A NEW CUBIC EQUATION OF STATE

A Thesis

by

MERT ATILHAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2004

Major Subject: Chemical Engineering

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ABSTRACT

A New Cubic Equation of State.

(May 2004)

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Chair of Advisory Committee: Dr. Kenneth R. Hall

Thermodynamic properties are essential for the design of chemical processes, and they are most useful in the form of an equation of state (EOS). The motivating force of this work is the need for accurate prediction of the phase behavior and thermophysical properties of natural gas for practical engineering applications.

This thesis presents a new cubic EOS for pure argon. In this work, a theoretically based EOS represents the *PVT* behavior of pure fluids. The new equation has its basis in the improved *Most General Cubic Equation of State* theory and forecasts the behavior of pure molecules over a broad range of fluid densities at both high and low pressures in both single and multiphase regions. With the new EOS, it is possible to make accurate estimations for saturated densities and vapor pressures. The density dependence of the equation results from fitting isotherms of test substances while reproducing the critical point, and enforcing the critical point criteria. The EOS includes analytical functions to fit the calculated temperature dependence of the new EOS parameters.

TO

MY PARENTS

TO

MY BROTHER AND SELMA

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I. INTRODUCTION

Given increased activity in petroleum, cryogenic, and chemical engineering, trustworthy estimates of thermodynamic properties and accurate experimental density measurements are necessary to design engineering processes. Accurate prediction of thermophysical properties is an essential requirement in optimum design and operation of most process equipment involved in petrochemical production, transportation, and processing. Vapor and liquid phases coexist in almost all areas of production operations including reservoirs, well bores, and processing plants, therefore an accurate knowledge of fluid properties and phase behavior is essential. Moreover, conversion of volumetric flow rates to mass or standard volumetric flow rates for custody transfer of natural gas requires density data. When experimental data are not available, a precise prediction of density is needed. In addition, equipment failure is often directly attributed to lack of accurate data. Indeed, comparatively small improvements in the accuracy of such data can improve operational efficiency substantially, consequently resulting in significant savings in the cost of manufacturing and operating chemical plant equipment (Assel *et al.*, 1978).

In chemical industries, obtaining thermophysical properties is always problematic. Mostly, thermophysical properties, such as PVT relations, come from experiments. Performing experiments to attain thermophysical data is not only time-consuming but

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also costly. Moreover, it is difficult to replicate all the conditions of actual industrial conditions in a laboratory environment. Thus, predictive models for thermophysical properties are undeniably an engineering necessity.

EOS can be either semi-theoretical or theoretical. Semi-theoretical EOS combine theory and experimental data while theoretical EOS are based in kinetic theory or statistical mechanics and involve intermolecular forces. Much research attention has been directed at developing more accurate EOS since the time of van der Waals (vdW) (1873). Two main reasons drive this constant search. EOS development is mathematically fascinating and challenging, because it seems so simple to the uninitiated. The second reason is the exceptional power and utility of an accurate equation of state.

The EOS that have appeared in the literature vary from simple expressions to multiple constant and convoluted types of equations. For high precision, industrial engineers may use the more complex equations, such as the Benedict-Webb-Rubin EOS. Today, these equations generally are not used for thermophysical property calculations, such as multi-component VLE, because they require complicated manipulation, extra computer storage, and time-consuming iterative calculations. Establishing their constants is often a lengthy task requiring curve fitting, careful weighting of the experimental data and the use of trial and error (Iglesias-Silva, 1987).

In most industrial design situations as well as research measurements of derived properties, the unknown variable is density, whereas the observables are pressure and temperature. Consequently, the density-cubic equations are of particular interest because they provide an analytical solution for the density, as compared to the more complicated

non-cubic and non-analytic equations of state, which require time consuming iterative procedures to solve for the density. Cubic equations are preferable when compared to the non-cubic types of equations because non-cubic equations have high-order density terms or exponential terms that makes their solutions complex. Also the non-cubic equations have many adjustable parameters, and it is difficult to make them work throughout the entire temperature range.

The presently available popular density cubic equations of state, like the Soave Redlich Kwong and Peng-Robinson equations, provide good descriptions of real fluid behavior in the two phase region and in the gas phase, but in the compressed liquid region they lack the accuracy levels attainable using the Benedict-Webb-Rubin, modified Benedict-Webb-Rubin, Beattie-Bridgeman equations (Soave, 1972).

An EOS is the representation of pressure (or compressibility factor) as a function of temperature and volume. EOS serve three primary objectives.

i) Representation of *PVT* data for data smoothing and interpolation, and for differentiation and integration of *PVT* data for calculation of derived thermodynamic properties.

ii) Prediction of fluid phase properties of pure fluids and their mixtures from a minimum of experimental data.

iii) Prediction of vapor-liquid equilibria of mixtures, especially at high pressures.

When combined with appropriate thermodynamic relationships, an EOS can predict isothermal changes in latent heats of vaporization, activity coefficients and vapor-liquid

equilibria (VLE), with good accuracy. EOS also provide a comprehensive technique for describing thermophysical properties such as density, compressibility factor, internal energy, Helmoltz Free Energy, equilibrium ratios, entropy, enthalpy, fugacity, isothermal compressibility, Joule-Thompson coefficient, volume expansion, surface tension, speed of sound, specific heat at constant volume, specific heat at constant pressure and Gibbs Free Energy.

The development of an EOS requires accurate density measurements. Generally, a set of PVT data is correlated to determine the EOS parameters; sometimes, as shown in table 1 the critical conditions generate the values of those parameters. The EOS is an adequate model if it has the following characteristics:

1. Agreement between predicted values and experimental data within the estimated experimental error.
2. A small number of characteristic parameters describe the entire fluid region and saturation curve.
3. Extrapolation capability within reasonable limits.
4. Physical and theoretical description of its parameters.
5. Applicability of the equation to different substances.

The main purpose of this study is to develop a four parameter equation of state that has good predictive capability for natural gas components. In order to achieve this goal, a new equation of state has been derived from the most general cubic EOS proposed by Kumar and Starling. (Kumar and Starling, 1980).

As mentioned above, many attempts have been made to describe the thermodynamic behavior of gases. These different types of EOS fall into three categories (Kumar and Starling, 1980).

1) First Class EOS: Equations in this category are basically density cubic equation of state. The density cubic equations of state give reasonable results for the thermodynamic behavior of real fluids (van der Waals, 1873; Redlich and Kwong, 1949; Soave, 1972; Peng and Robinson, 1976).

Table 1. Examples for most common density cubic EOS

Name (Year)	EOS	a	b
van der Waals (1873)	$P=\frac{RT}{V-b}-\frac{a}{V^2}$	$0.421875R^2T_c^2/P_c$	$0.125RT_c/P_c$
Redlich, Kwong (1949)	$P=\frac{RT}{V-b}-\frac{a}{T^{0.5}V\left(V+b\right)}$	$0.42748R^2T_c^{2.5}/P_c$	$0.08664RT_c/P_c$
Soave Redlich, Kwong (1972)	$P=\frac{RT}{V-b}-\frac{\theta^1}{V\left(V+b\right)}$	$0.42748R^2T_c^2/P_c$	$0.08664RT_c/P_c$
Peng, Robinson (1976)	$P=\frac{RT}{V-b}-\frac{\theta^2}{V^2+2bV-b^2}$	$0.45724R^2T_c^2/P_c$	$0.0778RT_c/P_c$

$$\theta^1=a\left[1+\left(0.480+1.574\omega-0.176\omega^2\right)\left(1-T_r^{0.5}\right)\right]^2 \quad (1)$$

$$\theta^2=a\left[1+\left(0.3764+1.5422\omega-0.26992\omega^2\right)\left(1-T_r^{0.5}\right)\right]^2 \quad (2)$$

When we look at the form of the density-cubic equations of state in chronological order, we discover the latest equations are more complex than the former ones.

2) Second Class EOS: These EOS are non-cubic forms. They are capable of providing accurate results for both vapor and liquid phases. The Benedict-Webb-

Rubin Equation is a good example for this class equation (Benedict, Webb and Rubin 1940; Kumar and Starling, 1980).

3) Third Class EOS: In this class are the non-analytic EOS that are highly constrained for some specific fluids (Goodwin, 1977). Even though they are constrained, they are capable of expressing real fluid thermodynamic properties precisely.

Among all these EOS, the first class EOS are more useful because they provide an analytical solution for the density as compared to the more complex and complicated non-cubic 2^{nd} type and non-analytic 3^{rd} type which require time consuming iterative calculations.

In general, the overall performance in fluid properties prediction is somewhat better using the Peng-Robinson equation compared to the Soave-Redlich-Kwong (SRK) and the SRK equation is better than the Redlich-Kwong (RK) that is more precise than the vdW EOS. Thus, temperature dependence leads to a more precise equation of state. In the same vein, we also can state that more density dependence leads to more accurate EOS. This is very important because if the most general density-cubic equation can provide precise results comparable to the 2^{nd} class of EOS for all fluids, it becomes highly desirable in situations where repetitive calculations for the density are required.

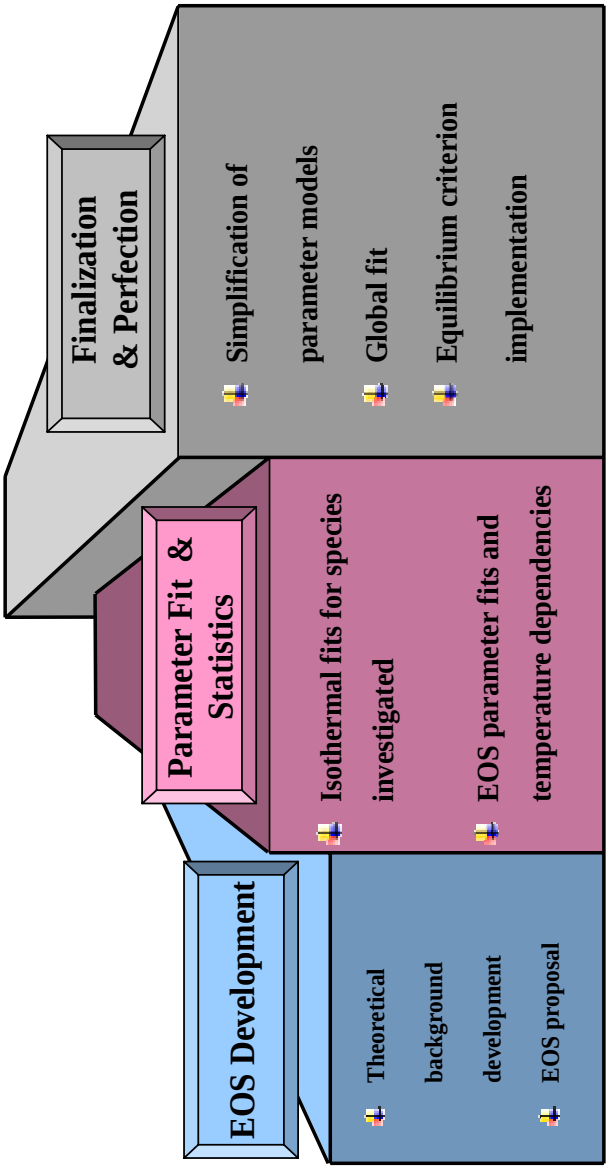

Figure 1. Overall research strategy

II. LITERATURE REVIEW

Since the time of Boyle, many studies have sought a better representation of the PVT relationship for fluids. In 1662 Boyle found that the volume of gas is inversely proportional to its pressure for a constant temperature. Charles showed that change in volume is proportional to change in temperature at constant pressure. In 1834 Clapeyron combined these two results into the Ideal Gas Law: $PV = RT$.

Then in 1800, Dalton proposed the law of partial pressures postulating that in a mixture, each gas behaves as if it occupied the entire volume alone. Eight decades later, Amagat (1880) proposed the concept of partial volumes. Ideal or perfect gases are pure or gas mixtures for which partial pressures and volumes can be additive and the relationship $PV = RT$ holds. Cagniard de la Tour (1822) discovered that, at a certain pressure and temperature, characteristic for each substance, the properties of the liquid and gas become indistinguishable, and some of the properties change significantly when approaching that condition. This condition is called the critical point, and comprehensive studies of the critical phenomena still continue today.

The ideal gas law is often not an adequate approximation of real gas behavior. The ideal gas law assumes zero molecular volume and no interactions among the gas molecules. These assumptions cannot be true for real gas molecules. For this reason, many attempts to describe PVT properties of gases and liquids using a theoretical EOS date to 1873, when van der Waals published his famous EOS. In 1901, Onnes (1909) proposed the virial EOS, which is an expression of the compressibility factor of gas in terms of a

power series in density. Although the virial equation was proposed as an empirical form, Davidson (1962) has shown that it results from statistical mechanics. The main disadvantage of this equation is its inability to describe multiple phase phenomena.

Several investigations proposed virial-type of EOS. Beattie and Bridgeman (1927) published a five constant equation that gives a satisfactory representation of volumetric properties except in the critical region. At densities greater than the critical density, the equation is inadequate. Later, Benedict, Webb and Rubin (1940) proposed an equation with eight characteristic constants. This equation has been extremely valuable and many modifications of this equation (Starling, 1972; Starling and Han, 1972 and Lee and Kesler, 1975) have been proposed to predict the entire PVT surface, however none of these equations have been completely adequate.

Almost fifty years later, Redlich and Kwong (1949) proposed a very successful equation. It was simple and moderately accurate in the estimation of thermodynamic properties for non-polar fluids and their mixtures. Shortly after van der Waals EOS appeared, researchers sought temperature dependence for the attraction parameter, ***a***. using this reasoning, Redlich and Kwong developed their popular EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V\left(V+b\right)T^{1/2}} \tag{3}$$

Principally, Redlich and Kwong noted that, when the system pressure goes to infinity $\left(P \to \infty\right)$, the molar volume of the substance shrinks to about 26 percent of its critical volume $\left(b = 0.26V_c\right)$.

In recent years, Zwanzig (1954) introduced the perturbation theory for atomic fluids, and Pople (1954) developed the theory for molecular fluids by separating the EOS into two terms: repulsive (hard body) and attractive. Percus and Yevick (1958), Wertheim (1964), and Longuet-Higgins and Widom (1964) developed equations for the hard sphere model. Later, Gibbons (1969) and Boublik (1975) proposed a more general equation to describe the behavior of hard convex bodies.

Alder and Hecht (1969) discussed the augmented vdW theory to provide a better representation of the vdW parameters. In this theory, the ***b*** term of the vdW EOS was replaced by the hard-sphere EOS and the ***a*** parameter was replaced by a value determined from perturbation theory. Later, Alder *et al*. (1972) showed that an excellent term for the long range potential function could be obtained from perturbation theory and molecular dynamics. Although their EOS predicted the internal energy well, it failed to predict compressibility factors (pressures) of pure fluids.

Based upon the fact that "the better the reproduction of the saturation conditions for pure substances, the better the results for mixtures," Soave (1972) modified the RK by replacing the term $\left(\frac{a}{T^{0.5}}\right)$ with a more general temperature dependent term, α. He did this by reproducing vapor pressures for non-polar substances at $T_r = 0.7$. The pressure explicit form of the Soave-Redlich-Kwong equation of state (SRK EOS) is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{4}$$

The coefficients and expressions for parameters *a(T)* and *b* come from applying the critical conditions:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{5}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{6}$$

The following relationship describes the temperature dependence:

$$a_i\left(T\right) = a_{ci}\alpha\left(T\right) \tag{7}$$

where $\alpha_i(T)$ is obtained by using experimental saturation data. A set of values of $\alpha_i(T)$ for each substance is obtained using the proposed EOS and the experimental saturation data. Then, he observed a linear relationship between $\alpha_i^{0.5}$ and $T_{ri}^{0.5}$. The following expression describes this observation

$$\alpha_i^{0.5} = 1 + m_i\left(1 - T_{ri}^{0.5}\right) \tag{8}$$

To introduce the characteristics of each component, the slope (m_i) in $\alpha_i^{0.5} = 1 + m_i\left(1 - T_{ri}^{0.5}\right)$ is correlated with respect to acentric factor (ω_i) for the compounds. Using pure component vapor pressure data, Soave found the following relationship for (m_i):

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \tag{9}$$

Using the critical conditions to determine parameters gives a fixed critical gas compressibility factor for all components. However this result does not agree with the

experimental values for the critical gas compressibility factor which ranges from 0.234-0.309 (Vera *et al*., 1984). The SRK predicts the critical compressibility factor as 0.333.

Peng and Robinson (1976) formulated their EOS to forecast saturated liquid densities more precisely. Their equation is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{10}$$

Peng and Robinson maintained the repulsion component of the vdW EOS. Furthermore, they defined the attraction term as a general function of temperature like Soave. The expressions for parameters *a(T)* and *b* result from applying the critical criteria. Peng and Robinson also adopted the Soave approach for calculating the parameter α. However their correlation for the slope $\alpha_i^{0.5} = 1 + m_i\left(1 - T_{ri}^{0.5}\right)$ with respect to acentric factor is different.

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{11}$$

The PR EOS improved the calculation of density near the critical point. The reason for that is they designed their equation of state such that the predicted critical compressibility is closer to the experimental value. Even though the PR EOS gives results closer to the experimental values for critical compressibility (0.307), it still has limitations.

The development of an EOS using augmented vdW theory has been emphasized because of its flexibility in predicting the behavior of pure fluids and their mixtures. Chen and Kreglevski (1977) combined the Alder (1972) and Boublik (1975) equations for arbitrary shape to obtain the BACK EOS. Recently, Prausnitz and Donohue (1976),

Vilmalchand and Donohue (1985), Kim *et al*. (1986), and Svedja and Kohler (1983) have proposed similar equations.

Patel and Teja (1982) proposed another EOS as an extension of the works of Soave, Peng-Robinson and Schmidt-Wenzel. They stated their equation as;

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + (b+c)V - bc} \tag{12}$$

The critical compressibility factor is defined by Patel and Teja by using:

$$\xi_c = \frac{P_c V_c}{rT_c} \tag{13}$$

Here, ξ is a correlation parameter for a non-polar component that is used for computational purposes:

$$\xi_{ci} = 0.329032 - 0.767992\omega_i + 0.0211947\omega_i^2 \tag{14}$$

Another interesting characteristic of the Patel-Teja EOS is, if ***c*** is 0, the equation reduces to the PR EOS. Likewise, when ***c*** equals ***b***, the Patel Teja EOS reduces to the PR EOS. All major historical development in EOS is tabulated in table 2.

Table 2. PVT relation determination and EOS development in history

Year	Author(s)	Accomplishment
1662	Boyle	Proportionality between pressure and volume at constant temperature
1787	Charles	Proportionality between ΔV and ΔT at constant pressure
1801	Dalton	Development of partial pressure of gases
1822	Carniard de la Tour	Determination of critical point characteristics
1834	Clapeyron	Development of ideal gas law, $PV = RT$
1873	van der Waals	The first EOS
1880	Amagat	Development of partial volume of gases
1901	Kammerlingh Onnes	The Virial EOS
1927	Beattie and Bridgeman	Development of five constant EOS
1940	Benedict et al.	Eight parameter, BWR EOS
1949	Redlich and Kwong	Thermodynamic property estimation for non-polar fluids, definition of acentric factor
1954	Zwanzig	Introduction of Perturbation theory for atomic fluids
1954	Pople	Introduction of repulsive and attractive terms for EOS
1955	Martin and Hou	Detailed PVT characteristics of gases
1969	Carnahan and Starling	Used statistical mechanics theory to improve EOS
1972	Soave-Redlich-Kwong	Modified form of Redlich-Kwong Equation
1972	Alder et al.	Acquisition of long range potential function from perturbation theory and molecular dynamics
1975	Boublik	Developed reference term for hard convex bodies
1977	Chen and Kreglewski	Developed four universal constant and five characteristic BACK EOS
1976	Prausnitz and Donohue	BACK EOS similar type four parameter EOS
1980	Kumar and Staling	The most general EOS
1982	Patel and Teja	Three parameter EOS, extension of Peng-Robinson EOS
1982	Kubic	Modified Martin EOS into simpler three parameter EOS
1987	Trebble and Bishnoi	Four parameter EOS with four different binary interaction coefficient pairs
1997	Nordin	Multiphase equilibria of PCB-contaminated systems

III. DEVELOPMENT OF THE NEW EQUATION OF STATE

Among the current cubic EOS, the Soave and Peng-Robinson equations appear to provide reasonable descriptions of real fluid behavior throughout phase space. However, in the compressed liquid region these popular EOS lack the accuracy levels achievable using the non-cubic form such as the Benedict-Webb-Rubin Equation of State.

Upon investigating cubic EOS in chorological order, it is noticeable that more recent equations have more complicated forms. For example the Redlich-Kwong EOS is more complicated than the van der Waals equation:

$$P = \frac{\rho RT}{1-\rho b} - a\rho^2 \tag{15}$$

$$P = \frac{\rho RT}{(1-\rho b)} - \frac{aT^{-0.5}\rho^2}{(1-\rho b)} \tag{16}$$

For two parameter EOS, the only constraint equations are the critical conditions, the first and second derivatives of pressure with respect to volume is zero:

$$\left(\frac{\partial P}{\partial V^2}\right)_{T_c}^{CP} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c}^{CP} \tag{17}$$

A 3-parameter equation of state utilizes either the critical compressibility factor or the co-volume definitions as an additional constraint to the critical conditions. Four parameter EOS use either compressibility factor or the co-volume along with the critical conditions. Two parameter EOS produce a fixed value of critical compressibility and, as a result, the predicted densities of the saturated liquids and the predicted critical volumes

differ considerably from experimental values. Four parameter EOS on the other hand are complex less used.

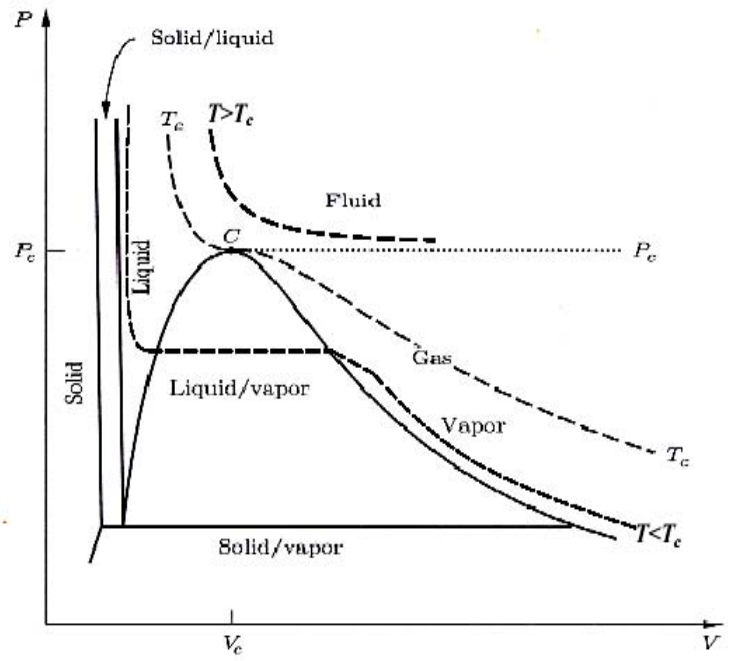

Figure 2. P-V diagram

Kumar and Starling (1982) proposed a so-called general cubic EOS. The characteristic of the Kumar-Starling EOS is the combination of the repulsive and attractive terms into a single term. Comparison of the vapor pressure, vapor/liquid density and enthalpy departure predictions for 32 non-polar substances, indicates that the Kumar-Starling EOS compares with the modified Benedict-Webb-Rubin EOS proposed by Brule *et al*. (1979) based upon three-parameter corresponding state theory. Nevertheless, the original Kumar-Starling EOS fails to predict the exact critical point of components. The present work is an extension of the work of Kumar and Starling (1982).

We propose a new equation of state starting from the Kumar-Starling general equation of state. In this work, we improve the representation of liquid phase densities, we improve the description of fluid phase behavior near the critical point as shown in figure 2, and we reproduce the true critical point. In order to accomplish these goals, we have modified the original Kumar-Starling EOS by eliminating some variables through defining relationships among the equation parameters.

3.1. Background information

The direct density expansion for a cubic EOS is similar to the virial EOS form through the third virial coefficient:

$$P = a_1 + a_2\rho + a_3\rho^2 + a_4\rho^3 \tag{18}$$

where ρ is the molar density and P is the absolute pressure. In this equation, a_1, a_2, a_3 and a_4 are temperature dependent parameters. This equation can describe both the gas and liquid phase behavior of a fluid:

$$P = \sum_{j=1}^{\infty} a_j \rho^{j-1} \tag{19}$$

Nevertheless, this equation has infinite order in density. The analytical polynomial function, which approximates the power of an infinite series in density in cubic form is a ratio of polynomials:

$$P = \frac{a_1 + a_2\rho + a_3\rho^2 + a_4\rho^3}{a_5 + a_6\rho + a_7\rho^2 + a_8\rho^3} \tag{20}$$

This cubic polynomial equation represents the general form of a cubic equation having a_1 to a_8 temperature and composition dependent parameters.

In terms of compressibility factor, it is possible to express this equation as

$$Z = \frac{\left(\frac{c_1}{\rho}\right) + c_2 + c_3\rho + c_4\rho^2}{a_5 + a_6\rho + a_7\rho^2 + a_8\rho^3} \tag{21}$$

where $c_i = \frac{a_i}{RT}$ and $i=1, 2, 3, 4$, R is the universal gas constant and T is the absolute temperature. Here, we need to consider the ideal gas limit: $\rho \to 0$ as $Z \to 1$ thereby preventing divergence of Z as $\rho \to 0$. For this purpose, c_1 is set equal to zero. Therefore, the form is:

$$Z = \frac{c_2 + c_3\rho + c_4\rho^2}{c_5 + c_6\rho + c_7\rho^2 + c_8\rho^3} \tag{22}$$

In the limit, this equation becomes:

$$\lim_{\rho\to\infty} Z = \frac{c_2}{c_5} \tag{23}$$

To satisfy the thermodynamic requirement of $\rho \to 0$ as $Z \to 1$, c_2 must equal to a_5. Therefore letting $c_2=a_5$ and dividing both denominator and numerator of the right hand side of equation (22) by c_2, we obtain:

$$Z = \frac{1 + d_1\rho + d_2\rho^2}{1 + d_3\rho + d_4\rho^2 + d_5\rho^3} \tag{24}$$

For calculation purposes, equation (24) also can be written in more convenient form by setting;

$$d_1 = A_5 \tag{25}$$

$$d_2=A_2 \tag{26}$$

$$d_3=A_3-A_1 \tag{27}$$

$$d_4=A_4-A_1A_3 \tag{28}$$

$$d_5=-A_1A_4 \tag{29}$$

and the equation takes the form:

$$Z=\frac{1+A_5\rho_r+A_2\rho_r^2}{\left(1-A_1\rho_r\right)\left(1+A_3\rho_r+A_4\rho_r^2\right)} \tag{30}$$

In this equation, Z is the compressibility factor and ρ_r is the reduced density $\left(\rho/\rho_c\right)$ and A_1 through A_5 are density independent parameters that depend upon temperature and composition:

$$A_1 = a_1 \tag{31}$$

$$A_2=\left(a_7+\frac{a_1}{T_r}+\frac{a_{12}}{T_r^2}\right)+\left(-\frac{a_2}{T_r}+\frac{10a_4}{T_r^2}+\frac{a_{11}}{10T_r^8}\right)\gamma \tag{32}$$

$$A_3=\left(\frac{a_9}{T_r}-\frac{a_4}{T_r^2}\right)+\left(\frac{a_6}{T_r}+\frac{10a_{12}}{T_r^2}+\frac{a_{10}}{T_r^3}+\frac{a_2}{T_r^4}\right)\gamma \tag{33}$$

$$A_4 = -a_1 \tag{34}$$

$$A_5=\left(\frac{a_3}{T_r^2}+\frac{a_4}{T_r^3}\right)+\left(\frac{a_8}{T_r}+\frac{a_3}{T_r^3}+\frac{a_5}{T_r^4}+\frac{a_3}{10^3T_r^8}\right)\gamma \tag{35}$$

Here, ρ_r and T_r are the reduced density and the reduced temperature, respectively. Also γ stands for the orientation parameter, and a_1-a_{12} are universal constants.

3.2 The proposed equation of state

Starting from the general EOS, we suggest the form:

$$\frac{P}{RT} = \frac{\beta_4\rho + \beta_5\rho^2 + \beta_6\rho^3}{\lambda_0 + \lambda_1\rho + \lambda_2\rho^2 + \lambda_3\rho^3} \tag{36}$$

Yet, this equation can be written in reduced form or in terms of $Z\left[=\frac{P}{RT\rho}\right]$ to suit the reader. Dividing both sides by ρ produces:

$$Z = \frac{\lambda_4 + \lambda_5\rho + \lambda_6\rho^2}{\lambda_0 + \lambda_1\rho + \lambda_2\rho^2 + \lambda_3\rho^3} \tag{37}$$

Factoring λ_0 from the numerator and denominator requires that $\frac{\lambda_4}{\lambda_0}$ must be unity ($\frac{\lambda_4}{\lambda_0} \to 1$) to satisfy the ideal gas boundary condition at zero density along any isotherm.

Therefore, equation (37) simplifies to a still-general form with up to five constants:

$$Z = \frac{1 + \left(\lambda_5/\lambda_0\right)\rho + \left(\lambda_6/\lambda_0\right)\rho^2}{1 + \left(\lambda_1/\lambda_0\right)\rho + \left(\lambda_2/\lambda_0\right)\rho^2 + \left(\lambda_3/\lambda_0\right)\rho^3} \tag{38}$$

Yet again, we can simplify the above equation by replacing the λ terms by μ to get:

$$Z = \frac{1 + \mu_1\rho + \mu_2\rho^2}{1 + \mu_3\rho + \mu_4\rho^2 + \mu_5\rho^3} \tag{39}$$

Going further, we can arrange the denominator of equation (39) while keeping it cubic:

$$Z = \frac{1 + \mu_1\rho + \mu_2\rho^2}{\left(1 - b\rho\right)\left(1 + \beta_1\rho + \beta_2\rho^2\right)} \tag{40}$$

At first, our new equation of state seemed to be a five-parameter cubic EOS. However, after trials of fitting isothermal argon data to equation(40), we have shown that the relation between β_1 and β_2 is:

$$\beta_1 = 2 * \beta_2 \tag{41}$$

After plugging this relation into equation (40) we get:

$$Z = \frac{1 + \mu_1\rho + \mu_2\rho^2}{(1 - b\rho)\left(1 + 2\beta_2\rho + \beta_2\rho^2\right)} \tag{42}$$

Equation (42) simplifies to:

$$Z = \frac{1 + \mu_1\rho + \mu_2\rho^2}{(1 - b\rho)(1 + \beta_2\rho)^2} = \frac{1 + a\rho + c\rho^2}{(1 - b\rho)(1 + d\rho)^2} \tag{1.43}$$

We have performed isothermal fits for argon by using equation(1.43). An outcome of this exercise is a relation between parameters ***b*** and ***d***.

3.3 Relation between *b* and *d* Parameters

Preliminary fits indicate a relation between ***b*** and ***d***:

$$d = \gamma(T)b^3 \tag{44}$$

Although ***d*** is replaced by equation (44), the number of parameters in the model equation remains the same. However, by replacing ***d*** with equation (44) in our model EOS, we get less temperature dependence parameter because γ has simple dependence. The relation between error in compressibility and the order of b parameter is shown in figure 3. After isothermal fits, the picture for ***b*** and ***d*** parameters plotted in figure 3.

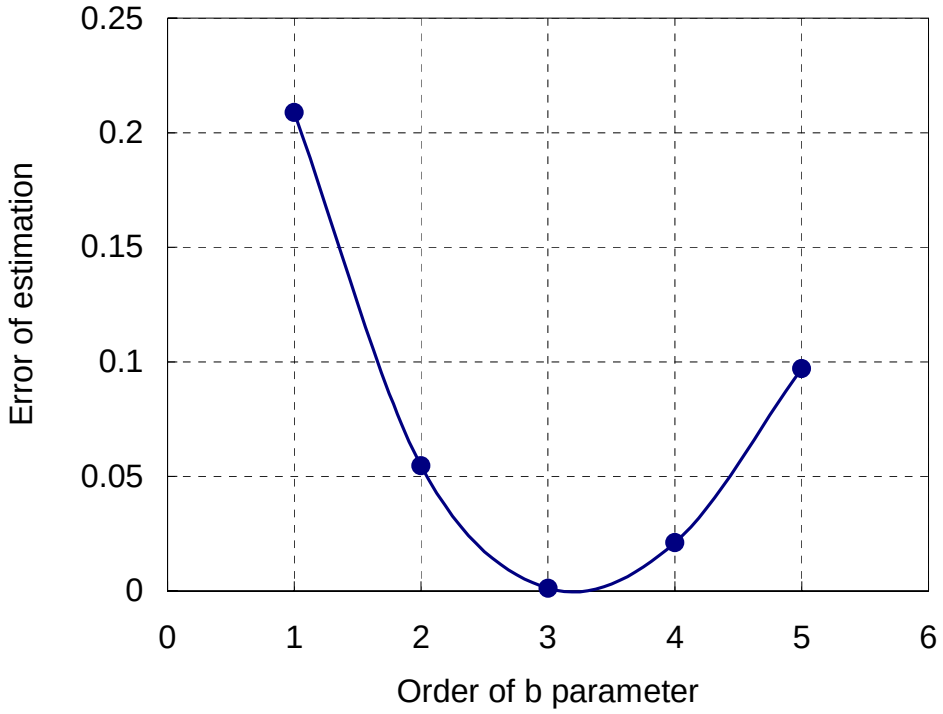

Figure 3. Error in compressibility factor during estimation with respect to different ***b*** parameter order of magnitudes

Table 3. Primary ***b*** and ***d*** parameter fit results after isothermal fits

Temp.[K]	B	D
90	1.98E-05	2.28E-06
100	2.09E-05	3.51E-06
110	2.24E-05	5.59E-06
120	2.42E-05	8.31E-06
130	2.62E-05	1.16E-05
135	2.74E-05	1.35E-05
140	2.88E-05	1.60E-05
143	2.97E-05	1.77E-05
146	3.08E-05	1.98E-05
148	3.15E-05	2.09E-05
150.7	3.29E-05	2.38E-05
153	3.30E-05	2.32E-05
155	3.25E-05	2.17E-05
157	3.24E-05	2.12E-05
160	3.19E-05	1.99E-05
165	3.05E-05	1.77E-05
170	2.77E-05	1.51E-05
175	2.42E-05	1.25E-05
180	2.01E-05	9.98E-06
200	1.23E-05	5.10E-06
220	2.25E-05	8.54E-06
235	2.83E-05	1.11E-05
250	2.80E-05	1.05E-05
265	2.80E-05	1.02E-05
280	2.78E-05	9.79E-06
295	2.77E-05	9.53E-06
310	2.67E-05	8.29E-06
340	2.69E-05	8.30E-06
370	2.72E-05	8.61E-06

As a result, our model equation becomes:

$$Z = \frac{1 + a\rho + c\rho^2}{(1 - b\rho)\left(1 + \gamma b^3 \rho\right)^2} \tag{45}$$

3.4 The effect of number of parameters

To make our equation accurate; as shown in figure 4, we require complicated temperature dependence for the parameters. This is not a significant computational burden because iterative solutions for density occur at constant temperature.

EOS have a pressure expression made up of the sum of repulsive and attraction terms:

$$P = P_{repulsion} + P_{attraction} \tag{46}$$

Most EOS employ the van der Waals repulsive term;

$$P_{repulsion} = \frac{RT}{V - b} \tag{47}$$

In equation(47), ***b*** is the co-volume parameter or the repulsion parameter.

Similarly, the attraction term is:

$$P_{attraction} = \frac{a}{g(V)} \tag{48}$$

In equation(48), ***a*** is an attraction parameter and *g(V)* is a function of molar volume.

The existence of additional parameters helps reduce errors in calculating critical volumes. For instance, the PR EOS contains only two parameters and the critical compressibility factor calculated is 0.307 for all components. No real fluid has such a large vale.

A fourth parameter is useful because it assists the EOS (the slope $\left(\frac{\partial P}{\partial V}\right)_T$) at elevated pressures.

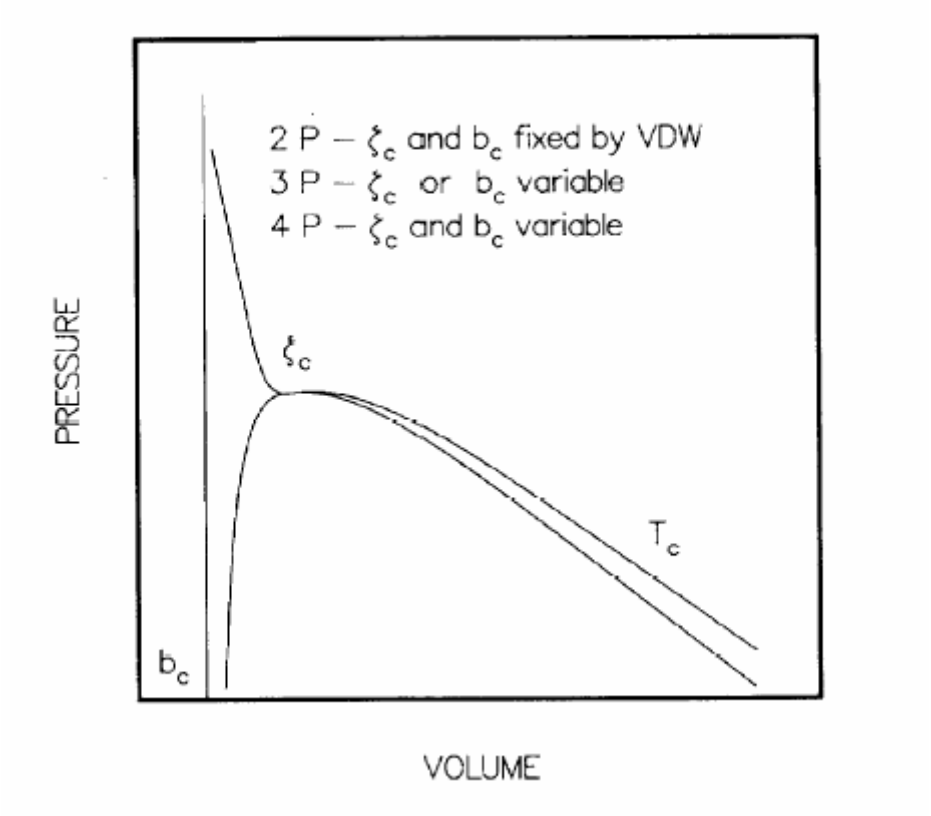

Figure 4. Effect of number of parameters on cubic equation of state

3.5 Critical point constraints

Applications of most of the equation of states are ultimately to vapor-liquid equilibria for mixtures. Application of the classical critical constraints of $\left(\frac{\partial P}{\partial V}\right)_{T_c}^{CP} = 0 = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c}^{CP}$ along the critical isotherm at the critical point (CP) leads to a serious problem for two-parameter, cubic EOS. These parameters do not follow the temperature dependence for other isotherms. The parameters can be described in terms of the critical temperature and critical pressure, the critical volume can be determined in

terms of the second parameter ***b*** and then the critical compressibility factor $Z_c\left[=\frac{P_cV_c}{RT_c}\right]$.

