

THERMODYNAMIC PROPERTIES OF GASEOUS PROPANE FROM MODEL INTERMOLECULAR POTENTIAL FUNCTIONS

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ABSTRACT

A fourth-order virial equation of state was combined with isotropic model potentials to predict accurate volumetric and caloric thermodynamic properties of propane in the gas phase. The parameters in the model were determined in a fit to speed-of-sound data alone; no other data were used. The approximation employed for the fourth virial coefficient included interaction graphs that contained at most one triplet potential. Predicted ordinary second and third virial coefficients are in good agreement with the experimental data of Thomas and Harrison (1982). Predicted compressibility factors deviated from experimental data by less than 0.05 % up to densities of 2 mol./dm³, or 0.4ρ_c. Predicted isobaric heat capacity were in agreement with experimental data to within uncertainties of 0.4 % at pressures up to 12 bar. As examples of results obtained, at 333.15 K the following properties at saturation were obtained: pressure, 21.162 bar; density, 1.1227 mol./dm³; compressibility factor, 0.68051; C_p/R = 14.8304, Joule-Thomson coefficient, 1.9265 K/bar and the speed of sound, 193.858 m/s.

Key Words: Propane, equation of state, model potential functions, virial coefficients, speed of sound.

INTRODUCTION

The virial equation of state (EOS) belongs to the class of methods that are based on rigorous theory. It can be derived from both the canonical (Temperley, 1979) and the grand canonical ensemble (Uhlenbeck and Ford, 1962), although the latter is the more elegant, using the method of cluster expansion. Its merits are that:

(a) few parameters, usually no more than 5, are required to apply the method to pure fluids and these can be given physical meanings.

- (b) The method can predict, as opposed to correlate, all interesting thermodynamic properties to their experimental uncertainties.
- (c) The resulting intermolecular potential functions, which are by-products of the method, can find use in computer simulation methods and in the prediction of transport properties of fluids.
- (d) There is a clear theoretical guide as to how the method may be extended to mixtures.

On the other hand, the virial equation of state is defective in some respects and these include:

- (a) The method is capable of very high accuracy only at a limited range of the sub-critical and supercritical states. Nevertheless it is now known that it can give useful results in the supercritical states even at ρ_c (Wiebke et al, 2011).
- (b) It is not valid at liquid-like densities and so it is not, by itself, useful for vapour-liquid equilibrium calculations.
- (c) The more useful implementations of the method require the investment of considerable computer resources (Monago and Otobrise, 2016).

In a previous paper, the second and third virial coefficients and their first two temperature derivatives were related to model intermolecular potential functions and the parameters in the potential functions were determined from experimental acoustic data for propane (Monago, 2006). The method predicted the thermodynamic properties of propane over a wide range of temperatures only when the density is not greater than one-fifth of the critical value. In this paper, we extend the method by incorporating the 4th virial coefficient in the procedure, in the hope of extending the density region in which the method is capable of high accuracy.

A more recent development is the use of Monte Carlo simulation techniques to calculate volumetric virial coefficients of real non-spherical molecules. Benjamin et al (2009) and Shaul et al (2011) have calculated volumetric virial coefficients up to the fifth order. However, the accuracy of calculated volumetric virial coefficients higher than the third cannot be verified because no experimental data on the higher volumetric virials exist. There is some

evidence to suppose that higher virials calculated by simulation are as yet not sufficiently accurate. For example, second and third virial coefficients calculated by Kim et al (2013) for mixtures of methane and ethane disagreed with experiment by between 5 – 10 and 20 – 30 percent, respectively. Also, the pressures of water calculated by Benjamin et al (2009) using a fifth-order virial EOS were deemed accurate only up to $\rho_c/2$!

