric heat capacity
- The speed of sound
- The Joule - Thomson coefficient

The equations will be compared on the complexity of the calculation, accuracy and range. The derivation of the above mentioned properties for mixtures will also be discussed.

2. Theoretical issues of the equations of state

In this section of the review the functional structure of the different equations of state for pure compounds will be discussed. The procedure of fitting the data to the equations and their complexity will also be discussed. Five equations of state are chosen for evaluation :

- The Schmidt Wagner EOS (SWEOS)
- The Bender EOS (20-MBWR)
- The Jacobsen Stewart EOS (32-MBWR)
- The Hill EOS
- The Goodwin EOS

The indexing of the equations differs from that used in the literature. The equations are usually indexed into equations explicit in the Helmholz energy and in the pressure. The new indexing is used in order to stress the differences in data fitting procedure and functional form of the thermodynamic surface. As stated in the introduction, the quality of an EOS depends not only on the functional form but also on the data and the fitting procedure.

2.1. The Schmidt - Wagner EOS

In 1985 Schmidt and Wagner[39] published a new equation of state for oxygen based on a new method of optimalisation. Schmidt and Wagner stated four goals for the development of the new EOS (SWEOS) :

- Simultaneous fit of the new equation of state to all kinds of measured thermodynamic data in order to represent all properties within the experimental accuracy.
- The new equation should cover the whole fluid region where data exists.
- Being of a simple functional form the equation should be simple to handle.
- In order to minimize the number of coefficients, the structure of the new equation of state should be developed using an optimization method.

In the discussion of the SWEOS the equation of state for methane developed by Setzmann and Wagner[6] is used as the reference.

2.1.1. Functional form of the thermodynamic surface

The fundamental equation is expressed in form of the Helmholz energy A with the two independent variables, density ρ and temperature T. The dimensionless Helmholz energy $\Phi = A/(RT)$ is split into a part depending on the ideal gas behavior Φ^0 and a part which takes into account the residual fluid behavior Φ^r :

$$\Phi(\delta,\tau) = \Phi^0(\delta,\tau) + \Phi^r(\delta,\tau) \qquad (2.1.1)$$

The Helmholz energy of an ideal gas is given by :

$$A^0(\rho,T) = H^0(T) - RT - TS^0(\rho,T) \qquad (2.1.2)$$

If the ideal gas heat capacity c_p^0 is known the following equation is obtained :

$$A^0(\rho,T) = \int_{T_0}^{T} C_p^0 dT + H_0^0 - RT - T\int_{T_0}^{T} \frac{C_p^0 - R}{T} dT - RT\ln\left(\frac{\rho}{\rho_c}\right) - TS_o^o \qquad (2.1.3)$$

$\rho_0 = \dfrac{P_o}{RT_o}$ is a reference density. Furthermore, arbitrary reference values for the temperature T_0, the pressure P_0, the entropy S_0^0 and the enthalpy H_0^0 have to be selected.

The development of the residual term of the Helmholz energy Φ^r is split into three steps:

1. The first step is the formulation of a general expression for the equation which functions a "bank of terms". For methane, this bank of terms of the residual part of the dimensionless Helmholz energy was formulated as :

$$\begin{aligned}\Phi^r(\delta,\tau) = {} & \sum_{i=1}^{10}\sum_{j=-1}^{9} n_i\delta^i\tau^{j/2} + e^{-\delta}\sum_{i=1}^{6}\sum_{j=0}^{5} n_i\delta^i\tau^j + e^{-\delta^2}\sum_{i=1}^{7}\sum_{j=0}^{10} n_i\delta^i\tau^j \\ & + e^{-\delta^3}\sum_{i=1}^{3}\sum_{j=0}^{13} n_i\delta^i\tau^{2j} + e^{-\delta^4}\sum_{i=1}^{6}\sum_{j=5}^{11} n_i\delta^i\tau^{2j} + e^{-\delta^5}\sum_{i=1}^{3}\sum_{j=7}^{13} n_i\delta^i\tau^j \\ & + (e^{-0.4\delta^6} - e^{-2\delta^6})\sum_{i=3}^{6}\sum_{j=10}^{15} n_i\delta^i\tau^{2j} + \sum_{i=1}^{27} n_i\delta^{d_i}\tau^{t_i}e^{-a_i(\delta-\Delta_i)^2-\beta_i(\tau-\gamma_i)^2} \qquad (2.1.4)\end{aligned}$$

2. The second step after selecting a suitable bank of terms is a mathematical statistical optimization to determine the most effective equation for Φ^r. This equation consist of the terms from equation (2.1.4) which gives the best representation of the data.

3. The third step is the optimization of the parameters n_i, in the obtained equation. In the optimization of the parameters the following information was used :

- p,ρ,T data
- The isochoric heat capacity
- The isopiestic heat capacity
- The second virial coefficient
- The speed of sound
- The enthalpy
- Vapor pressure

- Vapor density
- Liquid density

The steps 2 and 3 are repeated until the best equation and the best parameter set is found. For the case of methane the resulting equation was :

$$\Phi^r(\rho,T) = \sum_{i=1}^{13} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=14}^{36} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}} + \sum_{i=37}^{i=40} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta-\Delta_i)^2-\beta_i(\tau-\gamma_i)^2} \qquad (2.1.5)$$

In the literature there are three types of SWEOS mentioned. The methane type of SWEOS is already discussed here. The other equations of state are the oxygen type and the carbon dioxide type. The differences are in the banks of terms. In the bank of terms for the methane type of the SWEOS there are some extra terms added to give a better fit in the critical region. The first six sets of terms in (2.1.1) are used by the oxygen type SWEOS. By examining (2.1.5) it is evident that the Gaussian terms are the most effective in improving the fit in the critical region. In the bank of terms for the carbon dioxide type of SWEOS the following term is added to the methane type terms :

$$\sum_{i=1}^{2}\sum_{j=1}^{4}\sum_{k=1}^{3}\sum_{l=1}^{2}\sum_{m=1}^{3} n_{i,j,k,l,m} \Delta^{b_j} \delta \psi \qquad (2.1.6)$$

with

$$\Delta = \theta^2 + B_k\left[(\delta-1)^2\right]^{a_i}$$

$$\theta = (1-\tau) + A\left[(\delta-1)^2\right]^{\frac{1}{2\beta}}$$

$$\psi = e^{-C_l(\delta-1)^2 - D_m(\tau-1)^2}$$

The definition of the state variables are : $\tau = T_c/T$, $\delta = \rho/\rho_c$
All the other symbols represents fitted constants.

2.1.2. Data fitting procedure

The basic tools of the fit procedure are the multiproperty fit to determine the coefficients n_i of the vector n for a fixed form of $\Phi^r(\delta,\tau,n)$ and the optimization of the final functional form of the equation for Φ^r.
Since the Helmholz energy is not accessible to direct measurements, it is necessary to determine the unknown structure and the unknown coefficients n_i of the residual part of the dimensionless Helmholz energy from properties which are experimentally available. In paragraph 2.1.3. some of those quantities are listed. During the optimization process for determining the best structure for Φ^r, a lot of different forms of Φ^r equations have to be fitted to experimental data. The fitting process is explained using the general relationship z = z(x,y), where x, y and z denote general thermodynamic variables. The variable z might be U, H, C_v .... and x and y are δ and

τ. This means that that we have the experimental data $z_{exp}(x_{exp}, y_{exp})$ and the relationships to any correlation equation for Φ as $z = z(\Phi,\delta,\tau,n)$. With a known expression for Φ^0, Φ^r is fitted to the experimental data in such a way that the weighted sum of squares

$$\chi_j^2 = \sum_{m=1}^{M_j} \left[\frac{\left[z_{\text{exp}} - z(\Phi, x_{\text{exp}}, y_{\text{exp}}, n) \right]^2}{\sigma_{\text{exp}}^2} \right] = \sum_{m=1}^{M_j} \frac{\Delta z_{j,m}^2}{\sigma_{j,m}^2} \qquad (2.1.7)$$

is minimized. The index j denotes one particular property that is being considered. The weigthing factor corresponds to $1/\sigma_j^2$ with σ as the total uncertainty of the experimental data according to the Gaussian error propagation formula given by :

$$\sigma_{j,m}^2 = \left[\left[\frac{\partial \Delta z}{\partial x} \right]_{y,z}^2 \sigma_x^2 + \left[\frac{\partial \Delta z}{\partial y} \right]_{x,z}^2 \sigma_y^2 + \left[\frac{\partial \Delta z}{\partial z} \right]_{x,y}^2 \sigma_z^2 \right] \qquad (2.1.8)$$

The uncertainties with respect to the single variables z, x and y are σ_z, σ_x, and σ_y. The partial derivatives can be calculated from a preliminary equation of state. When Φ^r is fitted to more than one property, it is called a multiproperty fit and the resulting sum of squares

$$\chi^2 = \sum_{j=1}^{J} \chi_j^2 \qquad (2.1.9)$$

is to be minimized.

The optimization of the functional form is done using a evolutionary optimization method (EOM). The method is based on biological evolution. For a comprehensive discussion see Setzmann and Wagner[21].

2.1.3. Derivation of derivative properties

There are no iterations or integrations necessary in order to establish expressions for the derived properties. The derivative properties at interest are given below :

- The isochoric heat capacity

$$\frac{C_v(\delta,\tau)}{R} = -\tau^2(\Phi_{\tau\tau}^0 + \Phi_{\tau\tau}^r) \qquad (2.1.10)$$

- The isobaric heat capacity

$$\frac{C_p(\delta,\tau)}{R} = \frac{C_v(\delta,\tau)}{R} + \frac{\left(1+\delta\Phi^r_\delta - \delta\tau\Phi^r_{\delta\tau}\right)^2}{1+2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta}} \qquad (2.1.11)$$

- The speed of sound

$$\frac{w^2(\delta,\tau)}{RT} = 1+2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta} - \frac{\left(1+\delta\Phi^r_\delta - \delta\tau\Phi^r_{\delta\tau}\right)^2}{\tau^2\left(\Phi^0_{\tau\tau}+\Phi^r_{\tau\tau}\right)} \qquad (1.1.12)$$

- The Joule-Thomson coefficient

$$\mu(\delta,\tau)R\rho = \frac{-(\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta} + \delta\tau\Phi^r_{\delta\tau})}{(1+\delta\Phi^r_\delta - \delta\tau\Phi^r_{\delta\tau})^2 - \tau^2(\Phi^0_{\tau\tau}+\Phi^r_{\tau\tau})(1+2\delta\Phi^r_\delta+\delta^2\Phi^r_{\delta\delta})} \qquad (2.1.13)$$

The subscripts denote derivatives with respect to τ and/or δ.
The fact that only derivation of the thermodynamic surface with regard to temperature and density is necessary to obtain the derivative properties is an important advantage of the SWEOS. With other equations of state iterations or numerical integration might be necessary. The optimization of the functional form is important to get the best possible accuracy versus number of terms ratio.