The critical volume and compressibility factor are higher than the experimental values for real, pure fluids using the experimental values of P_c and T_c for vdW, RK and SRK equations, and they are usually high for PR equation of state. For most popular two parameter EOS, Z_c numerically equals$\left(\frac{3}{8}\right),\left(\frac{1}{3}\right),\left(\frac{1}{3}\right)$ and 0.307 respectively. In terms of the critical volume, this is the volume displacement (translation) problem.

3.5.1 Mathematical statement of critical constraints

Eubank and Hall (2004) have suggested a new technique to evaluate the critical isotherm parameters. The EOS written in quotient form is:

$$\frac{P}{RT}=\left[\frac{f(T,\rho)}{g(T,\rho)}\right]=\left[\frac{f(\rho)}{g(\rho)}\right] \quad \text{(T is constant)} \tag{49}$$

Where *f* and *g* are arbitrary mathematical functions for which we have chosen to use;

i. Density $\rho=V^{-1}$

ii. Not-reduced variables.

Let $f'\equiv\left[\frac{\partial f}{\partial\rho}\right]_{T_c}^{CP}$, $f''\equiv\left[\frac{\partial^2 f}{\partial\rho^2}\right]_{T_c}^{CP}$ *etc*. with similar functions for density derivatives of the function *g* and for the pressure *P* at the CP along the critical isotherm. Thus, operational equations become:

$$\frac{P}{RT}=\frac{f}{g} \tag{50}$$

$$\frac{P'}{RT} = \frac{f'g - fg'}{g^2} \tag{51}$$

$$\frac{P''}{RT} = \frac{f''g - fg''}{g^2} - 2\left(\frac{g'}{g}\right)\frac{P'}{RT} \tag{52}$$

$$\frac{P'''}{RT} = \frac{f'''g + f''g' - f'g'' - fg'''}{g^2} - 2\left(\frac{g'}{g}\right)\left[\frac{2P''}{RT} + 2\left(\frac{g'}{g}\right)\frac{P'}{RT}\right] - \frac{2P'}{RT}\left[\frac{g''}{g} - \left(\frac{g'}{g}\right)^2\right]$$

$$\frac{P'''}{RT} = \frac{f'''g + 2f''g' - 2f'g'' - fg'''}{g^2} - \frac{6P''}{RT}\left(\frac{g'}{g}\right) - \frac{4P''}{RT}\left[\frac{5g'}{2g} + \frac{g''}{g} - \left(\frac{g'}{g}\right)^2\right] -$$
$$\frac{2P'}{RT}\left\{\frac{g'''}{g} + \left(1 + \frac{g'}{g}\right)\frac{g''}{g} - \left(\frac{g'}{g}\right)^2 - 2\left(\frac{g'}{g}\right)\left[\frac{g''}{g} - \left(\frac{g'}{g}\right)^2\right]\right\}$$

By using critical constraints, equations (51) and (52) equal zero. Therefore:

$$\frac{P_C}{RT_C} = \frac{f}{g} = \frac{f'}{g'} = \frac{f''}{g''} \tag{53}$$

If we now assume that the third and fourth derivatives also equal zero depending on scaling hypothesis. If a system exhibits a phase transition of fractional order then scaling properties of the thermodynamic potentials in the vicinity of the critical point become a consequence of fractional calculus. In this way the standard scaling hypothesis follows from the classification scheme. As a consequence the critical amplitudes are related to fractional thermodynamic derivatives. We find that universal relations between critical scaling amplitudes in thermodynamics can be derived from fractional calculus.

As suggested by the scaling hypothesis and some experimental data:

$$f'''g + f''g' - f'g'' - fg''' = 0 = \frac{f'''}{g'''} + \frac{g'g''}{gg'''}\left[\frac{f''}{g''} - \frac{f'}{g'}\right] - \frac{f}{g} \tag{54}$$

$$f'''g + 2f''g' - 2f'g''' - fg'''' = 0 = \frac{f''''}{g''''} + \frac{2g'g'''}{gg''''}\left[\frac{f'''}{g'''} - \frac{f'}{g'}\right] - \frac{f}{g} \tag{55}$$

In equations (54) and (55), the terms in square brackets are zero from equation (53), thus equation (53) becomes:

$$\frac{P_C}{RT_C} = \frac{f}{g} = \frac{f'}{g'} = \frac{f''}{g''} = \frac{f'''}{g'''} = \frac{f''''}{g''''} \tag{56}$$

3.5.2 Application to the generalized cubic EOS

Kumar & Starling first published the generalized cubic EOS in 1980:

$$\frac{P}{RT} = \left[\frac{\lambda_4\rho + \lambda_5\rho^2 + \lambda_6\rho^3}{\lambda_0 + \lambda_1\rho + \lambda_2\rho^2 + \lambda_3\rho^3}\right] \tag{57}$$

Again, this equation can be written in reduced form or in terms of $Z=(P/RT\rho)$ to suit the reader. Factoring λ from the numerator and denominator requires that $\frac{\lambda_4}{\lambda_1}$ equal to unity to satisfy the ideal gas boundary condition at zero density along any isotherm. Thus, equation (57) simplifies to a still-general form with up to five constants

$$\frac{P}{RT} = \frac{\rho + (\lambda_5/\lambda_0)\rho^2 + (\lambda_6/\lambda_0)\rho^3}{1 + (\lambda_1/\lambda_0)\rho + (\lambda_2/\lambda_0)\rho^2 + (\lambda_3/\lambda_0)\rho^3} = \frac{\rho + \mu_1\rho^2 + \mu_2\rho^3}{1 + \mu_3\rho + \mu_4\rho^2 + \mu_5\rho^3} \tag{58}$$

where

$$\begin{aligned}
f &= \rho + \mu_1\rho^2 + \mu_2\rho^3 & g &= 1 + \mu_3\rho + \mu_4\rho^2 + \mu_5\rho^3 \\
f' &= 1 + 2\mu_1\rho + 3\mu_2\rho^2 & g' &= \mu_3 + 2\mu_4\rho + 3\mu_5\rho^2 \\
f'' &= 2\mu_1 + 6\mu_2\rho & g'' &= 2\mu_4 + 6\mu_5\rho \\
f''' &= 6\mu_2 & g''' &= 6\mu_5 \\
f'''' &= 0 & g'''' &= 0
\end{aligned} \tag{59}$$

Using equations (58) and (59) at the CP yields three equations for the classical critical point:

$$\frac{P_C}{RT_C} = \frac{\rho_C + \mu_1 \rho_C{}^2 + \mu_2 \rho_C{}^3}{1 + \mu_3 \rho_C + \mu_4 \rho_C{}^2 + \mu_5 \rho_C{}^3} = \frac{1 + 2\mu_1 \rho_C + 3\mu_2 \rho_C{}^2}{\mu_3 + 2\mu_4 \rho_C + 3\mu_5 \rho_C{}^2} = \frac{2\mu_1 + 6\mu_2 \rho_C}{2\mu_4 + 6\mu_5 \rho_C} \tag{60}$$

Solving these simultaneous equations, we obtain:

$$1 + \mu_1 \rho_C = \left[\frac{P_c}{RT_c} \right] \left(\mu_3 + \mu_4 \rho_C \right) \tag{61}$$

$$\mu_2 \rho_C^2 = \frac{1 - \left(\frac{P_C}{RT_C} \right) \left(\mu_3 - 3\mu_5 \rho_c^2 \right)}{3} \tag{62}$$

Substituting these expressions into equation (60) and simplifying produces:

$$\mu_3 = \frac{1 - 3Z_C}{Z_C \rho_C} \quad \text{or} \quad Z_C = \frac{1}{3 + \mu_3 \rho_C} \tag{63}$$

Substituting equation (63) into equations (61) and (62) gives:

$$Z_C = \frac{\mu_1 \rho_C}{\mu_4 \rho_c^2 - 3} = \frac{\mu_2 \rho_C^2}{1 + \mu_5 \rho_C^3} \tag{64}$$

Thus, for cubic EOS with two constants, the EOS fixes the value of Z_C, whereas for cubic EOS with three or more constants it is possible to set the experimental value of Z_C leaving zero, one or two free parameters for the three, four and five-constant cubic EOS, respectively.

Using the second virial coefficient and/or the limit of density at infinite pressure allows us to set additional parameters along the critical isotherm with constraints. Using the second virial coefficient as a constraint results in

$$\frac{BP_C}{RT_C} = -0.34 = Z_C \rho_C \left(\mu_1 - \mu_3 \right) \tag{65}$$

or

$$\frac{BP_C}{RT_C} = -0.34 = \mu_1 = \frac{0.66 - 3Z_C}{Z_C \rho_C} \tag{66}$$

Using only the classical critical point constraints thus allows us to establish three of the EOS constants at the CP:

$$\mu_1 = \frac{0.66 - 3Z_C}{Z_C \rho_C} \tag{67}$$

$$\mu_3 = \frac{1 - 3Z_C}{Z_C \rho_C} \tag{68}$$

$$\mu_4 = \frac{0.66 - 3Z_C (1 - Z_C)}{(Z_C \rho_C)^2} \tag{69}$$

We now examine the results from the above analysis for specific, well-known cubic EOS with two to five constants.

Table 6 contains a sample of cubic EOS. It is not an exhaustive list and does not imply a preference for the included EOS. This list is sufficient to illustrate the application of our analysis, which depends strongly upon the number of parameters.

3.6 Application of derived critical point criteria to proposed EOS

Previously, we proposed our final form of cubic equation of state as $Z = \frac{1 + a\rho + c\rho^2}{(1 - b\rho)\left[1 + \gamma b^3 \rho\right]^2}$. To specify the parameters at the critical point, we must

establish the EOS in terms of the general EOS form as $\frac{P}{RT}=\frac{\rho+\mu_1\rho^2+\mu_2\rho^3}{1+\mu_3\rho+\mu_4\rho^2+\mu_5\rho^3}$ or explicitly in Z as $Z=\frac{1+\mu_1\rho+\mu_2\rho^2}{1+\mu_3\rho+\mu_4\rho^2+\mu_5\rho^3}$.

If we expand the parenthesis in equation (45)

$$Z=\frac{1+a\rho+c\rho^2}{\left(1+b\rho\right)\left(1+2\gamma b^3\rho+\gamma^2b^6\rho^2\right)} \tag{70}$$

If we keep expanding the denominator, we get:

$$Z=\frac{1+a\rho+c\rho^2}{1+2\gamma b^3\rho+\gamma^2b^6\rho^2-b\rho-2\gamma b^4\rho^2-\gamma^2b^7\rho^3} \tag{71}$$

Yet again, if we take ρ and ρ^2 parenthesis to make it look like similar to the equation $Z=\frac{1+\mu_1\rho+\mu_2\rho^2}{1+\mu_3\rho+\mu_4\rho^2+\mu_5\rho^3}$, we get the following equation:

$$Z=\frac{1+a\rho+c\rho^2}{1+\left(2\gamma b^3-b\right)\rho+\left(\gamma^2b^6-2\gamma b^4\right)\rho^2-\gamma b^7\rho^3} \tag{72}$$

According to the above equation μ_1, μ_2, μ_3, μ_4 and μ_5 are expressed by utilizing the critical point criteria as;

$$\mu_1=a_c \tag{73}$$

$$\mu_2=c_c \tag{74}$$

$$\mu_3=\left(2\gamma_c b_c^3-b_c\right) \tag{75}$$

$$\mu_4=\left(\gamma_c^2b_c^6-2\gamma_c b_c^4\right) \tag{76}$$

$$\mu_5=-\gamma_c^2b_c^7 \tag{77}$$

Table 4. Critical properties for argon

	$P_c[MPa]$	$T_c[K]$	$\rho_c\left[\frac{mol}{m^3}\right]$	Z_c	$R\left[\frac{MPa*m^3}{mol*K}\right]$
Argon	4.863	150.687	13407.4	0.28951	$8.31451*10^{-6}$

If we apply these criteria to our screening sample argon by using the critical properties of argon as shown in above table 4, we would get the values for parameters at the critical region on behalf of our proposed equation as shown in table 5. Table 6 shows the result of the application of this theory to our sample - non-polar, spherical in shape substance, argon.

Table 5. Parameters of new equation of state at critical temperature for argon

a_c	b_c	c_c	γ_c
-5.173E-5	3.99E-5	1.401E-9	5.79E8

Table 6 contains a sample of cubic EOS and regarding parameters that are to be used in described critical point criteria for EOS parameters.

Table 6. Cubic Equation of state parameters

Equation of State	μ_1	μ_2	μ_3	μ_4	μ_5
vdW $\frac{P}{RT}=\frac{\rho}{1-b\rho}-(a/RT)\rho^2$	$-a/RT$	ab/RT	$-b$	0	0
RK $\frac{P}{RT}=\frac{\rho}{1-b\rho}-\frac{(a/RT^{1.5})\rho^2}{1+b\rho}$	$b-a/RT^{1.5}$	$ab/RT^{1.5}$	0	$-b^2$	0
SRK $\frac{P}{RT}=\frac{\rho}{1-b\rho}-\frac{(a/RT)\rho^2}{1+b\rho}$	$b-a/RT$	ab/RT	0	$-b^2$	0
PR $\frac{P}{RT}=\frac{\rho}{1-b\rho}-\frac{(a/RT)\rho^2}{1+2b\rho-b^2\rho^2}$	$2b-a/RT$	$ab/RT-b^2$	b	$-3b^2$	b^2
Patel-Teja $\frac{P}{RT}=\frac{\rho}{1-b\rho}-\frac{(a/RT)\rho^2}{1+(b+c)\rho-bc\rho^2}$	$c+b-a/RT$	$ab/RT-bc$	c	$-b(b+2c)$-	b^2c

IV. APPLICATION OF PROPOSED EOS TO ARGON

4.1 Regression model

In order to determine substance specific values for adjustable global constants in various EOS and re-fit existing EOS to the same data to allow fair comparisons, it is necessary to develop an appropriate data-fitting model. Because the proposed EOS is non-linear with respect to density, a non-linear least squares method appears appropriate to fit the isotherms of the sample substance, argon.

Fitting observed data to the model requires a non-linear regression analysis (NLIN). In addition to the model being non-linear, the temperature dependencies of the parameters are also nonlinear. The NLIN procedure produces least squares or weighted least squares estimates of the parameters a nonlinear model. Initial values for the parameters are necessary in the program. In SAS 8.0, the NLIN procedure incorporates five different iterative methods:

- steepest-descent or gradient method
- Newton method
- modified Gauss-Newton method
- Marquardt method
- multivariate secant or false position (DUD) method

In this work, we have use the method based upon the Levenberg-Marquardt algorithm in SAS 8.0.

4.2 Isothermal fits of argon

We have performed isothermal fits for argon using a set of data that is very accurate from Tegeler, Span and Wagner (1999). The reason for using pure argon is that it is essentially a spherical molecule. It is necessary to perform isothermal fits before global fits in order to define the model equations for the temperature dependent parameters. After results of isothermal fits are evaluated and temperature dependent parameter model equations are defined by using unconstrained multivariable nonlinear parameter optimization, these results can be integrated to the global fit process. The results of the isothermal fits appear in table 7. The regarding plot for ***a, b*** and ***c*** parameters are shown in figures 5-7. We have smoothed the values for γ in figure 8 on page 38.

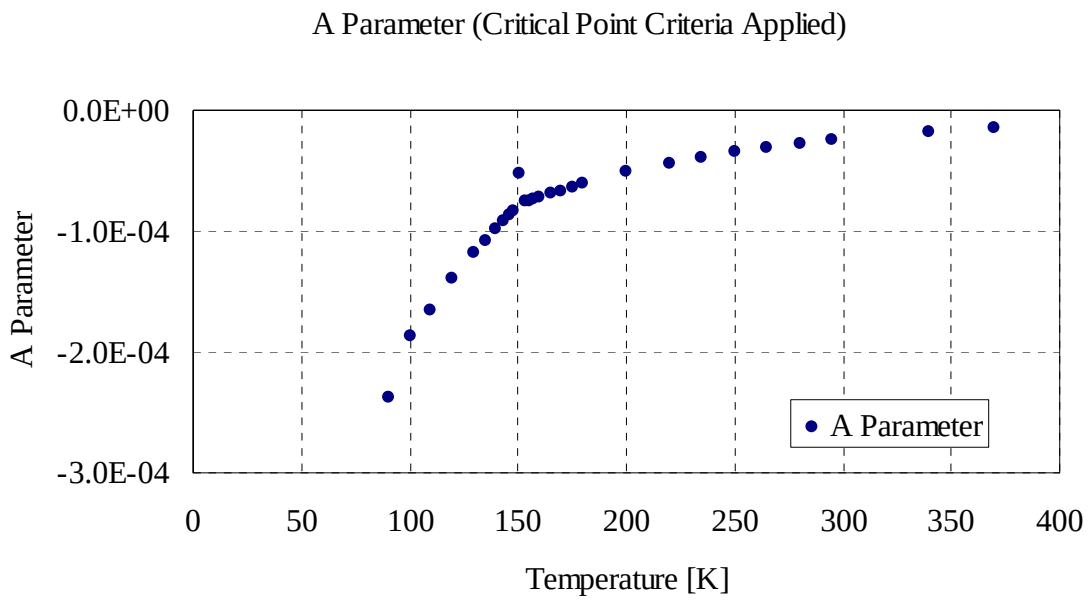

Figure 5. ***a*** parameter plot (after critical point criteria applied)

Table 7. Temperature dependent parameters values after isothermal fits

Temp. [K]	*a* Parameter	*b* Parameter	*c* Parameter	γ Parameter
90	-2.3754E-04	1.9079E-05	5.9055E-09	2.8342E+08
100	-1.8868E-04	2.0701E-05	4.9149E-09	3.6525E+08
110	-1.6309E-04	2.2165E-05	4.1842E-09	4.8333E+08
120	-1.4174E-04	2.3741E-05	3.6048E-09	5.9634E+08
130	-1.1823E-04	2.5877E-05	3.0643E-09	6.6254E+08
135	-1.0680E-04	2.7295E-05	2.7736E-09	6.7325E+08
140	-9.6579E-05	2.8943E-05	2.4677E-09	6.7114E+08
143	-9.1230E-05	2.9988E-05	2.2853E-09	6.6531E+08
146	-8.6510E-05	3.1001E-05	2.1130E-09	6.5735E+08
148	-8.3704E-05	3.1613E-05	2.0083E-09	6.5144E+08
150.7	-8.0321E-05	3.2293E-05	1.8849E-09	6.4352E+08
153	-7.7773E-05	3.2677E-05	1.7996E-09	6.3752E+08
155	-7.5777E-05	3.2823E-05	1.7418E-09	6.3346E+08
157	-7.3961E-05	3.2763E-05	1.6997E-09	6.3100E+08
160	-7.1522E-05	3.2255E-05	1.6643E-09	6.3168E+08
165	-6.8040E-05	3.0314E-05	1.6644E-09	6.5128E+08
170	-6.5057E-05	2.7338E-05	1.7028E-09	7.1340E+08
175	-6.2392E-05	2.3896E-05	1.7391E-09	8.7110E+08
180	-5.9934E-05	2.0492E-05	1.7488E-09	1.2285E+09
190	-5.5429E-05	N/A	1.6802E-09	3.1685E+09
200	-5.1319E-05	1.2263E-05	1.5556E-09	2.7739E+09
220	-4.4012E-05	2.2452E-05	1.3150E-09	7.2589E+08
235	-3.9211E-05	2.8287E-05	1.1668E-09	N/A
250	-3.4927E-05	2.8495E-05	1.0426E-09	4.9155E+08
265	-3.1119E-05	2.8009E-05	9.3893E-10	4.6589E+08
280	-2.7755E-05	2.7624E-05	8.5307E-10	4.5251E+08
295	-2.4801E-05	2.7361E-05	7.8281E-10	4.4469E+08
310	-2.2226E-05	2.7176E-05	7.2638E-10	4.3971E+08
340	-1.8098E-05	2.6940E-05	6.4926E-10	4.3398E+08
370	-1.5143E-05	2.6797E-05	6.1225E-10	4.3092E+08

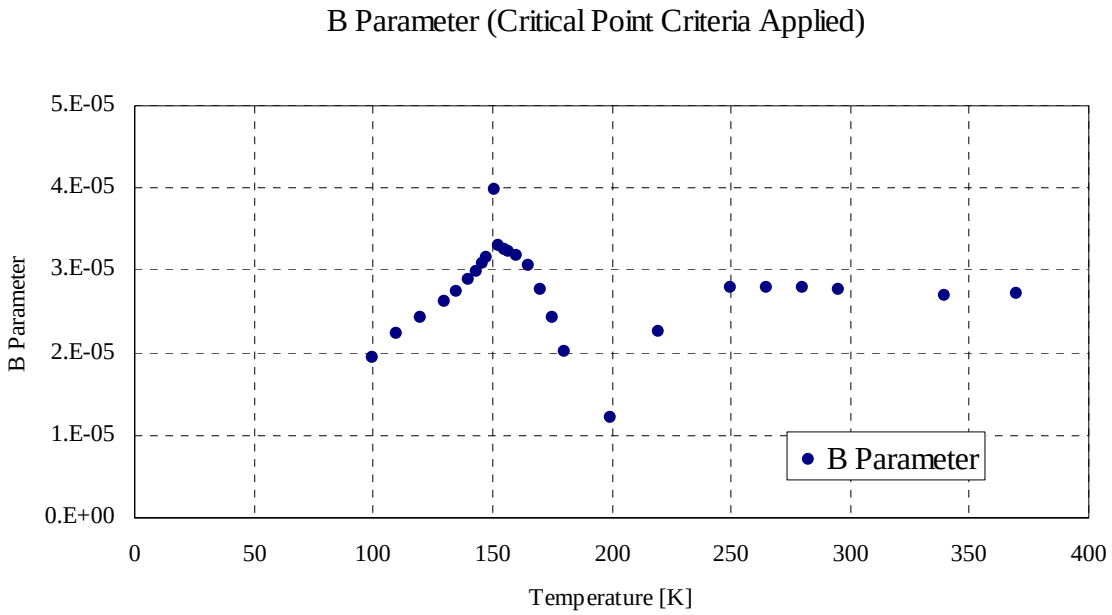

Figure 6. ***b*** Parameter plot (after critical point criteria applied)

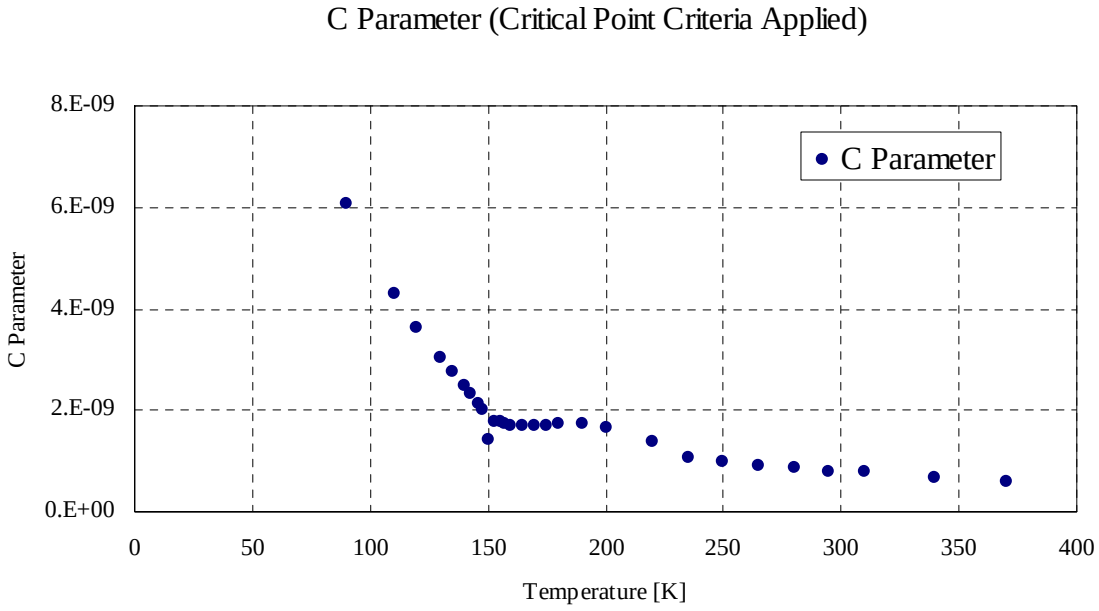

Figure 7. ***c*** Parameter plot (after critical point criteria applied)

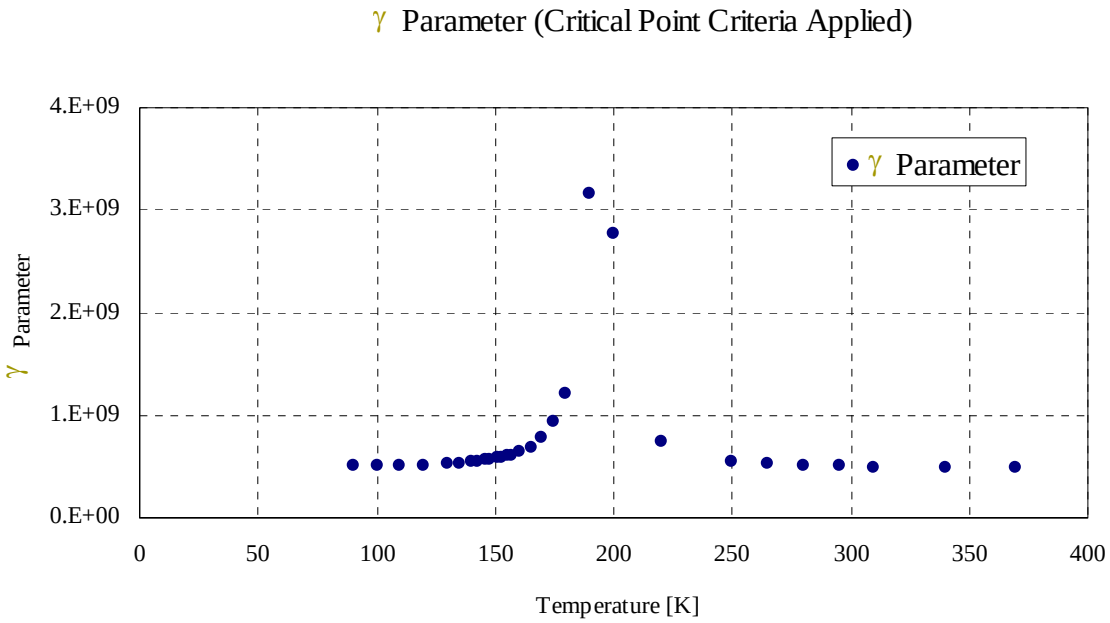

Figure 8. γ Parameter plot (after critical point criteria applied)

4.3 Temperature dependencies of the EOS parameters

The procedure followed in determining the temperature dependencies of the new cubic EOS is relatively straightforward. The overall algorithm is

1) calculate the values of four EOS parameters at several sub-critical temperatures by forcing EOS to meet the saturation pressure and saturated liquid and vapor specific volumes
2) For temperatures above critical point fit the EOS to Pρ data along individual isotherms by keeping all four parameters floating in the process of data fitting

3) Having defined the values of four parameters of EOS at all isotherms develop algebraic functions that fit the calculated values of the EOS as a function of temperature.

This procedure may seem simple; however, the problem is actually trying to fit the calculated values of EOS parameters as a function of temperature. This difficulty arises because the applied critical point criteria give an unusual shape to the parameter curves in the vicinity of the critical point and exactly at the critical point as shown in figures 7 to 10. The figures show that the EOS parameters have anomalous peaks near the critical point. In fact, this behavior is limited to the near critical region and the rest of the curve is a smooth function. The difficulty this behavior creates is that to preserve prediction of the critical point and enforce the critical point criteria, any temperature function used to fit the curves in figures 7 to 10 must pass through the critical point exactly. Regardless of the form of the algebraic equation used to describe temperature dependence of the EOS parameters and to fit the EOS parameter curves, this critical point problem arises unless the proposed EOS is altered in some way to reduce the strange characteristic behavior of the EOS parameters at vicinity of the critical point.

4.3.1 General approach

It is necessary to determine how the values of the EOS parameters vary with temperature. We accomplish this by using saturation data, saturated liquid and vapor specific volumes for one test sample -argon- and fitting PVT data.

At each temperature where data is available, we have determined values for the EOS parameters. Having determined the variation of these parameters with temperature, a trial and error procedure determines the best analytical description for the parameters as a function of temperature.

4.3.2 Temperature function development for new EOS parameters

For each parameter, we have determined the value of the parameter at discrete temperatures. To complete the EOS, it is necessary to develop mathematical functions capable of fitting the temperature dependence data.

In the critical region, it is a trade-off between achieving accuracy and predicting the critical point itself. We decided to reproduce the critical values of the parameters exactly by using an analytical expression depending upon the critical point criteria. In order to express the critical point accurately, we have applied our critical point correction criteria described in section three.

The nature of the second and third virial coefficients are described by using prior expressions. Because in our EOS ***a*** and ***c*** correspond to the second virial coefficient, we can use either an experimental value or a correlation.

As shown in figures 7 and 9, the observed ***a*** and ***c*** parameters indicate a “bump” in the vicinity of the critical point. The proposed inverse ordered polynomial function is not sufficient to describe this bump. At this point, determination an additional expression is necessary.

Based on these considerations, the first background temperature functions investigated for ***a*** and ***c*** parameters are the form of:

$$a = k_{1a} + \frac{k_{2a}}{T} + \frac{k_{3a}}{T^2} + \frac{k_{4a}}{T^3} \tag{78}$$

$$c = k_{1c} + \frac{k_{2c}}{T} + \frac{k_{3c}}{T^2} + \frac{k_{4c}}{T^3} \tag{79}$$

As expected, these background curves in figures 9 and 10 are well in describing the overall nature of the temperature dependencies for the second virial coefficient related ***a*** and ***c*** parameters. Having described the background equation for ***a*** and ***c*** parameters, we require a form to describe the critical region accurately.

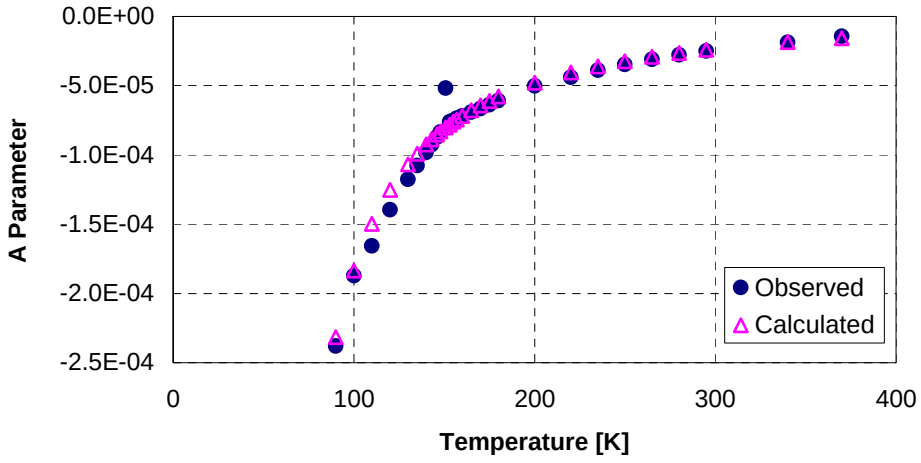

Figure 9. Background equation for parameter ***a***

As seen in figure 11 inverse third order equation works well for parameter A.

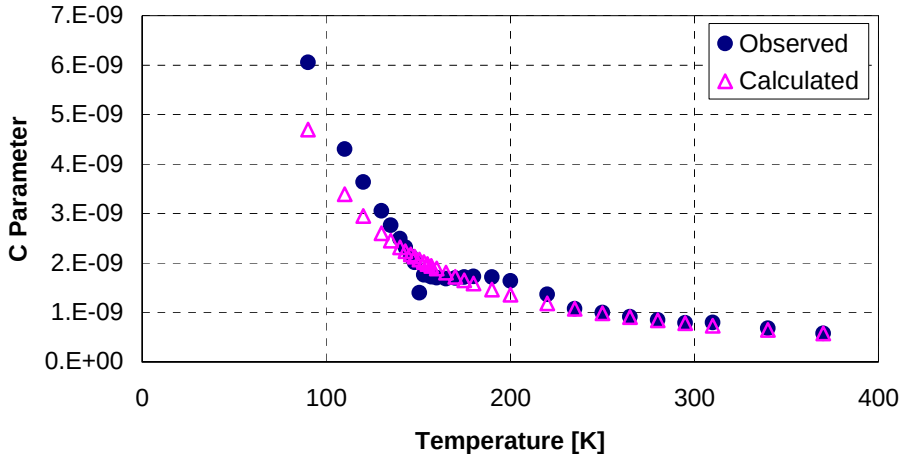

Figure 10. Background equation for parameter ***c***

Also as seen in figure 12, an inverse third order polynomial works well for parameter ***c***. However, the inverse third order polynomial function is insufficient to describe the low temperature values for both parameters. In order to fix this, we may either increase the temperature dependence introduce a new function as a background equation. Application of critical point criteria gives a sharp cusp shape right at the critical point. Because it is important to describe the critical point, the cusp function must be steep and sharp. We have selected equation(80).

$$g(T) = k_{1g} * \exp\left[-0.5\left(\frac{|T - k_{2g}|}{k_{3g}}\right)^2\right] \tag{80}$$

Also, it is more convenient to use normal Gaussian distribution function to describe the bump nature of the parameters in the vicinity of critical point.

$$h(T) = k_{1h} * \exp\left[-0.5\left(\frac{T - k_{2h}}{k_{3h}} \right)^2 \right] \tag{81}$$

The model equation for ***a*** and ***c*** are:

$$a = k_1 + \left(\frac{k_2}{T} \right) + \left(\frac{k_3}{T^3} \right) + k_4 * \exp\left[-0.5\left(\frac{T - T_c}{k_5} \right)^2 \right] \tag{82}$$

$$c = \left(\frac{k_{21}}{T} \right) + \left(\frac{k_{22}}{T^2} \right) + k_{23} * \left[\exp - 0.5 * \left(\frac{|T - k_{24}|}{k_{25}} \right)^2 \right] + k_{26} * \exp\left[-0.5 * \left(\frac{T - T_c}{k_{27}} \right)^2 \right] \tag{83}$$

The values for k_i in above equations after curve fitting for ***a*** and ***c*** parameters are shown in below tables 8 and 9.

Table 8. ***a*** Parameter model equation parameters fit results

Parameter	Estimate	Std. Error	Apprx. 95% Confidence Intervals		Skewness
			Lower	Upper	
k1	0.000016	1.775E-6	0.000013	0.000020	0.000494
k2	-0.0109	0.000599	-0.0121	-0.00964	-0.00044
k3	-98.1714	7.1078	-112.9	-83.4679	1.51E-6
k4	0.000033	2.121E-6	0.000028	0.000037	0.000039
k5	-1.3007	0.1529	-1.6169	-0.9845	0.1577

Table 9. ***c*** Parameter model equation parameters fit results

Parameter	Estimate	Std. Error	Apprx. 95% Confidence Intervals		Skewness
			Lower	Upper	
k21	1.037E-7	7.965E-9	8.722E-8	1.203E-7	-0.0186
k22	0.000040	1.762E-6	0.000036	0.000043	0.0480
k23	-4.9E-10	4.42E-11	-582E-12	-398E-12	0.00461
k24	155.3	1.1916	152.9	157.8	-0.2109
k25	15.7760	1.3169	13.0451	18.5070	0.3081
k26	-5.46E-10	6.67E-11	-684E-12	-408E-12	0.00448
k27	1.2686	0.2546	0.7405	1.7967	-0.4033

Fit results and % error obtained for the model equation of ***a, b, c*** and γ parameters are shown in tables 10, 11, 13 and 14 respectively.