Today, the virial EOS has found use in the gas-phase fiscal metering, or custody transfer, of natural gas in pipelines. Gas pipelines are characterised by high volumetric flowrates, which means that in a day an enormous amount of gas passes from the custody of one party to another. Current best practice requires custody transfer to be based on the actual amount of gas that is transferred; an even more stringent, but related, condition sometimes used is based on the gross calorific value of the fuel. In general, custody transfer flowmeters are either of the mass or volumetric type; however, irrespective of the type, in addition to temperature, pressure and composition, density is required in order to determine the amount of gas that is transferred. Gas density can either be measured with a gas densitometer or calculated from an EOS. However, whether measured or calculated, the accuracy of density is crucial as even a small error can add up fast, leading to financial exposure for one party, or the other, in the custody transfer transactions.

One of the joint venture partners in the Nigerian liquefied natural gas (NLNG) venture supplies a total of 1.2 billion standard cubic foot (BSCF) of gas per day to the NLNG plant from both on-shore and

off-shore gas facilities (NLNG, 2014). Assuming an accuracy of 0.1 percent in measurement, this level of uncertainty translates to a loss of some 1.2 MMSCF of gas per day and at current price of \$3.3 per 1000 cubic foot set by the Federal Government, the 0.1 percent inaccuracy translates to a potential financial loss of about 1.42 million (US) dollar per year to the partner or NLNG. The virial EOS enables the density of natural gas to be calculated with an accuracy of better than 0.05 % within the so-called custody transfer region; namely, $T/[K] = 300 \pm 30$ and $P/[MPa] \leq 12$ (Monago, 2012).

In this work, parameters in the equation of state model were determined by a fit to speed-of-sound data. The Choice of acoustic data makes sense because, perhaps more than any other thermodynamic property, speed-of-sound values can be determined with exceptionally high accuracy over wide ranges of temperature and density, including the difficult low temperature states where conventional *PVT* measurements encounter the difficulty of gas adsorption. However, any thermodynamic property that is accessible with high accuracy can be made this basis of the procedure.

THEORY

The basic definition that relates equilibrium speed of sound to other thermodynamic properties is

$$w^2 = -\frac{V^2}{M} \left(\frac{\partial P}{\partial V} \right)_s \quad (1)$$

Where, w is the sound-speed, V is molar volume, s is entropy and M is the molar mass. Using standard thermodynamics, the above definitional equation may be

transformed into a computational one, namely (Monago, 2005)

$$w^2 = -\frac{\gamma V^2}{M} \left(\frac{\partial P}{\partial V} \right)_T \quad (2)$$

in which $\gamma = C_p/C_v$ is the ratio of the two principal heat capacity functions and T is the thermodynamic temperature. Introducing the truncated virial equation of state,

$$Z = 1 + B/V + C/V^2 + D/V^3 \quad (3)$$

Where, B , C , D are, respectively, the second, third and fourth volumetric, or ordinary, virial coefficients; they are functions only of temperature. In terms of Eq. (3), one derives the following prescriptions:

$$V = ZRT/P \quad (4)$$

$$\frac{1}{\beta_r} = -\frac{V^2}{RT} \left(\frac{\partial P}{\partial V} \right)_T = 1 + 2B/V + 3C/V^2 + 4D/V^3 \quad (5)$$

$$C_v = C_v^{pg} - (R/V^3) [(2TB' + T^2 B'' V^2 + (2TC' + T^2 C'' V)/2 + (2TD' + T^2 D'' V^2)/3] \quad (6)$$

$$C_p = C_p^{pg} - \frac{1}{RT} \int_0^P T^2 \left(\frac{\partial^2 V}{\partial T^2} \right)_p dP \quad (7)$$