2.1.4. Accuracy of derivative properties

In table 1 the uncertainties in the derivative properties are given :

Table 1 Uncertainties in derivative properties from the SWEOS

Substance	C_v (%)	C_p (%)	Speed of sound (%)	Source
Carbon dioxide	-	from +/- 0.15 to +/- 1.5	from +/- 0.03 to +/- 1	R. Span and W. Wagner[25]
Methane	< 2	< 2	< 1	W. Wagner and R. Span[38]
Water (38 –coeff.)	< 5	< 2	< 0.5	A. Saul and W. Wagner[16]

The accuracy of the derived properties are often given in plots. In Figure 1 the uncertainty of the calculated isochoric heat capacity is shown :

Figure 1 Uncertainties in C_v for methane from the SWEOS

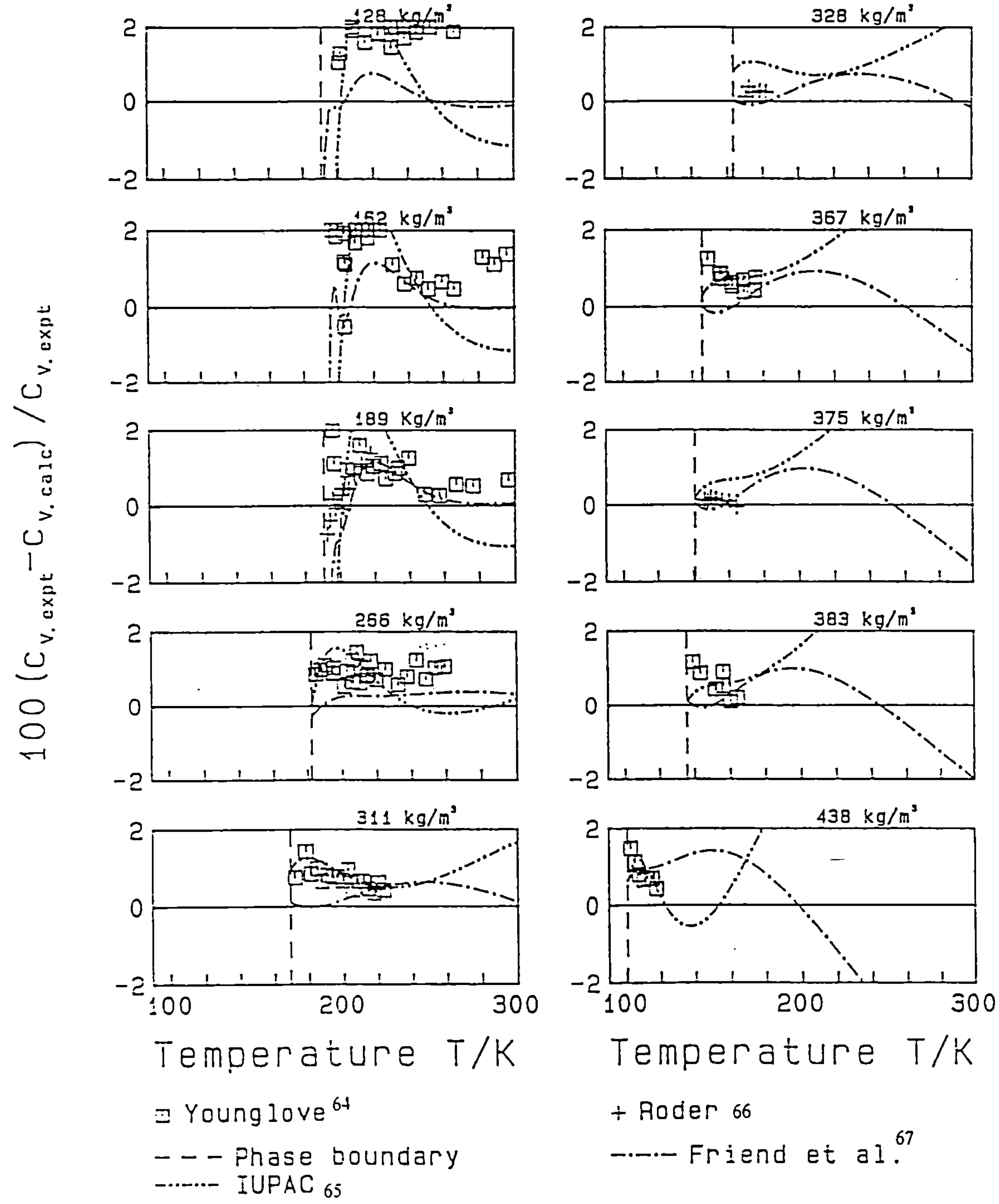
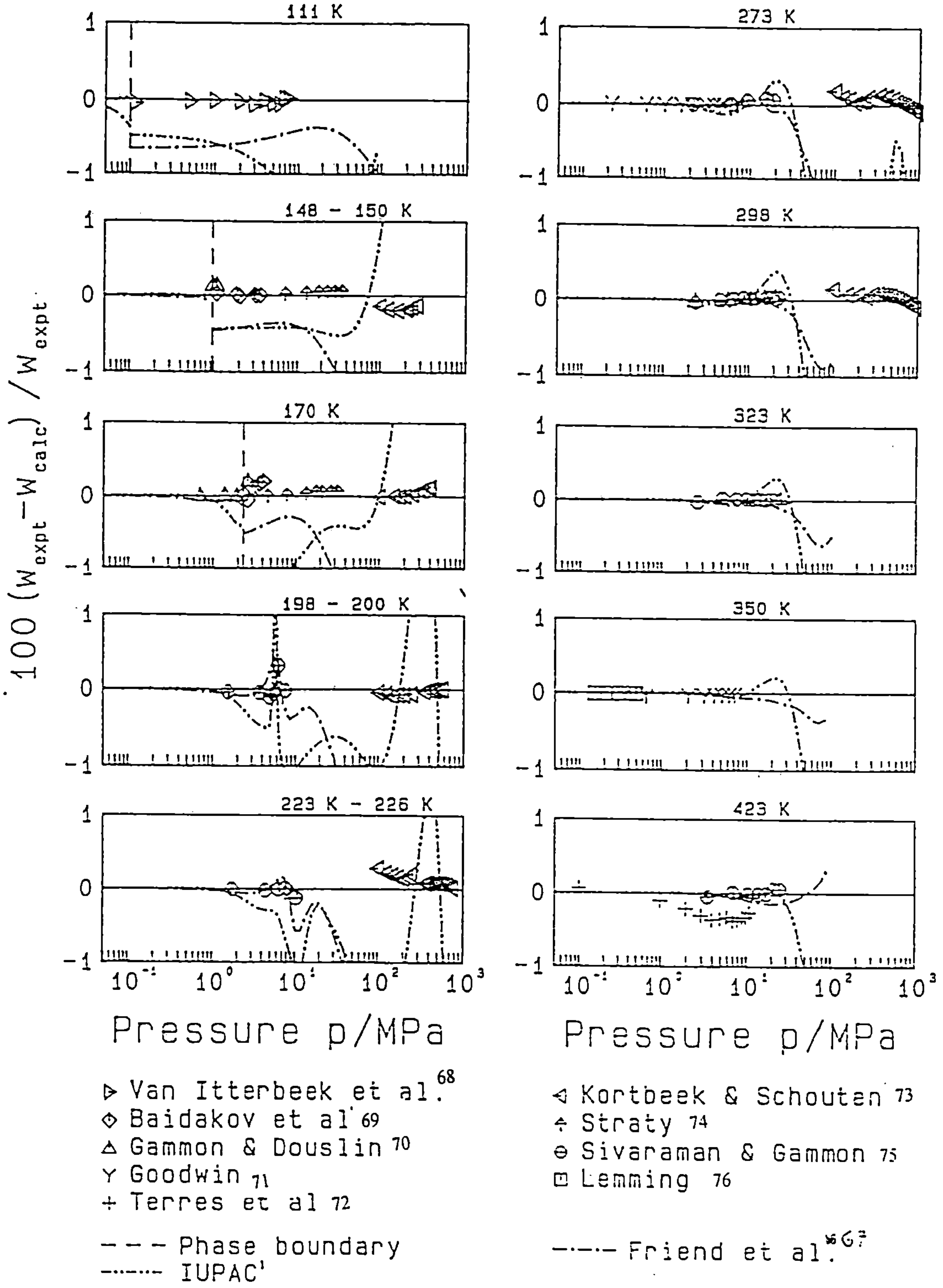


Figure 2 **Uncertainties speed of sound for methane from the SWEOS**



2.1.5. Validity of derivative properties in the critical region

Only the range of states were the SWEOS is not valid will be discussed. Normally the overall range will be determined by the availability of experimental data. In Table 2 the range of states will be given were the SWEOS is not accurate. The ranges are taken from different authors :

Table 2 Validity of the SWEOS in the critical region

Compound	Temperature range (K)	Density range	Source
Cyclohexane	$256<T<581$	$0.75<\rho_c<1.25$	S. G. Penoncello et. al[5]
Methane	$190.1<T<191.1$	-	W. Wagner and K. M. de Reuck[30]
Water (38 coefficients)	$645<T<665$	$0.6\rho_c<\rho<1.4\rho_c$	A. Saul and W. Wagner[16] (1989)
Water (58 coefficients)	*	*	A. Saul and W. Wagner[16] (1989)
Carbon dioxide	$303.8<T<304.2$	$0.9\rho<\rho<1.2\rho_c$	R. Span and W. Wagner[25] (1996)

*The authors are reporting that only one experimental value of C_v near the critical point is deviating from the model.

The IUPAC formulation (W. Wagner and K. M. de Reuck[30]) and the SWEOS for carbon dioxide are of the methane type. Table 2 shows that the methane and carbon dioxide type of SWEOS is valid closer to the critical point than the oxygen type of the SWEOS.