Table 10. ***a*** parameter fit results and % error for the model equation of ***a*** parameter

Temp. [K]	A Observed	Weight	A Predicted	A Residuals	% Error in Z
90	-2.3791E-04	1.77E+07	-2.3897E-04	1.0621E-06	-0.45%
100	-1.8713E-04	2.86E+07	-1.9049E-04	3.3648E-06	-1.80%
110	-1.6574E-04	3.64E+07	-1.5626E-04	-9.4834E-06	5.72%
120	-1.3953E-04	5.14E+07	-1.3111E-04	-8.4187E-06	6.03%
130	-1.1770E-04	7.22E+07	-1.1204E-04	-5.6631E-06	4.81%
135	-1.0757E-04	8.64E+07	-1.0416E-04	-3.4061E-06	3.17%
140	-9.8153E-05	1.04E+08	-9.7170E-05	-9.8348E-07	1.00%
143	-9.2542E-05	1.17E+08	-9.3339E-05	7.9650E-07	-0.86%
146	-8.7011E-05	1.32E+08	-8.9703E-05	2.6918E-06	-3.09%
148	-8.3378E-05	1.44E+08	-8.3664E-05	2.8635E-07	-0.34%
150.7	-5.1700E-05	3.74E+08	-5.1803E-05	1.0330E-07	-0.20%
153	-7.5936E-05	1.73E+08	-7.5325E-05	-6.1125E-07	0.80%
155	-7.5074E-05	1.77E+08	-8.0110E-05	5.0363E-06	-6.71%
157	-7.3578E-05	1.85E+08	-7.8363E-05	4.7853E-06	-6.50%
160	-7.1842E-05	1.94E+08	-7.5666E-05	3.8238E-06	-5.32%
165	-6.9122E-05	2.09E+08	-7.1494E-05	2.3723E-06	-3.43%
170	-6.6478E-05	2.26E+08	-6.7685E-05	1.2069E-06	-1.82%
175	-6.3683E-05	2.47E+08	-6.4194E-05	5.1066E-07	-0.80%
180	-6.0656E-05	2.72E+08	-6.0983E-05	3.2740E-07	-0.54%
200	-5.0055E-05	3.99E+08	-5.0379E-05	3.2393E-07	-0.65%
220	-4.3939E-05	5.18E+08	-4.2381E-05	-1.5583E-06	3.55%
235	-3.8780E-05	6.65E+08	-3.7567E-05	-1.2130E-06	3.13%
250	-3.4692E-05	8.31E+08	-3.3505E-05	-1.1866E-06	3.42%
265	-3.0874E-05	1.05E+09	-3.0032E-05	-8.4217E-07	2.73%
280	-2.7833E-05	1.29E+09	-2.7027E-05	-8.0640E-07	2.90%
295	-2.4863E-05	1.62E+09	-2.4400E-05	-4.6284E-07	1.86%
340	-1.8606E-05	2.89E+09	-1.8185E-05	-4.2086E-07	2.26%
370	-1.4245E-05	4.93E+09	-1.5026E-05	7.8145E-07	-5.49%

Table 11. ***c*** parameter fit results and % error for the model equation of ***c*** parameter

Temp. [K]	C Observed	Weight	C Predicted	C Residuals	% Error in Z
90	6.0560E-09	2.73E+16	6.0776E-09	-2.2E-11	-0.36%
110	4.3050E-09	5.4E+16	4.2370E-09	6.8E-11	1.58%
120	3.6360E-09	7.56E+16	3.6177E-09	1.83E-11	0.50%
130	3.0530E-09	1.07E+17	3.0685E-09	-1.5E-11	-0.51%
135	2.7650E-09	1.31E+17	2.7858E-09	-2.1E-11	-0.75%
140	2.4880E-09	1.62E+17	2.4919E-09	-3.9E-12	-0.16%
143	2.3130E-09	1.87E+17	2.3166E-09	-3.6E-12	-0.16%
146	2.1340E-09	2.2E+17	2.1500E-09	-1.6E-11	-0.75%
148	2.0100E-09	2.48E+17	2.0084E-09	1.58E-12	0.08%
150.7	1.4000E-09	5.1E+17	1.3818E-09	1.82E-11	1.30%
153	1.7600E-09	3.23E+17	1.7600E-09	2.12E-14	0.00%
155	1.7580E-09	3.24E+17	1.7817E-09	-2.4E-11	-1.35%
157	1.7240E-09	3.36E+17	1.7379E-09	-1.4E-11	-0.81%
160	1.7000E-09	3.46E+17	1.6969E-09	3.09E-12	0.18%
165	1.6790E-09	3.55E+17	1.6831E-09	-4.1E-12	-0.25%
170	1.6940E-09	3.48E+17	1.7038E-09	-9.8E-12	-0.58%
175	1.7120E-09	3.41E+17	1.7218E-09	-9.8E-12	-0.58%
180	1.7250E-09	3.36E+17	1.7161E-09	8.91E-12	0.52%
190	1.7150E-09	3.4E+17	1.6331E-09	8.19E-11	4.78%
200	1.6370E-09	3.73E+17	1.5121E-09	1.25E-10	7.63%
220	1.3620E-09	5.39E+17	1.2934E-09	6.86E-11	5.03%
235	1.0760E-09	8.64E+17	1.1615E-09	-8.6E-11	-7.95%
250	9.9400E-10	1.01E+18	1.0510E-09	-5.7E-11	-5.74%
265	9.1200E-10	1.2E+18	9.5739E-10	-4.5E-11	-4.98%
280	8.4900E-10	1.39E+18	8.7724E-10	-2.8E-11	-3.33%
295	7.9100E-10	1.6E+18	8.0803E-10	-1.7E-11	-2.15%
310	7.9300E-10	1.59E+18	7.4779E-10	4.52E-11	5.70%
340	6.8100E-10	2.16E+18	6.4835E-10	3.27E-11	4.80%
370	5.7800E-10	2.99E+18	5.7002E-10	7.98E-12	1.38%

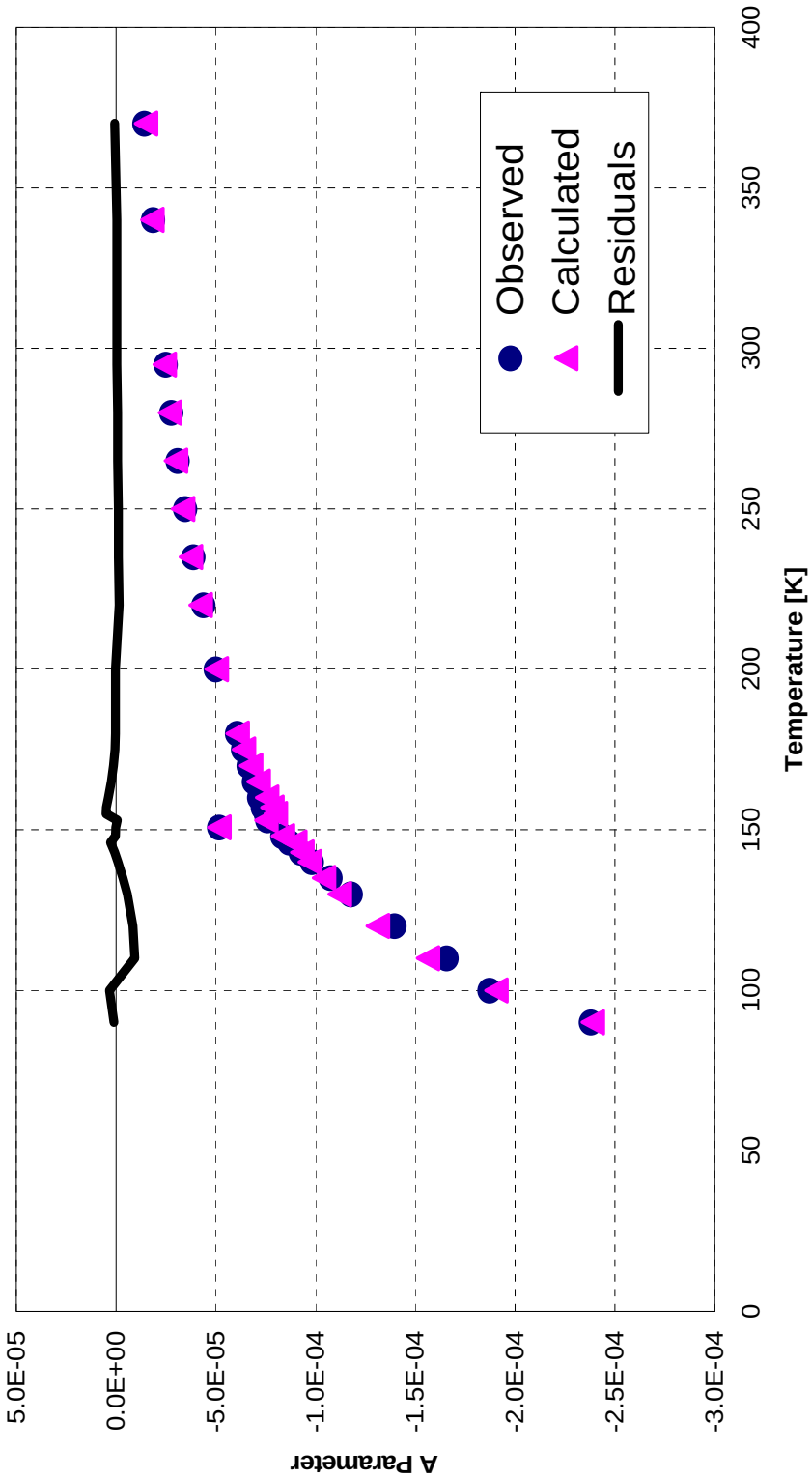

Figure 11. Observed and calculated ***a*** parameter plots with residuals

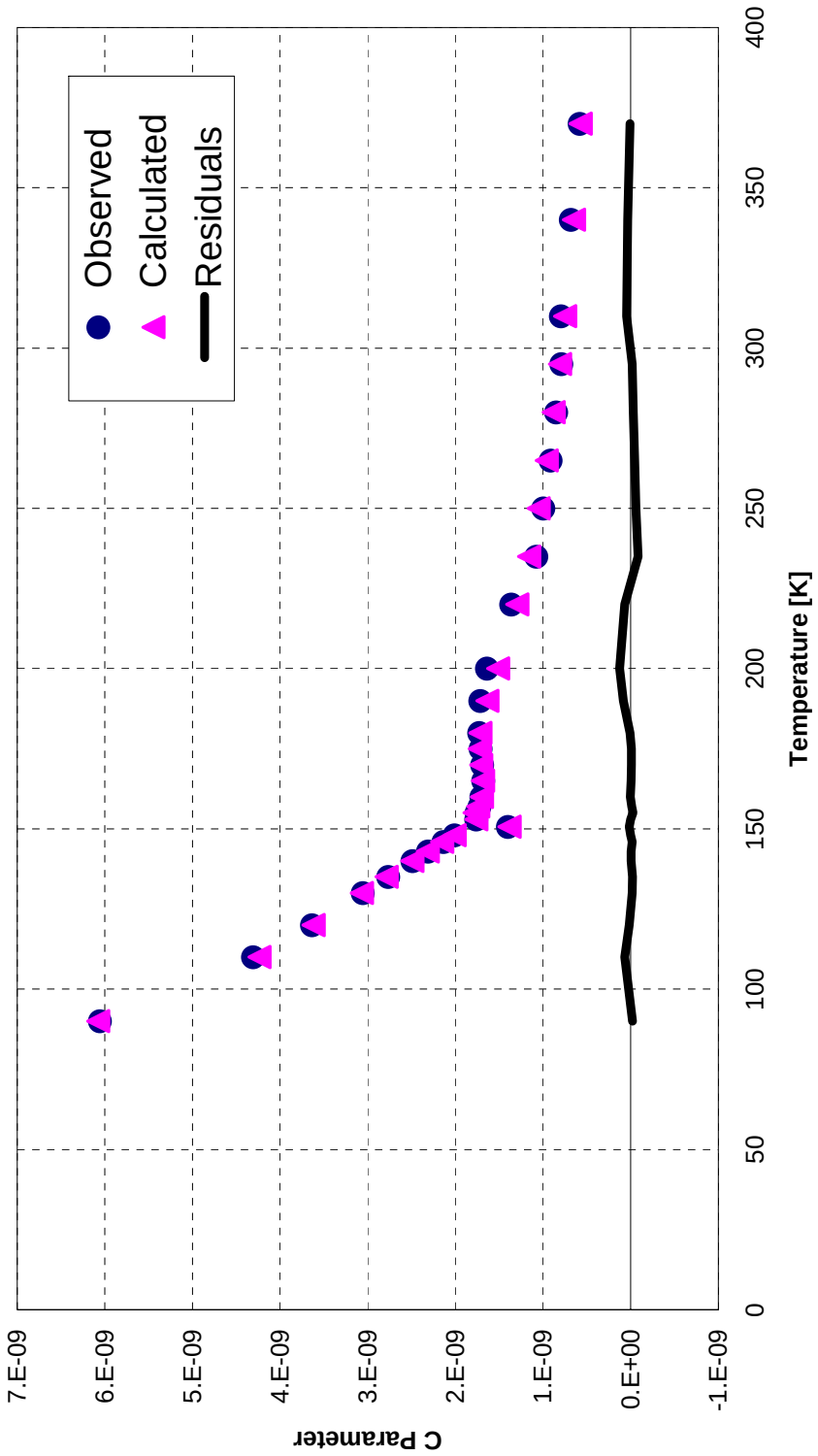

Figure 12. Observed and calculated ***c*** parameter plots with residuals

The model equation that describes the temperature dependence of ***c*** is:

$$b = k_6 \exp\left[-0.5\left(\frac{T-k_7}{k_8}\right)^2\right] k_9 \exp\left[-0.5\left(\frac{T-k_{10}}{k_{11}}\right)^2\right] + \frac{k_{12}T^{k_{14}}}{k_{13}^{k_{14}}+T^{k14}} + \frac{k_{15}}{1+\left(\frac{T-T_c}{k_{16}}\right)} \quad (84)$$

and the k_i values for above equation are given in below table 12 after fit process.

Table 12. ***b*** Parameter model equation parameters fit results

Parameter	Estimate	Std. Error	Apprx. 95% Confidence Intervals		Skewness
			Lower	Upper	
k6	0.000011	7.587E-7	9.629E-6	0.000013	0.4760
k7	161.6	0.4871	160.5	162.6	0.1898
k8	15.2430	0.6298	13.9006	16.5854	0.1769
k9	0.000025	3.812E-7	0.000024	0.000026	-0.1820
k10	132.3	1.4545	129.2	135.4	-0.4069
k11	46.4628	1.0355	44.2557	48.6699	-0.3316
k12	0.000027	1.124E-7	0.000027	0.000028	-0.00373
k13	214.7	0.8868	212.8	216.6	-0.4511
k14	28.6872	1.4763	25.5405	31.8339	0.4966
k15	8.14E-6	3.539E-7	7.386E-6	8.894E-6	0.00292
k16	-0.7027	0.1596	-1.0428	-0.3626	0.5016

Table 13. ***b*** parameter fit results and % error for the model equation of ***b*** parameter

Temp. [K]	B Observed	Weight	B Predicted	B Residuals	% Error in Z
100	1.9510E-05	2.63E+09	1.9571E-05	-6.1E-08	-0.31%
110	2.2397E-05	1.99E+09	2.2243E-05	1.54E-07	0.69%
120	2.4200E-05	1.71E+09	2.4334E-05	-1.3E-07	-0.55%
130	2.6197E-05	1.46E+09	2.6211E-05	-1.4E-08	-0.05%
135	2.7407E-05	1.33E+09	2.7352E-05	5.49E-08	0.20%
140	2.8775E-05	1.21E+09	2.8744E-05	3.07E-08	0.11%
143	2.9743E-05	1.13E+09	2.9687E-05	5.59E-08	0.19%
146	3.0814E-05	1.05E+09	3.0711E-05	1.03E-07	0.34%
148	3.1507E-05	1.01E+09	3.1618E-05	-1.1E-07	-0.35%
150.7	3.9900E-05	6.28E+08	3.9900E-05	-3.7E-10	0.00%
153	3.2967E-05	9.2E+08	3.2862E-05	1.05E-07	0.32%
155	3.2481E-05	9.48E+08	3.2577E-05	-9.6E-08	-0.29%
157	3.2398E-05	9.53E+08	3.2489E-05	-9.1E-08	-0.28%
160	3.1906E-05	9.82E+08	3.2098E-05	-1.9E-07	-0.60%
165	3.0532E-05	1.07E+09	3.0448E-05	8.37E-08	0.27%
170	2.7737E-05	1.3E+09	2.7622E-05	1.15E-07	0.42%
175	2.4246E-05	1.7E+09	2.4044E-05	2.02E-07	0.83%
180	2.0114E-05	2.47E+09	2.0300E-05	-1.9E-07	-0.93%
200	1.2253E-05	6.66E+09	1.2246E-05	6.5E-09	0.05%
220	2.2480E-05	1.98E+09	2.2487E-05	-6.8E-09	-0.03%
250	2.8029E-05	1.27E+09	2.8063E-05	-3.4E-08	-0.12%
265	2.7973E-05	1.28E+09	2.7757E-05	2.16E-07	0.77%
280	2.7833E-05	1.29E+09	2.7546E-05	2.87E-07	1.03%
295	2.7671E-05	1.31E+09	2.7452E-05	2.19E-07	0.79%
340	2.6919E-05	1.38E+09	2.7401E-05	-4.8E-07	-1.79%
370	2.7239E-05	1.35E+09	2.7400E-05	-1.6E-07	-0.59%

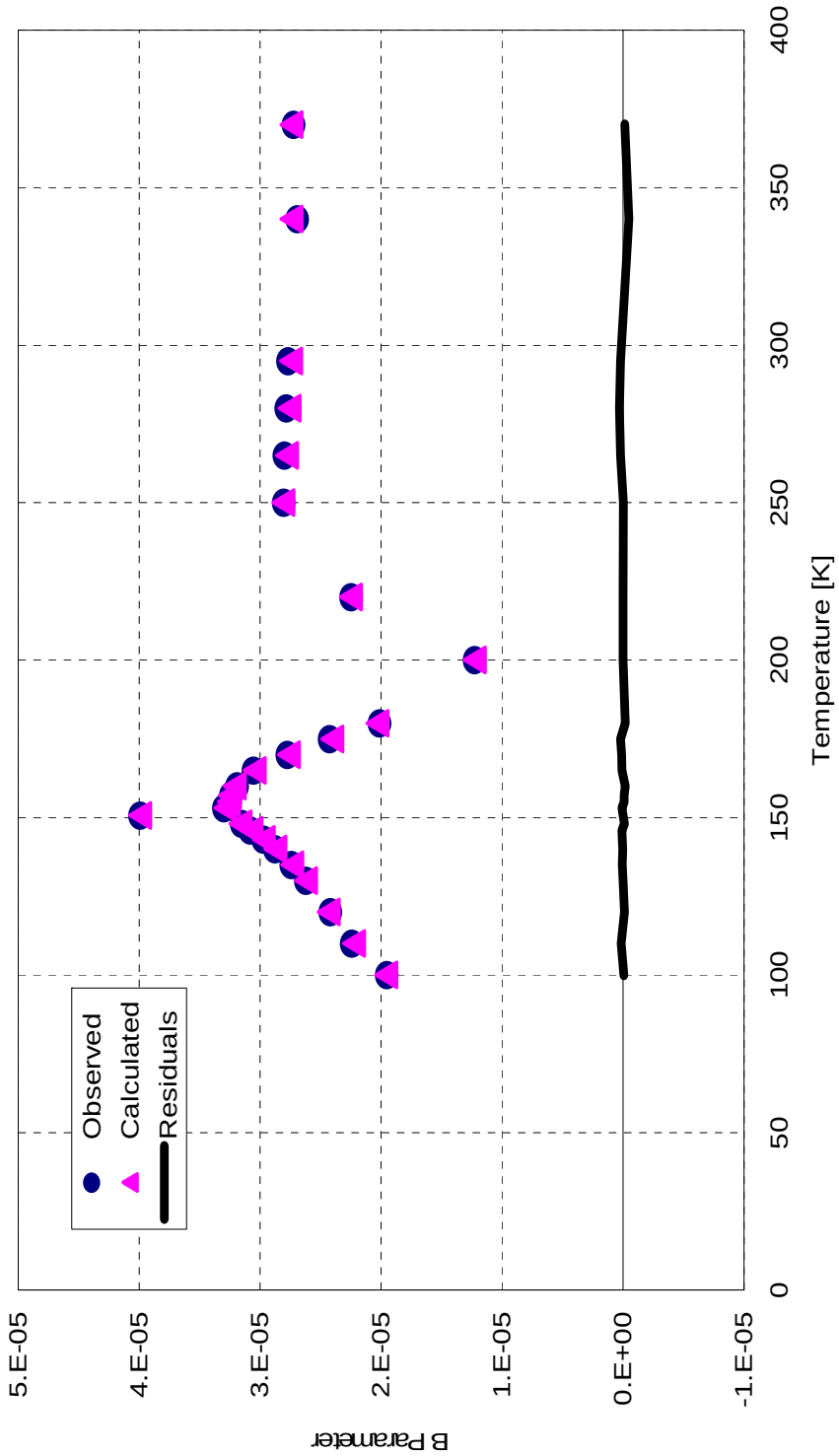

Figure 13. Observed and calculated ***b*** parameter plots with residuals

Finally, we obtain regression results for γ as shown in table 14 and these results are plotted in figure 14. Because of the smoothed nature of the data for γ, it is easier to fit the parameter:

$$\gamma = k_{24} + \frac{k_{25}}{1+\left(\frac{T-k_{26}}{k_{27}}\right)^2} \tag{85}$$

Table 14. γ parameter model equation parameters fit results

Parameter	Estimate	Std. Error	Apprx. 95% Confidence Intervals		Skewness
			Lower	Upper	
k24	4.8135E8	0.00724	4.8135E8	4.8135E8	-181E-13
k25	3.6842E9	0.2649	3.6842E9	3.6842E9	2.68E-10
k26	194.4	2.91E-10	194.4	194.4	1.5E-11
k27	7.2	4.48E-10	7.2	7.2	9.68E-11

Table 15. γ fit results and % error for the model equation of γ parameter

Temp. [K]	γ Observed	Weight	γ Predicted	γ Residuals	% Error in Z
90	4.9879E+08	4.02E-18	4.9879E+08	-0.01366	-2.7E-09
100	5.0266E+08	3.96E-18	5.0266E+08	0.009921	1.97E-09
110	5.0798E+08	3.88E-18	5.0798E+08	0.008979	1.77E-09
120	5.1554E+08	3.76E-18	5.1554E+08	0.027789	5.39E-09
130	5.2685E+08	3.6E-18	5.2685E+08	-0.02336	-4.4E-09
135	5.3472E+08	3.5E-18	5.3472E+08	-0.00326	-6.1E-10
140	5.4480E+08	3.37E-18	5.4480E+08	0.03865	7.09E-09
143	5.5228E+08	3.28E-18	5.5228E+08	-0.02996	-5.4E-09
146	5.6115E+08	3.18E-18	5.6115E+08	-9.4E-05	-1.7E-11
148	5.6801E+08	3.1E-18	5.6801E+08	-0.02924	-5.1E-09
150.7	5.7876E+08	2.99E-18	5.7876E+08	-0.02194	-3.8E-09
153	5.8957E+08	2.88E-18	5.8957E+08	0.000679	1.15E-10
155	6.0047E+08	2.77E-18	6.0047E+08	-0.00149	-2.5E-10
157	6.1309E+08	2.66E-18	6.1309E+08	0.007312	1.19E-09
160	6.3607E+08	2.47E-18	6.3607E+08	0.059241	9.31E-09
165	6.8995E+08	2.1E-18	6.8995E+08	-0.02972	-4.3E-09
170	7.7669E+08	1.66E-18	7.7669E+08	0.04127	5.31E-09
175	9.2782E+08	1.16E-18	9.2782E+08	0.055171	5.95E-09
180	1.2191E+09	6.73E-19	1.2191E+09	-0.11815	-9.7E-09
190	3.1675E+09	9.97E-20	3.1675E+09	0.016102	5.08E-10
200	2.7734E+09	1.3E-19	2.7734E+09	0.003385	1.22E-10
220	7.5119E+08	1.77E-18	7.5119E+08	-0.01338	-1.8E-09
250	5.4209E+08	3.4E-18	5.4209E+08	0.028669	5.29E-09
265	5.1926E+08	3.71E-18	5.1926E+08	-0.0043	-8.3E-10
280	5.0723E+08	3.89E-18	5.0723E+08	-0.01891	-3.7E-09
295	5.0012E+08	4E-18	5.0012E+08	0.003402	6.8E-10
310	4.9558E+08	4.07E-18	4.9558E+08	0.038505	7.77E-09
340	4.9034E+08	4.16E-18	4.9034E+08	-0.03028	-6.2E-09
370	4.8753E+08	4.21E-18	4.8753E+08	-0.02306	-4.7E-09

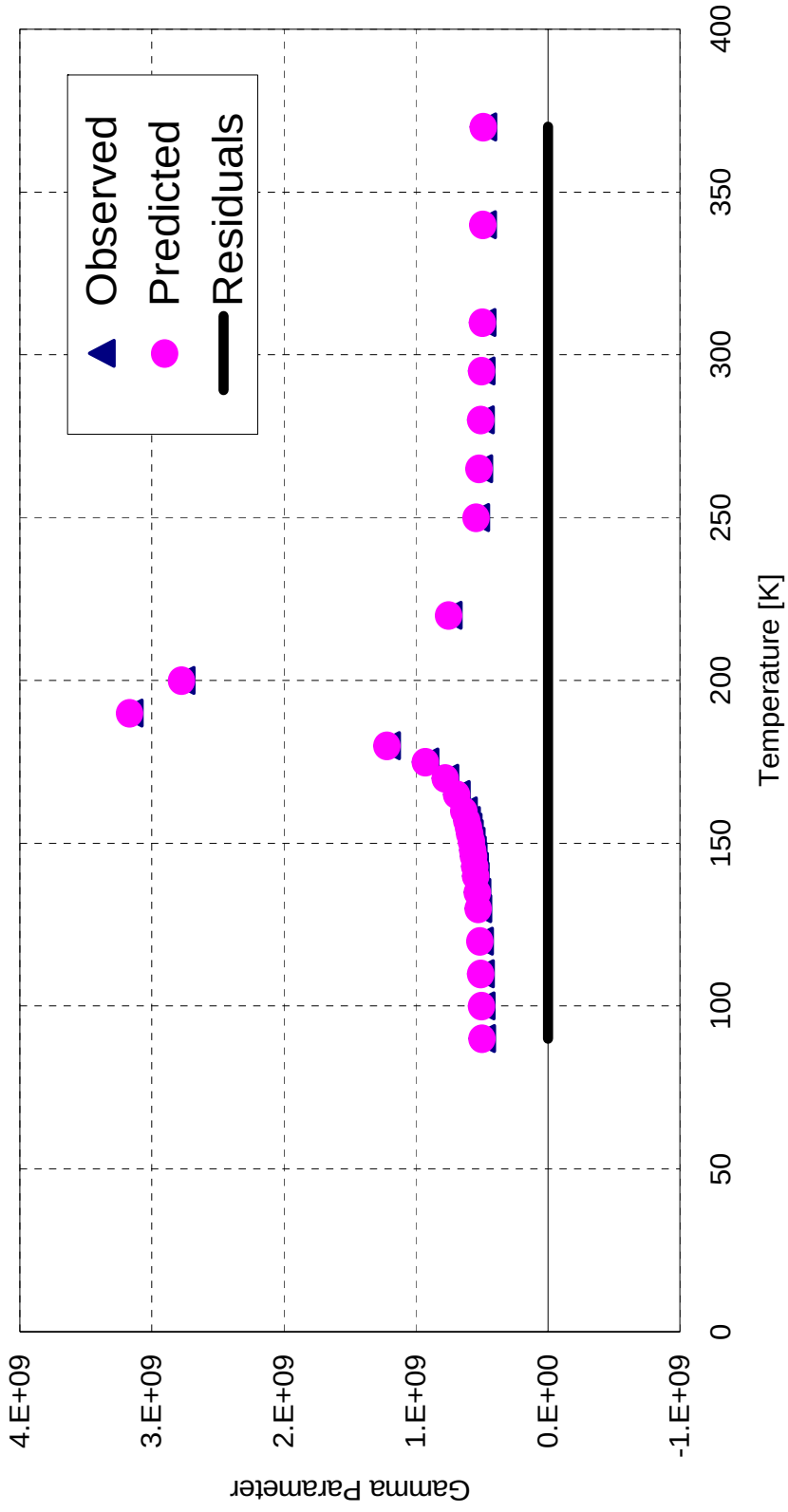

Figure 14. Observed and calculated γ parameter plots with residuals

4.4 Global fit

Finally, we require a global fit to determine the temperature dependence of the EOS. In the global fit, previously determined parameters are initial guesses. The compressibility form of the EOS is used to fit the all isotherms simultaneously. In order to obtain results for the parameters consistent with the results obtained from the isothermal fits, the model equations for the parameters must be accurate. This accuracy is controllable by looking at the skewness of the variables in the EOS parameter equations.

Weighted regression analysis is also important. Observations with small weights contribute less to sums of squares and thus provide less influence to the estimation parameters. Thus, it is logical to assign small weights to observations that are less reliable, and to assign larger weights to observations that are more reliable. However, it is not possible to determine the best possible weighting of the data set. Lacking such a method, this weight determination process is trial and error supported with the experience. In our isothermal fits and parameter fits, the weighting factor is:

$$weight = \frac{1}{Z^2} \tag{86}$$

Conversely, for global fits the weighting factor is:

$$weight = \frac{1}{Z^{0.5}} \tag{87}$$

The equations used in the global fit for the parameters are

$$a = k_1 + \left(\frac{k_2}{T}\right) + \left(\frac{k_3}{T^3}\right) + k_4 * \exp\left[-0.5\left(\frac{T - T_c}{k_5}\right)^2\right] \tag{88}$$

$$b = k_6 * \exp\left[-0.5\left(\frac{|T-k_7|}{k_8}\right)^2\right] + k_9 * \exp\left[-0.5\left(\frac{T-k_{10}}{k_{11}}\right)^2\right] + \frac{k_{12} * T^{k_{13}}}{k_{14}^{k_{13}} + T^{k_{13}}} + \frac{k_{15}}{1+\left(\frac{T-T_c}{k_{16}}\right)^2} \quad (89)$$

$$c = \left(\frac{k_{17}}{T}\right) + \left(\frac{k_{18}}{T^2}\right) + k_{19} * \exp\left[-0.5\left(\frac{|T-k_{20}|}{k_{21}}\right)^2\right] + k_{22} * \exp\left[-0.5\left(\frac{T-T_c}{k_{23}}\right)^2\right] \quad (90)$$

$$\gamma = k_{24} + \frac{k_{25}}{1+\left(\frac{T-k_{26}}{k_{27}}\right)^2} \quad (91)$$

Global fit results for k_i parameters are tabulated in table 16. Final parameter values for entire temperature range of argon after global fit for ***a***, ***b***, ***c*** and $\boldsymbol{\gamma}$ parameters are tabulated in table 17 and related plots for these parameters are shown in figures 15-18.

Table 16. Global fit results for parameter model equation variables

Parameter	Estimate	Approx Std Error	Approx. Confidence Limits		Skewness
			Lower	Higher	
k1	0.000039	2.082E-7	0.000039	0.000040	-0.3088
k2	-0.0156	0.000155	-0.0159	-0.0153	0.0654
k3	-82.5680	2.3715	-87.2239	-77.9120	-0.0312
k4	8.035E-6	3.261E-7	7.395E-6	8.675E-6	0.0636
k5	-9.1067	0.3755	-9.8439	-8.3695	-0.1438
k6	2.872E-6	1.579E-6	-2.28E-7	5.973E-6	0.4674
k7	121.0	0.6698	119.7	122.3	-0.5095
k8	-15.1824	2.3394	-19.7753	-10.5895	1.2067
k9	0.000020	2.771E-7	0.000020	0.000021	7.0871
k10	83.2211	21.6110	40.7928	125.6	-1.3539
k11	-73.0445	8.6166	-89.9614	-56.1277	-0.3036
k12	0.000028	2.42E-7	0.000027	0.000028	0.1565
k13	7.9027	0.8248	6.2834	9.5220	0.6472
k14	178.3	6.5235	165.5	191.1	0.2739
k15	0.000012	1.458E-6	9.281E-6	0.000015	0.7048
k16	-17.8364	1.1794	-20.1519	-15.5208	-0.1264
k17	2.17E-8	9.25E-9	3.536E-9	3.986E-8	0.0149
k18	0.000049	1.22E-6	0.000047	0.000052	0.00341
k19	-18E-11	3.64E-11	-252E-12	-109E-12	-0.9194
k20	152.0	0.3881	151.2	152.7	0.5213
k21	10.7433	0.6043	9.5569	11.9297	0.0310
k22	-212E-12	3.46E-11	-28E-11	-144E-12	1.0043
k23	8.0442	0.3449	7.3671	8.7213	-0.1284
k24	6.482E8	5396586	6.3761E8	6.588E8	-0.4613
k25	79941981	11998517	56385555	1.035E8	0.00160
k26	186.9	1.5808	183.8	190.0	-0.6452
k27	16.0160	3.1136	9.9031	22.1290	-0.2468

Table 17. Final parameter values for entire temperature range of argon after global fit

Temp[K]	*a* Parameter	*b* Parameter	*c* Parameter	γ Parameter
90	-0.000247595	N/A	6.29049E-09	650325838
100	-0.000199568	2.13506E-05	4.24677E-09	651523451
110	-0.000164852	2.21913E-05	3.58133E-09	652533383
120	-0.000138755	2.34451E-05	3.03648E-09	654068741
130	-0.000117975	2.46866E-05	2.76632E-09	655150932
135	-0.000108297	2.59447E-05	2.47101E-09	656548973
140	-9.84899E-05	2.69922E-05	2.28714E-09	657590433
143	-9.27069E-05	2.853E-05	2.11463E-09	658828654
146	-8.73472E-05	2.95968E-05	2.01532E-09	659787184
148	-8.41858E-05	3.05695E-05	1.9109E-09	661286613
150.7	-8.06072E-05	3.10455E-05	1.85231E-09	662787589
153	-7.82315E-05	3.13378E-05	1.82265E-09	664294294
155	-7.66304E-05	3.12227E-05	1.80859E-09	666023295
157	-7.5374E-05	3.08732E-05	1.80461E-09	669121980
160	-7.38882E-05	3.0351E-05	1.80111E-09	676056919
165	-7.15842E-05	2.9402E-05	1.767E-09	686025597
170	-6.87202E-05	2.78754E-05	1.70359E-09	699707037
175	-6.53206E-05	2.68125E-05	1.62659E-09	715627153
180	-6.1779E-05	2.62577E-05	1.4712E-09	725255178
200	-4.9321E-05	2.60854E-05	1.33349E-09	696097762
220	-3.96634E-05	2.69113E-05	1.11103E-09	663365861
235	-3.37452E-05	N/A	9.7962E-10	656178647
250	-2.86844E-05	2.77397E-05	8.708E-10	653038487
265	-2.43048E-05	2.7985E-05	7.79644E-10	651426196
280	-2.04756E-05	2.80391E-05	7.025E-10	650497828
295	-1.70976E-05	2.80182E-05	6.36616E-10	649917123
310	N/A	N/A	5.79886E-10	649530690
340	-8.98311E-06	2.79858E-05	4.87699E-10	649065378
370	-4.79223E-06	2.79655E-05	4.16574E-10	648807010