Finally,

$$w^2 = RT\gamma/M\beta_r \quad (8)$$

In Eq. (3) to (5), Z is the compressibility factor, β_r is dimensionless coefficient of isothermal compressibility and R is the molar gas constant. The other derived derivative properties required in the above expressions are determined from equations (3) and (4); the results are

$$\begin{aligned}
& -T^2 \left(\partial^2 V / \partial T^2 \right)_p = \\
& V[V^3 + (B + TB')V^2 + (C + TC')V + D + TD'] / d \\
& -V[(2TB' + T^2 B'')V^2 + (2TC' + T^2 C'')V + 2TD' + T^2 D''] / d \\
& -V[4V^3 + 3(B + TB')V^2 + 2(C + TC')V + D + TD'] [V^3 + (B + TB')V^2 + (C + TC')V + D + TD'] / d^2 \\
& + V[2TB'V^2 + 3TC'V + 4TD'] [V^3 + (B + TB')V^2 + (C + TC')V + D + TD'] / d^2 \\
& + V^2(3V^2 + 4BV + 3C)[V^3 + (B + TB')V^2 + (C + TC')V + D + TD']^2 / d^3
\end{aligned} \tag{9}$$

Where,

$$d = V^3 + 2BV^2 + 3CV + 4D$$

In Eq. (6) and (9), B' is the first temperature derivative of B and B'' is the second temperature derivative also of B ; C' and C'' , and D' and D'' are similarly defined.

The virial coefficients, which are functions only of temperature, are related to the potentials of interaction by integral expressions; in the language of linear graph (Monago, 2005; 2013):

$$\begin{aligned}
-2B &= \text{---} \\
-3C &= \triangle + \triangle \\
-8D &= 3 \begin{array}{c} \bullet \text{---} \bullet \\ | \\ \bullet \text{---} \bullet \end{array} + 6 \begin{array}{c} \bullet \text{---} \bullet \\ | \quad \diagdown \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \bullet \text{---} \bullet \\ | \quad \diagup \\ \bullet \text{---} \bullet \end{array} + 12 \begin{array}{c} \bullet \text{---} \bullet \\ | \quad \diagdown \quad \diagup \\ \bullet \text{---} \bullet \end{array} + 4 \begin{array}{c} \bullet \text{---} \bullet \\ | \quad \diagdown \quad \diagup \\ \bullet \text{---} \bullet \end{array} \\
& \quad \quad \quad D_a \quad \quad \quad D_b \quad \quad \quad D_c \quad \quad \quad D_d \quad \quad \quad D_e
\end{aligned}$$

The equation for D is exact only at the level of graphs that contain at most one triplet potential; higher graphs have been neglected. For the pair-potential, we use that proposed by Maitland and Smith (1973), namely

$$\phi(r_{ij}) = \frac{6\varepsilon}{n-6} \left\{ (r_m/r)^n - (n/6)(r_m/r)^6 \right\}; \tag{17}$$

It has four parameters; ε , the magnitude of the potential at its minimum; r_m , the radial distance where $\phi = -\varepsilon$ and two shape parameters m and κ , which determine the repulsive exponent according to the linear equation

$$n = m + \kappa \left\{ (r/r_m) - 1 \right\} \tag{18}$$

The shape parameters act also to simulate the contributions of multipoles that are higher than the dipole-dipole term of the attractive part of the pair-potential. Non-additive three-body forces are modeled by the Axilrod-Teller triple dipole term; hence,

$$\Delta\phi_3 = v_{123} (1 + 3 \cos\theta_1 \cos\theta_2 \cos\theta_3) / (r_{12} r_{13} r_{23})^3 \tag{19}$$

Equation (19) adds the fifth parameter to the model namely, v_{123} , the three-body strength coefficient.

NUMERICAL METHODS

Parameters in the model potential functions were determined by solving the nonlinear least square problem

$$\chi^2 = \mathbf{R}^T \mathbf{R} \quad (20)$$

Where,

$$R_i(\mathbf{x}) = (w_{i,\text{cal}} - w_{i,\text{expt}}) / s_i \sqrt{N - N_p} \quad (21)$$

Here, \mathbf{x} is the parameter vector, $w_{i,\text{expt}}$ is the i -th experimental speed of sound value, $w_{i,\text{cal}}$ is the calculated value for the speed of sound at the i -th data point, N is the total number of acoustic data points, N_p is the number of adjustable parameters in the model and s_i is the estimated standard deviation of $w_{i,\text{expt}}$.