2.2. The Jacobsen - Stewart EOS

The Jacobsen and Stewart EOS (32-MBWR EOS) is a modification of the Benedict-Webb-Rubin EOS. The 32-MBWR equation consists of an exponential term and what is essentially an expanded virial equation. The 32-MBWR equation has a proven ability to represent various classes of fluids including hydrocarbons, cryogenic fluids and refrigerants. The 32-MBWR equation is capable of providing highly accurate fits of the liquid, vapor and supercritical regions of a fluid as well as the saturation boundary.

2.2.1. Functional form of the thermodynamic surface

The MBWR equation represents pressure P as function of molar density ρ and temperature T :

$$P(\rho,T) = \sum_{i=1}^{9} a_i(T)\rho^i + \exp(-\delta^2)\sum_{i=10}^{15} a_i(T)\rho^{2i-17} \qquad (2.2.1)$$

where $\delta = \rho/\rho_c$, and the temperature dependencies of the a_i coefficients are :

$$\begin{aligned}
a_1 &= RT \\
a_2 &= b_1T + b_2T^{0.5} + b_3 + b_4/T + b_5/T^2 \\
a_3 &= b_6T + b_7 + b_8/T + b_9/T^2 \\
a_4 &= b_{10}T + b_{11} + b_{12}/T \\
a_5 &= b_{13} \\
a_6 &= b_{14}/T + b_{15}/T^2 \\
a_7 &= b_{16}/T \\
a_8 &= b_{17}/T + b_{18}/T^2 \\
a_9 &= b_{19}/T^2 \\
a_{10} &= b_{20}/T^2 + b_{21}/T^3 \\
a_{11} &= b_{22}/T^2 + b_{23}/T^4 \\
a_{12} &= b_{24}/T^2 + b_{25}/T^3 \\
a_{13} &= b_{26}/T^2 + b_{27}/T^4 \\
a_{14} &= b_{28}/T^2 + b_{29}/T^3 \\
a_{15} &= b_{30}/T^2 + b_{31}/T^3 + b_{32}/T^4
\end{aligned}$$

2.2.2. Data fitting procedure

Different authors use different fit procedures in finding estimates for the coefficients in the 32-MBWR EOS. By utilization of the EOS the fit procedure for the EOS at interest has to be critically reviewed. The fit procedure for the equations of state for R125 and R32 given by S. L. Outcalt and M. O. McLinden[23] will be discussed in this review. The 32-MBWR EOS has a fixed form, therefore the goal of the fit procedure is to find the best set of parameters. The whole machinery of multiproperty fitting as discussed in 1.2.2 can be used in the fitting of the equation. S. L. Outcalt and M. O. McLinden[23] used the following data in their fit procedure :

- P,V,T data
- Isochoric heat capacity
- Isopiestic heat capacity
- Saturation pressure

- Density of saturated liquid
- Density of saturated vapor

2.2.3. Derivation of derivative properties

The derivation of some of the derivative properties are given below. In order to derive the isochoric heat capacity an integration is necessary.

- The isochoric heat capacity :

$$C_v(\rho,T)=C_v^0-\int_0^{\rho}\left[\frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_{\rho}\right]d\rho \tag{2.2.2}$$

- The isobaric heat capacity :

$$C_p(\rho,T)=C_v(\rho,T)+\frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_{\rho}^2 \Bigg/ \left(\frac{\partial P}{\partial \rho}\right)_T \tag{2.2.3}$$

- The speed of sound :

$$w^2(\rho,T)=\left[\frac{C_p}{C_v}\left(\frac{\partial P}{\partial \rho}\right)_T\frac{10^6}{M_r}\right] \tag{2.2.4}$$

- The Joule-Thomson coefficient :

$$\mu(\rho,T)=\frac{1}{C_p}\left[\frac{T(\partial P/\partial T)_{\rho}}{\rho^2(\partial P/\partial \rho)_T}-\frac{1}{\rho}\right] \tag{2.2.5}$$

In order to obtain any of the derived properties given here, the isochoric heat capacity has to be derived. The derivation of the isochoric heat capacity involves an integration with respect to the density (2.2.2). This integration can be done analytically. Expressions for the isochoric heat capacity and the other derivative properties are given in S. Angus et al.[47].

2.2.4. Accuracy of derivative properties

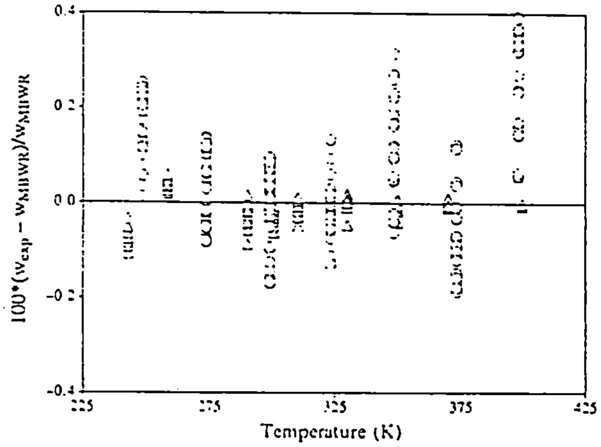
The accuracy of the derived properties is dependent on the fit procedure used, on the accuracy of the data and the ability of the EOS to give a good representation of the data. The deviations given here are taken from a number of authors :

Table 3 Uncertainties of derivative properties from the 32-MBWR EOS

Substance	Uncertainty C_v (%)	Uncertainty C_p (%)	Uncertainty speed of sound (%)
Methane	2	2	0.5
Ethane	1	2	0.6
Propane	2	2	1
Isobutane	2	2	1

The values in the table are taken from B. A. Younglove and J. F. Ely[8]

Figure 3 Uncertainties in speed of sound for R125a from the 32-MBWR EOS



Data of : Gillis[77] (Δ), and Ahn[78] (□)

2.2.5. Validity of derivative properties in the critical region

According to B. A. Younglove and J. F. Ely[8] the calorific properties are not accurate in the region :

- Temperature region :

$0.97T_c<T<1.03T_c$

- Density region :

$0.75\rho_c<\rho<1.25\rho_c$

2.3. The Bender EOS

The Bender EOS (20-MBWR) is also a modification of the Benedict - Webb - Rubin EOS.

2.3.1. Functional form of the thermodynamic surface

$$P(\rho,T)=\rho T\left(R+B\rho+C\rho^2+D\rho^3+E\rho^4+F\rho^5+(G+H\rho^2)\rho^2\exp(-a_{20}\rho^2)\right)\quad(2.3.1)$$

with

$$\begin{aligned}
B&=a_1+a_2/T+a_3/T^2+a_4/T^3+a_5/T^4\\
C&=a_6+a_7/T+a_8/T^2\\
D&=a_9+a_{10}/T\\
E&=a_{11}+a_{12}/T\\
F&=a_{13}/T\\
G&=a_{14}/T^3+a_{15}/T^4+a_{16}/T^5\\
H&=a_{17}/T^3+a_{18}/T^4+a_{19}/T^5
\end{aligned}$$

2.3.2. Data fitting procedure

The 20-MBWR EOS has a fixed functional form. It is not necessary to optimize the functional form of the equation. The goal of the data fitting is to find the 20 best parameters. A. Polt[17] used the following data in his parameter fit :

- P,V,T data
- The vapor pressure
- The orthobaric densities
- The Maxwell criterion

2.3.3. Derivation of derivative properties

The derivation of the derivative properties is equivalent to the derivation given in paragraph 2.2.3. :

- The isochoric heat capacity :

$$C_v(\rho,T)=C_v^0-\int_0^{\rho}\left[\frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_{\rho}\right]d\rho\qquad(2.3.2)$$

- The isobaric heat capacity :

$$C_p(\rho,T) = C_v(\rho,T) + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \bigg/ \left(\frac{\partial P}{\partial \rho}\right)_T \tag{2.3.3}$$

- The speed of sound :

$$w^2(\rho,T) = \left[\frac{C_p}{C_v}\left(\frac{\partial P}{\partial \rho}\right)_T \frac{10^6}{M_r}\right] \tag{2.3.4}$$

- The Joule-Thomson coefficient :

$$\mu(\rho,T) = \frac{1}{C_p}\left[\frac{T(\partial P/\partial T)_\rho}{\rho^2(\partial P/\partial \rho)_T} - \frac{1}{\rho}\right] \tag{2.3.5}$$

The calculation of the derivative properties is straight forward. Expressions for the derivative properties are given in U. Sievers, and S. Schulz[31].

2.3.4. Accuracy of derivative properties

The accuracy of the derived properties from the 20-MBWR EOS is discussed by A. Polt[17]. He obtained the coefficients for 14 substances, and discussed the accuracy of the derived properties were data where available. The accuracy's are given in Table 4 :

Table 4 Uncertainty of the derivative properties from the 20-MBWR EOS

	Heat of vaporization ΔH_v		Isochoric heat capacity $C_v(\rho,T)$		Speed of sound w(T,p)		Joule - Thomson coefficient μ(T,p)	
Substance	No. points	$\Delta(\Delta H_v)$ (%)	No. points	ΔC_v (%)	No. points	Δw (%)	No. points	$\Delta\mu$ (%)
N-Butane	15	0.91	-	-	-	-	26	5.4
I-Butane	50	1.32	-	-	-	-	-	-
N-Pentane	6	0.06	73	5.59	-	-	-	-
I-Pentane	3	0.04	-	-	-	-	-	-
Neopentane	4	0.20	-	-	-	-	-	-
Hexane	40	0.61	227	3.75	532	1.28	-	-
Heptane	36	0.95	238	5.76	124	1.71	-	-
Octane	42	0.78	48	6.60	36	1.93	-	-
Benzene	-	-	-	-	106	1.04	-	-
Methanol	19	1.61	-	-	9	5.48	-	-
Sulfurhexa-fluoride	-	-	-	-	-	-	66	2.04

The definition of the error is given by :

$$\Delta X = 100\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{X_{\exp}-X_{calc}}{X_{\exp}}\right)_i^2} \qquad (2.3.1)$$

X can be any of the properties mentioned in Table 4.