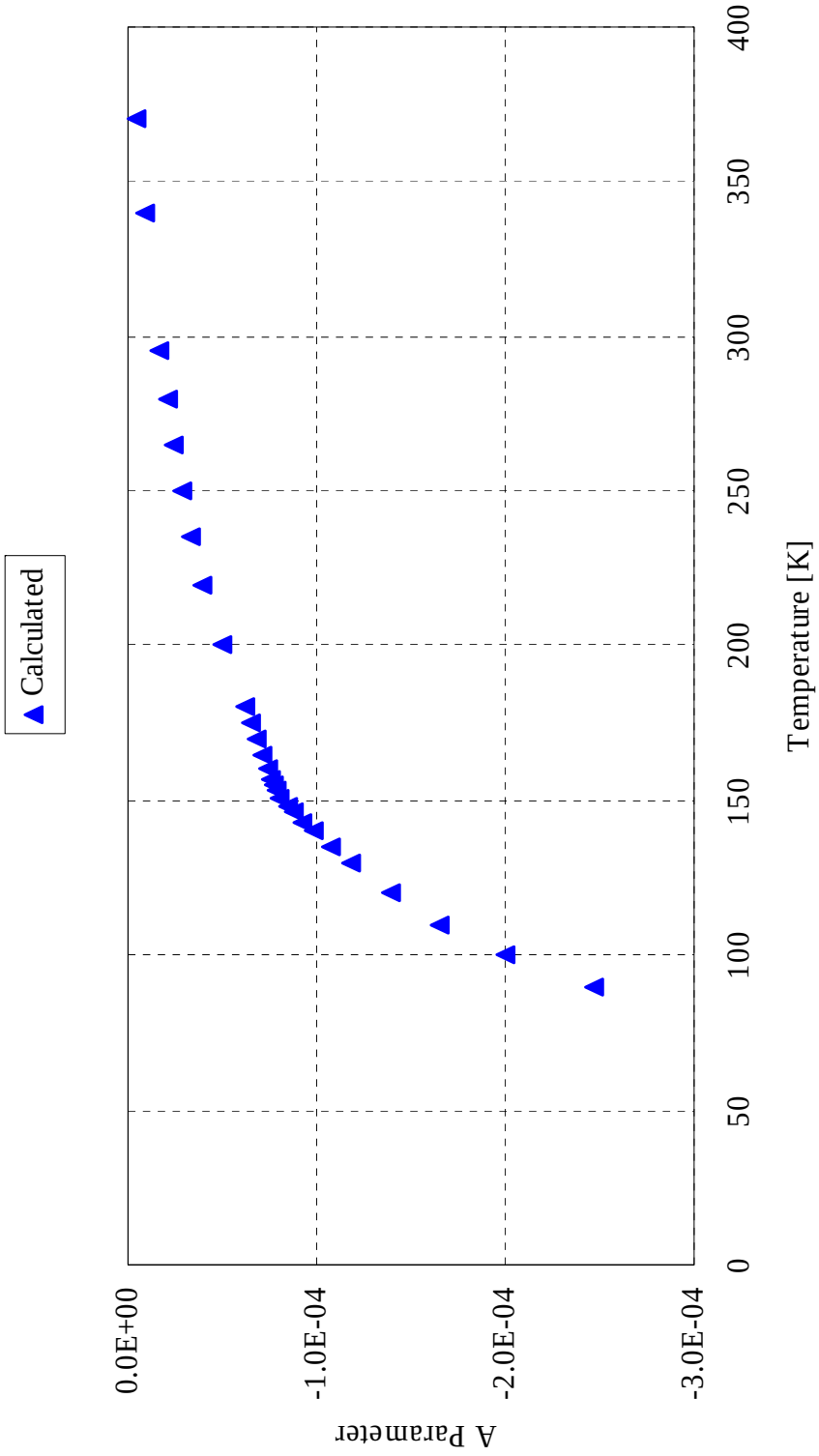

Figure 15. Final ***a*** parameter plot after global fit

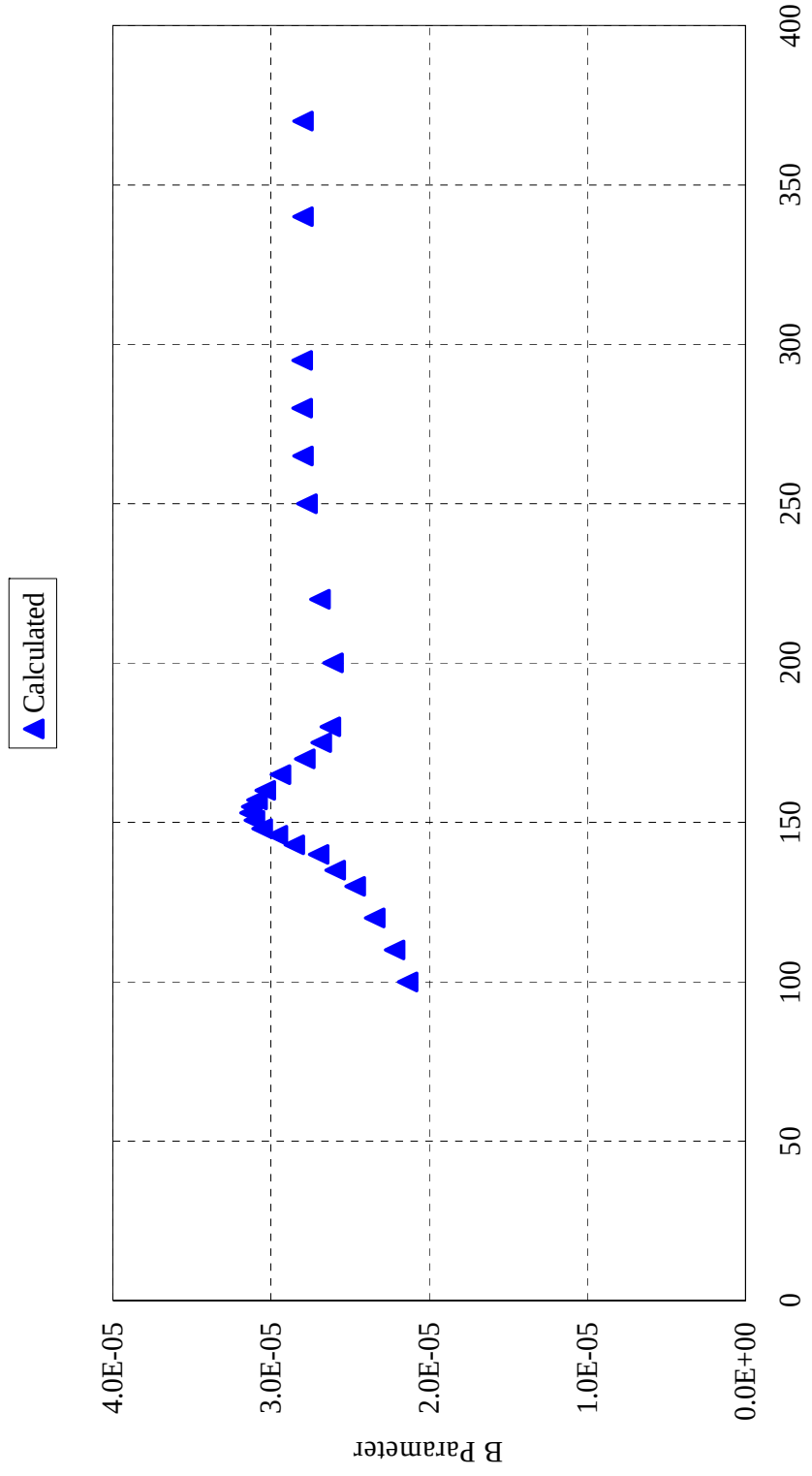

Figure 16. Final ***b*** parameter plot after global fit

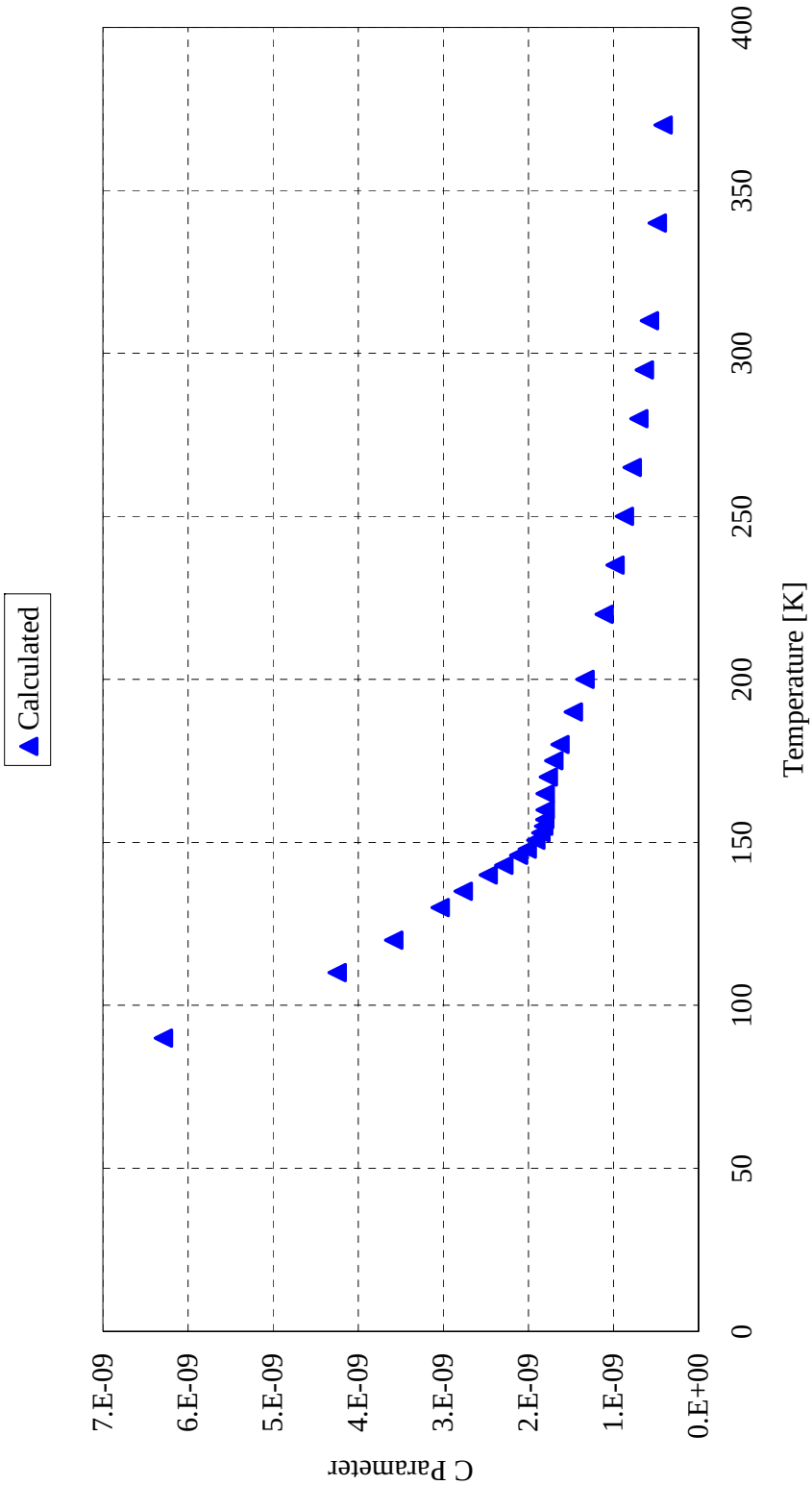

Figure 17. Final ***c*** parameter plot after global fit

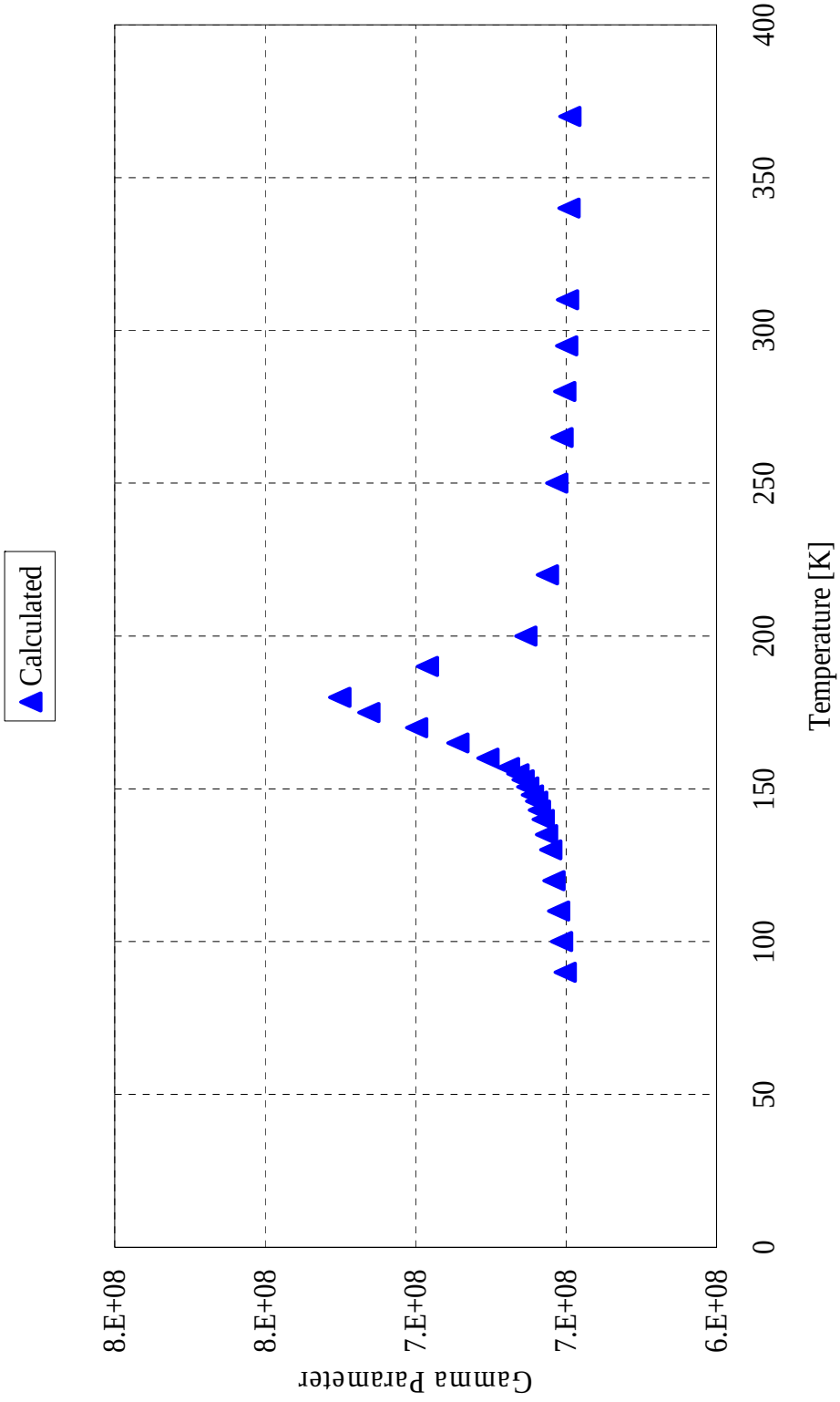

Figure 18. Final γ parameter plot after global fit

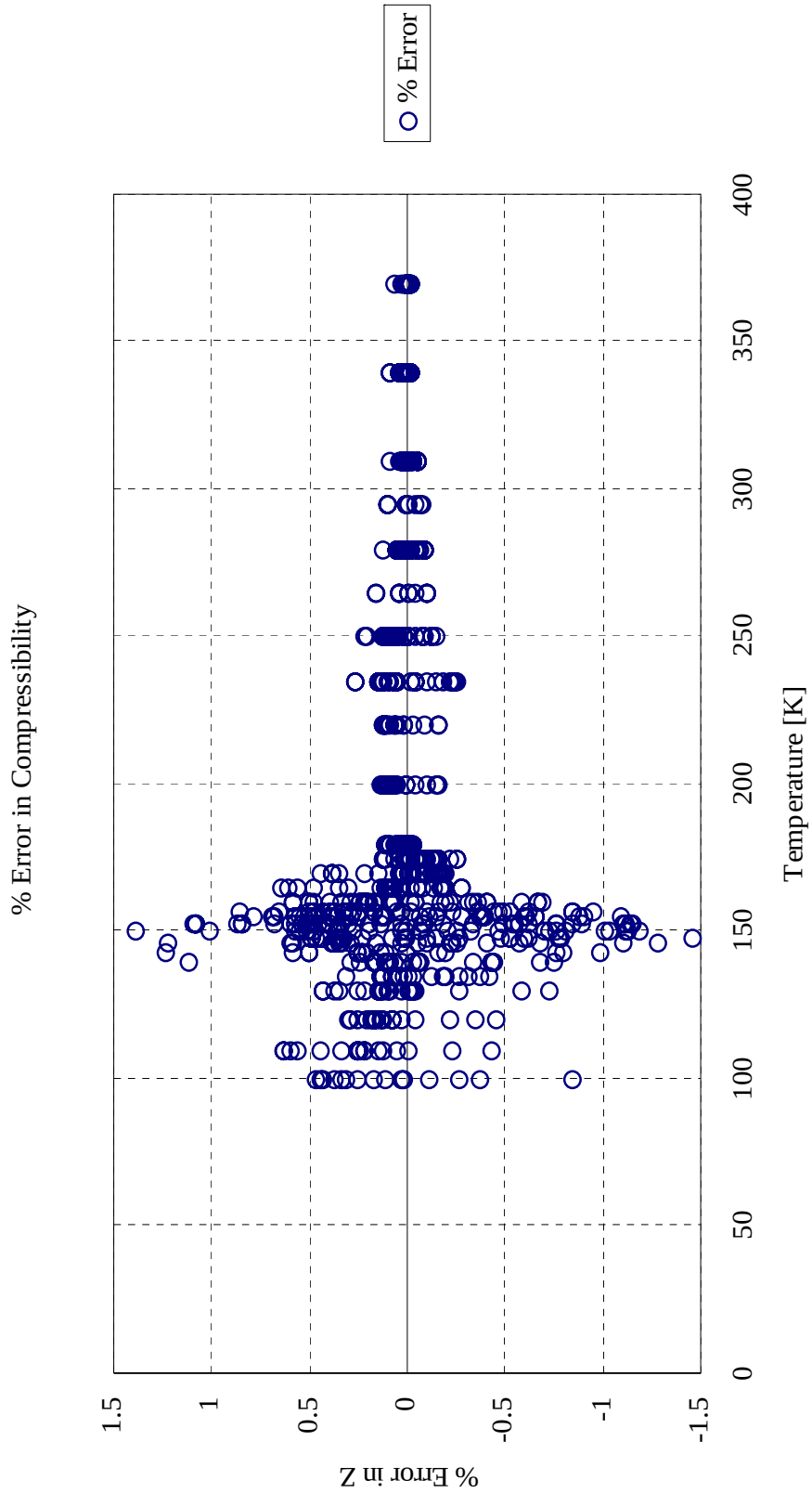

Figure 19. Deviation of compressibility factor [Z] in global fit

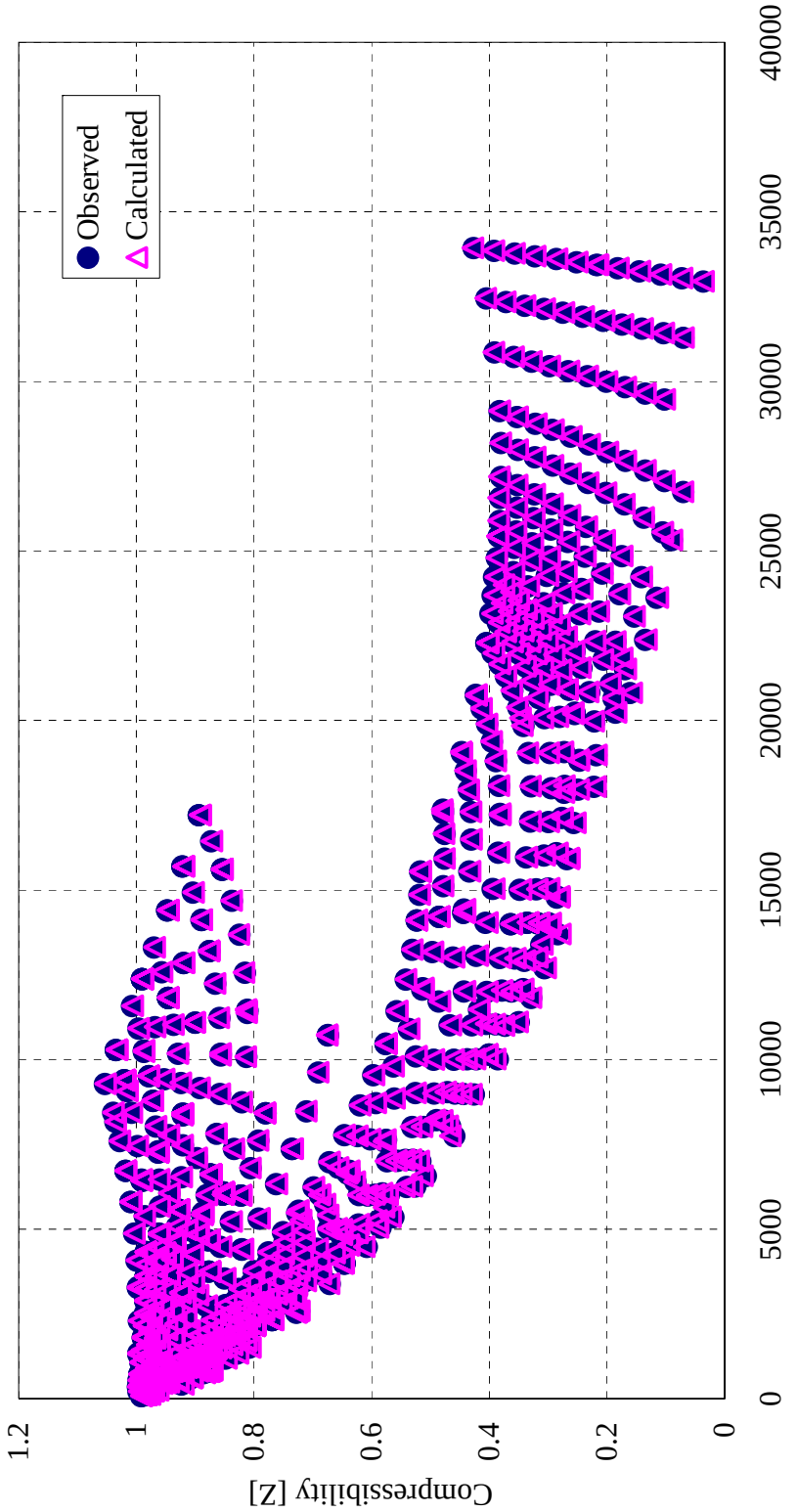

Figure 20. Observed and calculated compressibility factor [Z] in global fit

V. COMPARISON TO PREVIOUSLY PUBLISHED CUBIC EOS

Having plotted deviation of compressibility factor [Z] in global fit obtained with this new cubic equation in figure 19 and 20, we have chosen several cubic EOS for comparison to the new cubic EOS They are: vdW (1873), RK (1949), SRK (1972) and PR (1976) EOS.

Table 18. Real data for argon at entire critical isotherm

Temp [K]	Volume [cm^3/mol]	Compressibility [Z]
150.687	1158.7930	0.9279
150.687	740.9262	0.8887
150.687	528.6239	0.8463
150.687	400.5748	0.8006
150.687	312.0572	0.7493
150.687	246.6413	0.6909
150.687	194.5362	0.6217
150.687	166.4854	0.5707
150.687	142.6205	0.5165
150.687	124.3479	0.4663
150.687	99.8378	0.3855
150.687	90.0212	0.3492
150.687	78.6815	0.3055
150.687	72.9830	0.2834
150.687	52.6845	0.2182
150.687	50.0477	0.2208

Table 19. Calculated Z values for argon at entire critical isotherm

V [cm3/mol]	z-Real	z-BWR	z-vdW	z-SRK	z-RK	z-PR	z-NEW
1158.793	0.9279	0.9234	0.9350	0.9266	0.9264	0.9194	0.9247
740.926	0.8887	0.8819	0.8990	0.8870	0.8868	0.8769	0.8845
528.624	0.8463	0.8372	0.8596	0.8445	0.8442	0.8321	0.8416
400.575	0.8006	0.7892	0.8166	0.7989	0.7986	0.7849	0.7960
312.057	0.7493	0.7354	0.7674	0.7481	0.7477	0.7330	0.7455
246.641	0.6909	0.6744	0.7102	0.6905	0.6900	0.6755	0.6886
194.536	0.6217	0.6022	0.6405	0.6222	0.6218	0.6086	0.6217
166.485	0.5707	0.5491	0.5878	0.5720	0.5715	0.5601	0.5726
142.621	0.5165	0.4927	0.5304	0.5182	0.5179	0.5090	0.5202
124.348	0.4663	0.4405	0.4762	0.4681	0.4679	0.4618	0.4712
99.838	0.3855	0.3563	0.3879	0.3863	0.3864	0.3848	0.3899
90.021	0.3492	0.3186	0.3496	0.3491	0.3494	0.3493	0.3517
78.682	0.3055	0.2743	0.3106	0.3049	0.3057	0.3059	0.3041
72.983	0.2834	0.2532	0.2988	0.2838	0.2850	0.2840	0.2795
52.685	0.2182	0.2233	0.4970	0.2626	0.2669	0.2312	0.2181
50.048	0.2208	0.2352	0.6161	0.2782	0.2833	0.2340	0.2226

Table 20. %AAD results for critical isotherm with different EOS

Average Absolute Deviation				
BWR EOS	RK EOS	SRK EOS	PR EOS	NEW EOS
4.4449	3.3465	3.0606	1.8267	0.5900

Comparing the average absolute percent deviations (%AAD) in table 20 by using the calculated Z values shown in table 19 and real critical isotherm data shown in table 18, we see that for compressibility, the new EOS has the lowest value overall. The PR EOS is closer than the others to the new EOS. As shown in table 21, the New EOS had the lowest overall maximum absolute percent deviation (%MAD) for compressibility while PR has the second best %MAD. The %MAD occurs in the immediate vicinity of the critical point. Deviation for calculated volume and pressure at critical point is shown in table 22 and 23 respectively. Also percentage error in Z for different equations is shown in table 24. In figure 21, plot for critical isotherm values calculated by BWR, vdW, SRK, PR and New EOS is shown and in figure 22 percentage errors in Z at T_c calculated by BWR, vdW, SRK, PR and New EOS is plotted. In figure 23, percentage error for Z calculated by both PR and New EOS is plotted for entire fluid region.

Table 21. %MAD results for critical isotherm with different EOS

Maximum Absolute Deviation			
BWR EOS	**SRK EOS**	**PR EOS**	**NEW EOS**
10.6497	25.9787	5.9974	1.3838

Table 22. % error for calculated volume at T_c=150.687K and P_c=47.994atm

% Error in pressure w.r.t. V_c=74.585 cm^3/mol					
RK EOS	**BWR EOS**	**vdW EOS**	**SRK EOS**	**PR EOS**	**New EOS**
36.4081	10.158	16.709	30.038	17.86	2.605

Table 23. % error for calculated pressure at T_c=150.687K and V_c=74.585cm^3/mol

% Error in pressure w.r.t. P_c=47.994atm					
RK EOS	**BWR EOS**	**vdW EOS**	**SRK EOS**	**PR EOS**	**New EOS**
0.3958	10.556	4.038	0.0333	4.459	3.381

Table 24. Percentage error for Z

	% Error in z					
z-REAL	**BWR**	**vdW**	**SRK**	**RK**	**PR**	**New**
0.9279	-0.49	0.7623	-0.145	-0.162	-0.92	-0.345
0.8887	-0.767	1.1618	-0.192	-0.217	-1.323	-0.473
0.8463	-1.078	1.5767	-0.214	-0.249	-1.679	-0.555
0.8006	-1.429	1.9949	-0.206	-0.251	-1.966	-0.575
0.7493	-1.854	2.4106	-0.161	-0.216	-2.17	-0.507
0.6909	-2.382	2.7926	-0.06	-0.124	-2.235	-0.333
0.6217	-3.137	3.0176	0.0832	0.0105	-2.113	0
0.5707	-3.776	2.9969	0.2205	0.1464	-1.851	0.3329
0.5165	-4.612	2.6893	0.331	0.2626	-1.455	0.7164
0.4663	-5.542	2.1164	0.3958	0.3442	-0.974	1.0508
0.3855	-7.573	0.6128	0.216	0.2406	-0.183	1.1414
0.3492	-8.77	0.1161	-0.042	0.0592	0.0335	0.7159
0.3055	-10.22	1.6744	-0.211	0.0614	0.1364	-0.458
0.2834	-10.65	5.4312	0.158	0.5793	0.2099	-1.383
0.2182	2.3324	127.77	20.356	22.312	5.9792	-0.046
0.2208	6.5076	179.04	25.979	28.309	5.9975	0.8152

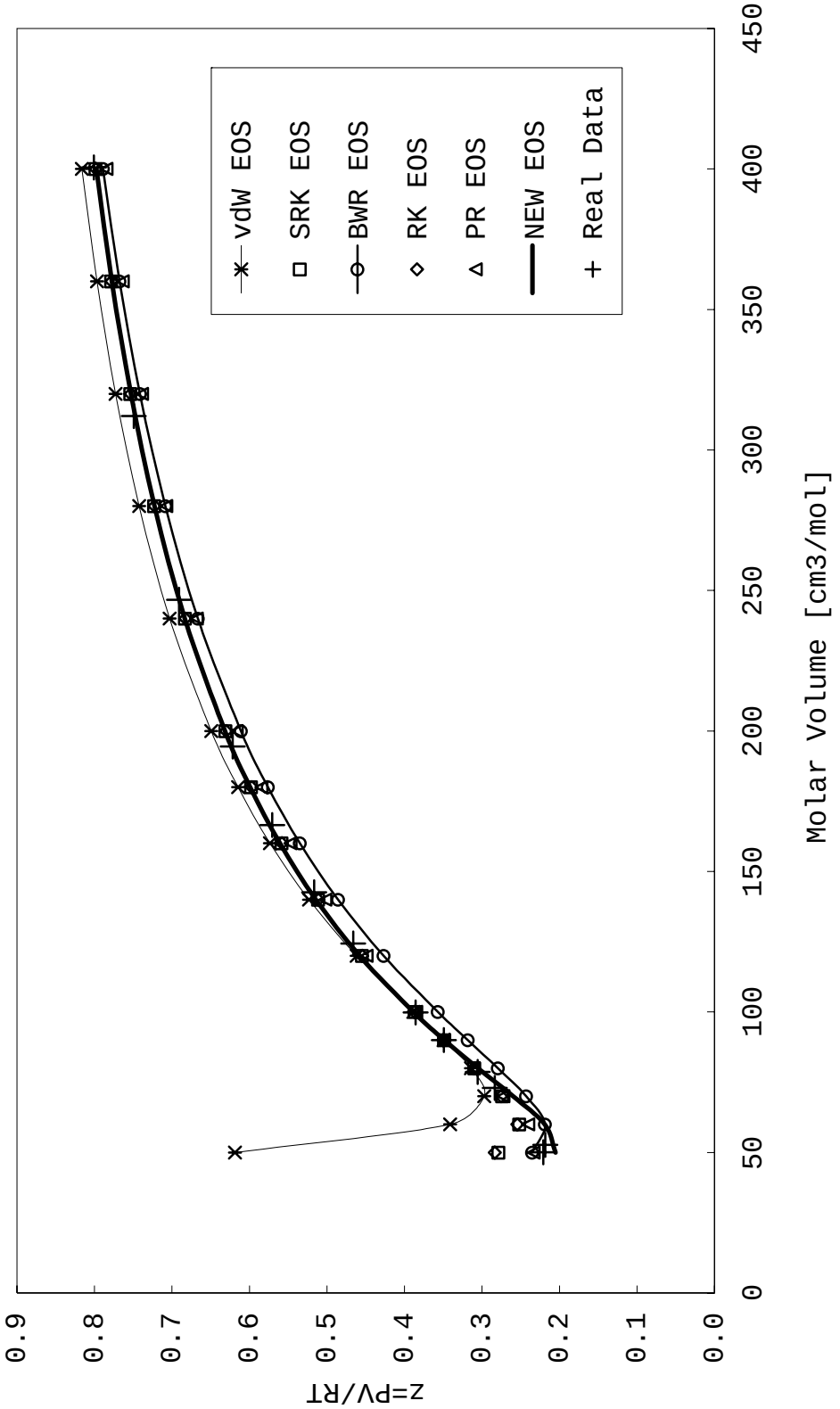

Figure 21. Critical isotherm calculated by BWR, vdW, SRK, PR and New EOS

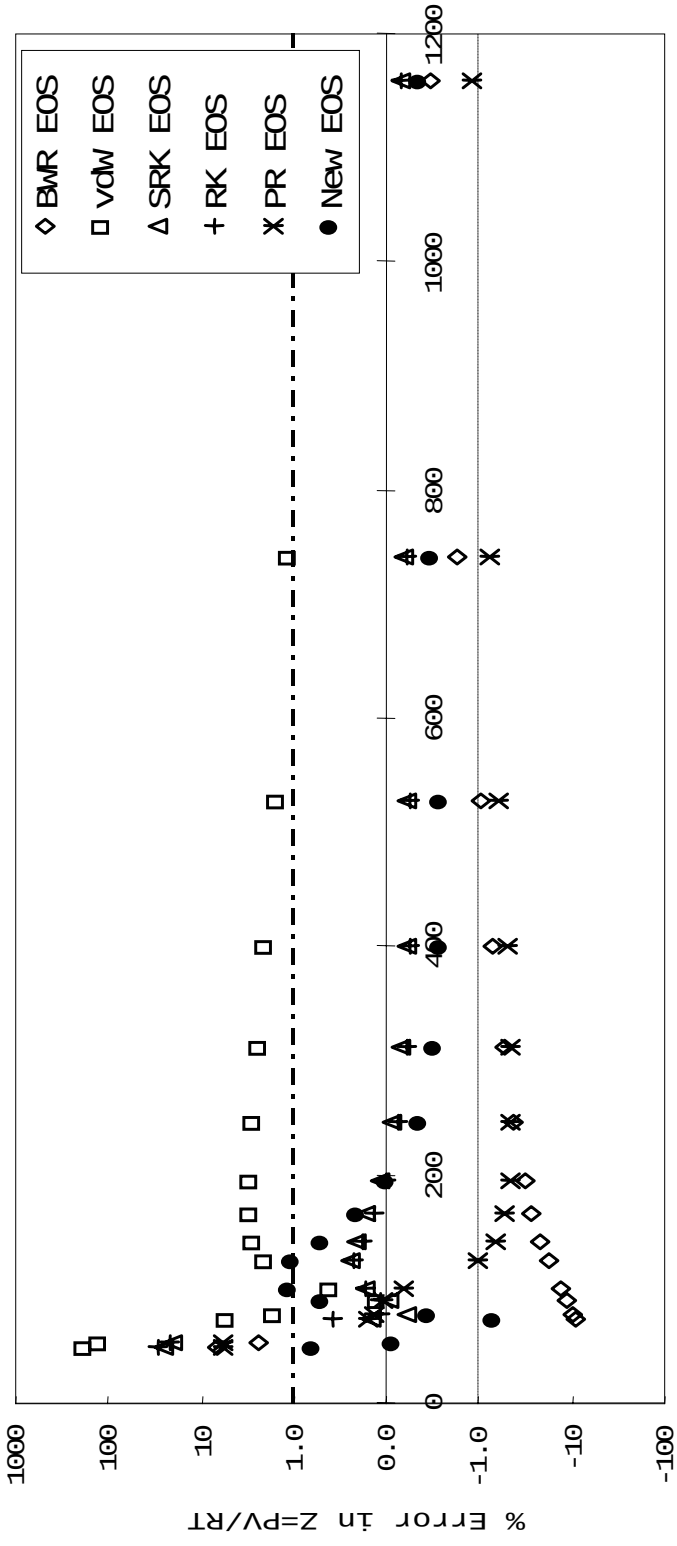

Figure 22. Percentage error in Z at critical isotherm calculated by BWR, vdW, SRK, PR and New EOS

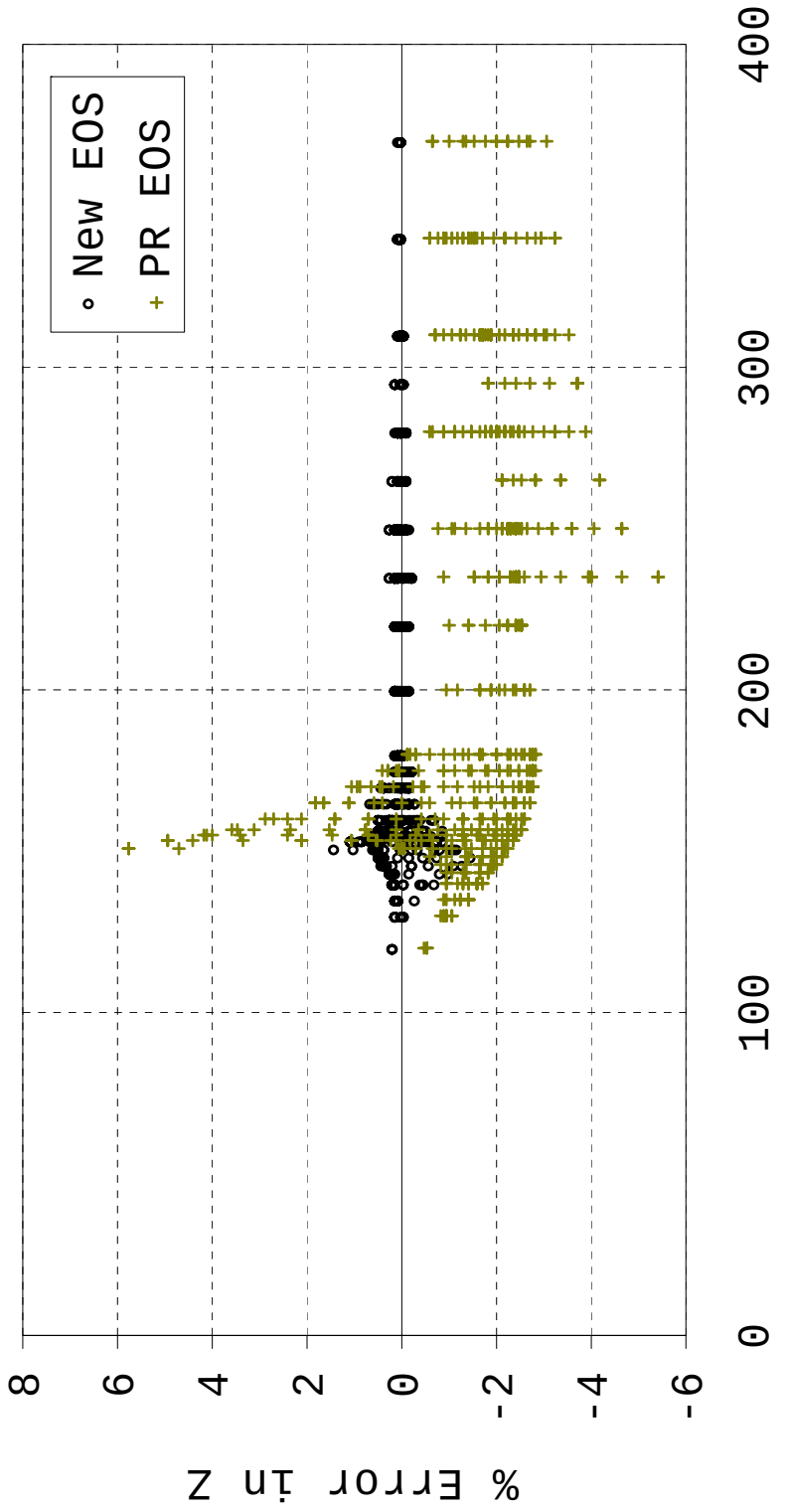

Figure 23.Percentage error for Z calculated by both PR and New EOS

VI. DISCUSSION AND COMMENTS

6.1 Discussion

A new EOS must have significant features that make it preferable to established equations. The goal in EOS development is to describe mixture properties of fluids precisely. No comparison of new EOS to common EOS would be complete without the description of mixture properties. However, before describing mixing rules the new EOS must show the ability to predict pure component properties. If a new EOS does not present advantages over previous EOS for pure components, it would be futile to apply it to mixtures.

Truly, developing a new EOS that performs better than previous equations is more complicated and challenging than it may appear. The challenging part is to propose the EOS - simple in form which describes pressure, temperature and volume properties of substances as well as predicts thermodynamic properties. Having highlighted this fact, considering the number of different thermodynamic properties and the complexity of these properties and the wide range of pressure and temperature that the new EOS must predict, it is not hard to understand why developing new EOS is difficult. Certainly, having more parameters can provide more accuracy. However, the fact is the greater the number of parameters, the more difficult the applicability of EOS to mixtures. In other words, it is a trade-off between accuracy of the EOS and ease of application to mixtures. In this view, a new EOS must strike a balance between obtaining accuracy with a large number of parameters and ease of application to mixtures with fewer parameters.

From this perspective, we have made an effort to identify a new cubic EOS that strikes the balance of accuracy and applicability. Clearly, for expressing the *P,V,T* properties of pure argon, our new EOS shows remarkable capabilities especially for critical isotherm description.

6.2 Temperature dependency of EOS parameters

At first sight, our procedure seems simple; however, the problem is actually trying to fit the calculated values of EOS parameters as a function of temperature. This difficulty arises because the applied critical point criterion gives an unusual shape to the parameter curves in the vicinity of the critical point as shown in figures 7 to 10. The figures show that the EOS parameters display anomalous peaks near the critical point. In fact, this behavior is limited to the near critical region and the rest of the curve is appears to line up smoothly with the values at temperatures removed from the critical point. The difficulty this behavior creates is that to preserve the exact prediction of the critical point and enforcement of critical point criterion, any temperature function used to fit the curves in figures 7 to 10 must pass through the critical point exactly. Regardless of the form of the algebraic equation used to describe temperature dependence of the EOS parameters and to fit the EOS parameter curves, this critical point problem arises unless the proposed EOS is altered in some way to reduce the strange characteristic behavior of the EOS parameters in vicinity of the critical point.

It would appear necessary to add additional density dependency in numerator and denominator as well as introducing extra parameters. If in doing so, a near critical term

could smooth out the curves, it would be much easier to fit the temperature dependencies by using simple algebraic functions having fewer parameters.

6.3 Parameters at critical point

Expressing density dependence of a proposed EOS by fitting density in a compressibility explicit equation along the critical isotherm of a pure component is conceivably the most challenging part of the EOS development. By far the most complicated characteristic of this challenge is achieving good fits in the vicinity of the critical point while having critical point constraints satisfied.

This work has shown that for a cubic EOS to provide a good fit in the vicinity of the critical point, it is convenient to utilize the newly introduced critical point criteria. With these considerations, figures C-1 to C-30 illustrate that the new cubic EOS achieves good balance between accuracy and applicability. The new EOS provides lower average errors in compressibility factor compared to the SRK and PR EOS for pure argon. Using the critical point criteria eliminates the volume displacement at the critical point.

6.4 Statistics

The regression procedure used a correlation matrix, obtained by normalizing the variance-covariance matrix, to improve the fit for argon. The correlation matrix indicates the strength of the cross correlation between the regressed parameters. It is beneficial to use the correlation matrix in coordination with skewness analysis of the parameters. In some cases, examination of these cross relations can improve the sensitivity analysis of

the regressed parameters for determining whether the equation needs more density dependence or more parameters to fit the data. The sensitivity analysis can yield information about all parameters in the equation, including those whose values are fixed by the critical constraints.

Besides the correlation matrix and skewness analysis, given the highly nonlinear nature of the parameter equations, it is preferable to generate different initial guesses for the parameters during the fitting process. The different starting points for different parameters can yield different results.

6.5 Future work

In absolute terms, the new cubic EOS fits pure argon remarkably well. Its performance is comparable to EOS with greater density dependence and more parameters. Further development of the new EOS (*i.e*. mixing rules determination) requires fitting more pure components (especially natural gas components). The new EOS shows enough promise to warrant further development. This development should focus upon improving the equation in the vicinity of the critical point and improving the prediction of the near critical isotherms. This may be possible by adding more density dependence to the equation.

These improvements would make the new EOS an excellent candidate for generalization and extension to fluid mixtures. Nevertheless, the adjustable parameters may be correlated to each other which can lead to non-unique regressed values for the parameters. This fact can make it difficult to develop mixing rules.

VII. CONCLUSIONS

In this research, a new cubic EOS has been developed that has shown promising results for representing *PVT* behavior of pure argon. The maximum absolute percentage error for compressibility factor is 1.463% throughout the entire database for saturation and supercritical data with 746 data points for argon. The functions chosen to express the temperature dependence of the parameters provide excellent fits of data for argon, except in the vicinity of the critical point. The percentage error in the intermediate vicinity of the critical point is 1.383%.

Besides these major outcomes, minor conclusions are:

1. When four parameters are available that vary with temperature, plots of the parameters as functions of temperature behave anomalously near the critical point, turning upward sharply over a small range of temperature. It is difficult to match the required values at the critical temperature using analytical temperature functions and still achieve good fit in the vicinity of the critical point without employing the newly introduced critical point criterion.
2. Analytical temperature functions expressing the temperature dependence of the EOS parameters in terms of reciprocal temperature generally give better fit results than functions written in terms of temperature directly.
3. The Levenberg-Marquardt unconstrained, multivariable non-linear regression algorithm provides the fits for critical pressure and the critical point conditions. Using this method to solve the resulting equations simultaneously for values of

all of the EOS parameters is not only simpler but also more reliable than using weighting factors in order reach precise fits in the vicinity of the critical point. The algorithm used for nonlinear regression is also robust and reliable for overall fitting of EOS parameters directly to the data of saturation and supercritical *PVT* data.

4. The new EOS generally performs better for fitting pure component properties than the SRK and PR equations in this work. Further work should focus upon improving the new EOS prediction of the critical point and minimizing the anomalous behavior of the values of the EOS at the critical point, either altering the equation by adding more molar volume dependence or developing a special term that becomes active only in the vicinity of the critical point.

LITERATURE CITED

Abbott, M., "Cubic Equations of State," *AIChE J.*, **19,** 596 (1973).