Each $w_{\text{cal}}(T_i, P_i)$ was calculated in the following way. First, the virial coefficients B , C and D together with their first two temperature derivatives were calculated along the 7 experimental isotherms from the integral expressions that relate them to $\phi(r_{ij})$ and $\Delta\phi_3$. Next, at each experimental temperature and pressure of the data points, the following equation was solved for Z

$$Z^4 - Z^3 - (BP/RT)Z^2 - C(P/RT)^2 Z - D(P/RT)^3 = 0 \quad (22)$$

Thereafter, V was calculated from Eq. (4), followed by C_v and C_p , respectively, from Eq. (6) and (7). Finally, $w_{\text{cal}}(T_i, P_i)$ was calculated from Eq. (8).

The dimensionless statistic, χ^2 was minimized using a method described by Fletcher (1987), which is a Newton-like method that incorporates a restricted step algorithm. The method requires values of the first partial derivatives of $w_{\text{cal}}(T_i, P_i)$ with respect to each adjustable parameters; these were calculated numerically using a first-order forward-difference formula.

The virial coefficients and their temperature derivatives were calculated numerically by a method that combined the composite Simpson's rule and a multi-panel Gaussian quadrature. The former was employed in the regions where the integrand is rapidly varying, while the latter was used in those sections where the integrand varied slowly.

The Fit to the Speed of Sound

The experimental speeds of sound data of Trusler and Zarari (1996) were given on seven isotherms in the region $0.61 \leq T/T_c \leq 1.01$ and $\rho \leq \rho_c/12$ and were estimated to possess a uniform standard deviation of 0.002ms^{-1} . In a previous work Monago (2006), the best fit for propane was obtained when κ , one of the shape parameters in the pair-potential, assumed the value 12. Consequently, only four model parameters were allowed to vary in the present fit, κ was assigned a fixed value of 12.