2.3.5. Validity of derivative properties in the critical region

According to A. Polt and G. Maurer[27] the region were the equation is not valid is defined by :

- Temperature region :

$$T_c-1.0\text{ K} < T < T_c+1.0\text{ K}$$

- Density region :

$$\rho''(T_c+1.0\text{ K}) < \rho < \rho'(T_c-1.0\text{ K})$$

2.4. The Goodwin EOS

2.4.1. Functional form of the thermodynamic surface

The EOS for methanol published by R. D. Goodwin[1] serves as the basis for the discussion of the Goodwin EOS. The following isochoric EOS (2.4.4) gives pressure as function of temperature along paths of constant density which originate on the liquid - vapor coexistence boundary specified by vapor pressure (2.4.1)

$$\ln(P_\sigma) = a/x + b + cx + dx^2 + ex^3 + f(1-x)^p \qquad (2.4.1)$$

and by orthobaric densities :

$$\ln(\rho_g/\rho_c) = a(1-1/x) + bu^\beta + cu + du^2 \qquad (2.4.2)$$

$$(\rho_l/\rho_c - 1) = au^\beta + b(x-1) + c(x^2-1) + d(x^3-1) \qquad (2.4.3)$$

For any isochore the coexistence temperature $T_\sigma(\rho)$ as found by iteration from equation (2.4.2) and (2.4.3) and thus the vapor pressure $P_\sigma[T_\sigma(\rho)]$ becomes a function of density.

$$P - P_\sigma(\rho) = \rho R\left[T - T_\sigma(\rho)\right] + \sigma(\rho R T_c)F(\rho,T) \qquad (2.4.4)$$

with

$$F(\rho,T) = B(\rho)\Phi(\rho,T) + C(\rho)\Psi(\rho,T) \qquad (2.4.5)$$

$$\Phi(\rho,T) = \ln\left[(1+u^2)/2\right] \qquad (2.4.6)$$

$$\Psi(\rho,T) = (1/x)\ln[1+\varepsilon(u-1)]/\varepsilon \qquad (2.4.7)$$

$$B(\rho) = B_1\sigma\exp(-\gamma\sigma) \qquad (2.4.8)$$

$$C(\rho) = [C_1 + C_2\sigma + C_3\sigma^2](\sigma-\sigma^0)\exp(-\delta\sigma) \qquad (2.4.9)$$

and the following dimensionless variables :

$$\sigma = \rho/\rho_c \quad x(T) = T/T_c \quad u(\rho,T) = T/T_\sigma(\rho)$$

The constants in the expression are :

γ, δ, ε, σ_0, B_1, C_1, C_2, and C_3

2.4.2. Data fitting procedure

In the literature the function F(ρ,T) sometimes has a different form than the one mentioned in this review (R. D. Goodwin[3,4]). However the procedure of finding the best parameter set is the same for all the equations. The equation is only fit to P,V,T data. The procedure of fitting is the least squares program given by McCarty[29]. To obtain a well behaved critical isotherm the slope of the critical isochore is constrained to equal the slope of the vapor pressure (2.4.1) at the critical point.

2.4.3. Derivation of derivative properties

- The isopiestic heat capacity :

  The calculation of the isochoric heat capacity in the homogenous domain is started with the ideal gas state function at zero density, and then integrated numerically along isotherms using the EOS (2.4.1) in the following relation :

$$C_v(\rho,T) = C_v^0 - \int_0^\rho \left[\frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho\right] d\rho \qquad (2.4.10)$$

For each P,V state reached by the above mention computation the following properties can be caclulated :

- The isobaric heat capacity :

$$C_p(\rho,T) = C_v(\rho,T) + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \Big/ \left(\frac{\partial P}{\partial \rho}\right)_T \qquad (2.4.11)$$

- The speed of sound :

$$w^2(\rho,T)=\left[\frac{C_p}{C_v}\left(\frac{\partial P}{\partial\rho}\right)_T\frac{10^6}{M_r}\right] \tag{2.4.12}$$

- The Joule - Thomson coefficient :

$$\mu(\rho,T)=\frac{1}{C_p}\left[\frac{T(\partial P/\partial T)_\rho}{\rho^2(\partial P/\partial\rho)_T}-\frac{1}{\rho}\right] \tag{2.4.13}$$

2.4.4. Accuracy of derivative properties

The accuracy of the derived properties is has not been extensively discussed.

2.4.5. Validity of derivative properties in the critical region

The Goodwin EOS is not valid near the critical point. The exact range were the equation fails is not discussed.

2.5. The parametric crossover EOS

Phillip G. Hill published an EOS for water in 1990. He used an equation explicit in the Helmholz energy. The main contribution of this equation was the combination of a classic "far field" Helmholz function with the scaling equation published by Levelt Sengers et al.[63]. All analytic equations of state fails to produce thermodynamically consistent values of the isochoric and isobaric heat capacity in the near critical region. With the use of the scaling equation the equation was able to give a better representation of the calorific data in the critical region. This EOS is taken as an example of an EOS incorporating scaling in the critical region.

2.5.1. Functional form of the thermodynamic surface

The thermodynamic surface is given as the Helmholz energy as function of density and temperature :

$$\Phi=\Phi_f+F(\Phi_n-\Phi_f) \tag{2.5.1}$$

with $\Phi = A/RT$

Φ_f is the far field function and the function $F(\bar{\rho},\bar{T})$ with $\bar{\rho}=\rho/\rho_c$ and $\bar{T}=-T_c/T$ is unity at the critical point, where all derivatives are zero; it descends to zero inside the region of validity of Φ_n, and is zero everywhere else. Φ_n is the scaling low describing the thermodynamic properties in the critical region.

$$F = 1 - \exp(-1/Z) \tag{2.5.2}$$

$$Z = \exp\left[(\xi/\delta)^4\right] - 1 \tag{2.5.3}$$

$$\zeta = \sqrt{(\Delta\bar{\rho}/\Delta\bar{\rho}_0)^2 + (\Delta\bar{T}/\Delta\bar{T}_0)^2} \tag{2.5.4}$$

with $\Delta\bar{T} = 1 + \bar{T}$ and $\Delta\bar{\rho} = \bar{\rho} - 1$

The far field function is in the form :

$$\Phi_f = \ln\bar{\rho} + \Phi_0 + \Phi_1(\bar{\rho},\bar{T}) \tag{2.5.5}$$

The function Φ_1 can be written as :

$$\Phi_1 = W_1 + EW_2 + GW_3 + HW_4 \tag{2.5.6}$$

in which

$$W_1 = \sum_{i=1}^{N_{R1}}\sum_{j=1}^{N_{T1}} A_1(i,j)R_1(i)T_1(j)$$

$$W_2 = \sum_{i=1}^{N_{R2}}\sum_{j=1}^{N_{T2}} A_2(i,j)R_2(i)T_2(j)$$

$$W_3 = \sum_{i=1}^{N_{R13}}\sum_{j=1}^{N_{T3}} A_3(i,j)R_3(i)T_3(j)$$

$$W_4 = \sum_{i=1}^{N_{R4}}\sum_{j=1}^{N_{T14}} A_4(i,j)R_4(i)T_4(j)$$

$$R_1(i) = (1-E)(\bar{\rho})^{i-2}$$

$$R_1(2) = (1-E)\ln\bar{\rho} - \bar{\rho}^2\ln\bar{\rho} + \bar{\rho}^2/2$$

$$R_2(i) = (\bar{\rho})^i$$

$$R_3(i) = (\bar{\rho})^{i+1}$$

$$R_4(i) = R_1(i)$$

$$T_1(j) = (\bar{T})^{j-1}$$

$$T_2(j) = (\overline{T})^{j+1}$$

$$E = \exp(-\overline{\rho}^2)$$

$$G = \exp(-\alpha\Delta\overline{T} - \beta\Delta\overline{\rho} - \gamma\Delta\overline{T}^2 - \delta\Delta\overline{\rho}^2)$$

$$H = \exp(-\nu(\overline{T} + 3))$$

The indices are given by :

$N_{R1} = 7N_{T1} = 7$
$N_{R2} = 7N_{T2} = 12$
$N_{R3} = 5N_{T3} = 5$
$N_{R4} = 5N_{T4} = 10$

$A_1(i,j)$, $A_2(i,j)$, $A_3(i,j)$ and $A_4(i,j)$ are the coefficients in the expression.

2.5.2. Data fitting procedure

The fit procedure used by Hill[7] was the one given by Wagner[28]. The method has already been discussed in paragraph 2.1.2. The coefficients of the nonlinear terms were adjusted one at a time while finding optimum values. Special care has to be taken in fitting the data close to the critical point.

2.5.3. Derivation of derivative properties

- The isochoric heat capacity :

$$\overline{C}_v = \frac{C_v}{R} = \overline{C}_{vf} + F(\overline{C}_{vn} - \overline{C}_{vf}) + 2\overline{T}^2 \frac{\partial F}{\partial \overline{T}}(\overline{U}_n - \overline{U}_f) - \overline{T}^2 \frac{\partial^2 F}{\partial \overline{T}^2}(\Phi_n - \Phi_f)$$

(2.5.7)

- The isopiestic heat capacity :

$$\overline{C}_p = \frac{C_p}{R} = \overline{C}_v + \left[\overline{T}\left(\frac{\partial \overline{P}}{\partial \overline{T}}\right)_{\overline{\rho}} - \overline{P}\right]^2 \Big/ \left[\overline{\rho}^2\left(\frac{\partial \overline{P}}{\partial \overline{\rho}}\right)_{\overline{T}}\right] \qquad (2.5.8)$$

- The speed of sound :

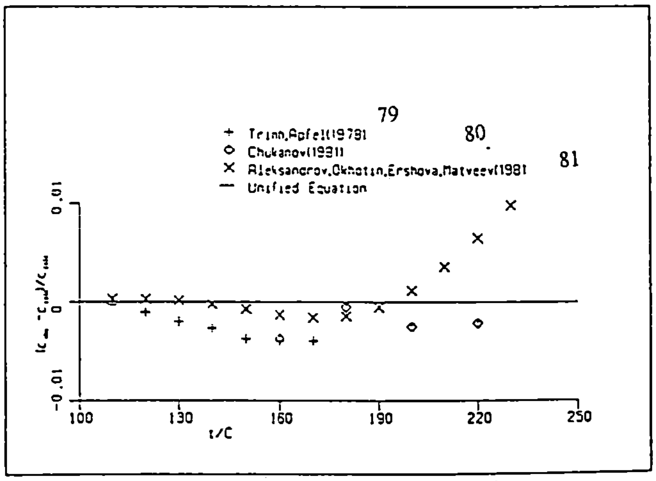
$$\bar{w} = \frac{w}{\sqrt{RT_c}} = \sqrt{-\frac{\bar{C}_p}{\bar{C}_v}\frac{1}{\bar{T}}\left(\frac{\partial \bar{P}}{\partial \bar{\rho}}\right)_{\bar{T}}} \qquad (2.5.9)$$

The derivation of the Joule - Thomson coefficient is not given by Hill[7]. The derivation of the calorific properties is complex. The far field function, equivalent in complexity to the SWEOS surface, and the scaling equation has to be derived. For example in order to derive the isochoric heat capacity there are two extra terms containing derivatives, compared to the equivalent SWEOS based equation.