Alder, B.J. and Hecht, C.E., "Studies in Molecular Dynamics. VII.," *J. Chem. Phys.*, **50**, 2032 (1969).

Alder, B.J., Young, D.A. and Mark, M.A., "Studies in Molecular Dynamics. X.," *J. Chem. Phys.*, **56**, 3013 (1972).

Assel, M.J., Nieto de Castro, C.A. and Wakeham, W.A., "The Estimation of Physical Properties of Fluids, Part II, the Economic Advantage of Accurate Transport Property Data," *ChemPor'78*, 16.1 (1978).

Barrow, D., Belmonte, A., Boggess A., Bryant, J., Kiffe, T., Morgan, J., Rahe, M., Smith, K. and Stecher M., *Solving Differential Equations with Maple V*, 4th Edition, Brooks/Cole Publishing Co., Pacific Grove, CA (1998).

Beattie, J.A. and Bridgeman, O.C., "A New Equation of State for Fluids: I.Application to gaseous ethyl ether and carbon dioxide," *J. Amer. Chem. Soc.*, **49**, 1665 (1927).

Benedict, M., Webb, G.B., and Rubin, L.C., "Empirical Equations for Thermodynamic Properties of Light Hydrocarbons and their Mixtures," *J. Chem. Phys.*, **8**, 334 (1940).

Boublik, T., "An Equation of State of Hard Convex Body Fluids," *Molec. Phys.*, **42**, 209 (1981).

Boublik, T., "Statistical Thermodynamics of Convex Molecular Fluids," *Molec. Phys.*, **27**, 1415 (1975).

Bradley, M., "Franco-Russian Engineering Links: The Careers of Lame and Clapeyron," *Ann. of Sci.*, **38**, 291 (1981).

Cagniard de la Tour, C., *Ann. Chim. Phys.*, **22**, 127

Chen., S.S. and Kreglewski, A., "Applications of the Augmented van der Waals Theory of Fluids," *Beichte de Bunsen-Gelleschaft*, **81**, 1048 (1977).

Davidson, N., *Statistical Mechanics*, Mc Graw Hill, NY (1962).

Edgar, T.F., Himmelblau, D.M. and Lasdon, L.S., *Optimization of Chemical Processes*, 2nd Edition, Mc Graw Hill Book Co., NY (2001).

Erdogmus, M., "Development of a Modified Patel-Teja Equation of State," PhD Dissertation, Pennsylvania State University, University Park, PA (2000).

Freund, R.J. and Little, R.C., *SAS System for Regression*, 3rd Edition, SAS Institute Inc., Cary, NC (2000).

Gibbons, R.M., "The Scaled Particle Theory for Particles of Arbitrary Shape," *Molec. Phys.*, **17**, 81 (1969).

Goodwin, R.D., "Provisional Thermodynamic Functions of Propane, from 85 to 700 K at Pressure to 700 bar," *NBSIR*, **77**, 860 (1977).

Hall, K.R. and Eubank, P.T., "New Identities for Critical-Point Constraints with Application to Cubic Equations of State," *I. & E. C. Res.*, accepted (2004).

Han, M.S. and Starling, K.E., " Thermodynamic Data Refined for LPG. Part 14: Mixtures," *Hydrocarbon Processing*, **51**, 129 (1972).

Heal, K.M., Hansen, M.L and Rickard, K.M., *Maple V, Learning Guide*, Hamilton Printing Co., Rensselaer, NY (1996).

Holste, J.C., Hall, K.R. and Iglesias-Silva, G.A., "Log-Linear Plots for Data Representation," *AIChE J.*, **42**, 296 (1996).

Hunter, M., *Robert Boyle Reconsidered*, Cambridge Co., Cambridge University Press NY (1994).

Iglesias-Silva, G.A., "A New Equation of State: Theory and Experiment," PhD Dissertation, Texas A&M University, College Station, TX (1987).

Iglesias-Silva, G.A., "Optimization of the BACK EOS," Ms Thesis, Texas A&M University, College Station, TX (1983).

Jiuxun, S., "Totally Inclusive Cubic Equation of State with Five Parameters for Pure Fluids," *Fluid Phase Equilib.*, **193**, 1 (2002).

Kedge, C.J., "A New Non-Cubic Equation of State," PhD Dissertation, University of Calgary, Alberta, Canada (2000).

Kim, H., Lin, H.M. and Chao, K.C., "Cubic Chain-of-Rotators Equation of State," *Ind. Eng. Chem. Fundam.*, **25**, 75 (1986).

Kreglewski, A., *Equilibrium Properties of Fluids and Fluid Mixtures, TEES Monograph Series No.1*, Texas A&M University Press, College Station, TX (1984).

Kubic, W.L., "A Modification of the Martin Equation of State for Calculating Vapor Liquid Equilibria," *Fluid Phase Equilib.*, **9**, 79 (1982).

Kumar, H.E. and Starling K.E., "Modification of the Kumar-Starling Five-parameter Cubic Equation of State and Extension to Mixtures," *Fluid Phase Equilib.*, **77**, 181 (1992).

Kumar, H.E. and Starling K.E., "The Most General Density-Cubic Equation of State: Application to Non-polar Fluids," *Ind. Eng. Chem. Fundam.*, **21**, 255 (1982).

Kumar, K.H. and Staling, K.E., "Comments on Cubic Equation of State-Which?," *Ind. Eng. Chem. Fund.*, **19**, 128 (1980).

Kumar, K.H., "Development of the Most General Density-Cubic Equation of State," PhD Dissertation, University Oklahoma, Norman (1980).

Lee, B.I. and Kesler, M.G., "A Generalized Thermodynamics Correlation Based on Three-Parameter Corresponding States," *AIChE J.*, **21**, 510 (1975).

Levenberg, K., "A Method for the Solution of Certain Nonlinear Problems in Least Squares,", *Quart. Appl. Math.*, **2**, 164 (1944).

Levine, I.N., *Physical Chemistry*, 4th Edition, Mc Graw Hill Book Co., NY (1994).

Longuet-Higgins, H.C. and Widom, B., "A Rigid Sphere Model for the Melting of Argon," *Molec. Phys.*, **8**, 549 (1964).

Marquardt, D.W., "An Algorithm for Least-Squares Estimation of Nonlinear Parametrs," *J. SIAM*, **11**, 2 (1963).

Martin, J.J. and Stanford, T.G., "Development of High Precision Equations of State for Wide Ranges of Density Utilizing a Minimum of Input Information: Example-Argon," *AIChE Symp.*, Ser.760, No.140 (1974)

Martin. J.J. and Hou, Y.C., "Development of an Equation of State for Gases," *AIChE J.*, **1**, 142 (1955)

Mathias, P.M. and Copeman, T.W., "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the various forms of the Local Composition Concept," *Fluid Phase Equilib.*, **13**, 91 (1980).

Mohsen-Nia, M., Nodarress, H. and Mansoori, G.A., "A Cubic Hord-Core Equation of State," *Fluid Phase Equilib.*, **206**, 27 (2003).

Monagan, M.B., Geddes, K.O., Labahn, G. and Vorkoetter, S., *Maple V Programming Guide*, Hamilton Printing Co., Rensselaer, NY (1996).

Naslifor, K. and Moshfeghion, M., "A New Cubic Equarion of State for Simple Fluids: Pure and Mixture," *Fluid Phase Equilib.*, **190**, 73 (2001).

Onnes, K.H., "On the Lowest Temperature Yet Obtained," *Comm. Phys. Lab. Univ.*, 159, Leiden, The Netherlands (1922).

Orbey, H. and Vera, J.H., "Correlation fot the 3rd Virial Coefficient Using T_c, P_c and ω as Parameters," *AIChE J.*, **29**, 107 (1983).

Patel, N.C. and Teja, A.S., "A New Cubic Equation of State for Fluids and Fluid Mixtures," *Chem. Eng. Science*, **37**, 463 (1982)

Patel, N.C., "The Calculation of Thermodynamic Properties and Phase Equilibria Using a New Cubic Equation of State," PhD Dissertation, Loughborough University, Loughborough, UK (1980).

Peng, D.Y. and Robinson, D.B., "A New Two-Constant Equation of State," *Ind. Eng. Chem.Fundementals*, **15**, 1 (1976).

Percus, J.K. and Yevick, G.J., "Analysis of Classical Mechanics by Means of Collective Coordinates," *Phys. Rev.*, **110**, 1 (1958).

Pitzer, K.S., "The Volumetric and Thermodynamic Properties of Fluids," *J. Amer. Chem. Soc.*, **77**, No.13, 3427 (1955).

Polpe, J.A., "The Statistical Mechanics of Assemblies of Axial Symmetric Molecules. I. General Theory," *Proc. Roy. Soc.*, **221A**, 498 (1954).

Pope, G.A., Chappelear, P.S. and Kobayashi, R., "Virial Coefficients of Argon, Methane, and Ethane at Low Reduced Temperatures," *J. Chem. Phys.*, **59**, 423 (1973).

Prausnitz, J.M. and Donohue, M.D., *Thermodynamic Properties of Fluids Mixtures from Perturbed-Hard-Chain Theory*, Proceedings of the 55th Convention of Gas Processors Assoc., Tulsa, OK (1976).

Press, W.H., Flammery, B.P., Teukolsky, S.A. and Vetterling, W.T., *Numerical Recepies*, Cambridge University Press, Cambridge, UK (1986).

Redlich, O. and Kwong, J.N.S., "On the Thermodynamics of Solutions. An Equation of State. Fugacities of Gaseous Solutions," *Chem Rev.*, **44**, 233 (1949).

Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., *The Properties of Gases and Liquids*, Mc Graw Hill Book Co., NY (1977).

SAS, *SAS/GRAPH User's Guide*, 1st Edition, SAS Institute Inc., Cary, NC (1993).

SAS, *SAS/STAT User's Guide*, Release 6.03 Edition, SAS Institute Inc., Cary, NC (1991).

Schimdt, G. and Wenzel, H., "A Modified van der Waals Type of Equation of State," *Chem. Eng. Science*, **35**, 1503 (1980).

Schwartzentruber, J. and Renon, H., "Development of a New Cubic Equation of State for Phase Equilibrium Calculations," *Fluid Phase Equilib.*, **52**, 127 (1989).

SigmaPlot, *SigmaPlot 2000 Programming Guide*, SPSS Inc., Chicago, IL (2000).

Smith, J.M., Van Ness, H.C. and Abbott, M.M., *Introduction to Chemical Engineering Thermodynamics*, Mc Graw Hill Book Co., NY (1996).

Smyth, A.L., John Dalton, 1766-1884: A Bibliography of Works by him and about him, by A. L. Smyth, Manchester University Press, Manchester, UK (1966).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Science*, **27**, 1197 (1972).

Sodus, R.J., "New Dieterici-Type Equations of State for Fluid Phase Equilibria," *Fluid Phase Equilib.*, **212**, 31 (2003).

Starling, K.E., "Thermo Data Refined for LPG. Part 1: Equation of State and Computer Prediction," *Hydrocarbon Process.*, **50**, 101 (1972)

Starling, K.E., *Fluid Thermodynamic Properties for Light Petroleum Systems, Gulf Pub. Co.*, Houston, TX (1973).

Starling, K.E. and Han, M.S., "Thermo Data Refined for LPG. Part 14: Mixtures," *Hydrocarbon Process.*, **51**, 129 (1972)

Strett, W.B. and Staveley, L.A.K., "Experimental Study of the Equation of State of Liquid Argon," *J. Chem. Phys.*, **50**, 2302 (1969).

Stryjek, R. and Vera, J.H., "PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures," *Can. J. Chem. Eng.*, **64**, 323 (1986).

Svejda, P. and Kohler, F., "A Generalized van der Waals Equation of State I. Treatment of Molecular Shape in Terms of the Boubilic-Nezbeda Equation," *Ber. Busenges. Phys. Chem.*, **87**, 672 (1983).

Tegeler, Ch., Span, R. and Wagner, W., "A New Equation of State fot Argon Covering the Fluid Region for Temperatures From Melting Point Line to 700K at Pressures up to 1000MPa," *J. Phys. Ref. Data*, **28**, 779 (1999)

Trebble, M.A. and Kedge, C.J., "Development of a New Empirical Non-cubic Equation of State," *Fluid Phase Equilib.*, **158**, 219 (1999).

Trebble, M.A. and Bishnoi, P.R., "Extension of the Trebble-Bishnoi Equation of State to Fluid Mixtures," *Fluid Phase Equilib.*, **40**, 1 (1988).

Trebble, M.A. and Bishnoi, P.R., "Development of a New Four Parameter Cubic Equation of State," *Fluid Phase Equilib.*, **35**, 1 (1987).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **20**, 263 (1974).

van der Waals, J.D., "On the Continuity of the Gaseous and Liquid States," Ph.D. Dissertation, University of Leiden, Sijthoff, Leiden, The Netherlands (1873).

Vera, J. H., Huran, M.J. and Vidal, J., "On the Flexibility and Limitations of Cubic Equations of State," *Chem. Eng. Com.*, **26**, 311 (1984).

Vilmalchand, P. and Donohue, M.D., "Thermodynamics of Quadrupolar Molecules: The Peturbed-Anisotropic-Chain Theory," *Ind. Eng. Chem. Fundam.*, **24**, 246 (1985).

Wagner, W., "New Vapor Pressure Measurements for Argon and Nitrogen and a New Method for Establishing Rational Vapor Pressure Equations," *Cryogenics*, **13**, 470 (1973).

Wertheim, M., "Analytical Solution of the Percus-Yevick Equation," *J. Math. Phys.*, **5**, 643 (1964).

Zwanzig, R.W., “High-Temperature Equation of State by Perturbation Method,” *J. Chem. Phys.*, **22**, 1420 (1954).

APPENDIX A. NOTATION

a	van der Waals, RK and new equation of state parameters
a_c	value of attraction parameter
$a_i(T)$	temperature dependence of SRK and PR EOS parameter
A_j	constants in equations
a_j	general EOS parameters
B	2^{nd} virial coefficient
b	van der Waals, RK, SRK, PR and New EOS parameters
b_c	value of repulsion parameter
c	Patel-Teja and New EOS constant
c_j	a_j / RT in equation (22)
d_j	constants in equation (24)
f	arbitrary function
g(V)	function of molar volume
I	identity matrix
L	lower triangle matrix
L^T	transpose of lower triangle matrix
m_i	slope
P	pressure
P_c	critical pressure
R	universal gas constant

T temperature

T_c critical temperature

T_{ci} critical temperature of species

T_{ri} reduced temperature of species T / T_{ci}

V volume

V_c critical volume

Z compressibility factor

Greek Letters

$\alpha_i(T)$

$\beta_{i:}$ constants in equation (41)

Δ difference

ε_i sensitivity

$\gamma(T)$ new EOS parameter

γ_i orientation parameter in equations (32-35)

λ_i parameters in raw EOS in equation (36-57)

μ_i generalized cubic EOS parameters in equation (39)

θ^1 SRK EOS parameter

θ^2 PR EOS parameter

ω_i acentric factor of species

ζ_c correlation

Subscripts and Supercripts

c critical

calc calculated

EOS Equation of State

err percentage error

liq liquid

PR: Peng - Robinson

PT Patel - Teja

r reduced

res residuals

RK Redlich - Kwong

sat saturated

SRK Soave - Redlich - Kwong

vap vapor

vdW van der Waals

VLE vapor liquid equilibria

Symbols

∇ divergence

APPENDIX B. SAS PROGRAM FOR THE CALCULATION OF GLOBAL FIT

```
TITLE 'GLOBAL FIT RESULTS';
DATA compress;
INPUT T P Rho Z;
w=1/z**0.5;

CARDS;
(HERE ALL OBSERVED PRESSURE, DENSITY, COMPRESSIBILITY FACTOR VALUES)

PROC NLIN NOITPRINT  METHOD=marquardt HOUGAARD CONVERGE=1E-6
MAXITER=25000; _weight_=(w);

A=k1+(k2/T)+(k3/T**3)+k27*exp(-0.5*((T-150.7)/k4)**2);

B=k5*exp(-0.5*(abs(T-k6)/k7)**2)+ k8*exp(-0.5*((T-
k9)/k10)**2)+k11*T**k12/(k13**k12+T**k12)+k14/(1+((T-150.7)/k15)**2);

C=(k16/T)+(k17/T**2)+k18*exp(-0.5*((abs(T-k19)/k20)**2))+k26*exp(-
0.5*((T-150.7)/k21)**2);

G=k22+ k23/(1+((T-k24)/k25)**2);

MODEL Z=(1+A*Rho+C*Rho**2)/((1-B*Rho)*(1+(G*B**3)*Rho)**2);

PARMS
k1   =      0.000016
k2   =     -0.0109
k3   =     -97.8036
k4   =     -1.3023
k5   =      0.000011
k6   =      161.6
k7   =     -15.24
k8   =      0.000025
k9   =      132.3
k10  =     -46.46
k11  =      0.000027
k12  =      28.6872
k13  =      214.7
k14  =      8.14E-6
k15  =     -0.7027
k16  =      1.029E-7
k17  =      0.000040
k18  =     -545E-12
k20  =      13.1124
k19  =      155.0
k21  =      1.1798
k22  =      4.8135E8
k23  =      3.6842E9
k24  =      194.4
k25  =      7.1999
```

```
k26  =      -545e-12
k27  =      0.000032;

OUTPUT OUT=out2 PREDICTED=Zp RESIDUAL=Zr ;
DATA new;
SET out2;
perc=Zr*100/Z;

PROC PRINT;
VAR T P Rho Z Zp Zr perc ;

PROC PLOT;
PLOT Z*Rho='0' Zp*Rho='+'/OVERLAY;
RUN;
```