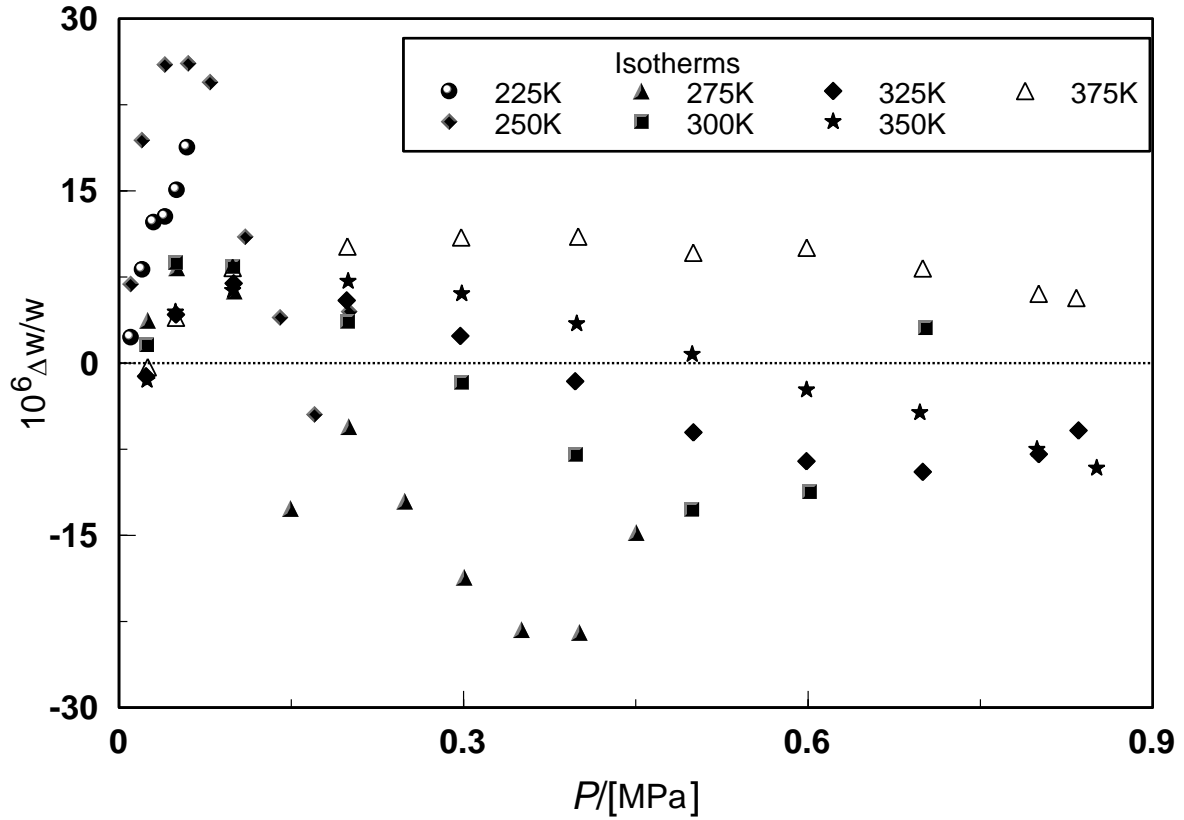


Fig. 1: Fractional uncertainties, $\Delta w/w_{\text{expt}}$, in experimental speed-of-sound of propane from the fit. $\Delta w = w_{\text{expt}} - w_{\text{cal}}$.

The final parameter values obtained were as follows

$$\left. \begin{aligned} r_m &= 0.486572 \text{ nm} \\ \varepsilon / k &= 560.81 \text{ K} \\ m &= 67.655 \\ \kappa &= 12 \\ \nu_{123} &= 0.044342 \text{ K nm}^9 \end{aligned} \right\} \quad (23)$$

The maximum absolute deviation was 0.006 and $\chi^2=1.6$. The deviations of the experimental speeds of sound from those given by the final model are displayed in fig. 1.

COMPARISON WITH OTHER EXPERIMENTAL DATA

All residual thermodynamic properties of gaseous propane may be calculated from the

present truncated virial equation of state; however, to calculate caloric properties, one needs values for the perfect-gas heat capacity at each temperature of interest as an independent specification. As mentioned previously, the perfect-gas heat capacity required for parameter optimisation were obtained from Trusler and Zarari (1996), who derived their values from a low-density analyses of their acoustic data. Trusler(1997) has parameterised these heat capacity values for use in the temperature range $225 \leq T/\text{K} \leq 375$. We have used Trusler's expression in calculating C_p^{pg} for use in the calculation of all caloric properties presented in this paper.

Experimental volumetric data for propane are available from the work of Thomas and

Harrison (1982); their data extended in temperature between $258.15 \leq T/K \leq 623.15$ for the density range $\rho_n \geq 0.8 \text{ mol dm}^{-3}$. The fractional uncertainties in the experimental compressibility factor were quoted to vary between $(0.3-3) \times 10^{-3}$, which depended on temperature and density. The greatest density along any given isotherm employed in this work in the parameter optimization was not greater than $\rho_c/12$; consequently, the minimum density of the data of Thomas and Harrison(1982) is more than twice the

maximum density along any of the 7 isotherms used for parameter optimization. Accordingly, comparison of the predictions of the equation of state with the data of Thomas and Harrison provides a severe test on the ability of the model to extrapolate not only in density, but also in temperature. Fig 2 shows deviations, ΔZ , in compressibility factors along four isochores from Thomas and Harrison; namely, $\rho_n/[\text{mol dm}^{-3}] = 0.8, 1.0, 1.5, \text{ and } 2.0$. This figure suggests that compressibility factors calculated with the