2.5.4. Accuracy of derivative properties

Hill is only giving deviation plots for the speed of sound. It's really more relevant to look at the isochoric heat capacity. If the isochoric heat capacity is accurate the other derivative properties will also most likely be accurate. The deviations in the speed of sound are given in Figure 4.

Figure 4 **Uncertainties in speed of sound for water from the Hill EOS**

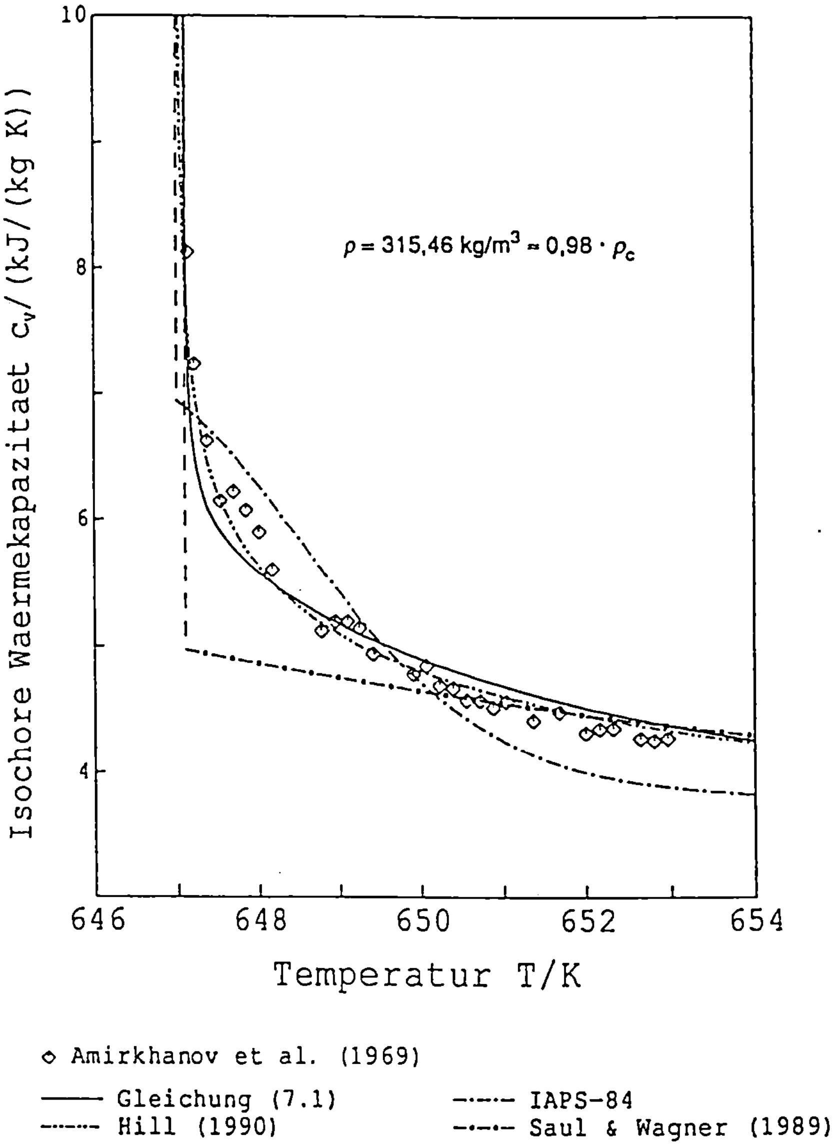


2.2.5. Validity of derivative properties in the critical region

Andreas Pruss[36] made a comparison of the behavior of different equations of state for water in the critical region. In the analyses he included the EOS proposed by Hill[7] and the one proposed by himself. His own EOS was of the SWEOS of the methane type.

The comparison in Figure 5 is made between the IAPS-84 equation, the Hill EOS, the oxygen type SWEOS (Saul & Wagner[16]) and the methane type SWEOS (A. Pruss[36])

Figure 5 Comparison of C_v for water in the critical region from different equations of state



The IAPS-84 formulation is clearly not correct. The oxygen type SWEOS is not able to give the right values of the C_v. The methane type SWEOS is giving much better value for the C_v. It is evident that the Hill EOS is giving the best representation of the C_v in the critical region. This is due to the switching from an analytic far field function to a scaling law function in the critical region.

3. Equations of state for mixtures

Two ways of representing thermodynamic properties of mixtures will be discussed. The Bender procedure is based on developing composition dependent parameters derived from the pure component parameters. The extended corresponding states principle (ECS) is based on prediction of reducing parameters for a mixture. The (ECS) procedure is the most widely used one.

3.1. The Bender procedure

3.1.1 Functional form of the thermodynamic surface

The Bender procedure is based on knowledge of the pure component EOS for all the components in the mixture. The equations of state have to be of the same type. The parameters for the mixture is then correlated to the pure mixture parameters by means of mixing rules. E. Bender[11] used the following thermodynamic surface in studying the ternary system of nitrogen, argon and oxygen :

$$P = \rho T\left[R + \left(a_1 - \frac{a_2}{T}\overline{B}\right)\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 + \left(G + H\rho^2\right)\rho^2 \exp(-a_{20}\rho^2)\right]$$

(3.1.1)

In equation (3.1.1) P is pressure, T is temperature, ρ is the molar density and R is the universal gas constant. The coefficients a_i and the temperature functions B, C, D, E, F, G, H are dependent on the mole fractions ψ_k of the components and are combined with the coefficients of the pure fluids by the following rules :

for a_2, B, a_{20} : $$X = \left(\sum_{k=1}^{N} \psi_k X_k^{1/2}\right)^2 \qquad (3.1.2)$$

for a_1, D, E, F, H $$X = \sum_{k=1}^{N} \psi_k X_k \qquad (3.1.3)$$

The subscript k refers to the pure component k of total N components and X means any one of the quantities given on the left.

$$C = \left(\sum_{k=1}^{N} \psi_k C_k^{1/3}\right)^3 \qquad (3.1.4)$$

$$G = \sum_{k=1}^{N} \psi_k G_k + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left[\alpha_{ij}(T_0 / T)^{m_{ij}} + \beta_{ij}\right]\psi_i \psi_j \qquad (3.1.5)$$

The temperature functions of the equations of state for the pure fluid k are :

$$B_k = \frac{a_{3k}}{T^2} + \frac{a_{4k}}{T^3} + \frac{a_{5k}}{T^4}$$

$$C_k = a_{6k} + \frac{a_{7k}}{T} + \frac{a_{8k}}{T^2}$$

$$D_k = a_{9k} + \frac{a_{10k}}{T}$$

$$E_k = a_{11k} + \frac{a_{12k}}{T}$$

$$F_k = \frac{a_{13k}}{T}$$

$$G_k = \frac{a_{14k}}{T^3} + \frac{a_{15k}}{T^4} + \frac{a_{16k}}{T^5}$$

$$H_k = \frac{a_{17k}}{T^3} + \frac{a_{18k}}{T^4} + \frac{a_{19k}}{T^5}$$

The coefficients α_{ij}, β_{ij} and m_{ij} are the binary interaction coefficients. The constant T_0 is set equal to 100 K.

3.3.2. Derivation of derivative properties

The derivation of the calorific properties is the same as for the 20-MBWR and the 32-MBWR EOS (Paragraph 2.3.3.). The derivation for a mixture is more complex than for a pure compound because of the mixing rules. The advantage of the Bender mixing rules is the simplicity of the calculation of thermodynamic properties. No extra iterations are necessary for the calculation of the derivative properties.

3.3.3. Accuracy of derivative properties

The accuracy of the derived properties for mixtures calculated by means of the Bender mixing rules is not extensively tested. Bender developed his theory for mixtures with the aim of calculating phase equilibria for air.

3.3.4. Validity of derivative properties in the critical region

The range of valid mole fractions are dependent on the quality of the mixing rules. In the case of the Bender mixing rules three binary interaction parameters must be estimated. The validity of the equation in the critical region is given by the pure substance equations. According to A. Polt and G. Maurer[27] the region were the equation is not valid is defined by :

- Temperature region :

  T_c-1.0 K < T < T_c+1.0 K

- Density region :

  ρ"(T_c+1.0 K) < ρ < ρ'(T_c-1.0 K)

3.2. The procedure of the extended corresponding states

3.2.1 Functional form of the thermodynamic surface

This procedure is based on the extended corresponding states principle (ECS). The extended corresponding states method is based on the following relationships :

$$z_i(\rho,T) = z_0(\rho h_{i,o}, T / f_{i,o}) \tag{3.2.1}$$

and

$$a_i(\rho,T) = a_0(\rho h_{i,0}, T / f_{i,0}) \tag{3.2.2}$$

z is the compressibility factor (z = Z-1 and a is the dimensionless residual Helmholz free energy.(a = [A-A^0]/RT) ρ and T are the density and temperature, where the subscripts denote the reference fluid (0) and target fluid (i). The $f_{i,0}$ and $h_{i,0}$ are transformation parameters, defined by

$$f_{i,0} = (T_c^i / T_c^0)\theta(T_r,\rho_r) \tag{3.2.3}$$

and

$$h_{i,0} = (\rho_c^0 / \rho_c^i)\phi(T_r,\rho_r) \tag{3.2.4}$$

where T_c and ρ_c are the critical temperature and volume for the fluids. T_r and ρ_r are defined as T_i/T^c_i and ρ_i/ρ^c_i, respectively. The functions $\phi(\rho_r,T_r)$ and $\theta(\rho_r,T_r)$ are shape factors. Given a state point defined by ρ and T plus the transformation variables $f_{i,0}$ and $h_{i,0}$ the equations (3.2.1) and (3.2.2) defines an exact transformation from one pure fluid surface to another. The pressure P_i becomes $(f_{i,0}/h_{i,0})P_0$. The shape factors $\phi(\rho_r,T_r)$ and $\theta(\rho_r,T_r)$ can by approximated in a number of ways, but if the equation of state is known both for the (0) fluid and the (i) fluid the exact calculation of $h_{i,0}$ and $f_{i,0}$ is possible for each state points. This eliminates the need to approximate the shape factors. The extension of this procedure to mixtures is accomplished by the following mixing rules :

$$f_{ij} = \varepsilon_{i,j}(f_{ii,0}f_{jj,0})^{1/2} \tag{3.2.5}$$

$$h_{ij} = \eta_{i,j}(\tfrac{1}{2}h_{ii,0}^{1/3} + \tfrac{1}{2}h_{jj,0}^{1/3})^{3} \tag{3.2.6}$$

$$h_{x,0} = \sum_i \sum_j x_i x_j h_{ij,0} \tag{3.2.7}$$

$$f_{x,0}h_{x,0} = \sum_i \sum_j x_i x_j f_{ij,0} h_{ij,0} \tag{3.2.8}$$

where x_i and x_j are the mole fractions of the pure components. The η_{ij} and the ε_{ij} are binary interaction parameters. The previously defined $h_{i,0}$ and $f_{i,0}$ becomes $h_{ii,0}$ and $f_{ii,0}$. The only adjustable parameters are the η_{ij} and the ε_{ij}. An equation of state has to be chosen to represent the pure fluids. In the literature the 32-MBWR and SWEOS are the most frequently used equations.