APPENDIX C. ISOTHERMAL FIT RESULTS

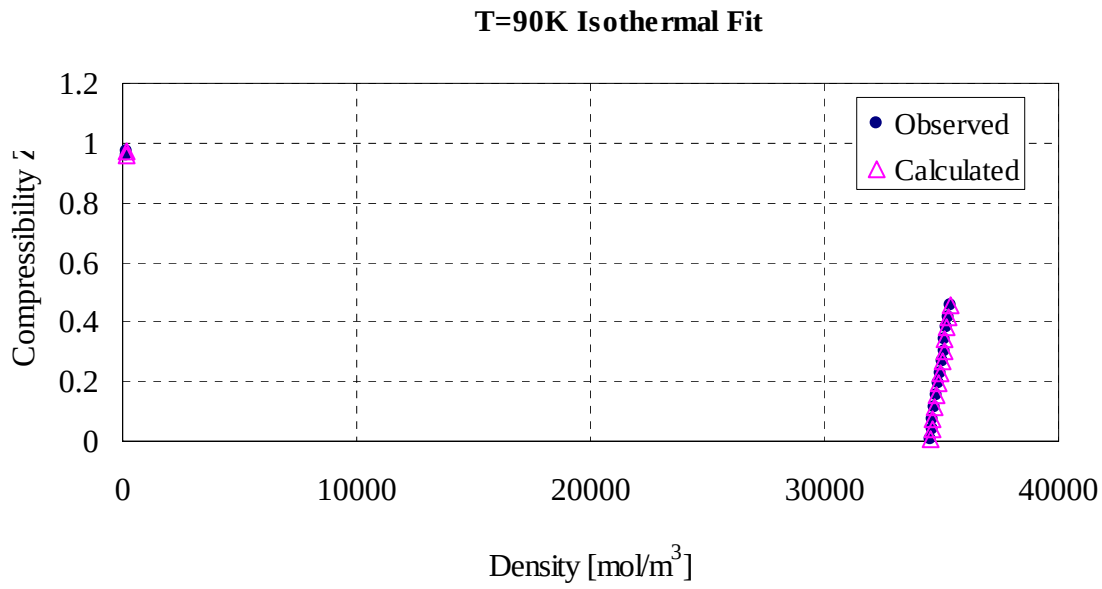

Figure C-1. Observed and calculated compressibility plots for 90K isotherm

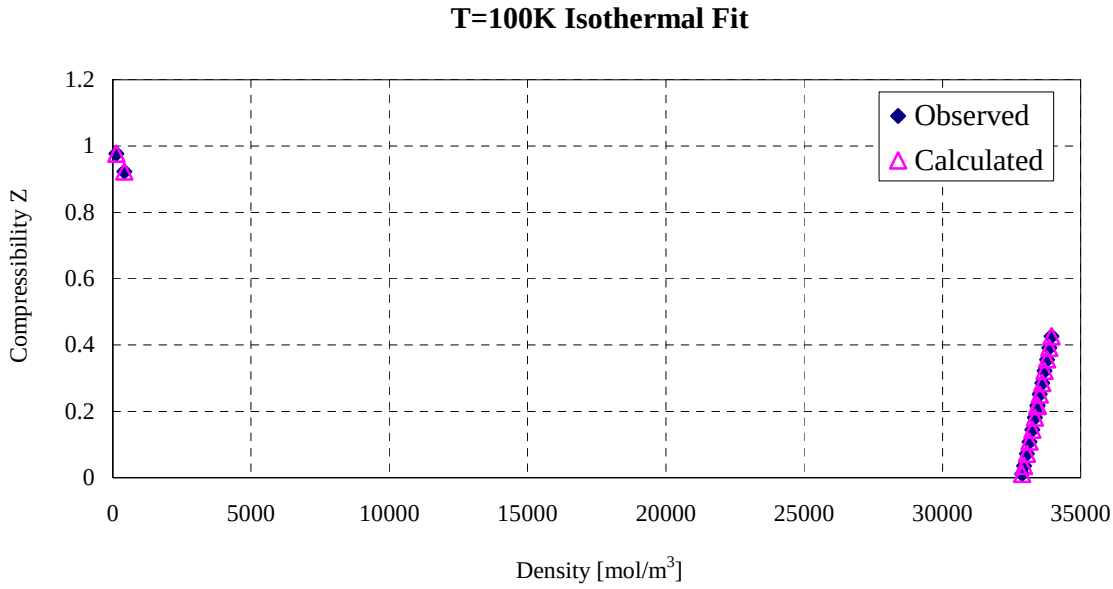

Figure C-2. Observed and calculated compressibility plots for 100K isotherm

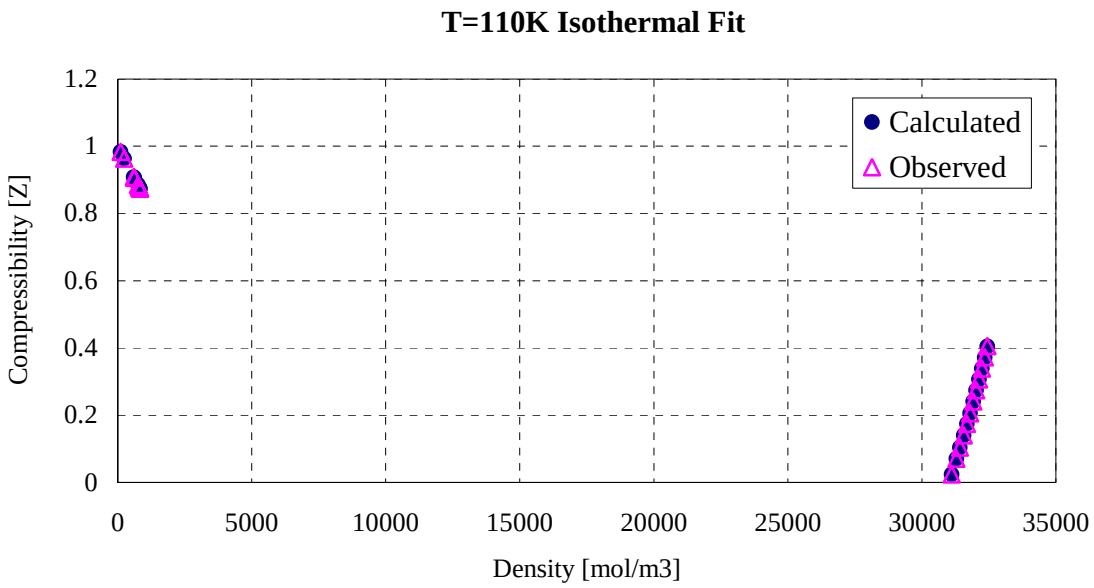

Figure C-3. Observed and calculated compressibility plots for 110K isotherm

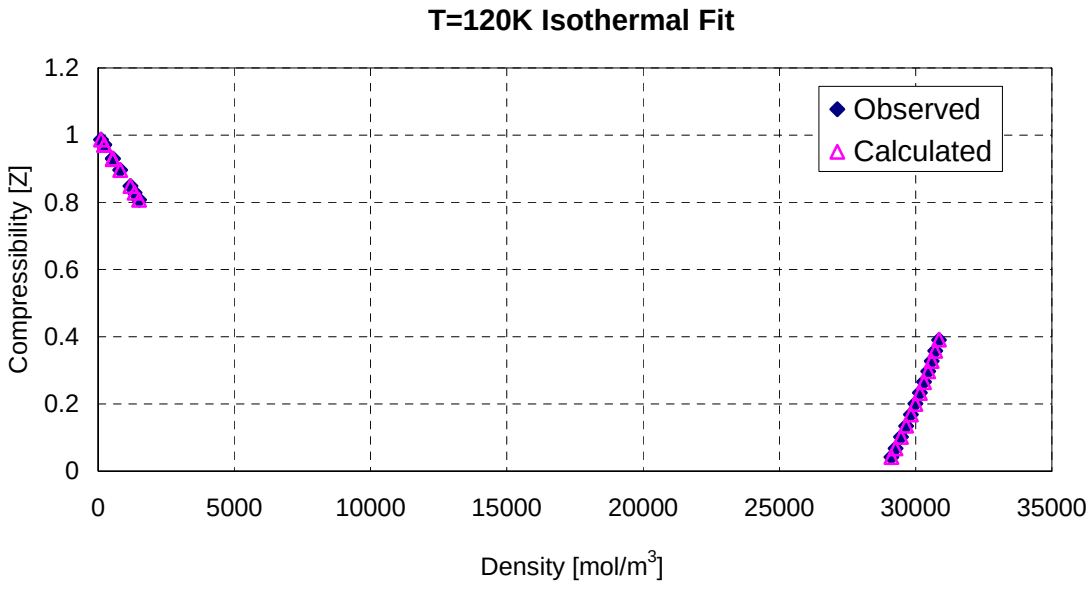

Figure C-4. Observed and calculated compressibility plots for 120K isotherm

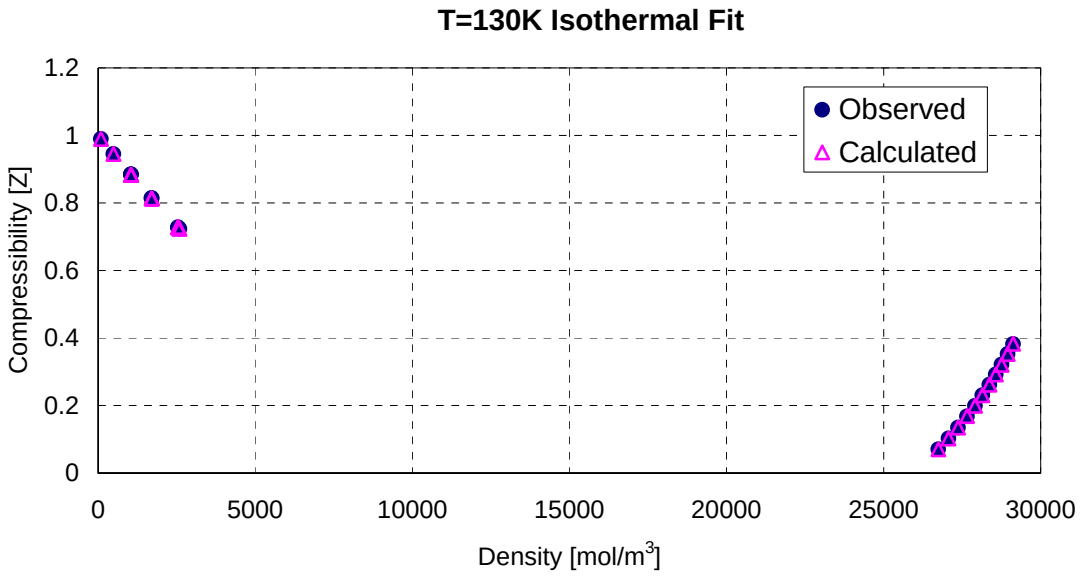

Figure C-5. Observed and calculated compressibility plots for 130K isotherm

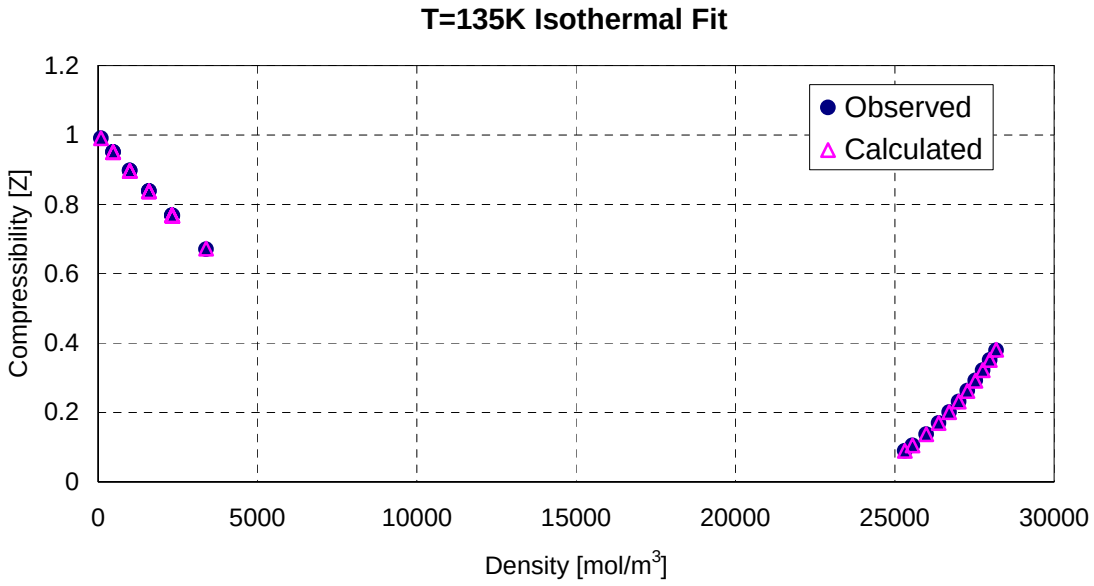

Figure C-6. Observed and calculated compressibility plots for 135K isotherm

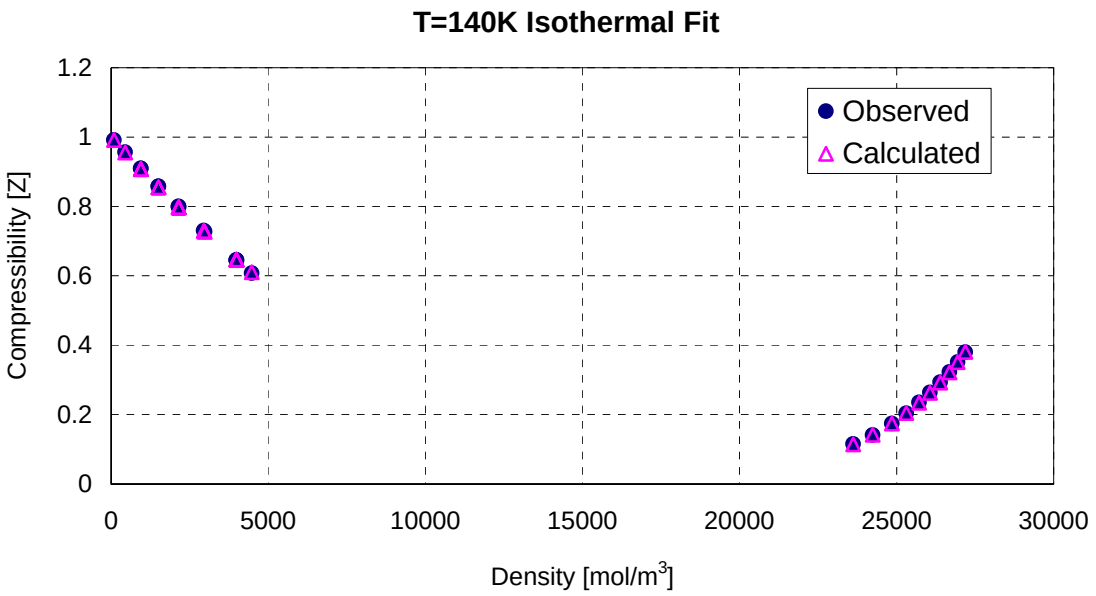

Figure C-7. Observed and calculated compressibility plots for 140K isotherm

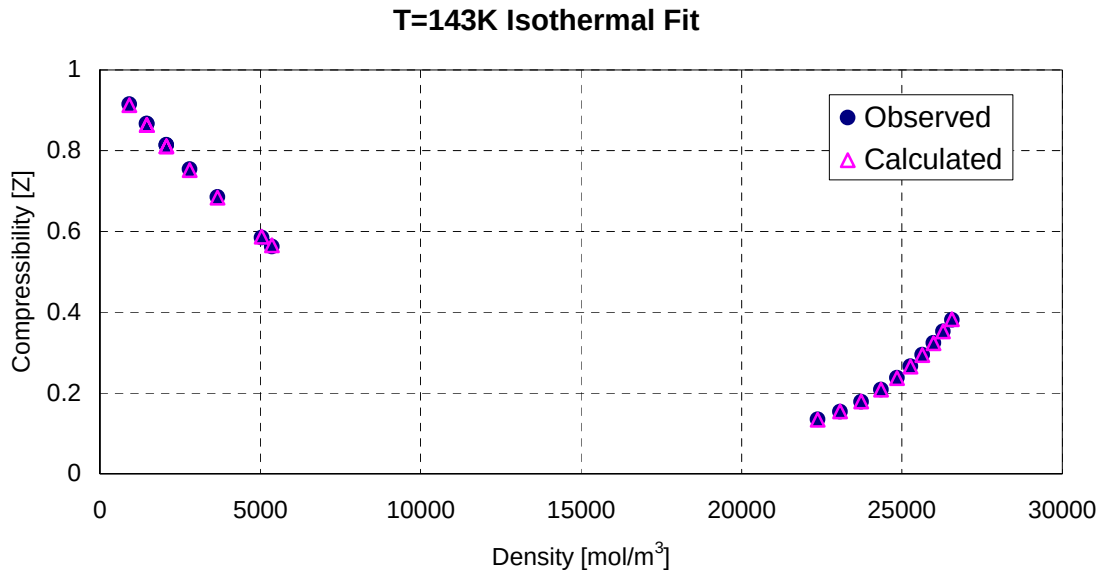

Figure C-8. Observed and calculated compressibility plots for 143K isotherm

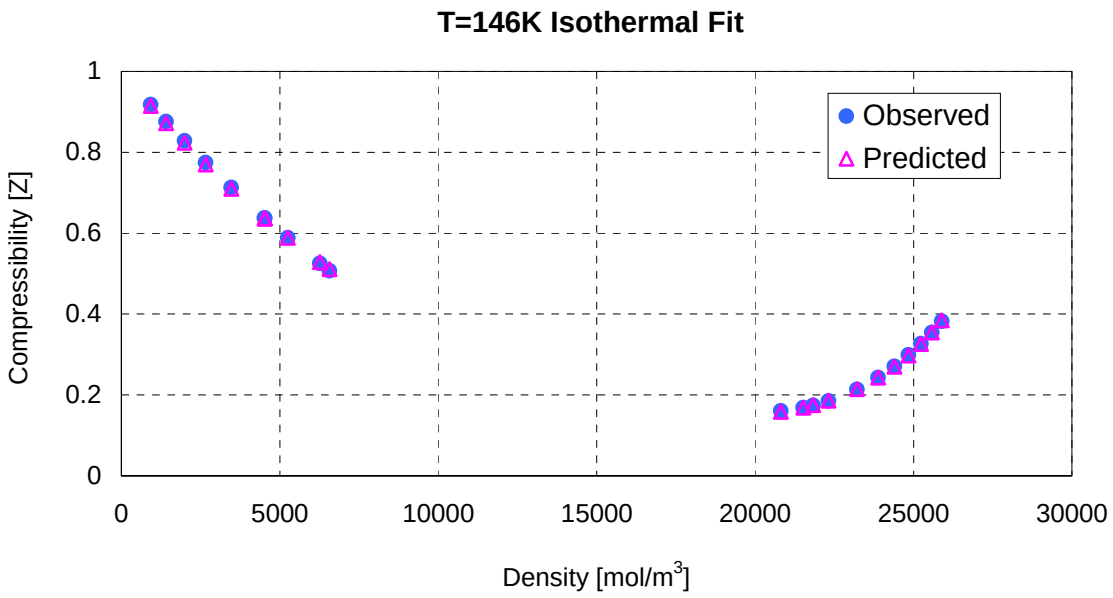

Figure C-9. Observed and calculated compressibility plots for 146K isotherm

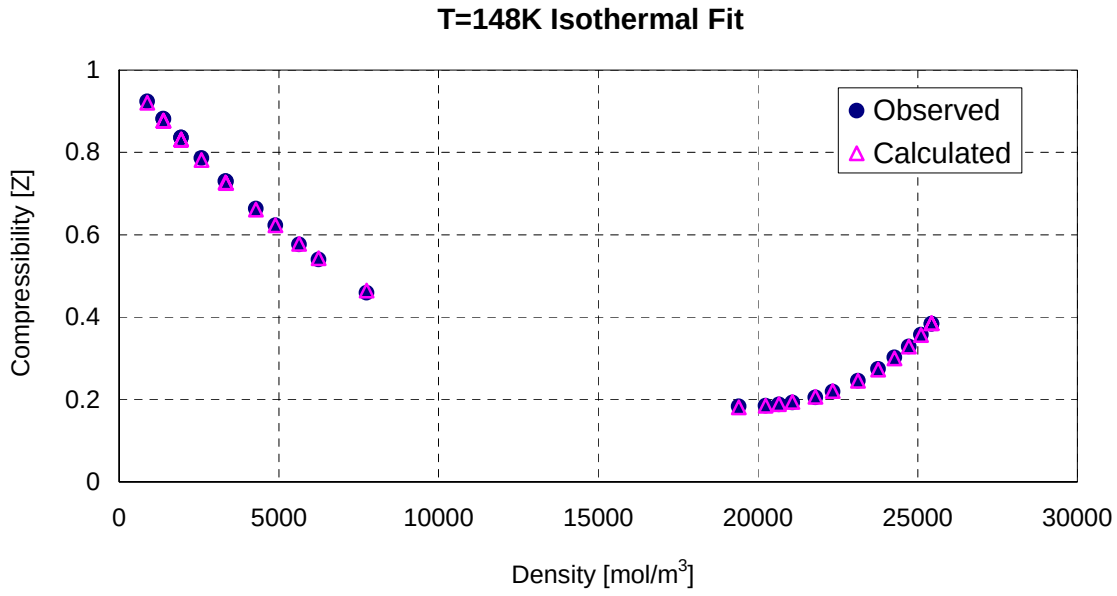

Figure C-10. Observed and calculated compressibility plots for 148K isotherm

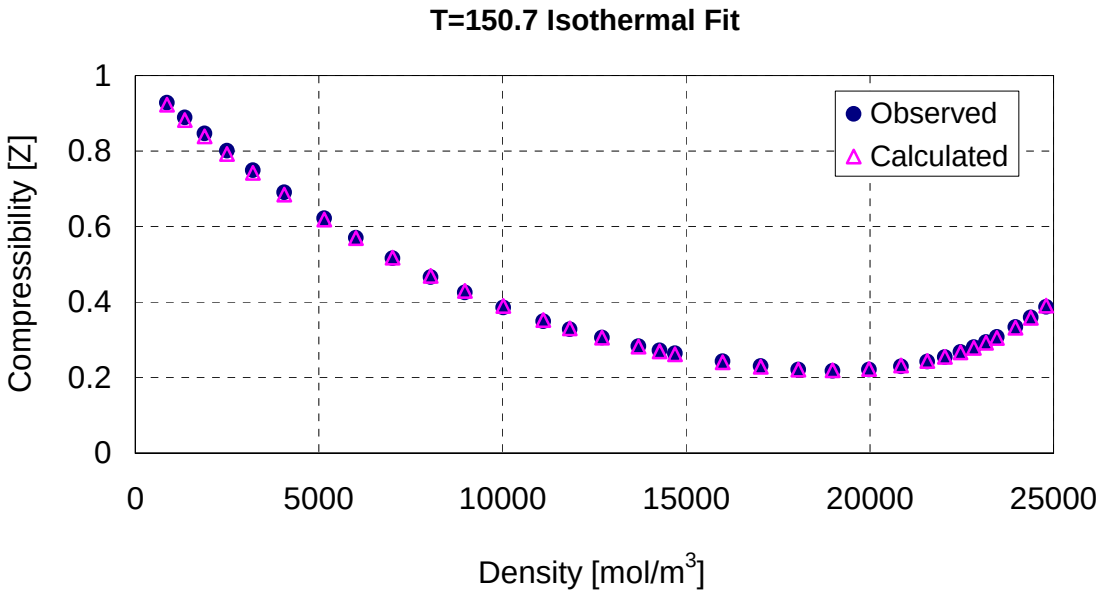

Figure C-11. Observed and calculated compressibility plots for 150.7K isotherm

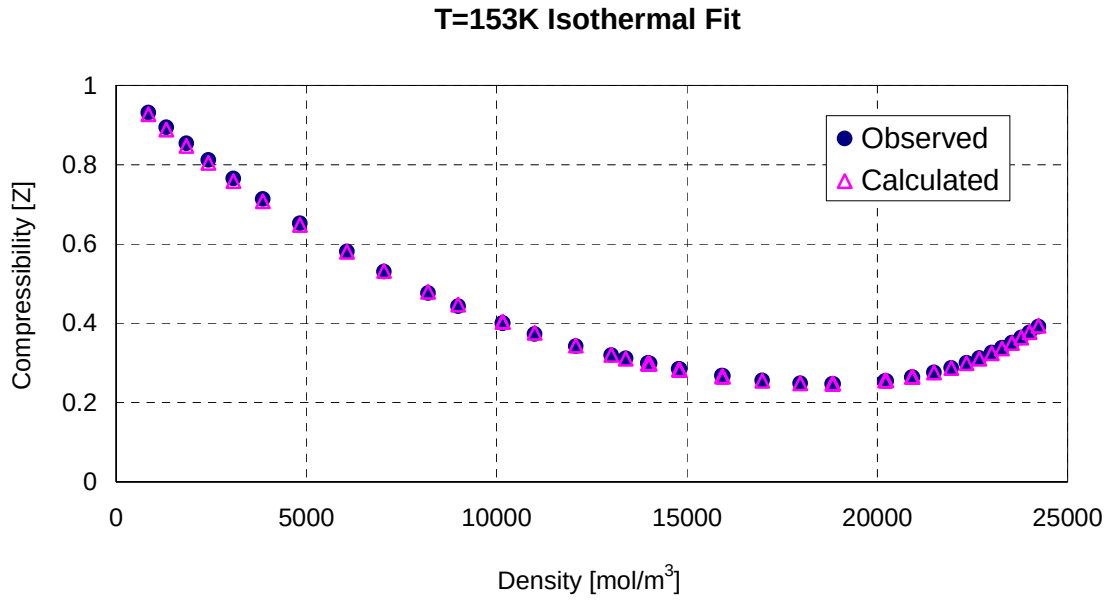

Figure C-12. Observed and calculated compressibility plots for 153K isotherm

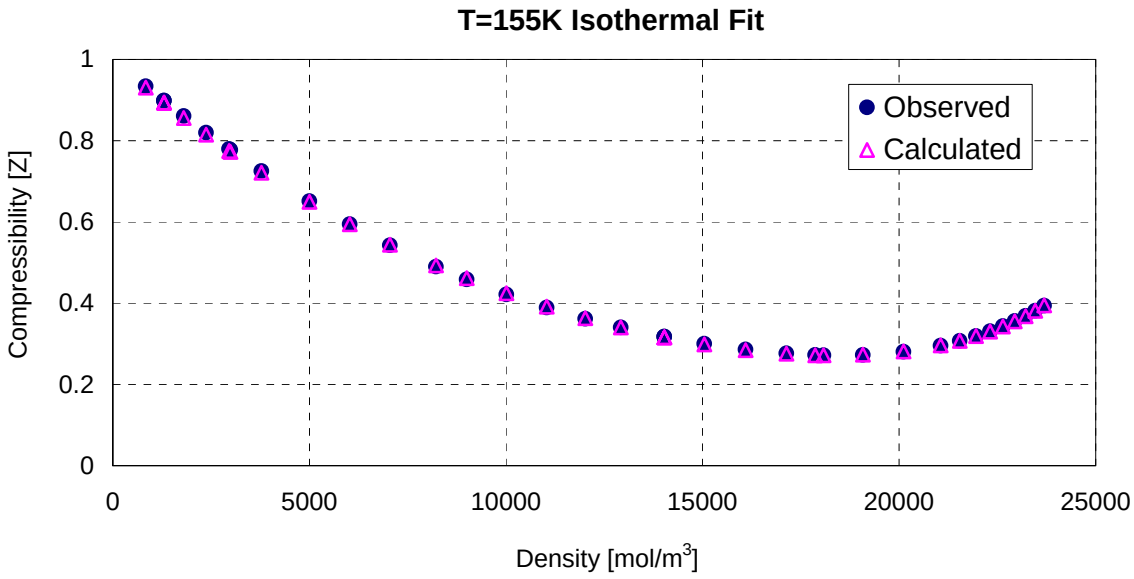

Figure C-13. Observed and calculated compressibility plots for 155K isotherm

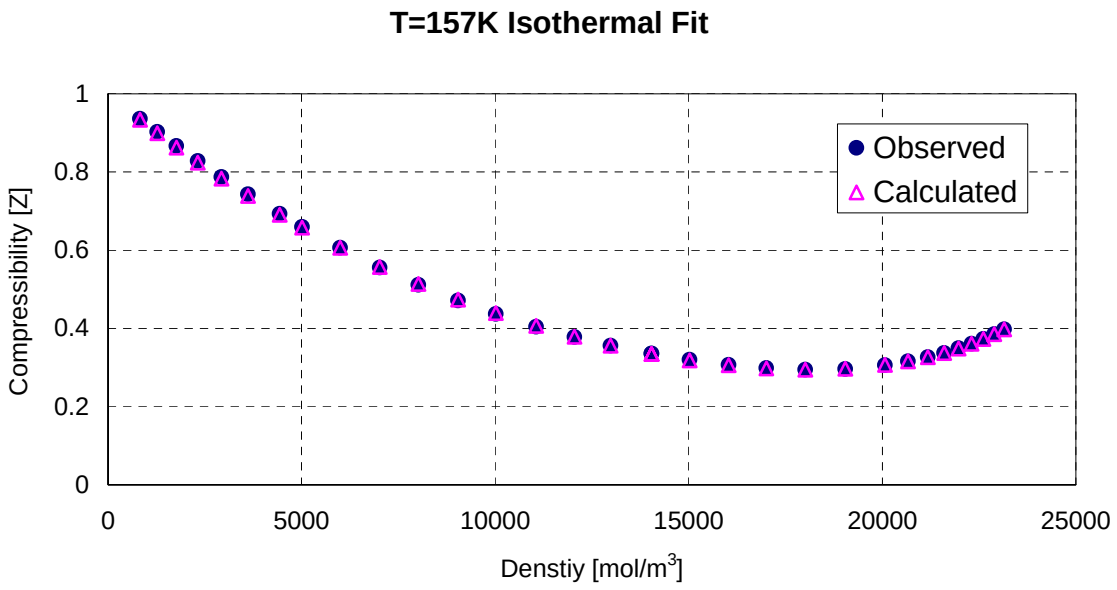

Figure C-14. Observed and calculated compressibility plots for 157K isotherm

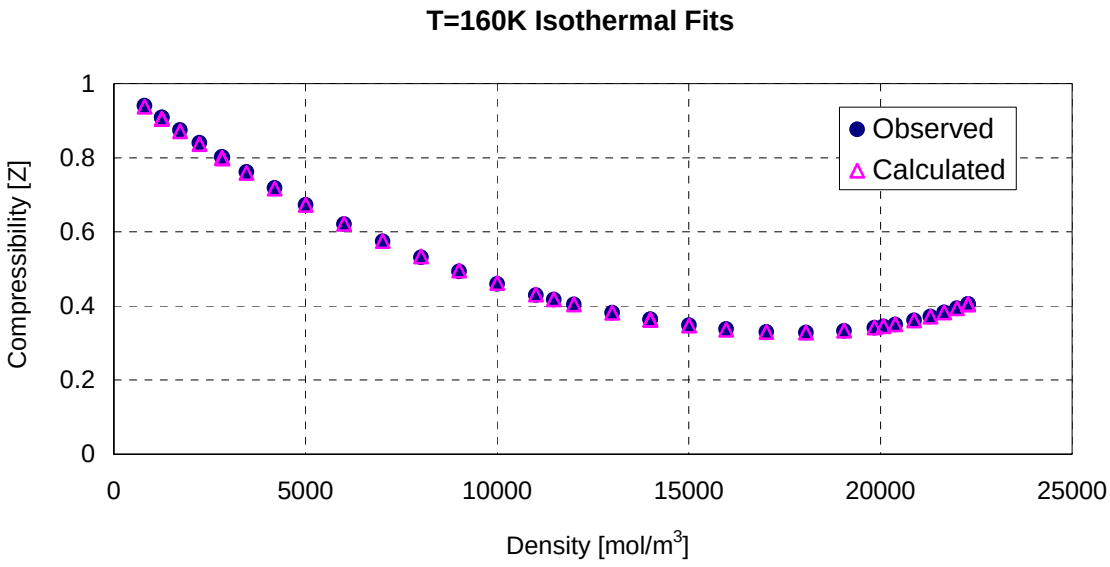

Figure C-15. Observed and calculated compressibility plots for 160K isotherm

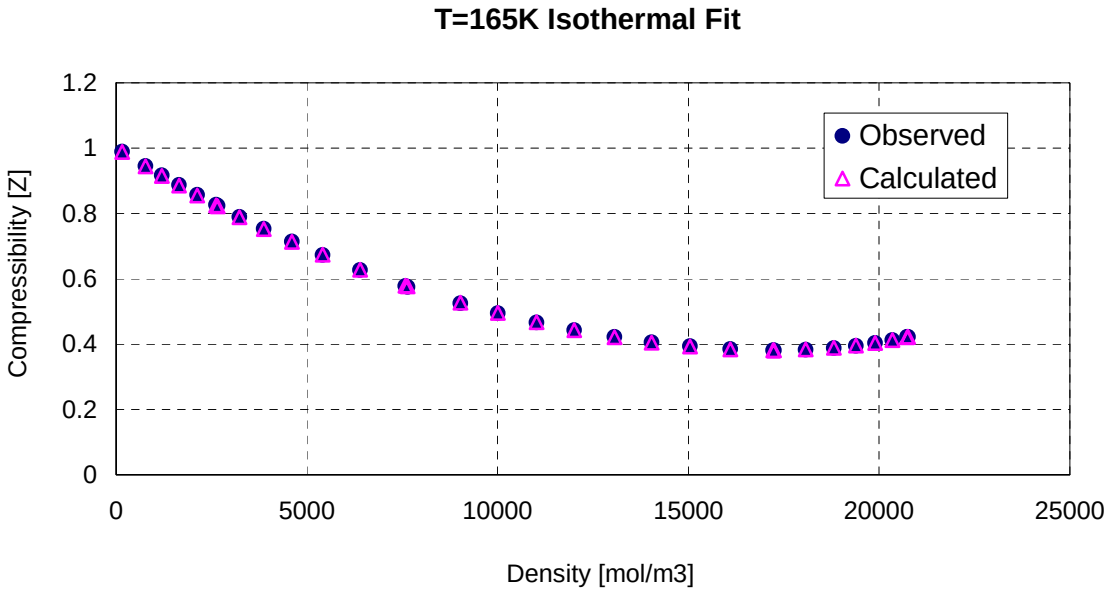

Figure C-16. Observed and calculated compressibility plots for 165K isotherm

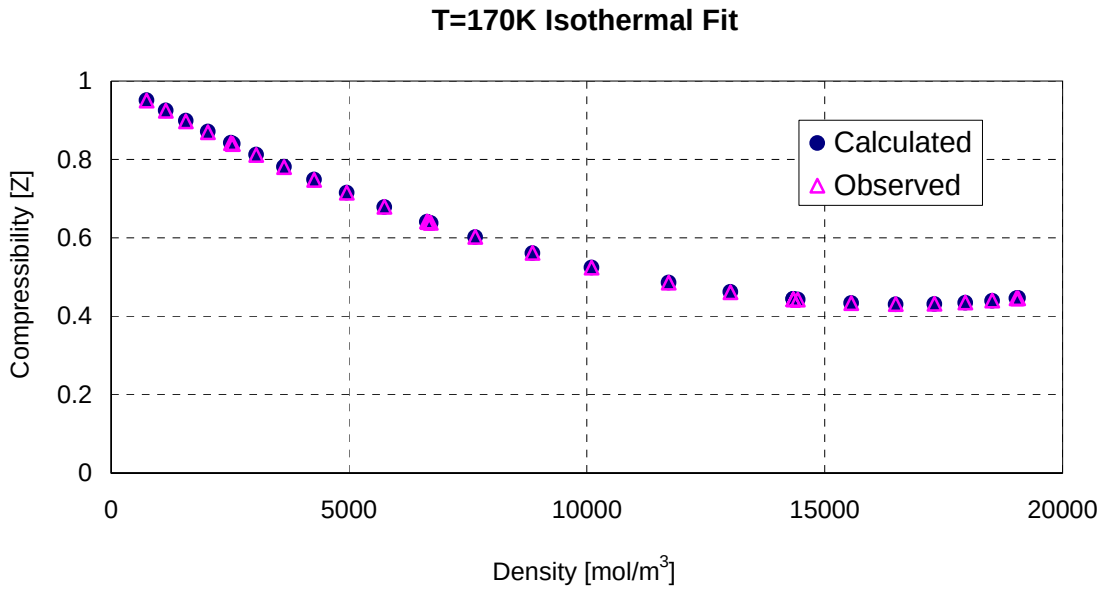

Figure C-17. Observed and calculated compressibility plots for 170K isotherm

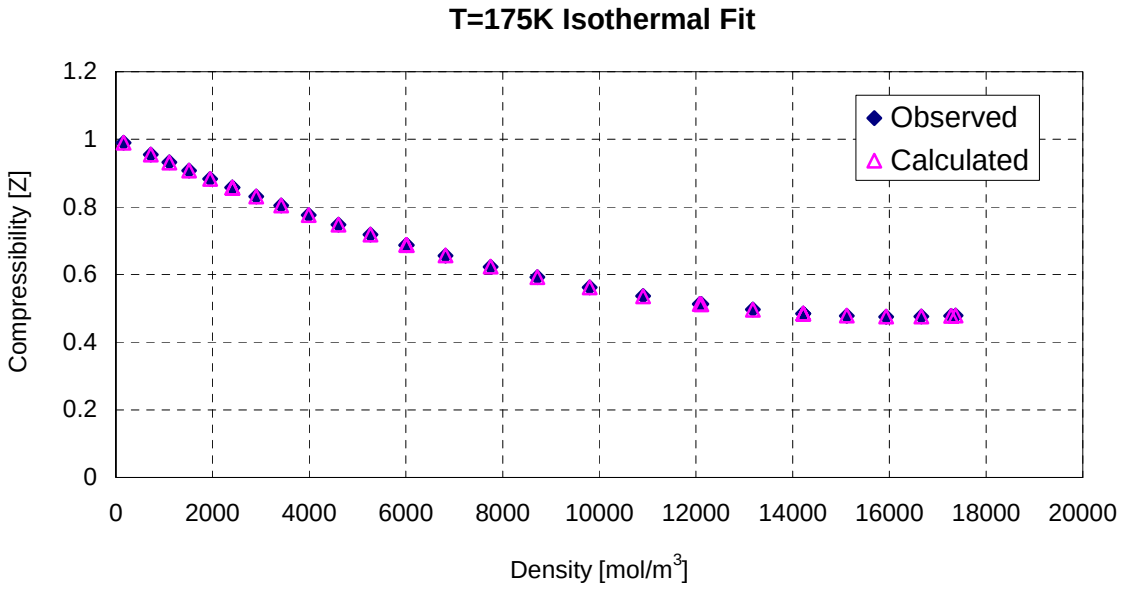

Figure C-18. Observed and calculated compressibility plots for 175K isotherm

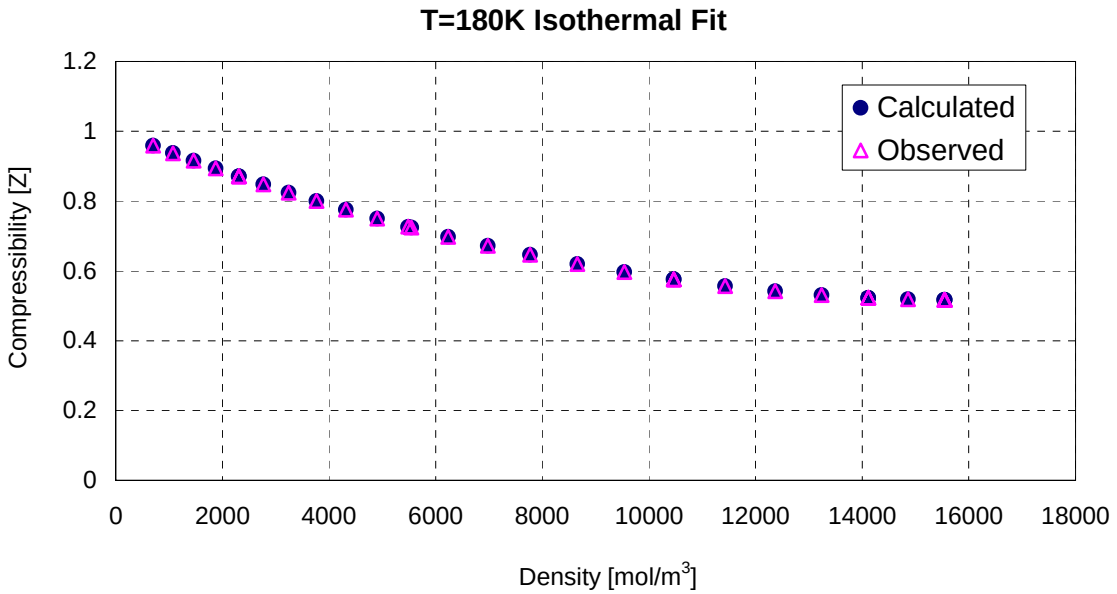

Figure C-19. Observed and calculated compressibility plots for 180K isotherm

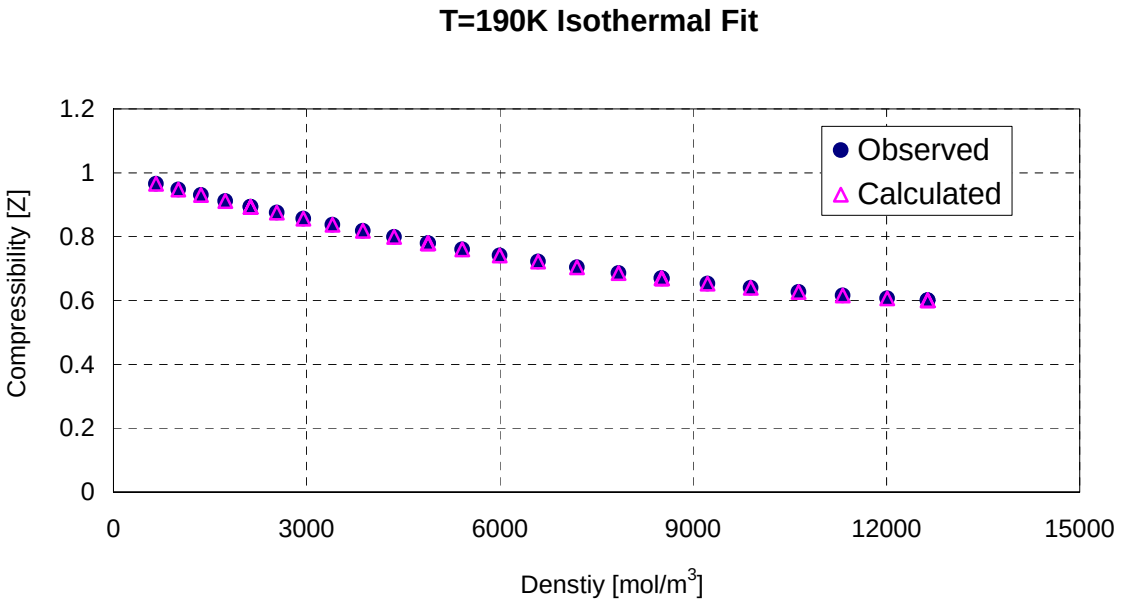

Figure C-20. Observed and calculated compressibility plots for 190K isotherm

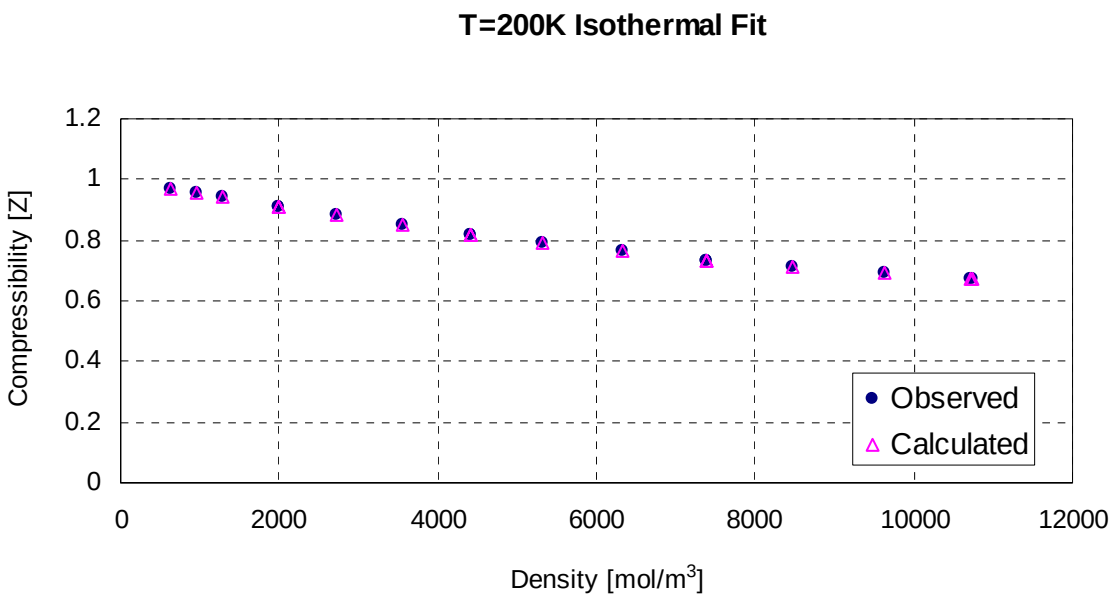

Figure C-21. Observed and calculated compressibility plots for 200K isotherm

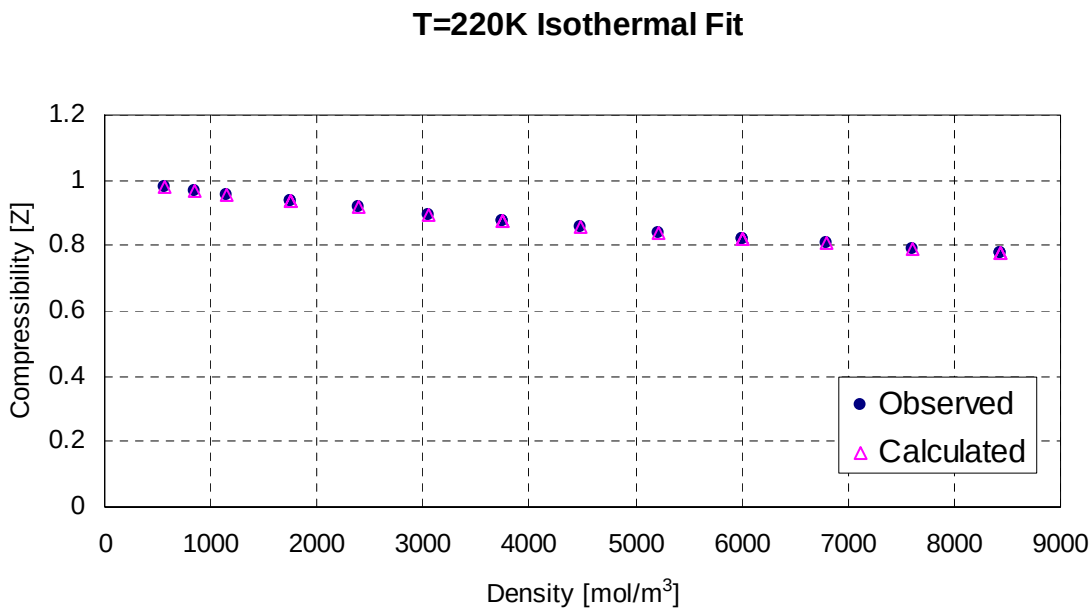

Figure C-22. Observed and calculated compressibility plots for 220K isotherm

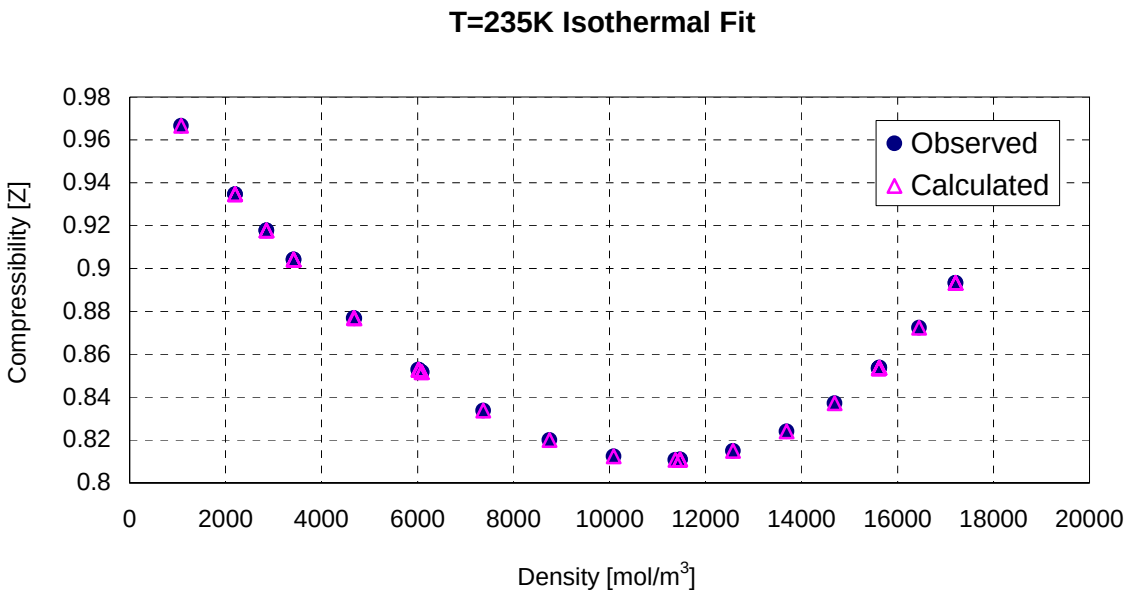

Figure C-23. Observed and calculated compressibility plots for 235K isotherm

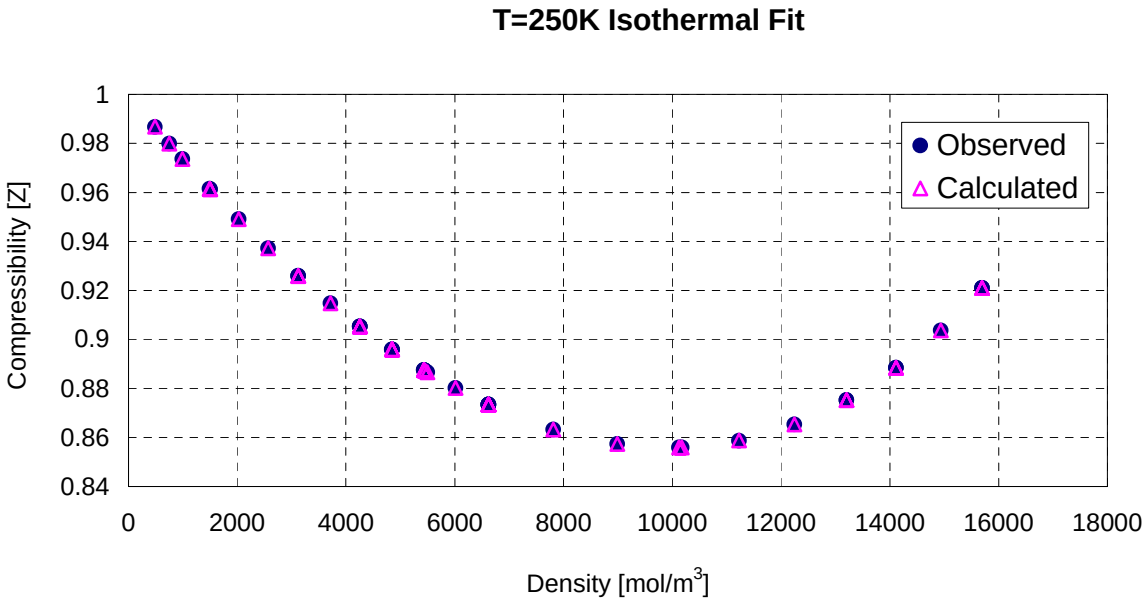

Figure C-24. Observed and calculated compressibility plots for 250K isotherm

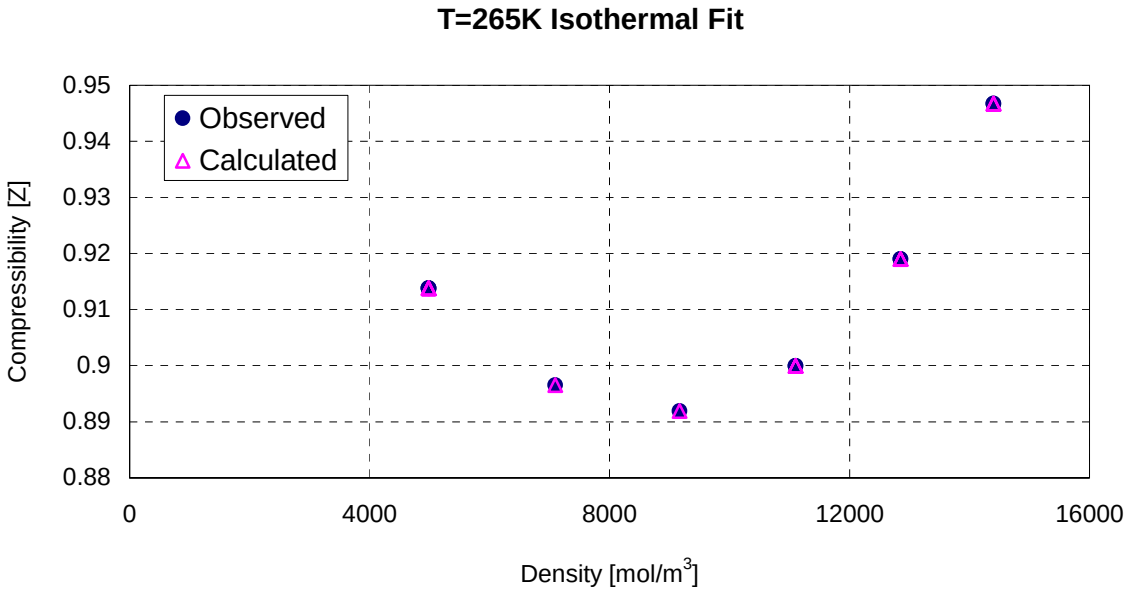

Figure C-25. Observed and calculated compressibility plots for 265K isotherm

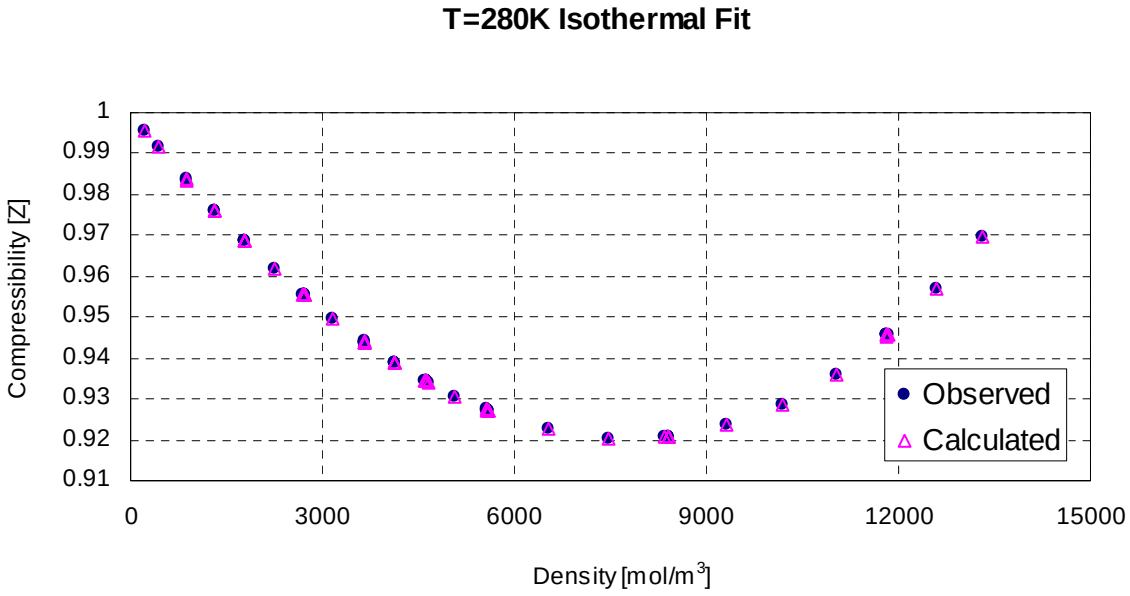

Figure C-26. Observed and calculated compressibility plots for 280K isotherm

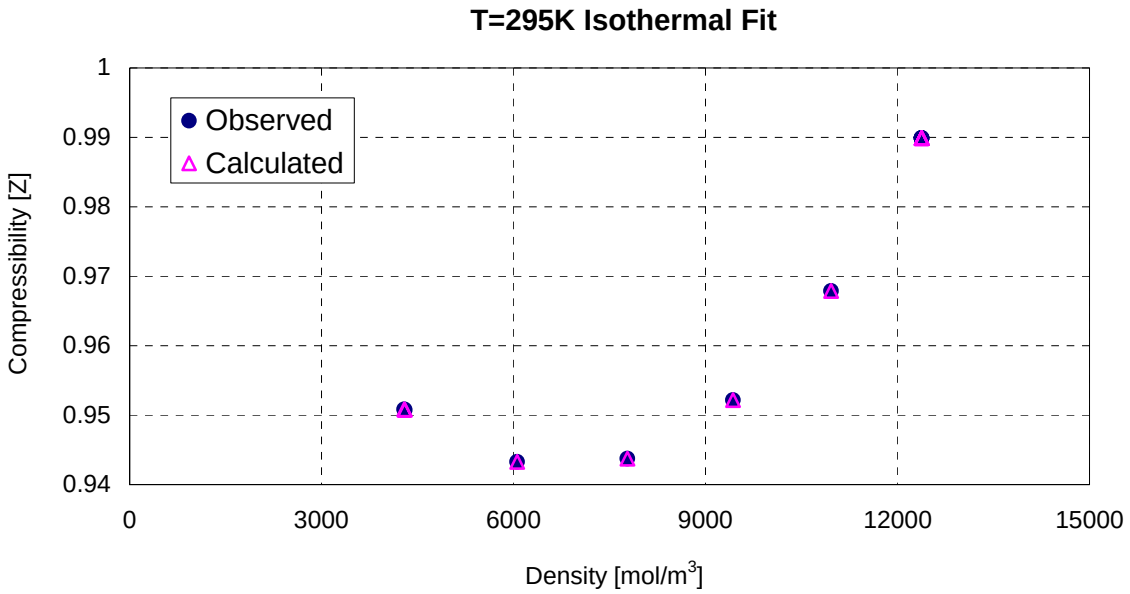

Figure C-27. Observed and calculated compressibility plots for 295K isotherm

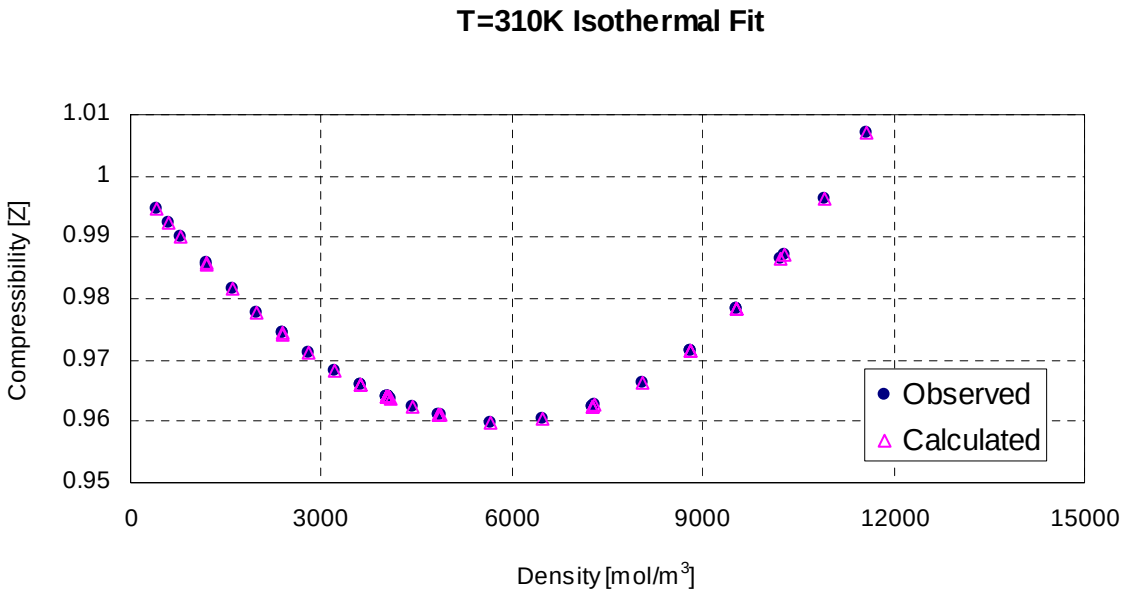

Figure C-28. Observed and calculated compressibility plots for 310K isotherm

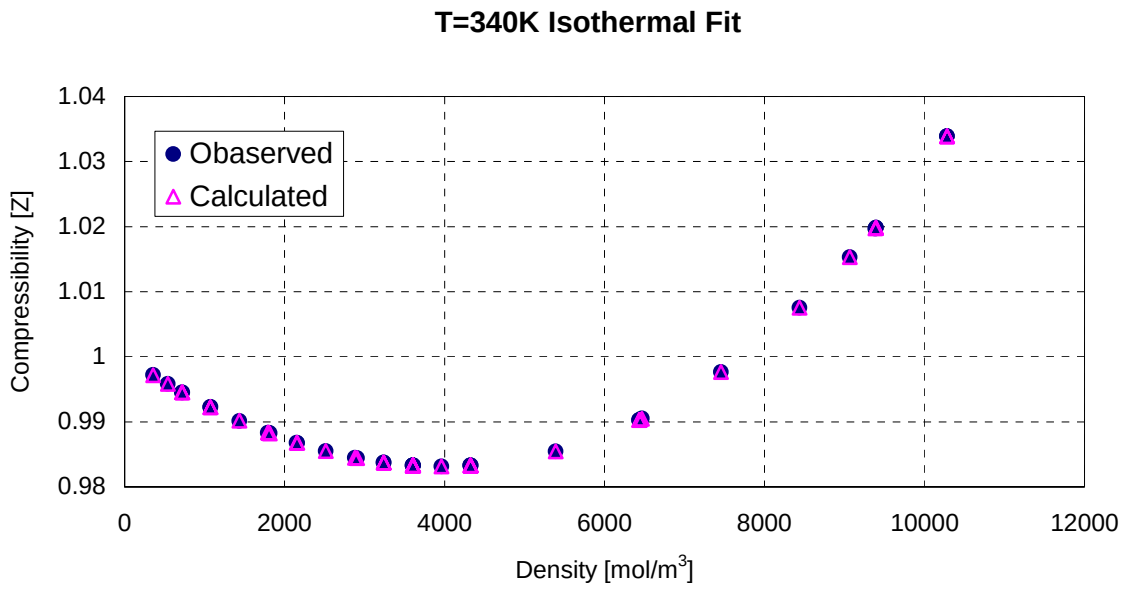

Figure C-29. Observed and calculated compressibility plots for 340K isotherm

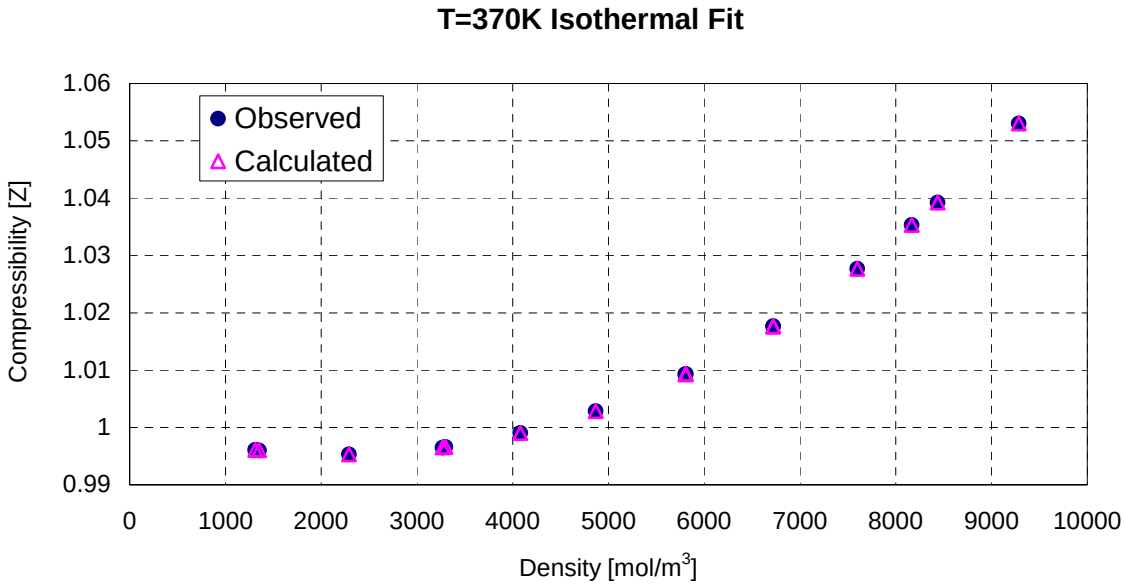

Figure C-30. Observed and calculated compressibility plots for 370K isotherm

APPENDIX D. GLOBAL FIT RESULTS

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
100	0.3238	421.98	0.92283	0.91996	0.002866679	0.31064
100	0.1000	123.04	0.97750	0.97652	0.000981790	0.10044
100	0.9728	32951.84	0.03551	0.03581	-.000302982	-0.85323
100	1.9840	33053.97	0.07219	0.07218	0.000005677	0.00786
100	2.9911	33152.60	0.10851	0.10811	0.000395762	0.36472
100	3.9996	33248.97	0.14468	0.14401	0.000671069	0.46383
100	5.0266	33344.85	0.18130	0.18051	0.000792675	0.43722
100	6.0014	33433.46	0.21589	0.21496	0.000929429	0.43051
100	6.0581	33439.97	0.21789	0.21752	0.000371279	0.17040
100	7.0083	33523.33	0.25144	0.25062	0.000817321	0.32506
100	7.9833	33608.19	0.28570	0.28498	0.000718337	0.25143
100	9.0329	33698.56	0.32239	0.32232	0.000071748	0.02225
100	10.0102	33780.41	0.35640	0.35682	-.000419935	-0.11783
100	11.0221	33863.52	0.39147	0.39253	-.001057798	-0.27021
100	12.0285	33944.13	0.42620	0.42783	-.001628348	-0.38206
110	0.2113	239.73	0.96348	0.96232	0.001158451	0.12024
110	0.5105	616.04	0.90613	0.90401	0.002120808	0.23405
110	0.6085	751.33	0.88549	0.88329	0.002198214	0.24825
110	0.6369	791.93	0.87933	0.87710	0.002230048	0.25361
110	0.6530	815.24	0.87576	0.87355	0.002210127	0.25237
110	0.6653	833.20	0.87300	0.87082	0.002181828	0.24992
110	0.1000	111.23	0.98295	0.98247	0.000484386	0.04928
110	0.5000	602.03	0.90807	0.90616	0.001908640	0.21019
110	2.0022	31294.93	0.06995	0.06980	0.000145473	0.20797
110	2.9826	31425.10	0.10377	0.10315	0.000616551	0.59415
110	4.0388	31560.78	0.13992	0.13905	0.000867988	0.62035
110	5.0454	31685.19	0.17411	0.17303	0.001081098	0.62093
110	5.9881	31798.09	0.20590	0.20477	0.001131269	0.54943
110	7.0340	31919.50	0.24094	0.23990	0.001041739	0.43236
110	8.0374	32032.14	0.27435	0.27345	0.000902156	0.32883
110	9.0029	32138.03	0.30629	0.30585	0.000439246	0.14341
110	10.0001	32243.92	0.33910	0.33912	-.000020349	-0.00600
110	10.9928	32347.30	0.37157	0.37247	-.000896124	-0.24117
110	12.0127	32450.19	0.40476	0.40652	-.001763529	-0.43570
120	0.2112	217.85	0.97168	0.97105	0.000632213	0.06506
120	0.2152	222.10	0.97117	0.97049	0.000683255	0.07035
120	0.5052	544.77	0.92941	0.92820	0.001210005	0.13019
120	0.7192	804.35	0.89621	0.89469	0.001524971	0.17016
120	1.1057	1337.38	0.82866	0.82726	0.001401815	0.16917
120	1.2130	1505.49	0.80757	0.80638	0.001192899	0.14771
120	0.1000	101.57	0.98673	0.98646	0.000269095	0.02727
120	0.5000	538.80	0.93009	0.92898	0.001114554	0.11983
120	1.0000	1181.59	0.84824	0.84677	0.001467251	0.17298
120	1.9764	29267.30	0.06768	0.06836	-.000677838	-1.00153
120	2.9867	29466.06	0.10159	0.10195	-.000359066	-0.35345
120	3.9860	29650.30	0.13474	0.13464	0.000098339	0.07298
120	5.0168	29830.53	0.16856	0.16815	0.000411659	0.24422
120	6.0034	29994.49	0.20060	0.20001	0.000593258	0.29574
120	7.0105	30154.20	0.23301	0.23236	0.000648394	0.27827
120	8.0227	30307.90	0.26531	0.26479	0.000518697	0.19551
120	9.0429	30456.34	0.29758	0.29737	0.000208740	0.07015
120	10.0118	30591.52	0.32801	0.32816	-.000154611	-0.04714
120	10.9745	30721.44	0.35803	0.35882	-.000785170	-0.21930
120	12.0285	30859.12	0.39067	0.39247	-.001803329	-0.46160
130	1.0007	1046.78	0.88444	0.88322	0.001224847	0.13849
130	1.0013	1047.41	0.88442	0.88315	0.001273954	0.14404
130	1.5033	1708.73	0.81394	0.81290	0.001043289	0.12818
130	2.0073	2556.30	0.72646	0.72673	-.000273250	-0.03761
130	2.0254	2592.60	0.72277	0.72314	-.000368578	-0.05100

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
130	0.1000	93.50	0.98947	0.98928	0.000185966	0.01879
130	0.5000	489.34	0.94533	0.94454	0.000789032	0.08347
130	1.0000	1046.03	0.88445	0.88330	0.001154619	0.13055
130	1.5000	1704.09	0.81436	0.81338	0.000979341	0.12026
130	2.0000	2541.80	0.72796	0.72817	-.000210811	-0.02896
130	2.0254	26739.26	0.07008	0.07059	-.000512547	-0.73137
130	2.9859	27069.19	0.10205	0.10265	-.000601078	-0.58900
130	3.9803	27373.84	0.13452	0.13489	-.000366105	-0.27216
130	5.0291	27664.46	0.16818	0.16819	-.000010085	-0.00600
130	6.0108	27913.04	0.19923	0.19881	0.000423231	0.21243
130	7.0153	28148.59	0.23057	0.22977	0.000801843	0.34777
130	8.0292	28370.13	0.26184	0.26074	0.001103562	0.42146
130	9.0295	28575.15	0.29234	0.29110	0.001241204	0.42458
130	9.9811	28759.64	0.32108	0.31991	0.001170820	0.36465
130	11.0334	28952.89	0.35256	0.35169	0.000867695	0.24611
130	12.0292	29126.61	0.38209	0.38175	0.000341134	0.08928
135	0.5013	469.55	0.95107	0.95038	0.000687839	0.07232
135	1.0023	994.72	0.89769	0.89655	0.001136728	0.12663
135	1.5006	1594.91	0.83819	0.83714	0.001052315	0.12555
135	2.0013	2319.77	0.76859	0.76829	0.000300724	0.03913
135	2.0084	2331.35	0.76749	0.76721	0.000275303	0.03587
135	2.0096	2333.31	0.76731	0.76703	0.000276640	0.03605
135	2.5509	3389.63	0.67046	0.67229	-.001829669	-0.27290
135	0.1000	89.94	0.99056	0.99039	0.000174538	0.01762
135	0.5000	468.28	0.95124	0.95051	0.000726164	0.07634
135	1.0000	992.21	0.89789	0.89681	0.001084015	0.12073
135	1.5000	1594.32	0.83819	0.83720	0.000994913	0.11870
135	2.0000	2317.74	0.76877	0.76848	0.000292027	0.03799
135	2.5509	25319.16	0.08976	0.08949	0.000272006	0.30304
135	3.0097	25550.72	0.10494	0.10515	-.000209503	-0.19964
135	4.0055	25989.54	0.13731	0.13790	-.000586573	-0.42719
135	5.0204	26373.29	0.16959	0.17013	-.000544641	-0.32115
135	6.0333	26710.22	0.20124	0.20151	-.000270320	-0.13433
135	7.0257	27007.36	0.23176	0.23180	-.000037700	-0.01627
135	8.0399	27283.47	0.26253	0.26234	0.000186657	0.07110
135	9.0214	27530.79	0.29194	0.29184	0.000103093	0.03531
135	10.0294	27766.10	0.32180	0.32192	-.000121522	-0.03776
135	11.0364	27986.13	0.35133	0.35198	-.000648859	-0.18469
135	12.0063	28185.39	0.37950	0.38092	-.001423265	-0.37504
140	1.0006	945.43	0.90917	0.90779	0.001384431	0.15227
140	1.5007	1503.37	0.85754	0.85610	0.001442636	0.16823
140	1.9995	2147.93	0.79970	0.79881	0.000894103	0.11180
140	2.0044	2154.88	0.79909	0.79820	0.000887714	0.11109
140	2.5065	2946.18	0.73089	0.73132	-.000431848	-0.05909
140	2.5254	2979.97	0.72802	0.72855	-.000527336	-0.07243
140	2.9977	3986.13	0.64607	0.64891	-.002842160	-0.43992
140	3.0032	4000.18	0.64497	0.64784	-.002870636	-0.44508
140	3.1683	4477.05	0.60796	0.61209	-.004131643	-0.67959
140	0.1000	86.65	0.99150	0.99130	0.000200245	0.02020
140	0.5000	449.18	0.95627	0.95545	0.000823046	0.08607
140	1.0000	944.90	0.90918	0.90784	0.001344791	0.14791
140	1.5000	1502.70	0.85754	0.85616	0.001382347	0.16120
140	2.0000	2148.79	0.79960	0.79873	0.000869161	0.10870
140	3.0000	3991.94	0.64561	0.64847	-.002858905	-0.44282
140	3.1683	23622.21	0.11522	0.11394	0.001280073	1.11098
140	3.9822	24237.51	0.14115	0.14107	0.000075902	0.05377
140	5.0316	24847.00	0.17397	0.17409	-.000116590	-0.06702
140	6.0193	25312.91	0.20429	0.20411	0.000181617	0.08890
140	7.0292	25719.94	0.23479	0.23425	0.000543339	0.23141
140	7.9915	26061.13	0.26343	0.26269	0.000741031	0.28130
140	9.0140	26387.80	0.29346	0.29297	0.000490165	0.16703
140	10.0289	26681.44	0.32291	0.32302	-.000114380	-0.03542
140	11.0232	26946.03	0.35144	0.35266	-.001219325	-0.34695
140	12.0169	27191.35	0.37966	0.38252	-.002860988	-0.75357
143	1.0006	919.68	0.91509	0.91323	0.001859967	0.20326

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
143	1.5046	1459.44	0.86709	0.86496	0.002125843	0.24517
143	1.5053	1460.14	0.86705	0.86490	0.002147280	0.24765
143	2.0033	2068.48	0.81456	0.81276	0.001800973	0.22110
143	2.0080	2074.60	0.81405	0.81225	0.001803130	0.22150
143	2.5077	2796.74	0.75413	0.75335	0.000777603	0.10311
143	2.9904	3671.35	0.68506	0.68615	-.001093302	-0.15959
143	3.5058	5043.23	0.58466	0.58934	-.004683540	-0.80107
143	3.5877	5362.45	0.56270	0.56825	-.005552102	-0.98669
143	3.5877	22378.14	0.13484	0.13319	0.001648908	1.22286
143	4.2150	23075.00	0.15363	0.15343	0.000202763	0.13198
143	5.0223	23726.09	0.17803	0.17803	0.000001007	0.00057
143	6.0221	24345.75	0.20804	0.20752	0.000523052	0.25142
143	7.0151	24843.90	0.23749	0.23631	0.001176931	0.49557
143	8.0056	25266.85	0.26648	0.26494	0.001538592	0.57738
143	8.9932	25636.33	0.29504	0.29358	0.001462658	0.49575
143	10.0177	25979.02	0.32432	0.32360	0.000723764	0.22316
143	11.0087	26279.41	0.35233	0.35302	-.000687345	-0.19509
143	12.0427	26566.29	0.38126	0.38418	-.002918383	-0.76546
146	1.0321	926.34	0.91784	0.91524	0.002600166	0.28329
146	1.5043	1414.37	0.87616	0.87300	0.003163772	0.36110
146	2.0043	1993.97	0.82806	0.82488	0.003177997	0.38379
146	2.5063	2666.67	0.77424	0.77172	0.002516831	0.32507
146	3.0015	3467.36	0.71310	0.71203	0.001070119	0.15007
146	3.4982	4517.95	0.63783	0.63928	-.001450559	-0.22742
146	3.5027	4529.24	0.63706	0.63853	-.001471771	-0.23103
146	3.7545	5257.23	0.58830	0.59167	-.003373284	-0.57340
146	3.9956	6262.72	0.52557	0.53141	-.005843545	-1.11185
146	4.0477	6573.85	0.50722	0.51377	-.006554769	-1.29229
146	4.0477	20812.58	0.16021	0.15826	0.001950673	1.21757
146	4.4023	21521.70	0.16850	0.16846	0.000042485	0.02521
146	4.6125	21836.59	0.17400	0.17446	-.000455276	-0.26165
146	5.0112	22322.22	0.18493	0.18569	-.000760606	-0.41129
146	6.0188	23219.51	0.21353	0.21377	-.000236972	-0.11098
146	7.0443	23887.00	0.24293	0.24210	0.000832731	0.34279
146	8.0192	24399.87	0.27074	0.26918	0.001555419	0.57451
146	9.0081	24841.59	0.29872	0.29695	0.001766315	0.59129
146	10.0215	25236.81	0.32712	0.32590	0.001222046	0.37358
146	11.0061	25579.50	0.35445	0.35465	-.000196003	-0.05530
146	12.0136	25896.92	0.38215	0.38477	-.002619705	-0.68552
148	1.0018	881.19	0.92383	0.92082	0.003007573	0.32555
148	1.5027	1384.80	0.88183	0.87804	0.003788928	0.42967
148	1.5070	1389.29	0.88147	0.87767	0.003803056	0.43144
148	2.0028	1945.83	0.83642	0.83239	0.004029194	0.48172
148	2.0029	1946.05	0.83640	0.83237	0.004026913	0.48146
148	2.5023	2585.64	0.78645	0.78281	0.003644174	0.46337
148	2.9958	3331.81	0.73070	0.72815	0.002549623	0.34893
148	3.0076	3351.38	0.72928	0.72676	0.002519053	0.34542
148	3.5000	4287.77	0.66335	0.66285	0.000503399	0.07589
148	3.7509	4890.46	0.62329	0.62426	-.000968818	-0.15544
148	3.9974	5636.68	0.57631	0.57911	-.002800611	-0.48596
148	4.1511	6244.59	0.54020	0.54439	-.004194303	-0.77644
148	4.3797	7749.32	0.45928	0.46600	-.006723338	-1.46389
148	4.6120	20242.37	0.18515	0.18473	0.000424513	0.22928
148	4.7856	20661.08	0.18823	0.18875	-.000515925	-0.27409
148	5.0091	21084.56	0.19306	0.19423	-.001170122	-0.60609
148	5.5114	21798.56	0.20547	0.20709	-.001620269	-0.78857
148	6.0254	22346.78	0.21912	0.22048	-.001360976	-0.62111
148	6.9985	23133.82	0.24584	0.24610	-.000255352	-0.10387
148	8.0146	23764.32	0.27407	0.27320	0.000872019	0.31817
148	9.0209	24276.66	0.30197	0.30052	0.001448942	0.47983
148	10.0107	24723.64	0.32904	0.32904	0.000003581	0.00109
148	11.0319	25100.63	0.35716	0.35710	0.000056259	0.01575
148	12.0130	25437.32	0.38378	0.38581	-.002031053	-0.52922
148	12.0193	25439.32	0.38395	0.38599	-.002043176	-0.53215
150.7	1.0034	862.97	0.92792	0.92468	0.003243591	0.34955

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
150.7	1.5028	1349.66	0.88866	0.88451	0.004152302	0.46725
150.7	2.0059	1891.70	0.84626	0.84164	0.004624283	0.54644
150.7	2.5042	2496.41	0.80057	0.79603	0.004541515	0.56729
150.7	3.0086	3204.54	0.74929	0.74546	0.003829230	0.51105