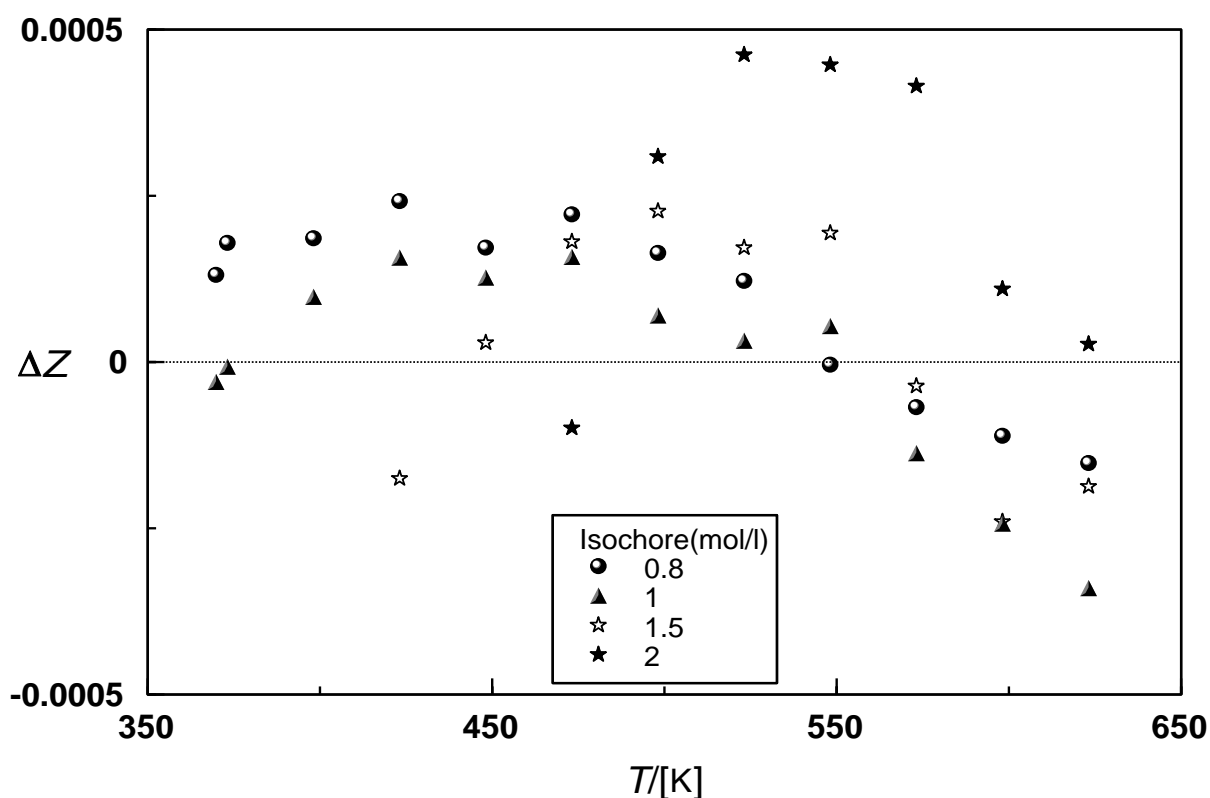


Fig.2: Deviations in compressibility factors of propane predicted by Eq. (23) along four isochores.

present equation of state is not in error by more than 0.03 percent in the whole of the supercritical temperature region at densities of 2 mol dm^{-3} ($0.4\rho_c$) or less. Indeed, the

maximum density at which the equation of state may predict Z that falls within the experimental uncertainties is $\rho_c/2$ for $T/K \geq 400$; this is shown in fig 3.