3.3.2. Derivation of derivative properties

The fundamental thermodynamic properties are defined as follows :

$$u_i = (1 - F_T)u_0 - H_T z_0 \tag{3.3.1}$$

$$s_i = s_0 - F_T u_0 - H_T z_0 \tag{3.3.2}$$

$$h_i = h_0 + (F_\rho - F_T)u_0 + (H_\rho - H_T)z_0 \tag{3.3.3}$$

$$g_i = g_0 + H_\rho z_0 + F_\rho u_0 \tag{3.3.4}$$

$$\ln \phi_i = g_0 + u_0 F_{n_i} + z_0 H_{n_i} \tag{3.3.5}$$

$u = [U-U^0]/RT$, $h = [H-H^0]/RT$, $s = [S-S^0]/R$, $g = [G-G^0]/RT$, ϕ = fugacity coefficient

The functions F_T, H_T, F_T and F_ρ are defined as :

$$F_T = \left(\frac{\partial f_{i,0}}{\partial T}\right)\frac{T}{f_{i,0}} \tag{3.3.6}$$

$$H_T = \left(\frac{\partial h_{i,0}}{\partial T}\right)\frac{T}{h_{i,0}} \tag{3.3.7}$$

$$F_\rho = \left(\frac{\partial f_{i,0}}{\partial \rho}\right)\frac{\rho}{f_{i,0}} \tag{3.3.8}$$

$$H_\rho = \left(\frac{\partial h_{i,0}}{\partial \rho}\right)\frac{\rho}{h_{i,0}} \tag{3.3.9}$$

The functions H_ρ and H_T are given by :

$$H_\rho = \frac{[(\kappa_i - \kappa_o)u_0]}{[(\kappa_0 - 1)u_0 + (\gamma_0 - 1)z_0]} \tag{3.3.10}$$

$$H_T = \frac{[(\gamma_i - \gamma_0)u_0 - (\gamma_0 - 1)(u_i - u_0)]}{[(\kappa_0 - 1)u_0 + (\gamma_0 - 1)z_0]} \tag{3.3.11}$$

F_ρ is obtained from the following relationship :

$$z_0 H_\rho = -u_0 F_\rho \tag{3.3.12}$$

F_T is obtained from equation (3.3.1). The definitions of γ κ are given by :

$$\gamma = \frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{3.3.13}$$

$$\kappa = \frac{\rho}{P}\left(\frac{\partial P}{\partial \rho}\right)_T \tag{3.3.14}$$

The index i denotes the property from the target fluid derived with basic thermodynamic relationships. The index 0 denotes the same thermodynamic properties derived from the reference surface. To obtain heat capacities speed of sound and other derivative properties the second derivatives of the functions $f_{i,0}$ and $h_{i,0}$ has to be calculated. Deriving these second derivatives is a difficult task. Using numerical procedures is a way to solve that problem.

The derivative properties are given by :

- The isochoric heat capacity :

$$C_v(\rho,T) = \left(\frac{\partial U_i}{\partial T}\right)_\rho \tag{3.3.15}$$

- The isobaric heat capacity :

$$C_p(\rho,T) = C_v(\rho,T) + \frac{P_i}{\rho T}\frac{\gamma_i^2}{\kappa_i} \tag{3.3.16}$$

- The speed of sound :

$$w^2(\rho,T) = \left[\frac{C_p}{C_v}\frac{P_i\gamma_i}{T}\frac{10^6}{M_r}\right] \tag{3.3.17}$$

- The Joule - Thomson coefficient :

$$\mu(\rho,T) = \frac{1}{C_p}\left[\frac{\gamma_i}{\rho\kappa_i} - \frac{1}{\rho}\right] \tag{3.3.18}$$

Calculation of the derived properties from the ECS principle is a complex process. For each state point the $f_{i,0}$ and the $h_{i,0}$ have to be calculated. This calculation is impossible without iterations. Then the derivatives of the $f_{i,0}$ and the $h_{i,0}$ have to be calculated with the equations (3.3.10), (3.3.11), (3.3.12) and (3.3.1). The fundamental thermodynamic properties H and U have to be calculated for every state point. The derivatives of the fundamental thermodynamic properties has to be calculated for every state point (3.3.15), (3.3.16).

3.3.2. Accuracy of derived properties

The accuracy in the calculated properties is dependent on :

- The accuracy of the pure component thermodynamic surface
- The accuracy of the mixing rules
- The accuracy of the experimental data used to develop pure component surfaces

There has been published several articles using the ECS theory to calculate thermodynamic properties of mixtures. There are essentially two ways of using the theory. If the thermodynamic surface for all the components in the mixture is known the $f_{i,0}$ and the $h_{i,0}$ plus their first derivatives can be evaluated for every state point. If only the thermodynamic surface of the reference fluid is known the shape factors θ and ϕ have to be estimated.

The graphs showing the error in the derived properties are taken from authors calculating the exact shape factors for every state point.

Figure 6 **Deviation in the C_v for air calculated by the ECS procedure**

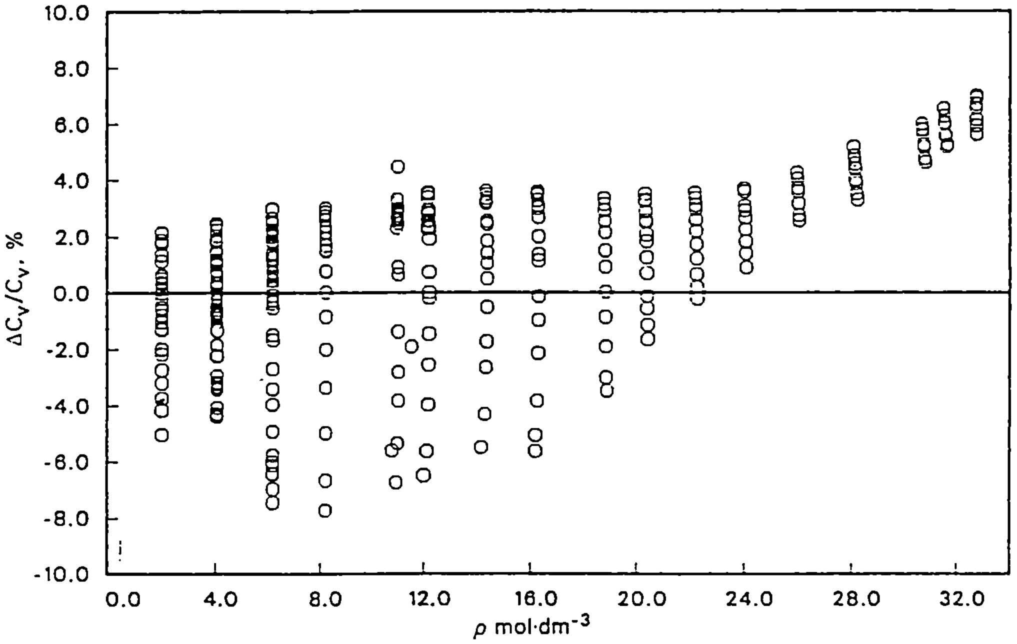
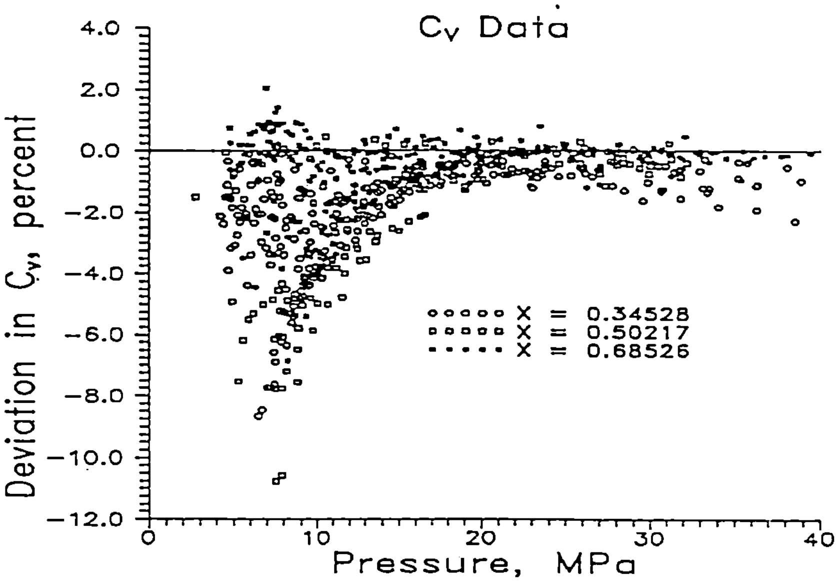
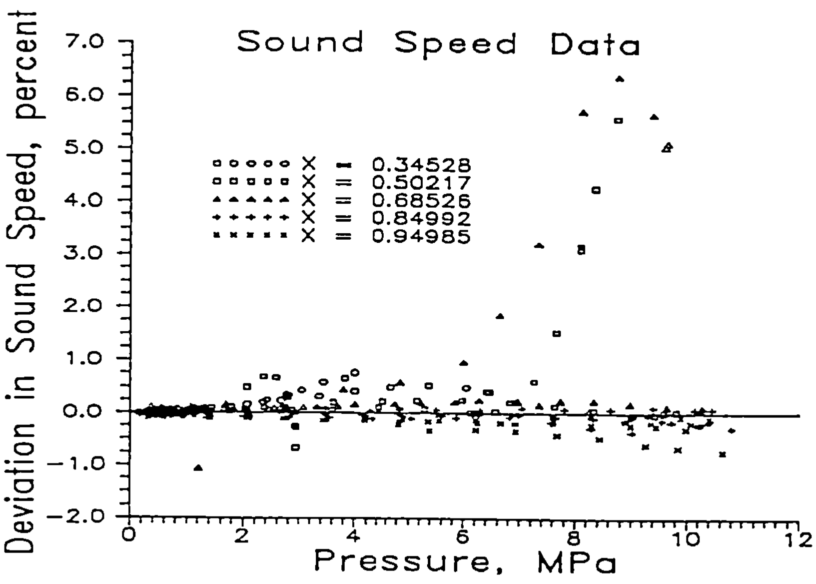