150.7	3.5101	4054.47	0.69094	0.68860	0.002339923	0.33866
150.7	4.0041	5140.43	0.62166	0.62166	-.000003835	-0.00062
150.7	4.2954	6006.53	0.57073	0.57259	-.001864426	-0.32667
150.7	4.5376	7011.62	0.51649	0.52016	-.003672384	-0.71103
150.7	4.6991	8041.95	0.46634	0.47117	-.004832324	-1.03622
150.7	4.7872	8977.30	0.42558	0.43067	-.005085865	-1.19504
150.7	4.8386	10016.25	0.38554	0.38991	-.004368689	-1.13314
150.7	4.8599	11108.49	0.34915	0.35170	-.002551494	-0.73077
150.7	4.8641	11827.75	0.32821	0.32908	-.000868440	-0.26460
150.7	4.8653	12709.47	0.30551	0.30406	0.001449447	0.47444
150.7	4.8656	13701.81	0.28340	0.27948	0.003921739	1.38382
150.7	4.8657	14272.30	0.27208	0.26888	0.005004075	-1.17612
150.7	4.8661	14692.98	0.26431	0.26175	0.005557342	-0.96742
150.7	4.8766	15987.58	0.24344	0.24065	0.005787048	-1.14484
150.7	4.9143	17025.03	0.23037	0.22793	0.004433243	-1.05613
150.7	5.0116	18052.67	0.22156	0.21932	0.002237260	1.00978
150.7	5.1890	18980.90	0.21818	0.21812	0.000062064	0.02845
150.7	5.5287	19980.95	0.22083	0.22264	-.001810442	-0.81984
150.7	5.9991	20845.70	0.22968	0.23226	-.002584307	-1.12518
150.7	6.5514	21559.90	0.24251	0.24497	-.002457211	-1.01324
150.7	7.0248	22039.70	0.25438	0.25633	-.001950368	-0.76671
150.7	7.5317	22470.89	0.26750	0.26877	-.001270867	-0.47509
150.7	8.0230	22832.48	0.28044	0.28103	-.000593879	-0.21177
150.7	8.5347	23165.29	0.29404	0.29397	0.000069873	0.02376
150.7	9.0352	23458.02	0.30739	0.30680	0.000591925	0.19256
150.7	10.0305	23968.06	0.33399	0.33283	0.001159978	0.34731
150.7	10.9683	24383.45	0.35900	0.35803	0.000972228	0.27082
150.7	12.0272	24797.06	0.38709	0.38734	-.000251540	-0.06498
153	1.0011	844.90	0.93143	0.92837	0.003063549	0.32891
153	1.5039	1322.30	0.89406	0.89005	0.004014765	0.44905
153	2.0053	1845.20	0.85431	0.84977	0.004538650	0.53127
153	2.5042	2425.31	0.81165	0.80709	0.004562861	0.56217
153	3.0019	3084.08	0.76514	0.76105	0.004089148	0.53443
153	3.4978	3854.59	0.71333	0.71034	0.002994358	0.41977
153	4.0053	4829.35	0.65195	0.65074	0.001205065	0.18484
153	4.4818	6063.81	0.58101	0.58214	-.001128392	-0.19421
153	4.7499	7041.15	0.53028	0.53292	-.002635465	-0.49700
153	4.9696	8202.41	0.47627	0.47993	-.003661021	-0.76869
153	5.0716	8990.69	0.44343	0.44721	-.003782431	-0.85299
153	5.1727	10157.08	0.40033	0.40342	-.003091195	-0.77216
153	5.1727	10157.15	0.40033	0.40342	-.003088549	-0.77150
153	5.2206	10999.95	0.37308	0.37511	-.002031317	-0.54447
153	5.2643	12083.23	0.34248	0.34275	-.000268886	-0.07851
153	5.2942	13010.34	0.31988	0.31862	0.001262742	0.39475
153	5.3062	13394.11	0.31142	0.30959	0.001827184	0.58673
153	5.3251	13977.27	0.29949	0.29697	0.002518393	0.84089
153	5.3251	13977.27	0.29949	0.29697	0.002518393	0.84089
153	5.3267	14021.85	0.29862	0.29606	0.002558678	0.85683
153	5.3560	14785.57	0.28476	0.28169	0.003069569	1.07795
153	5.3572	14813.23	0.28429	0.28121	0.003076246	1.08208
153	5.4191	15914.84	0.26767	0.26480	0.002872003	1.07296
153	5.4211	15940.30	0.26734	0.26448	0.002860778	1.07009
153	5.5215	16977.87	0.25565	0.25394	0.001709697	0.66876
153	5.6863	17974.37	0.24869	0.24862	0.000068510	0.02755
153	5.9092	18819.34	0.24683	0.24821	-.001383420	-0.56047
153	5.9176	18845.80	0.24683	0.24827	-.001436568	-0.58201
153	6.5305	20202.29	0.25411	0.25702	-.002911361	-1.14571
153	6.5534	20240.56	0.25452	0.25745	-.002934800	-1.15307
153	7.0220	20910.16	0.26398	0.26692	-.002944745	-1.11552
153	7.0366	20929.03	0.26429	0.26725	-.002956129	-1.11852
153	7.5360	21485.78	0.27571	0.27820	-.002488691	-0.90265

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
153	8.0287	21941.10	0.28765	0.28946	-.001806179	-0.62791
153	8.5348	22342.80	0.30028	0.30132	-.001043878	-0.34763
153	9.0144	22678.03	0.31247	0.31278	-.000305341	-0.09772
153	9.5397	23007.03	0.32595	0.32553	0.000419869	0.12881
153	10.0159	23277.56	0.33824	0.33725	0.000985169	0.29126
153	10.5214	23541.45	0.35133	0.34987	0.001459345	0.41538
153	11.0237	23783.69	0.36435	0.36257	0.001781974	0.48908
153	11.5127	24003.68	0.37703	0.37511	0.001924167	0.51035
153	12.0552	24231.70	0.39108	0.38920	0.001879708	0.48065
155	1.0043	834.35	0.93396	0.93127	0.002694779	0.28853
155	1.5060	1300.76	0.89835	0.89482	0.003526813	0.39259
155	1.5087	1303.38	0.89817	0.89462	0.003547710	0.39499
155	2.0019	1804.16	0.86099	0.85701	0.003975844	0.46178
155	2.5124	2377.91	0.81982	0.81578	0.004044023	0.49328
155	2.9737	2959.87	0.77958	0.77589	0.003691007	0.47346
155	3.0012	2996.90	0.77707	0.77342	0.003654260	0.47026
155	3.5359	3782.17	0.72543	0.72271	0.002718347	0.37472
155	4.1964	5000.75	0.65114	0.65037	0.000766359	0.11769
155	4.6140	6023.58	0.59436	0.59525	-.000889821	-0.14971
155	4.9296	7050.59	0.54252	0.54473	-.002206472	-0.40671
155	5.1882	8219.49	0.48979	0.49280	-.003005676	-0.61367
155	5.3153	9002.58	0.45813	0.46118	-.003052004	-0.66619
155	5.4391	10014.54	0.42143	0.42397	-.002542381	-0.60327
155	5.5323	11036.82	0.38895	0.39045	-.001501327	-0.38599
155	5.6036	12017.70	0.36181	0.36207	-.000257682	-0.07122
155	5.6623	12923.08	0.33999	0.33914	0.000850520	0.25016
155	5.7355	14028.69	0.31724	0.31544	0.001799910	0.56737
155	5.7355	14028.69	0.31724	0.31544	0.001799910	0.56737
155	5.8163	15048.81	0.29990	0.29788	0.002021369	0.67401
155	5.9288	16091.34	0.28590	0.28441	0.001491577	0.52171
155	6.0969	17137.45	0.27605	0.27577	0.000282390	0.10230
155	6.2665	17870.23	0.27210	0.27288	-.000777360	-0.28569
155	6.3260	18082.13	0.27146	0.27256	-.001102978	-0.40631
155	6.6910	19081.38	0.27209	0.27451	-.002415847	-0.88789
155	7.2586	20111.87	0.28005	0.28314	-.003085619	-1.10181
155	8.0153	21055.85	0.29538	0.29806	-.002675527	-0.90579
155	8.5194	21543.61	0.30685	0.30886	-.002011668	-0.65559
155	9.0204	21958.57	0.31875	0.31996	-.001212090	-0.38026
155	9.5124	22316.99	0.33074	0.33111	-.000374608	-0.11326
155	10.0145	22644.54	0.34316	0.34270	0.000457171	0.13322
155	10.5140	22939.62	0.35564	0.35439	0.001248267	0.35099
155	11.0262	23216.43	0.36852	0.36653	0.001989297	0.53981
155	11.5233	23464.50	0.38106	0.37846	0.002601933	0.68281
155	12.0146	23693.05	0.39348	0.39040	0.003084132	0.78381
157	1.0053	822.32	0.93649	0.93429	0.002195049	0.23439
157	1.5018	1274.23	0.90285	0.89997	0.002883867	0.31942
157	2.0032	1770.14	0.86690	0.86369	0.003211363	0.37044
157	2.5085	2319.84	0.82836	0.82512	0.003238331	0.39093
157	3.0093	2928.06	0.78731	0.78439	0.002916186	0.37040
157	3.5094	3619.93	0.74267	0.74045	0.002220790	0.29903
157	4.0115	4434.59	0.69297	0.69182	0.001148640	0.16576
157	4.3177	5015.95	0.65942	0.65910	0.000323398	0.04904
157	4.7480	5997.97	0.60642	0.60740	-.000976926	-0.16110
157	5.0975	7023.88	0.55596	0.55798	-.002022938	-0.36386
157	5.3584	8022.53	0.51167	0.51419	-.002521441	-0.49279
157	5.5625	9045.33	0.47110	0.47358	-.002477921	-0.52599
157	5.7127	10014.82	0.43698	0.43892	-.001940626	-0.44410
157	5.8426	11061.28	0.40464	0.40561	-.000974372	-0.24080
157	5.9470	12046.46	0.37818	0.37811	0.000071079	0.01879
157	6.0401	12984.88	0.35634	0.35539	0.000954840	0.26796
157	6.1488	14037.40	0.33556	0.33399	0.001565980	0.46668
157	6.1488	14037.40	0.33556	0.33399	0.001565980	0.46668
157	6.2676	15025.21	0.31956	0.31798	0.001581959	0.49504
157	6.4221	16029.84	0.30691	0.30592	0.000987208	0.32166
157	6.6274	17009.24	0.29849	0.29856	-.000074947	-0.02511

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
157	6.9268	18014.92	0.29455	0.29594	-.001393839	-0.47321
157	7.3744	19049.34	0.29656	0.29909	-.002531019	-0.85346
157	8.0137	20067.59	0.30592	0.30885	-.002934332	-0.95918
157	8.5100	20664.94	0.31547	0.31813	-.002664332	-0.84456
157	9.0190	21172.52	0.32633	0.32837	-.002042468	-0.62589
157	9.5167	21598.03	0.33755	0.33880	-.001254033	-0.37151
157	10.0143	21972.04	0.34915	0.34951	-.000356184	-0.10201
157	10.5185	22310.88	0.36116	0.36056	0.000604640	0.16742
157	11.0189	22615.48	0.37325	0.37168	0.001567973	0.42009
157	11.5182	22893.81	0.38542	0.38292	0.002500061	0.64866
157	12.0129	23148.69	0.39754	0.39418	0.003362249	0.84576
160	1.0036	802.28	0.94028	0.93879	0.001488045	0.15826
160	1.5082	1248.29	0.90818	0.90634	0.001842148	0.20284
160	1.5095	1249.38	0.90819	0.90626	0.001930578	0.21257
160	2.0096	1726.86	0.87477	0.87272	0.002049249	0.23426
160	2.5014	2237.91	0.84019	0.83816	0.002027264	0.24129
160	3.0078	2818.14	0.80228	0.80055	0.001726209	0.21516
160	3.0262	2840.29	0.80090	0.79915	0.001748569	0.21833
160	3.5103	3463.15	0.76194	0.76071	0.001227657	0.16112
160	4.0098	4195.85	0.71837	0.71788	0.000489999	0.06821
160	4.4836	5008.39	0.67294	0.67329	-.000348631	-0.05181
160	4.9655	6008.96	0.62116	0.62242	-.001255547	-0.20213
160	5.3539	7013.14	0.57385	0.57567	-.001817095	-0.31665
160	5.6648	8017.82	0.53109	0.53306	-.001970018	-0.37094
160	5.9121	9007.53	0.49337	0.49504	-.001672813	-0.33906
160	6.1165	10000.73	0.45974	0.46075	-.001013807	-0.22052
160	6.2943	11013.09	0.42962	0.42973	-.000113623	-0.02645
160	6.3700	11480.67	0.41707	0.41674	0.000328619	0.07879
160	6.4512	12003.65	0.40399	0.40321	0.000777965	0.19257
160	6.6045	13001.15	0.38186	0.38037	0.001493440	0.39110
160	6.7651	13996.30	0.36333	0.36152	0.001810486	0.49830
160	6.7651	13996.30	0.36333	0.36152	0.001810486	0.49830
160	6.9511	15005.31	0.34822	0.34658	0.001641460	0.47139
160	7.1698	15976.52	0.33734	0.33637	0.000970929	0.28782
160	7.4772	17026.18	0.33011	0.33027	-.000157586	-0.04774
160	7.8882	18057.55	0.32837	0.32973	-.001361282	-0.41456
160	8.4309	19049.26	0.33269	0.33492	-.002228913	-0.66997
160	9.0093	19844.95	0.34126	0.34365	-.002386846	-0.69942
160	9.2078	20077.88	0.34473	0.34705	-.002320388	-0.67310
160	9.4969	20388.25	0.35014	0.35223	-.002087078	-0.59607
160	10.0176	20882.87	0.36059	0.36208	-.001494708	-0.41452
160	10.5305	21306.07	0.37153	0.37221	-.000679332	-0.18285
160	11.0218	21666.04	0.38240	0.38215	0.000247262	0.06466
160	11.5231	21997.52	0.39377	0.39248	0.001293182	0.32841
160	12.0015	22286.20	0.40480	0.40245	0.002354462	0.58164
160	12.0116	22292.36	0.40503	0.40267	0.002361428	0.58303
165	0.2110	155.54	0.98891	0.98872	0.000190412	0.01925
165	1.0034	773.36	0.94576	0.94512	0.000644441	0.06814
165	1.5069	1197.66	0.91709	0.91626	0.000830500	0.09056
165	2.0079	1649.44	0.88734	0.88649	0.000851388	0.09595
165	2.5006	2127.32	0.85680	0.85605	0.000754062	0.08801
165	2.9697	2619.53	0.82636	0.82579	0.000566623	0.06857
165	3.0100	2663.79	0.82366	0.82313	0.000532777	0.06468
165	3.5029	3232.48	0.78989	0.78965	0.000240269	0.03042
165	4.0053	3875.51	0.75333	0.75351	-.000183511	-0.02436
165	4.5131	4608.02	0.71391	0.71452	-.000607558	-0.08510
165	5.0012	5415.37	0.67317	0.67415	-.000975608	-0.14493
165	5.5073	6398.74	0.62737	0.62857	-.001202748	-0.19171
165	6.0106	7583.18	0.57776	0.57880	-.001043075	-0.18054
165	6.0345	7645.94	0.57529	0.57632	-.001029778	-0.17900
165	6.5038	9023.36	0.52538	0.52566	-.000281019	-0.05349
165	6.7889	10009.24	0.49440	0.49389	0.000509681	0.10309
165	7.0532	11018.20	0.46661	0.46525	0.001360950	0.29167
165	7.3003	12012.79	0.44297	0.44088	0.002085096	0.47071
165	7.5621	13063.36	0.42195	0.41940	0.002546131	0.60342

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
165	7.8217	14041.30	0.40604	0.40346	0.002582049	0.63591
165	8.1215	15044.11	0.39351	0.39134	0.002169187	0.55124
165	8.5000	16102.46	0.38478	0.38348	0.001304990	0.33915
165	9.0054	17218.93	0.38122	0.38109	0.000134917	0.03539
165	9.0226	17251.55	0.38123	0.38111	0.000117836	0.03091
165	9.5016	18079.15	0.38309	0.38376	-.000668618	-0.17453
165	10.0226	18812.01	0.38835	0.38943	-.001083537	-0.27901
165	10.5127	19390.21	0.39520	0.39631	-.001108841	-0.28058
165	11.0127	19898.39	0.40342	0.40424	-.000818143	-0.20280
165	11.5208	20351.03	0.41265	0.41290	-.000245775	-0.05956
165	11.9989	20731.60	0.42188	0.42142	0.000463095	0.10977
165	12.0398	20762.57	0.42269	0.42216	0.000527609	0.12482
170	1.0011	744.95	0.95073	0.95050	0.000225495	0.02372
170	1.5062	1152.31	0.92477	0.92450	0.000274190	0.02965
170	2.0013	1575.92	0.89846	0.89823	0.000234559	0.02611
170	2.5030	2033.40	0.87087	0.87073	0.000139837	0.01606
170	2.9985	2517.82	0.84253	0.84259	-.000060058	-0.00713
170	3.0402	2560.20	0.84011	0.84018	-.000065354	-0.00778
170	3.5037	3050.99	0.81246	0.81276	-.000298188	-0.03670
170	4.0126	3635.63	0.78084	0.78140	-.000556652	-0.07129
170	4.5119	4265.45	0.74835	0.74916	-.000814700	-0.10887
170	5.0023	4950.46	0.71489	0.71591	-.001016604	-0.14220
170	5.5085	5743.22	0.67857	0.67972	-.001149007	-0.16933
170	6.0115	6638.15	0.64069	0.64179	-.001098601	-0.17147
170	6.0282	6669.70	0.63943	0.64051	-.001077792	-0.16856
170	6.0548	6720.66	0.63738	0.63845	-.001066190	-0.16728
170	6.5098	7655.30	0.60162	0.60239	-.000770832	-0.12813
170	7.0196	8854.79	0.56085	0.56096	-.000109377	-0.01950
170	7.4871	10100.88	0.52441	0.52367	0.000737310	0.14060
170	8.0464	11717.76	0.48581	0.48413	0.001677895	0.34538
170	8.4961	13015.85	0.46181	0.45982	0.001993658	0.43171
170	8.9959	14339.09	0.44385	0.44217	0.001684950	0.37962
170	8.9959	14339.09	0.44385	0.44217	0.001684950	0.37962
170	9.0357	14436.62	0.44281	0.44116	0.001649192	0.37244
170	9.5342	15555.75	0.43362	0.43269	0.000927879	0.21398
170	10.0301	16491.56	0.43029	0.43013	0.000155181	0.03606
170	10.5420	17303.17	0.43103	0.43150	-.000471492	-0.10939
170	11.0239	17954.97	0.43437	0.43518	-.000812790	-0.18712
170	11.5057	18521.60	0.43949	0.44038	-.000889871	-0.20248
170	12.0011	19034.82	0.44605	0.44679	-.000740916	-0.16611
170	12.0368	19069.11	0.44657	0.44728	-.000709500	-0.15888
175	0.2276	157.97	0.98999	0.98993	0.000061267	0.00619
175	1.0008	720.15	0.95507	0.95496	0.000111356	0.01166
175	1.5009	1106.96	0.93181	0.93167	0.000135238	0.01451
175	2.0047	1517.81	0.90773	0.90763	0.000101226	0.01115
175	2.5036	1948.18	0.88319	0.88319	0.000004277	0.00048
175	3.0071	2409.73	0.85763	0.85781	-.000178323	-0.02079
175	3.0134	2415.69	0.85732	0.85749	-.000165950	-0.01936
175	3.5108	2902.50	0.83130	0.83166	-.000357073	-0.04295
175	4.0057	3421.65	0.80457	0.80514	-.000574892	-0.07145
175	4.5094	3991.24	0.77648	0.77727	-.000786958	-0.10135
175	5.0103	4605.89	0.74762	0.74859	-.000965683	-0.12917
175	5.5019	5263.59	0.71839	0.71949	-.001097166	-0.15273
175	6.0064	6004.21	0.68752	0.68867	-.001148092	-0.16699
175	6.0139	6015.80	0.68705	0.68820	-.001152081	-0.16769
175	6.5098	6820.37	0.65597	0.65707	-.001101061	-0.16785
175	7.0290	7752.80	0.62310	0.62399	-.000885940	-0.14218
175	7.5174	8718.98	0.59255	0.59308	-.000532649	-0.08989
175	8.0216	9800.87	0.56250	0.56257	-.000071058	-0.01263
175	8.5110	10909.28	0.53618	0.53584	0.000337184	0.06289
175	9.0200	12074.77	0.51339	0.51279	0.000600480	0.11696
175	9.0360	12111.04	0.51277	0.51216	0.000613192	0.11958
175	9.5180	13176.13	0.49646	0.49592	0.000542858	0.10935
175	10.0296	14221.49	0.48469	0.48451	0.000179375	0.03701
175	10.0296	14221.49	0.48469	0.48451	0.000179375	0.03701