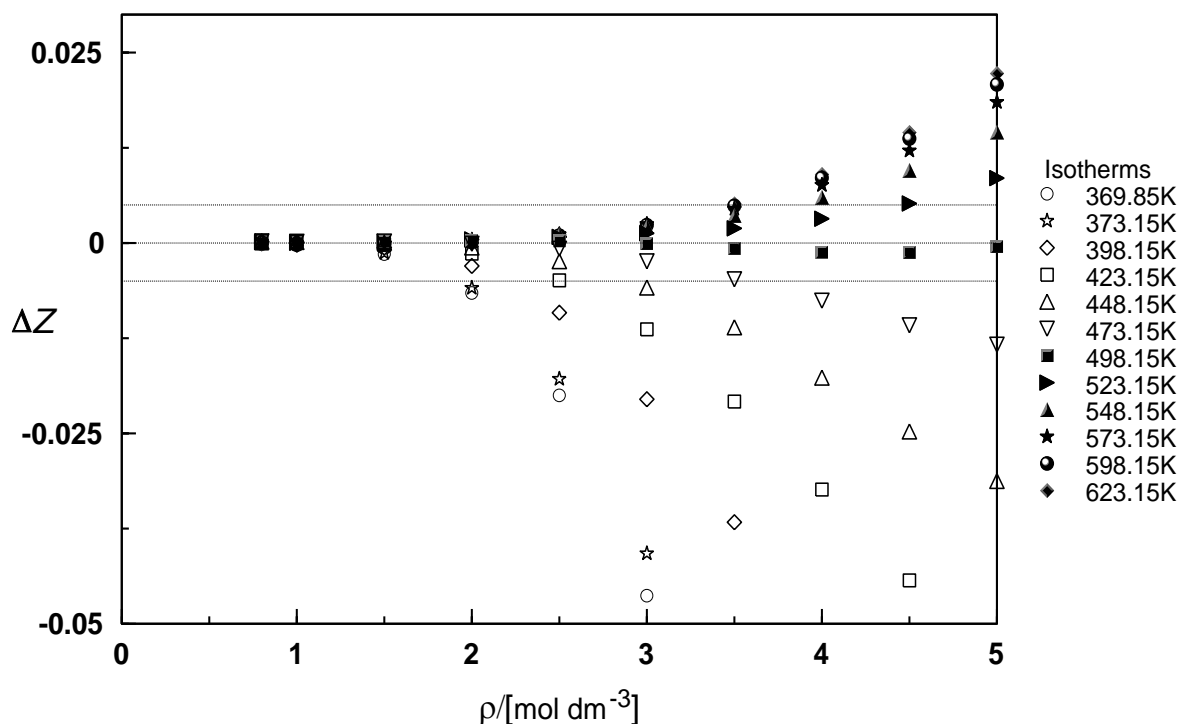


Fig.3: Deviations in compressibility factors of propane predicted by Eq. (23) from experimental values in the temperature range 369. 85 – 623.15 K..

Furthermore, calculated values of Z are not in error by more than 2 percent at ρ_c for $T/K \geq 450$. One may, therefore, conclude that the virial equation of state is convergent in the supercritical temperature region up to at least ρ_c .

In the sub-critical region, Thomas and Harrison(1982) reported vapour pressures P_σ of propane at temperatures $T/K \geq 258.15$ and orthobaric vapour densities for $T/K \geq 323.15$. From these data, we have calculated compressibility factors for the saturated vapour, $Z_{\sigma, \text{exp}}$, with which we compared those predicted by the present model. The fractional error in Z_σ at 323.15K was 0.0008; at 333.15K the error was 0.002. These results are in apparent contradiction of those obtained in the supercritical temperature region and those obtained

previously with a virial equation of state that was truncated after the 3rd coefficient (Monago, 2006). In the latter case, the errors in Z_σ are 0.0002 and 0.0006 at 323.15K and 333.15K, respectively. It appears, therefore, that the present virial equation of state, truncated after the 4th coefficient, is less accurate at sub-critical temperature states than one that is truncated after the 3rd coefficient.

Experimental isobaric heat capacity data at four sub-critical isotherms in the temperature range $293.15 \leq T/K \leq 353.15$ are available from the work of Ernst and Büsser(1970); these data have a claimed uncertainties of 0.1 percent. The experimental C_p data are compared with those predicted from our model in Fig 4.