Figure 7 **Deviation in C_v for the mixture methane/ethane from the ECS procedure**



The data in Figure 7 is taken from : Mayrath and Magee[82]

Figure 8 Deviation in speed of sound for the mixture methane/ethane from the ECS procedure



The data in Figure 8 is taken from Younglove and Frederick[83]

If we compare de deviations in Figure 7 with the deviations in Figure 8 it is evident that they are of they same order of magnitude. If we compare the above mentioned figures for mixtures with the ones given for pure substances we see that the deviations for the pure compound a magnitude lower is. The increased deviations for the mixture is probably connected to the failure of the mixing rules.

3.3.3. Validity of derivative properties in the critical region

The SWEOS surface has a better representation of the critical region. Therefore it is expected that the SWEOS used as reference surface will yield better representation in the critical region. The density is calculated with increased accuracy Figure 9, but the better representation of the derivative properties has not yet been proved (D. G. Friend and J. F. Ely[15]).

Figure 9 Comparison of SWEOS and 32-MBWR as reference surface for the ECS procedure

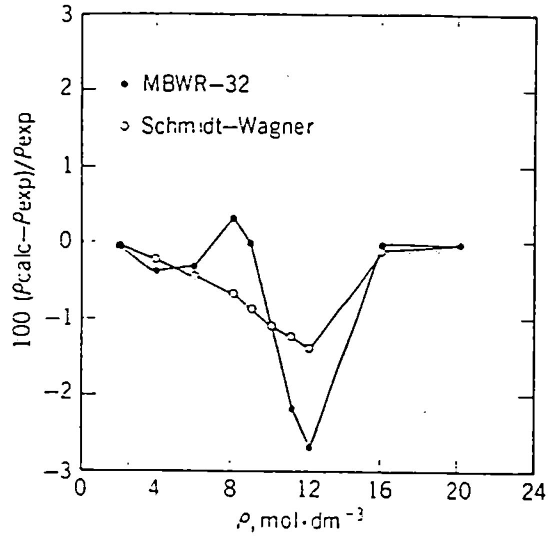


Fig. 4. Comparison of the density deviations obtained with DDMIX and those obtained with the Schmidt-Wagner equation of state as the reference fluid at 310 K.

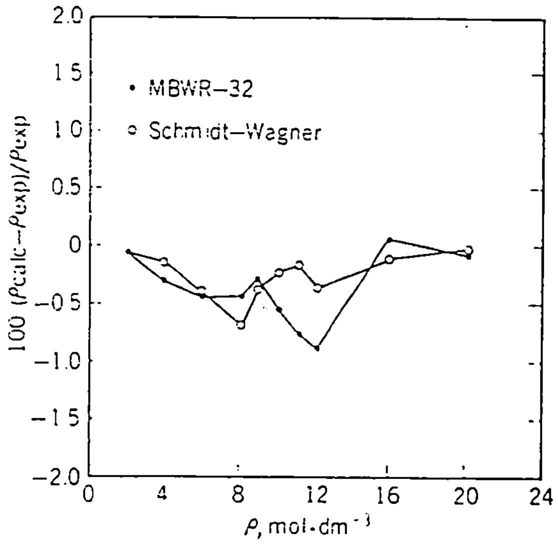


Fig. 5. Comparison of the density deviations obtained with DDMIX and those obtained with the Schmidt-Wagner equation of state as the reference fluit at 320 K.

4. Comparison of the equations of state

4.1. Pure substances

4.1.1. Accuracy of derivative properties

The parameters in the Goodwin EOS is not fitted with a multiproperty procedure. Therefore the accuracy of the derivative properties is not guaranteed.
The Bender EOS is fitted to P,V,T data and saturation properties. Multiproperty fit is not utilized. The relative low number of parameters (20) and the lack of multiproperty fit implies a low accuracy in the derivative properties. If we compare the accuracy of the 32-MBWR and the 20-MBWR (Table 3 and Table 4) we see that the accuracy of the derivative properties derived from the 32-MBWR are better. This is a result of the higher number of parameters and the multiproperty fit used in obtaining the 32-MBWR. The SWEOS is giving derived properties with a comparable accuracy to those given by the 32-MBWR. (Figure 2 and Figure 3) The Hill EOS is giving derivative properties comparable to the ones given by the SWEOS. (Figure 2 and Figure 4)

4.1.2. Validity of derivative properties in the critical region

According to A. Polt and G. Maurer[27] the Bender EOS is not valid in the region :

- Temperature region :
  $T_c-1.0\ K < T < T_c+1.0\ K$

- Density region :

  $\rho''(T_c+1.0\ K) < \rho < \rho'(T_c-1.0\ K)$

The according to B. A. Younglove and J. F. Ely[8] the 32-MBWR is not valid in the region :

- Temperature region :

  $0.97T_c<T<1.03T_c$

- Density region :

  $0.75\rho_c<\rho<1.25\rho_c$

The Bender EOS is claimed to be valid in a larger region than the 32-MBWR EOS. The basic structure of the two equations of state is the same. The 32-MBWR EOS has a larger number of parameters. It is therefore not likely that the Bender EOS has a better representation of the derivative properties in the critical region.
The SWEOS has is valid in a greater region near the critical point than the 32-MBWR equation (Table 1 and paragraph 2.2.5.). The region of validity of the SWEOS is dependent on the bank of terms used in optimizing the functional structure. The Hill EOS has the best representation of the derivative data in the critical region Figure 5. The Hill EOS is giving values for the derivative properties within the experimental uncertainty in the critical region. The validity of the Goodwin equation in the critical region has not been studied in detail.

4.1.3. Complexity of the calculation of derivative properties

The complexity of the calculation of the derivative properties is dependent on the number of terms used in the EOS. The Goodwin EOS has a low number of parameters, but numerical calculations are necessary in order to obtain the derivative properties. The Bender EOS has a relative low number of parameters, and all the derivative properties are derived by analytic differentiation. The 32-MBWR EOS has a greater number of terms, but all the derivative properties are still obtained by means of analytic differentiation. The SWEOS usually has more parameters (Dependent on the optimization of the functional structure) than the 32-MBWR. Because the thermodynamic surface is given as the free Helmholz energy as function of density and temperature more complex differentiation's has to be conducted to obtain the derivative properties. The derivative properties are still obtained by means of analytic differentiation. The derivation of the derivative properties from the Hill EOS is very complex. Due to the switching function a great number of differentiation's has to be conducted in order to obtain the derivative properties.

4.2. Mixtures

4.2.1. Accuracy of derivative properties

The accuracy of the derivative properties obtained from the ECS procedure is given in Figure 6, Figure 7 and Figure 8. Compared to the pure compound equations of state the ECS procedure is not able to produce the same accuracy in the derivative properties (Figure 1, Figure 2 and Figure 3). The mixing rules given by Bender has not been extensively tested against experimental data.

4.2.2. Validity of derivative properties in the critical region

The representation of the derivative properties in the critical region is dependent on the accuracy of the pure component equation. The representation is expected to be better for a SWEOS than for a 32-MBWR reference fluid.

4.2.3. Complexity of calculation of derivative properties

The complexity of the calculations using the ECS procedure is high. For every state point iterations and numerical differentiation have to be utilized. The Bender procedure requires no such steps.

D. McCarty[1] studied the binary mixtures of N_2-CH_4 and CH_4-C_2H_6. He experienced problems in calculating the $f_{i,0}$ and $h_{i,0}$ for densities below 3 mol/l due to convergence problems. In this region he had to use estimates for the shape factors.

If the shape factors as function of thermodynamic state are known it's not necessary to calculate $f_{i,0}$ and $h_{i,0}$ by means of iterations.

5. Discussion

For the calculation of derivative properties for a pure compound using the 32-MBWR or the SWEOS is recommended. The two equations of state are comparable on the accuracy of the derivative properties. The SWEOS is better in representing the derivative properties in the critical region, but it is more complex than the 32-MBWR. The advantage of the 32-MBWR is the high number of equations published in the literature (Table 7), and the fact that only the parameterset differs from substance to substance. This is a great advantage when writing computer code for the calculation of derivative properties. If a good representation of the derivative properties in the critical region is needed the SWEOS is a good choice. The Hill equation fails because of its high complexity. If the critical region is of special interest a scaling equation should be used.

The Bender equation fails to give the same accuracy in the derivative properties as the 32-MBWR and the SWEOS. The Goodwin equation has not proved its usefulness in representing the derivative properties. An additional draw back is the need for numerical integration in order to obtain the derivative properties.

When calculating the derivative properties for mixtures, the ECS procedure is recommended. The ECS procedure is the most widely used method for the calculations. The Bender mixing rules have not proved their usefulness in calculating the derivative properties. The Bender EOS it self is not accurate enough to give a good representation of the derivative data.

This review has focused on the ability of some wide range high precision equations of state to represent derivative properties in the homogenous region. The conclusions reached are based on the trend found in the literature. In making use of the equations mentioned care has to be taken to ensure that the equations are valid in the region at interest. The procedure used in fitting the parameters and the experimental data should also be critically reviewed before utilizing the equations.