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
175	10.5204	15119.73	0.47820	0.47848	-.000277900	-0.05811
175	11.0225	15932.89	0.47546	0.47619	-.000729504	-0.15343
175	11.5341	16661.79	0.47576	0.47685	-.001089672	-0.22904
175	12.0223	17275.81	0.47827	0.47951	-.001240159	-0.25930
175	12.1032	17370.26	0.47887	0.48010	-.001227242	-0.25628
180	1.0086	703.02	0.95864	0.95834	0.000299699	0.03126
180	1.5095	1075.83	0.93749	0.93707	0.000416486	0.04443
180	2.0068	1463.94	0.91597	0.91553	0.000438423	0.04786
180	2.5102	1876.71	0.89371	0.89328	0.000428431	0.04794
180	3.0111	2309.83	0.87105	0.87066	0.000391463	0.04494
180	3.0139	2312.31	0.87091	0.87053	0.000379307	0.04355
180	3.5118	2767.47	0.84787	0.84755	0.000320792	0.03784
180	4.0038	3244.52	0.82454	0.82432	0.000220509	0.02674
180	4.5071	3763.99	0.80009	0.80001	0.000080833	0.01010
180	5.0072	4315.49	0.77527	0.77531	-.000041954	-0.00541
180	5.5078	4907.45	0.74991	0.75006	-.000151688	-0.02023
180	5.9644	5486.28	0.72641	0.72662	-.000210596	-0.02899
180	6.0120	5548.86	0.72395	0.72416	-.000209704	-0.02897
180	6.5143	6237.86	0.69778	0.69801	-.000229143	-0.03284
180	7.0135	6976.72	0.67170	0.67188	-.000177739	-0.02646
180	7.5126	7771.98	0.64588	0.64595	-.000072173	-0.01117
180	8.0330	8659.63	0.61983	0.61971	0.000124324	0.02006
180	8.5225	9542.53	0.59675	0.59643	0.000324283	0.05434
180	9.0133	10460.57	0.57573	0.57524	0.000494375	0.08587
180	9.0183	10469.44	0.57556	0.57505	0.000513790	0.08927
180	9.5256	11429.21	0.55689	0.55627	0.000623948	0.11204
180	10.0307	12368.98	0.54186	0.54127	0.000593679	0.10956
180	10.5183	13236.68	0.53095	0.53049	0.000462877	0.08718
180	11.0449	14112.37	0.52294	0.52271	0.000228699	0.04373
180	11.0449	14112.37	0.52294	0.52271	0.000228699	0.04373
180	11.5347	14859.82	0.51866	0.51865	0.000014988	0.00289
180	12.0174	15532.82	0.51695	0.51710	-.000152274	-0.02946
180	12.0279	15547.06	0.51693	0.51709	-.000161996	-0.03134
200	1.0000	619.36	0.97097	0.97041	0.000559090	0.05758
200	1.5097	949.81	0.95587	0.95520	0.000665533	0.06963
200	2.0084	1283.33	0.94111	0.94026	0.000849652	0.09028
200	3.0106	1987.15	0.91107	0.91004	0.001032430	0.11332
200	3.0190	1993.25	0.91081	0.90978	0.001026883	0.11274
200	4.0069	2735.21	0.88094	0.87984	0.001103050	0.12521
200	5.0187	3549.81	0.85019	0.84916	0.001029302	0.12107
200	6.0049	4401.75	0.82038	0.81950	0.000875623	0.10673
200	6.0214	4416.57	0.81987	0.81901	0.000859761	0.10487
200	6.9907	5313.96	0.79111	0.79046	0.000649386	0.08209
200	8.0225	6334.38	0.76162	0.76126	0.000360727	0.04736
200	9.0154	7375.96	0.73502	0.73501	0.000005105	0.00069
200	9.0162	7376.74	0.73501	0.73500	0.000013316	0.00181
200	10.0217	8478.17	0.71084	0.71117	-.000329068	-0.04629
200	11.0423	9623.86	0.68999	0.69071	-.000717386	-0.10397
200	12.0232	10723.74	0.67423	0.67530	-.001067847	-0.15838
200	12.0312	10732.68	0.67411	0.67519	-.001079960	-0.16021
220	1.0013	559.18	0.97894	0.97845	0.000485919	0.04964
220	1.5020	847.97	0.96836	0.96774	0.000623360	0.06437
220	2.0029	1143.15	0.95784	0.95707	0.000772346	0.08063
220	2.9946	1746.94	0.93714	0.93613	0.001006515	0.10740
220	3.0102	1756.54	0.93685	0.93581	0.001039866	0.11100
220	4.0106	2393.20	0.91615	0.91503	0.001115670	0.12178
220	5.0036	3052.97	0.89598	0.89487	0.001109615	0.12384
220	6.0078	3749.00	0.87607	0.87509	0.000982452	0.11214
220	6.0110	3751.20	0.87602	0.87503	0.000992652	0.11331
220	7.0173	4477.52	0.85679	0.85600	0.000786118	0.09175
220	8.0120	5222.71	0.83866	0.83819	0.000470728	0.05613
220	9.0129	5997.12	0.82160	0.82150	0.000101731	0.01238
220	9.0172	6000.55	0.82153	0.82143	0.000101517	0.01236
220	10.0244	6800.82	0.80582	0.80614	-.000321336	-0.03988
220	11.0275	7613.02	0.79188	0.79267	-.000786751	-0.09935

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
220	12.0243	8427.86	0.77998	0.78124	-.001256643	-0.16111
220	12.0274	8430.48	0.77994	0.78120	-.001263191	-0.16196
235	2.0226	1070.95	0.96655	0.96573	0.000823877	0.08524
235	4.0193	2201.00	0.93459	0.93338	0.001207968	0.12925
235	4.0193	2200.97	0.93461	0.93338	0.001227093	0.13129
235	5.1128	2851.08	0.91779	0.91652	0.001270098	0.13839
235	5.1128	2851.08	0.91780	0.91652	0.001280098	0.13947
235	6.0328	3414.74	0.90419	0.90292	0.001271489	0.14062
235	6.0329	3414.76	0.90419	0.90292	0.001272072	0.14069
235	8.0075	4673.30	0.87693	0.87594	0.000991983	0.11312
235	8.0227	4683.24	0.87674	0.87574	0.000996459	0.11366
235	10.0243	6016.12	0.85277	0.85230	0.000473649	0.05554
235	10.0396	6026.41	0.85262	0.85214	0.000484236	0.05679
235	10.0398	6026.61	0.85260	0.85213	0.000467359	0.05482
235	10.1239	6083.56	0.85170	0.85125	0.000450555	0.05290
235	10.1300	6087.76	0.85162	0.85118	0.000435395	0.05113
235	12.0062	7370.48	0.83369	0.83387	-.000177587	-0.02130
235	14.0112	8745.32	0.81996	0.82084	-.000881820	-0.10754
235	16.0126	10088.19	0.81235	0.81385	-.001502556	-0.18496
235	18.0209	11374.91	0.81082	0.81276	-.001939696	-0.23923
235	18.1691	11466.83	0.81093	0.81290	-.001971122	-0.24307
235	18.1812	11474.34	0.81094	0.81291	-.001974004	-0.24342
235	20.0179	12571.77	0.81492	0.81701	-.002087040	-0.25610
235	22.0383	13687.62	0.82404	0.82591	-.001869564	-0.22688
235	24.0320	14693.08	0.83709	0.83838	-.001294058	-0.15459
235	26.0283	15609.19	0.85342	0.85378	-.000355488	-0.04165
235	26.0284	15609.17	0.85342	0.85378	-.000355012	-0.04160
235	26.0606	15623.61	0.85369	0.85405	-.000360421	-0.04222
235	26.0614	15623.96	0.85369	0.85406	-.000367115	-0.04300
235	28.0374	16447.93	0.87241	0.87156	0.000848478	0.09726
235	30.0320	17206.09	0.89330	0.89098	0.002323141	0.26006
235	30.0344	17206.99	0.89332	0.89100	0.002318053	0.25949
250	1.0030	489.02	0.98673	0.98639	0.000339581	0.03441
250	1.5275	749.90	0.97993	0.97941	0.000516161	0.05267
250	2.0148	995.47	0.97369	0.97303	0.000663902	0.06818
250	2.9803	1491.15	0.96152	0.96066	0.000861153	0.08956
250	3.0056	1504.27	0.96123	0.96034	0.000889028	0.09249
250	3.9984	2026.67	0.94913	0.94808	0.001046910	0.11030
250	5.0060	2569.49	0.93728	0.93616	0.001117456	0.11922
250	6.0069	3120.78	0.92600	0.92490	0.001097130	0.11848
250	6.0132	3124.31	0.92593	0.92483	0.001096477	0.11842
250	7.0652	3715.78	0.91474	0.91370	0.001035650	0.11322
250	8.0074	4255.01	0.90534	0.90441	0.000930772	0.10281
250	8.0116	4257.58	0.90527	0.90437	0.000903269	0.09978
250	8.0116	4257.61	0.90527	0.90437	0.000903681	0.09982
250	9.0228	4845.05	0.89591	0.89517	0.000741490	0.08276
250	9.0287	4848.25	0.89591	0.89512	0.000789012	0.08807
250	9.0354	4852.21	0.89584	0.89506	0.000777635	0.08681
250	10.0229	5433.19	0.88749	0.88693	0.000562260	0.06335
250	10.0230	5433.24	0.88749	0.88693	0.000562920	0.06343
250	10.0367	5441.17	0.88741	0.88682	0.000587462	0.06620
250	10.0576	5453.79	0.88720	0.88666	0.000543309	0.06124
250	10.1335	5498.57	0.88661	0.88607	0.000538382	0.06072
250	10.9981	6011.49	0.88015	0.87977	0.000375772	0.04269
250	12.0146	6617.58	0.87344	0.87330	0.000144499	0.01654
250	12.0162	6618.65	0.87342	0.87328	0.000135071	0.01546
250	12.0168	6619.21	0.87339	0.87328	0.000110479	0.01265
250	12.0169	6619.31	0.87338	0.87328	0.000101462	0.01162
250	14.0227	7815.08	0.86322	0.86361	-.000387445	-0.04488
250	16.0228	8990.39	0.85740	0.85823	-.000828254	-0.09660
250	18.0070	10121.01	0.85594	0.85708	-.001141507	-0.13336
250	18.1005	10173.02	0.85598	0.85713	-.001147171	-0.13402
250	20.0405	11227.42	0.85872	0.85999	-.001274260	-0.14839
250	22.0214	12243.89	0.86526	0.86642	-.001156770	-0.13369
250	24.0261	13205.79	0.87527	0.87604	-.000770914	-0.08808

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
250	24.0265	13205.99	0.87527	0.87604	-.000773295	-0.08835
250	26.0670	14114.92	0.88846	0.88856	-.000098942	-0.01114
250	26.0681	14115.10	0.88848	0.88856	-.000081692	-0.00919
250	28.0546	14934.54	0.90372	0.90293	0.000787044	0.08709
250	30.0502	15696.10	0.92104	0.91914	0.001901058	0.20640
250	30.0510	15696.38	0.92105	0.91915	0.001904672	0.20679
265	10.0361	4984.48	0.91382	0.91351	0.000308285	0.03374
265	10.0361	4984.50	0.91382	0.91351	0.000308554	0.03377
265	10.0446	4988.94	0.91378	0.91346	0.000316036	0.03459
265	14.0156	7095.10	0.89654	0.89692	-.000384689	-0.04291
265	18.0107	9164.99	0.89190	0.89284	-.000939539	-0.10534
265	22.0130	11101.53	0.89994	0.90086	-.000922635	-0.10252
265	22.0133	11101.68	0.89994	0.90086	-.000923734	-0.10264
265	26.0240	12852.11	0.91900	0.91913	-.000129750	-0.01412
265	26.0245	12852.28	0.91901	0.91913	-.000122151	-0.01329
265	30.0372	14399.84	0.94671	0.94523	0.001483374	0.15669
265	30.0387	14400.45	0.94672	0.94524	0.001481246	0.15646
280	0.5085	219.36	0.99572	0.99566	0.000061782	0.00620
280	1.0144	439.42	0.99157	0.99143	0.000143739	0.01450
280	2.0001	873.29	0.98377	0.98344	0.000326542	0.03319
280	2.0327	887.77	0.98353	0.98319	0.000344834	0.03506
280	3.0015	1320.77	0.97615	0.97571	0.000439975	0.04507
280	3.0048	1322.25	0.97612	0.97569	0.000434661	0.04453
280	4.0152	1780.29	0.96878	0.96830	0.000484916	0.05005
280	4.0177	1781.39	0.96878	0.96828	0.000502010	0.05182
280	4.0193	1782.22	0.96872	0.96827	0.000454859	0.04695
280	5.0067	2235.60	0.96197	0.96147	0.000496983	0.05166
280	6.0034	2698.66	0.95556	0.95507	0.000490003	0.05128
280	6.0217	2707.22	0.95543	0.95496	0.000473300	0.04954
280	6.0277	2710.05	0.95539	0.95492	0.000470694	0.04927
280	6.0277	2710.07	0.95538	0.95492	0.000461025	0.04826
280	6.0404	2715.88	0.95534	0.95484	0.000497734	0.05210
280	7.0083	3170.45	0.94950	0.94910	0.000398345	0.04195
280	8.0021	3641.01	0.94403	0.94371	0.000321810	0.03409
280	8.0232	3651.02	0.94393	0.94360	0.000330495	0.03501
280	8.0236	3651.20	0.94393	0.94360	0.000332395	0.03521
280	8.0239	3651.40	0.94392	0.94360	0.000324566	0.03438
280	9.0111	4122.13	0.93899	0.93877	0.000216797	0.02309
280	9.0145	4123.66	0.93900	0.93876	0.000241524	0.02572
280	9.0328	4132.47	0.93890	0.93867	0.000226389	0.02411
280	10.0272	4609.12	0.93448	0.93438	0.000102077	0.01092
280	10.0294	4610.14	0.93447	0.93437	0.000100700	0.01078
280	10.0324	4611.67	0.93444	0.93436	0.000083525	0.00894
280	10.0466	4618.45	0.93439	0.93430	0.000090428	0.00968
280	10.0469	4618.55	0.93440	0.93430	0.000101267	0.01084
280	10.1550	4670.40	0.93397	0.93387	0.000102218	0.01094
280	10.9885	5071.19	0.93075	0.93077	-.000019137	-0.00206
280	12.0026	5559.18	0.92741	0.92756	-.000146903	-0.01584
280	12.0303	5572.64	0.92730	0.92748	-.000177032	-0.01909
280	12.0432	5578.78	0.92728	0.92744	-.000160817	-0.01734
280	12.0472	5580.63	0.92727	0.92743	-.000159898	-0.01724
280	14.0233	6529.14	0.92257	0.92303	-.000455301	-0.04935
280	16.0259	7479.65	0.92034	0.92103	-.000691936	-0.07518
280	17.9084	8355.91	0.92059	0.92141	-.000821877	-0.08928
280	18.0070	8401.92	0.92059	0.92149	-.000902140	-0.09800
280	18.0146	8405.18	0.92063	0.92150	-.000868048	-0.09429
280	18.0146	8405.18	0.92063	0.92150	-.000868048	-0.09429
280	20.0362	9319.57	0.92347	0.92439	-.000916861	-0.09928
280	22.0007	10178.06	0.92849	0.92940	-.000909984	-0.09801
280	24.0257	11024.96	0.93606	0.93665	-.000585497	-0.06255
280	26.0180	11820.34	0.94547	0.94565	-.000181094	-0.01915
280	26.0323	11826.00	0.94554	0.94572	-.000183098	-0.01936
280	26.0332	11826.37	0.94554	0.94573	-.000187881	-0.01987
280	26.0476	11831.86	0.94563	0.94580	-.000167771	-0.01774
280	28.0201	12579.80	0.95676	0.95636	0.000396641	0.04146

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
280	30.0535	13310.25	0.96987	0.96874	0.001128545	0.11636
295	10.0065	4290.58	0.95084	0.95087	-.000030229	-0.00318
295	10.0339	4302.69	0.95076	0.95079	-.000034631	-0.00364
295	14.0150	6057.68	0.94325	0.94371	-.000458365	-0.04859
295	18.0106	7780.82	0.94372	0.94447	-.000754791	-0.07998
295	22.0208	9428.88	0.95217	0.95287	-.000698144	-0.07332
295	26.0257	10963.00	0.96786	0.96803	-.000170437	-0.01761
295	30.0507	12376.97	0.98988	0.98897	0.000911620	0.09209
295	30.0525	12377.59	0.98989	0.98898	0.000910757	0.09201
295	30.0527	12377.67	0.98989	0.98898	0.000909453	0.09187
295	30.0531	12377.77	0.98989	0.98898	0.000907716	0.09170
310	1.0420	406.39	0.99479	0.99467	0.000121693	0.01223
310	1.5399	602.01	0.99238	0.99224	0.000142438	0.01435
310	2.0115	788.14	0.99018	0.99001	0.000173643	0.01754
310	3.0166	1187.30	0.98574	0.98549	0.000249833	0.02534
310	3.0261	1191.09	0.98570	0.98545	0.000250984	0.02546
310	4.0289	1592.54	0.98152	0.98128	0.000239913	0.02444
310	5.0051	1985.95	0.97779	0.97755	0.000235409	0.02408
310	6.0057	2391.50	0.97431	0.97409	0.000222057	0.02279
310	6.0103	2393.35	0.97430	0.97407	0.000227040	0.02330
310	6.9935	2793.71	0.97121	0.97103	0.000184147	0.01896
310	8.0084	3208.45	0.96839	0.96826	0.000127796	0.01320
310	9.0126	3619.83	0.96597	0.96592	0.000051827	0.00537
310	9.0331	3628.14	0.96595	0.96587	0.000075086	0.00777
310	9.9997	4024.78	0.96393	0.96400	-.000069862	-0.00725
310	10.0085	4028.34	0.96393	0.96398	-.000054741	-0.00568
310	10.0188	4032.52	0.96392	0.96397	-.000046996	-0.00488
310	10.0420	4042.10	0.96386	0.96393	-.000066457	-0.00689
310	10.0426	4042.36	0.96386	0.96393	-.000065401	-0.00679
310	10.0430	4042.53	0.96386	0.96392	-.000064663	-0.00671
310	10.0456	4043.53	0.96387	0.96392	-.000050442	-0.00523
310	10.1393	4081.83	0.96373	0.96376	-.000030804	-0.00320
310	10.9880	4429.78	0.96236	0.96247	-.000110480	-0.01148
310	12.0199	4852.16	0.96110	0.96129	-.000193967	-0.02018
310	12.0238	4853.76	0.96109	0.96129	-.000200324	-0.02084
310	12.0558	4866.90	0.96105	0.96126	-.000210670	-0.02192
310	14.0320	5671.62	0.95987	0.96025	-.000377923	-0.03937
310	16.0129	6469.29	0.96032	0.96083	-.000510944	-0.05321
310	18.0092	7259.89	0.96242	0.96301	-.000594553	-0.061777
310	18.0094	7259.94	0.96243	0.96301	-.000584743	-0.060757
310	18.1204	7303.17	0.96263	0.96318	-.000551310	-0.057271
310	20.0100	8035.25	0.96616	0.96676	-.000602870	-0.062399
310	22.0098	8789.88	0.97148	0.97200	-.000519181	-0.053442
310	22.0098	8789.88	0.97148	0.97200	-.000519181	-0.053442
310	24.0139	9523.26	0.97832	0.97865	-.000334498	-0.034191
310	24.0140	9523.33	0.97831	0.97866	-.000345261	-0.035292
310	26.0182	10231.83	0.98657	0.98662	-.000050478	-0.005116
310	26.1349	10272.05	0.98711	0.98712	-.000009540	-0.000966
310	28.0346	10918.29	0.99619	0.99585	0.000340080	0.034138
310	30.0766	11585.84	1.00717	1.00633	0.000842016	0.083602
340	1.0004	354.86	0.99721	0.99712	0.000089480	0.008973
340	1.5174	538.98	0.99586	0.99573	0.000128059	0.012859
340	2.0151	716.75	0.99452	0.99446	0.000060273	0.006060
340	2.0372	724.59	0.99453	0.99441	0.000124832	0.012552
340	3.0095	1072.86	0.99227	0.99211	0.000156171	0.015739
340	3.0129	1074.07	0.99228	0.99211	0.000173690	0.017504
340	4.0135	1433.88	0.99014	0.99001	0.000127972	0.012925
340	5.0087	1792.73	0.98832	0.98820	0.000120311	0.012173
340	5.0322	1801.16	0.98830	0.98816	0.000139576	0.014123
340	5.0734	1816.03	0.98824	0.98809	0.000148431	0.015020
340	6.0038	2152.19	0.98680	0.98666	0.000137872	0.013972
340	6.0215	2158.65	0.98675	0.98664	0.000112964	0.011448
340	7.0083	2515.62	0.98549	0.98539	0.000098138	0.009958
340	8.0101	2878.19	0.98448	0.98441	0.000068829	0.006991
340	8.0916	2907.66	0.98441	0.98434	0.000065886	0.006693

T[K]	P[MPa]	ρ[mol/m^3]	Z[OBS]	Z[PRD]	Z[Residual]	% ERROR
340	9.0045	3237.81	0.98376	0.98372	0.000036758	0.003736
340	9.0196	3243.32	0.98375	0.98371	0.000035076	0.003566
340	10.0076	3600.18	0.98331	0.98332	-.000009244	-0.000940
340	10.0096	3600.93	0.98330	0.98332	-.000018710	-0.001903
340	10.0276	3607.41	0.98330	0.98331	-.000014152	-0.001439
340	10.0278	3607.51	0.98329	0.98331	-.000024082	-0.002449
340	10.0307	3608.52	0.98330	0.98331	-.000013387	-0.001361
340	11.0137	3962.70	0.98316	0.98321	-.000048194	-0.004902
340	12.0071	4319.57	0.98329	0.98339	-.000098092	-0.009976
340	12.0248	4325.97	0.98328	0.98339	-.000113964	-0.011590
340	12.0317	4328.45	0.98328	0.98340	-.000116259	-0.011824
340	15.0125	5388.93	0.98545	0.98568	-.000228164	-0.023153
340	18.0068	6432.39	0.99026	0.99052	-.000262463	-0.026504
340	18.0225	6437.87	0.99028	0.99055	-.000274924	-0.027762
340	18.1067	6466.41	0.99051	0.99073	-.000215105	-0.021717
340	21.0235	7454.27	0.99766	0.99788	-.000222111	-0.022263
340	24.0362	8438.95	1.00754	1.00756	-.000015522	-0.001541
340	26.0230	9066.56	1.01531	1.01511	0.000195891	0.019294
340	27.0546	9385.28	1.01971	1.01939	0.000324508	0.031824
340	27.0842	9394.29	1.01985	1.01951	0.000339400	0.033279
340	27.0846	9394.41	1.01985	1.01951	0.000337661	0.033109
340	30.0513	10281.99	1.03388	1.03304	0.000841855	0.081427
340	30.0536	10282.72	1.03389	1.03305	0.000839795	0.081227
370	4.0251	1313.59	0.99606	0.99602	0.000040128	0.004029
370	4.1449	1352.73	0.99600	0.99595	0.000045601	0.004578
370	7.0185	2292.13	0.99532	0.99532	0.000002434	0.000244
370	10.0242	3269.90	0.99650	0.99659	-.000088707	-0.008902
370	10.1129	3298.54	0.99659	0.99666	-.000066179	-0.006641
370	12.5413	4080.65	0.99902	0.99918	-.000156772	-0.015693
370	15.0162	4867.30	1.00284	1.00306	-.000216574	-0.021596
370	18.0160	5802.54	1.00926	1.00948	-.000224219	-0.022216
370	18.0432	5810.80	1.00934	1.00955	-.000210008	-0.020806
370	21.0373	6719.94	1.01762	1.01779	-.000165466	-0.016260
370	21.0376	6720.04	1.01762	1.01779	-.000166483	-0.016360
370	24.0255	7599.35	1.02768	1.02769	-.000011899	-0.001158
370	26.0153	8168.02	1.03532	1.03516	0.000157575	0.015220
370	26.9749	8437.34	1.03924	1.03900	0.000236630	0.022770
370	30.0767	9284.42	1.05302	1.05240	0.000616262	0.058523

APPENDIX E. CORRELATION MATRIX FOR VARIABLES IN EOS PARAMETERS EQUATIONS

Approximate Correlation Matrix (1)

	k1	k2	k3	k27	k4	k5	k6
k1	1.0000000	-0.7409236	0.6146045	0.4090955	-0.4516503	-0.3825101	-0.2523251
k2	-0.7409236	1.0000000	-0.9529554	-0.6676971	0.6391012	0.3781213	0.2684527
k3	0.6146045	-0.9529554	1.0000000	0.4910674	-0.5646143	-0.3174363	-0.2125898
k27	0.4090955	-0.6676971	0.4910674	1.0000000	-0.4414064	-0.2795982	-0.2364907
k4	-0.4516503	0.6391012	-0.5646143	-0.4414064	1.0000000	0.3781059	0.3821914
k5	-0.3825101	0.3781213	-0.3174363	-0.2795982	0.3781059	1.0000000	0.3726539
k6	-0.2523251	0.2684527	-0.2125898	-0.2364907	0.3821914	0.3726539	1.0000000
k7	0.3838113	-0.3978990	0.2913965	0.4137696	-0.4730714	-0.9342098	-0.3264729
k8	-0.0675715	0.0245330	-0.0307642	0.0853278	0.1173495	0.5043485	0.4599849
k9	0.3712863	-0.3772840	0.3321136	0.2540896	-0.3207986	-0.9807447	-0.3080363
k10	0.3334276	-0.4823140	0.4268109	0.3954966	-0.4963645	-0.6356630	-0.0748070
k11	-0.4294708	0.8106013	-0.7988995	-0.5795880	0.6499009	0.0536079	0.0500046
k12	0.1199864	-0.2790977	0.2281312	0.2992418	-0.4281232	-0.0717216	0.0826661
k13	0.3245529	-0.2584990	0.2070230	0.1740344	-0.2495470	-0.9557020	-0.4790820
k14	-0.1181181	-0.0284211	-0.0091749	0.1822266	-0.2457598	0.5640875	0.1020737
k15	-0.1541897	0.2943121	-0.2587306	-0.1773001	0.7068973	-0.0879347	0.2323461
k16	0.6130546	-0.9820997	0.9787973	0.6320186	-0.6321940	-0.3448023	-0.2370931
k17	-0.5939226	0.9604054	-0.9973312	-0.5330059	0.5899363	0.3230320	0.2148233
k18	0.1443692	0.1209712	-0.0548848	-0.3909594	0.1942446	0.1291614	0.2807999
k19	0.4081175	-0.2155082	0.2144214	-0.0625713	-0.2454113	-0.1062342	0.1064756
k20	0.5140395	-0.4430863	0.4470186	0.0512284	-0.6105188	-0.2441025	-0.0354899
k26	-0.3235329	0.1349651	-0.1368614	0.0178966	-0.0326215	-0.0185783	-0.2072740
k21	0.5115572	-0.5828874	0.5236447	0.3077287	-0.8944613	-0.2977819	-0.2890214
k22	0.7546522	-0.7926494	0.7536798	0.4254377	-0.5686099	-0.3481909	-0.0798444
k23	-0.1363373	0.4278191	-0.4478942	-0.3011962	0.3006856	-0.2804001	-0.3902292
k24	0.5221404	-0.5824820	0.5274048	0.3870425	-0.5078105	-0.5450733	-0.5056935
k25	-0.6419952	0.6921092	-0.6484777	-0.4093407	0.4978381	0.4836623	0.1888599

Approximate Correlation Matrix (2)

	k7	k8	k9	k10	k11	k12	k13
k1	0.3838113	-0.0675715	0.3712863	0.3334276	-0.4294708	0.1199864	0.3245529
k2	-0.3978990	0.0245330	-0.3772840	-0.4823140	0.8106013	-0.2790977	-0.2584990
k3	0.2913965	-0.0307642	0.3321136	0.4268109	-0.7988995	0.2281312	0.2070230
k27	0.4137696	0.0853278	0.2540896	0.3954966	-0.5795880	0.2992418	0.1740344
k4	-0.4730714	0.1173495	-0.3207986	-0.4963645	0.6499009	-0.4281232	-0.2495470
k5	-0.9342098	0.5043485	-0.9807447	-0.6356630	0.0536079	-0.0717216	-0.9557020
k6	-0.3264729	0.4599849	-0.3080363	-0.0748070	0.0500046	0.0826661	-0.4790820
k7	1.0000000	-0.3571524	0.9043897	0.7312420	-0.1824591	0.2946244	0.8421861
k8	-0.3571524	1.0000000	-0.6025066	-0.5259727	-0.1150228	-0.2516973	-0.4920195
k9	0.9043897	-0.6025066	1.0000000	0.7200841	-0.0767756	0.1602787	0.9113040
k10	0.7312420	-0.5259727	0.7200841	1.0000000	-0.5038294	0.7849381	0.4132092
k11	-0.1824591	-0.1150228	-0.0767756	-0.5038294	1.0000000	-0.5823826	0.1458161
k12	0.2946244	-0.2516973	0.1602787	0.7849381	-0.5823826	1.0000000	-0.1598893
k13	0.8421861	-0.4920195	0.9113040	0.4132092	0.1458161	-0.1598893	1.0000000
k14	-0.3032435	0.2009054	-0.5335619	0.1512592	-0.4540765	0.7171068	-0.6855541
k15	-0.1175480	0.0866409	0.0946591	-0.4355343	0.5935792	-0.7610109	0.2274795
k16	0.3551178	-0.0104719	0.3479057	0.4728007	-0.8416762	0.2838354	0.2197979
k17	-0.3078885	0.0199231	-0.3337593	-0.4419379	0.8198776	-0.2485886	-0.2061196
k18	-0.1511281	0.1826571	-0.1083217	-0.1246108	0.0338499	-0.1041247	-0.1612440
k19	0.1425832	0.1810095	0.0919733	0.1204362	-0.2791407	0.0627713	0.0036878
k20	0.2818271	0.0939995	0.2101739	0.2798088	-0.4795227	0.1898181	0.1195738
k26	-0.0106084	-0.2359580	0.0083303	-0.0226853	0.1897461	-0.0006441	0.0956370
k21	0.3928319	-0.0633764	0.2558417	0.4550929	-0.6467433	0.4200592	0.1524801
k22	0.3717775	0.0396731	0.3519515	0.4536696	-0.7671268	0.2605315	0.1898738
k23	0.2310257	-0.2206132	0.2139194	-0.1964476	0.6487468	-0.3274918	0.4785488
k24	0.4958774	0.0396427	0.4358878	0.0910121	-0.2913153	-0.2740822	0.5707085
k25	-0.5357336	0.0042075	-0.4695076	-0.4966988	0.6589528	-0.2645798	-0.3390448

Approximate Correlation Matrix (3)

	k14	k15	k16	k17	k18	k19	k20
k1	-0.1181181	-0.1541897	0.6130546	-0.5939226	0.1443692	0.4081175	0.5140395
k2	-0.0284211	0.2943121	-0.9820997	0.9604054	0.1209712	-0.2155082	-0.4430863
k3	-0.0091749	-0.2587306	0.9787973	-0.9973312	-0.0548848	0.2144214	0.4470186
k27	0.1822266	-0.1773001	0.6320186	-0.5330059	-0.3909594	-0.0625713	0.0512284
k4	-0.2457598	0.7068973	-0.6321940	0.5899363	0.1942446	-0.2454113	-0.6105188
k5	0.5640875	-0.0879347	-0.3448023	0.3230320	0.1291614	-0.1062342	-0.2441025
k6	0.1020737	0.2323461	-0.2370931	0.2148233	0.2807999	0.1064756	-0.0354899
k7	-0.3032435	-0.1175480	0.3551178	-0.3078885	-0.1511281	0.1425832	0.2818271
k8	0.2009054	0.0866409	-0.0104719	0.0199231	0.1826571	0.1810095	0.0939995
k9	-0.5335619	0.0946591	0.3479057	-0.3337593	-0.1083217	0.0919733	0.2101739
k10	0.1512592	-0.4355343	0.4728007	-0.4419379	-0.1246108	0.1204362	0.2798088
k11	-0.4540765	0.5935792	-0.8416762	0.8198776	0.0338499	-0.2791407	-0.4795227
k12	0.7171068	-0.7610109	0.2838354	-0.2485886	-0.1041247	0.0627713	0.1898181
k13	-0.6855541	0.2274795	0.2197979	-0.2061196	-0.1612440	0.0036878	0.1195738
k14	1.0000000	-0.7833167	0.0460719	-0.0124197	-0.1159437	-0.0610545	0.0106205
k15	-0.7833167	1.0000000	-0.3038959	0.2778200	0.1355735	-0.1106358	-0.3700665
k16	0.0460719	-0.3038959	1.0000000	-0.9895737	-0.1415691	0.1776797	0.4220941
k17	-0.0124197	0.2778200	-0.9895737	1.0000000	0.0856110	-0.1994935	-0.4400149
k18	-0.1159437	0.1355735	-0.1415691	0.0856110	1.0000000	0.8737875	0.6344763
k19	-0.0610545	-0.1106358	0.1776797	-0.1994935	0.8737875	1.0000000	0.8950959
k20	0.0106205	-0.3700665	0.4220941	-0.4400149	0.6344763	0.8950959	1.0000000
k26	0.0614929	-0.0821101	-0.0982483	0.1200870	-0.9264488	-0.9269997	-0.7136822
k21	0.2425253	-0.6669486	0.5618186	-0.5371447	0.2408858	0.6170641	0.8510051
k22	-0.0316582	-0.2686756	0.7521992	-0.7490654	0.2682845	0.5887702	0.7090975
k23	-0.3251696	0.2278525	-0.4688922	0.4622302	-0.0956967	-0.2465807	-0.3120551
k24	-0.4097741	-0.0011332	0.5535931	-0.5338089	0.0256496	0.3269048	0.4753266
k25	0.0870632	0.2340400	-0.6589565	0.6491547	-0.2974377	-0.6234354	-0.6787674

Approximate Correlation Matrix (4)

	k26	k21	k22	k23	k24	k25
k1	-0.3235329	0.5115572	0.7546522	-0.1363373	0.5221404	-0.6419952
k2	0.1349651	-0.5828874	-0.7926494	0.4278191	-0.5824820	0.6921092
k3	-0.1368614	0.5236447	0.7536798	-0.4478942	0.5274048	-0.6484777
k27	0.0178966	0.3077287	0.4254377	-0.3011962	0.3870425	-0.4093407
k4	-0.0326215	-0.8944613	-0.5686099	0.3006856	-0.5078105	0.4978381
k5	-0.0185783	-0.2977819	-0.3481909	-0.2804001	-0.5450733	0.4836623
k6	-0.2072740	-0.2890214	-0.0798444	-0.3902292	-0.5056935	0.1888599
k7	-0.0106084	0.3928319	0.3717775	0.2310257	0.4958774	-0.5357336
k8	-0.2359580	-0.0633764	0.0396731	-0.2206132	0.0396427	0.0042075
k9	0.0083303	0.2558417	0.3519515	0.2139194	0.4358878	-0.4695076
k10	-0.0226853	0.4550929	0.4536696	-0.1964476	0.0910121	-0.4966988
k11	0.1897461	-0.6467433	-0.7671268	0.6487468	-0.2913153	0.6589528
k12	-0.0006441	0.4200592	0.2605315	-0.3274918	-0.2740822	-0.2645798
k13	0.0956370	0.1524801	0.1898738	0.4785488	0.5707085	-0.3390448
k14	0.0614929	0.2425253	-0.0316582	-0.3251696	-0.4097741	0.0870632
k15	-0.0821101	-0.6669486	-0.2686756	0.2278525	-0.0011332	0.2340400
k16	-0.0982483	0.5618186	0.7521992	-0.4688922	0.5535931	-0.6589565
k17	0.1200870	-0.5371447	-0.7490654	0.4622302	-0.5338089	0.6491547
k18	-0.9264488	0.2408858	0.2682845	-0.0956967	0.0256496	-0.2974377
k19	-0.9269997	0.6170641	0.5887702	-0.2465807	0.3269048	-0.6234354
k20	-0.7136822	0.8510051	0.7090975	-0.3120551	0.4753266	-0.6787674
k26	1.0000000	-0.3832380	-0.4633192	0.2184631	-0.1905462	0.4950691
k21	-0.3832380	1.0000000	0.6736874	-0.3407785	0.4924344	-0.6256805
k22	-0.4633192	0.6736874	1.0000000	-0.4500900	0.5524258	-0.8882036
k23	0.2184631	-0.3407785	-0.4500900	1.0000000	0.1478935	0.2095241
k24	-0.1905462	0.4924344	0.5524258	0.1478935	1.0000000	-0.5976617
k25	0.4950691	-0.6256805	-0.8882036	0.2095241	-0.5976617	1.0000000

VITA

Mert Atilhan, son of Atilla and Muzaffer Atilhan and younger brother of Cevat Rifat Atilhan, was born in Izmir, Turkey in 1979. He graduated from Ege University, Department of Chemical Engineering, in June 2002. In the fall of 2002, he enrolled in Texas A&M University to pursue a graduate degree. He completed his research and received a Master of Science in Mechanical Engineering in May of 2004. Following graduation, Mert continued his studies at Texas A&M University as a Doctor of Philosophy student in the same department. His permanent address is:

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