Overview of some available equations of state

Table 5 Availability of the SWEOS in the literature

Substance	Pressure to : (MPa)	Temperature range (K)	Reference
Cyclohexane	80	Melting line-700	S. G. Penoncello et. al[5] (1995)
Methane	1000	Melting line-625	U. Setzmann and W. Wagner[6] (1991)
Water	25000	Melting line - 1273	A. Saul, and W. Wagner[16] (1989)
Oxygen	82	54 - 300	R. Schmidt and W. Wagner[39] (1985)
Carbon dioxide	800	Triple point - 1100	R. Span and W. Wagner[25] (1996)
1,1,1,2-Tetrafluoroethane (HFC-134a)	70	170-455	R. Tillner-Roth and H. D. Baehr[26] (1994)
Water	1000	Melting line to 1273	A. Pruss[36] (1994)
Argon	30	270-350	W. Wagner and R. Span[38] (1993)
Methane	30	270-350	W. Wagner and R. Span[38] (1993)
Nitrogen	30	270-350	W. Wagner and R. Span[38] (1993)
Methanol	800	Melting line - 620	K. M. de Reuck and R. J. B. Craven[49] (1993)
Ethylene	270	Melting line - 450	R. T. Jacobsen et al.[46] (1988)
Fluorine	20	55-300	K. M. de Reuck[48] (1990)
Oxygen	100	Melting line - 400	W. Wagner and K. M. de Reuck[44] (1987)
Methane	1000	Melting line - 620	W. Wagner and K. M. de Reuck[50] (1996)
R12	200	Melting line - 525	V. Marx et al.[57] (1992)
R22	200	Melting line - 525	V. Marx et al.[57] (1992)
R11	200	Melting line - 525	V. Marx et al.[57] (1992)

(Table 5 Continued)

R113	200	Melting line - 525	V. Marx et al.[57] (1992)
Sulfurhexafluoride	55	222 - 525	W. A. Cole and K. M. de Reuck[58] (1990)

Table 6 Availability of the 20-MBWR EOS in the literature

Substance	Pressure to : (MPa)	Temperature range (K)	Reference
Cyclopropane	28	293-473	A. Polt et al.[17] (1992)
I-Butane	34.72	120-498	A. Polt et al.[17] (1992)
N-Butane	30	140-589	A. Polt et al.[17] (1992)
N-Pentane	30	238-573	A. Polt et al.[17] (1992)
I-Pentane	7.34	283-553	A. Polt et al.[17] (1992)
Neopentane	20	303-498	A. Polt et al.[17] (1992)
Hexane	506.6	223-623	A. Polt et al.[17] (1992)
Octane	200	258-393	A. Polt et al.[17] (1992)
Heptane	506.6	273-393	A. Polt et al.[17] (1992)
Benzene	77.7	283-635	A. Polt et al.[17] (1992)
Toluene	25	298-673	A. Polt et al.[17] (1992)
Propylene	31.8	323-474	A. Polt et al.[17] (1992)
Methanol	62.51	298-703	A. Polt et al.[17] (1992)
Sulfurhexafluoride	40	233-523	A. Polt et al.[17] (1992)
Krypton	374	120-778	A. Polt and G. Maurer[27] (1992)
Neon	99	27-723	A. Polt and G. Maurer[27] (1992)
Fluorine	25	54-300	A. Polt and G. Maurer[27] (1992)
Sulfur dioxide	32	283-523	A. Polt and G. Maurer[27] (1992)
Water	80	273-924	A. Polt and G. Maurer[27] (1992)
Argon	-	-	E. Bender[11] (1973)
Oxygen	-	-	E. Bender[11] (1973)
Nitrogen	-	-	E. Bender[11] (1973)
Carbon dioxide	-	-	E. Bender[32] (1970)
Hydrogen	50	18-700	E. Bender[33] (1982)
Ethylene	-	-	E. Bender[34] (1975)
Propylene	-	-	E. Bender[34] (1975)
Ethane	-	-	A. S. Teja and A. Singh[35] (1977)

(Table 6 Continued)

Propane	-	-	A. S. Teja and A. Singh[35] (1977)
Ethylene			E. Bender[60] (1975)
Propylene			E. Bender[60] (1975)
Hydrogen	50	18 - 700	E. Bender[61] (1981)
Ethylene	100	T_σ(0.01 MPa) - 573	K. Bühner et al.[62] (1981)
Propylene	100	T_σ(0.01 MPa) - 573	K. Bühner et al.[62] (1981)
Propane	100	T_σ(0.01 MPa) - 573	K. Bühner et al.[62] (1981)
Ethane	100	T_σ(0.01 MPa) - 573	K. Bühner et al.[62] (1981)
Methane	100	T_σ(0.01 MPa) - 573	K. Bühner et al.[62] (1981)
Methane	50	91-625	U. Sievers and S. Schulz[31] (1986)

Table 7 Availability of the Jacobsen Stewrt EOS in the literature

Substance	Pressure range (MPa)	Temperature range (K)	Reference
Methane	0-200	Melting line -600	B. A. Younglove et al.[8] (1987)
Ethane	0-70	Melting line -600	B. A. Younglove et al.[8] (1987)
Propane	0-100	Melting line - 600	B. A. Younglove et al.[8] (1987)
I-butane	0-35	Melting line - 600	B. A. Younglove et al.[8] (1987)
N-butane	0-70	Melting line - 500	B. A. Younglove et al.[8] (1987)
1,1-Diflouroethane (R152a)	0-35	162-453	S. L. Outcalt and M. O. McLinden[9] (1986)
Nitrogen	1000	63-2000	R. T. Jacobsen, and R. B. Stewart[22] (1973)
Difluoroethane (R32)	35	160-393	S. L. Outcalt and M. O. McLinden[23] (1995)
Pentafluoroethane (R125)	68	174-448	S. L. Outcalt and M. O. McLinden[23] (1995)
Nitrogen	-	-	B. A. Younglove[37] (1982)

(Table 7 Continued)

Argon	-	-	B. A. Younglove[37] (1982)
Ethylene	-	-	B. A. Younglove[37] (1982)
Parahydrogen	-	-	B. A. Younglove[37] (1982)
Nitrogen Trifluoride	-	-	B. A. Younglove[37] (1982)
Methane	1000	Melting line -620	S. Angus et al.[47] (1978)
Oxygen	-	-	B. A. Younglove[37] (1982)
Nitrogen	1000	Melting line - 1100	S. Angus et al.[45] (1979)
R134a	10	233 - 450	M. O. McLinden et al.[56] (1989)
R123	10	255 - 450	M. O. McLinden et al.[56] (1989)
2,2-Dichloro-1,1,1-Trifluoroethane (R123)	40	166 - 500	B. A. Younglove and M. O. McLinden[24] (1994)

Table 8 Availability of the Goodwin EOS in the literature

Substance	Pressure to : (MPa)	Temperature range (K)	Reference
Methanol	70	176-673	R. D. Goodwin[1] (1987)
Carbon monoxide	100	68-1000	R. D. Goodwin[2] (1985)
Benzene	100	279-900	R. D. Goodwin[3] (1988)
Toluene	100	178-800	R. D. Goodwin[4] (1989)
Methane	70	90-700	R. D. Goodwin[20] (1974)
Propane	70	85-700	R. D. Goodwin and W. M. Haynes[41] (1982)
I-Butane	70	114-700	R. D. Goodwin and W. M. Haynes[42] (1982)
N-Butane	70	135-700	W. M.. Haynes, and R. D. Goodwin[43] (1982)

Table 9 Availability of equations of state for mixtures in the literature

Mixture	Pure fluid equation	Temperature range (K)	Pressure range (MPa)	Reference
CH_4-C_2H_6	32-MBWR	-	-	R. D. McCarty[10] (1986)
N_2-CH_4	32-MBWR	-	-	R. D. McCarty[10] (1986)
N_2-Ar-O_2	20-MBWR	-	-	E. Bender[11] (1973)
N_2-O_2	32-MBWR	-	-	J. F. Ely[12] (1990)
CH_4-C_2H_6	32-MBWR	100-320	0-35	W. M. Haynes et. al[13] (1985)
CO_2-H_2O	SWEOS	400-1000	0-100	J. S. Gallagher et. al[14] (1993)
CH_4-C_2H_6	SWEOS	-	-	D. G. Friend, and J. F. Ely[15] (1992)
CO_2-N_2	32-MBWR	250-330	0-34	J. F. Ely et. al[18] (1989)
CO_2-C_2H_6	32-MBWR / SWEOS	345-400	0-35	G. J. Sherman et. al[19]

List of symbols

A	Helmholz energy	[J/mol]
a	Residual dimensionless Helmholz energy $[A-A^0]/RT$	[-]
C_p	Isobaric heat capacity	[J/K.mol]
C_v	Isochoric heat capacity	[J/K.mol]
f	Transformation parameter in the ECS principle	[-]
G	Gibbs energy	[J/mol]
g	Residual dimensionless Gibbs energy $[G-G^0]/RT$	[-]
H	Enthalpy	[J/mol]
h	Residual dimensionless enthalpy $[H-H^0]/RT$	[-]
h	Transformation parameter ECS principle	[-]
m_{ij}	Binary interaction parameter Bender EOS for mixtures	[-]
P	Pressure	[MPa]
R	Universal gas constant	[J/K.mol]
S	Entropy	[J/K.mol]
s	Residual dimensionless entropy $[S-S^0]/R$	[-]
T	Temperature	[K]
U	Internal energy	[J/mol]
u	Residual internal energy $[U-U^0]/RT$	[-]
w	Speed of sound	[m/s]
x	Mole fraction	[-]
Z	Compressibility factor	[-]
z	Residual compressibility factor Z-1	

Greek :

α_{ij}	Binary interaction parameter Bender EOS for mixtures	[-]
β_{ij}	Binary interaction parameter Bender EOS for mixtures	[-]
ε_{ij}	Binary interaction parameter ECS mixing rules	[-]
η_{ij}	Binary interaction parameter ECS mixing rules	[-]
ρ	Density	[mol/L]
Φ	Dimensionless Helmholz energy A/RT	[-]
τ	Temperature variable (T_c/T)	[-]
δ	Density variable (ρ/ρ_c)	[-]
μ	The Joule - Thomson coefficient	[K/Pa]
ϕ	Shape factor ECS principle	[-]
ϕ	Fugacity factor	[-]
θ	Shape factor ECS principle	[-]

Subscript :

c	Critical properties
i	Target fluid
0	Reference fluid

0	Reference state
σ	Saturation properties
g	Gas property
l	Liquid property
f	Far field function Hill EOS
n	Critical region equation Hill EOS

Superscript :

r	Residual property
0	Ideal gas property

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