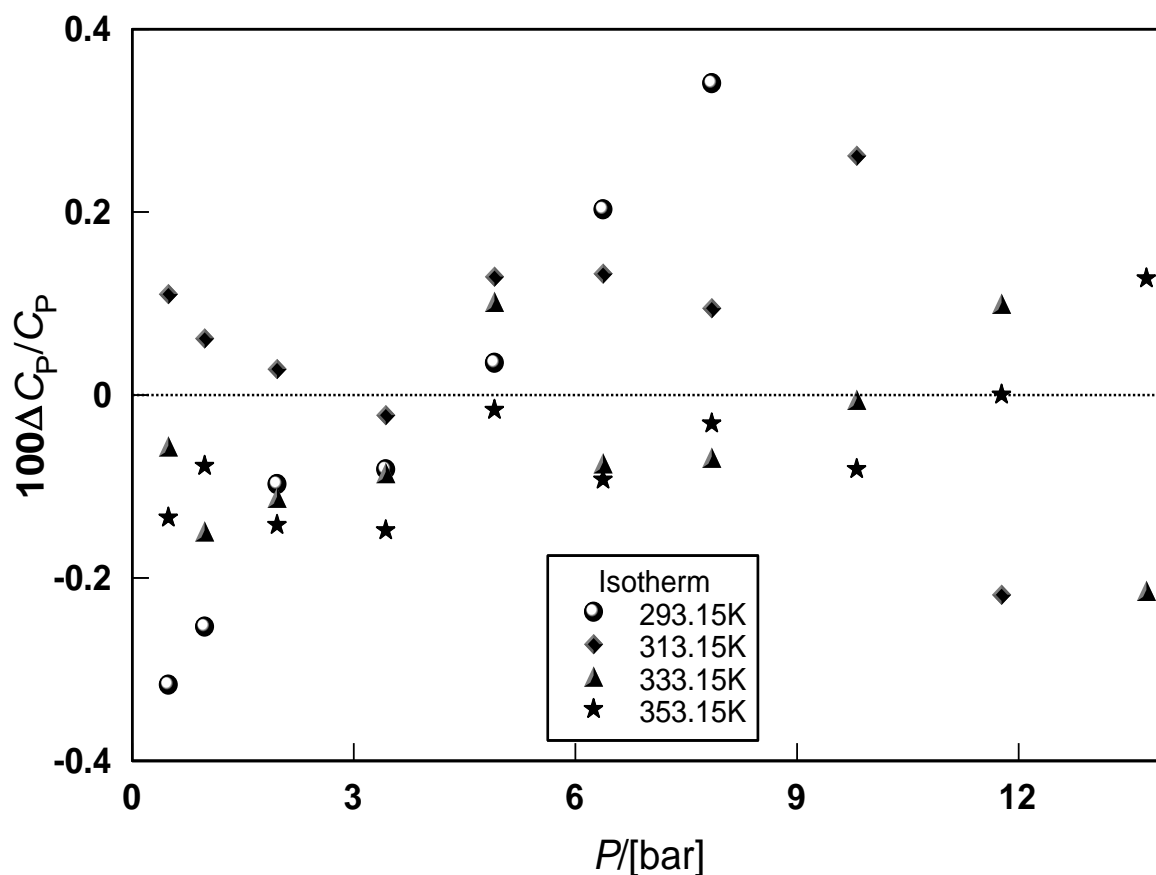


Fig 4: Fractional errors in isobaric heat capacity of propane predicted from Eq. (23) with respect to the data of Ernst and Busser (1970) in the temperature range 293 – 353 K.

These results, like those calculated with a three-term virial equation (Monago, 2006), generally, agree with the experimental data of Ernst and Young(1970) to within 0.2 percent.

The Virial Coefficients of Propane

Thomas and Harrison(1982) determined the second virial coefficients of propane in the temperature range $323.15 \leq T/K \leq 623.15$, the third coefficients in the range $343.15 \leq T/K \leq 623.15$ and the fourth coefficients in the range $373.15 \leq T/K \leq 623.15$ from the analyses of their volumetric data.

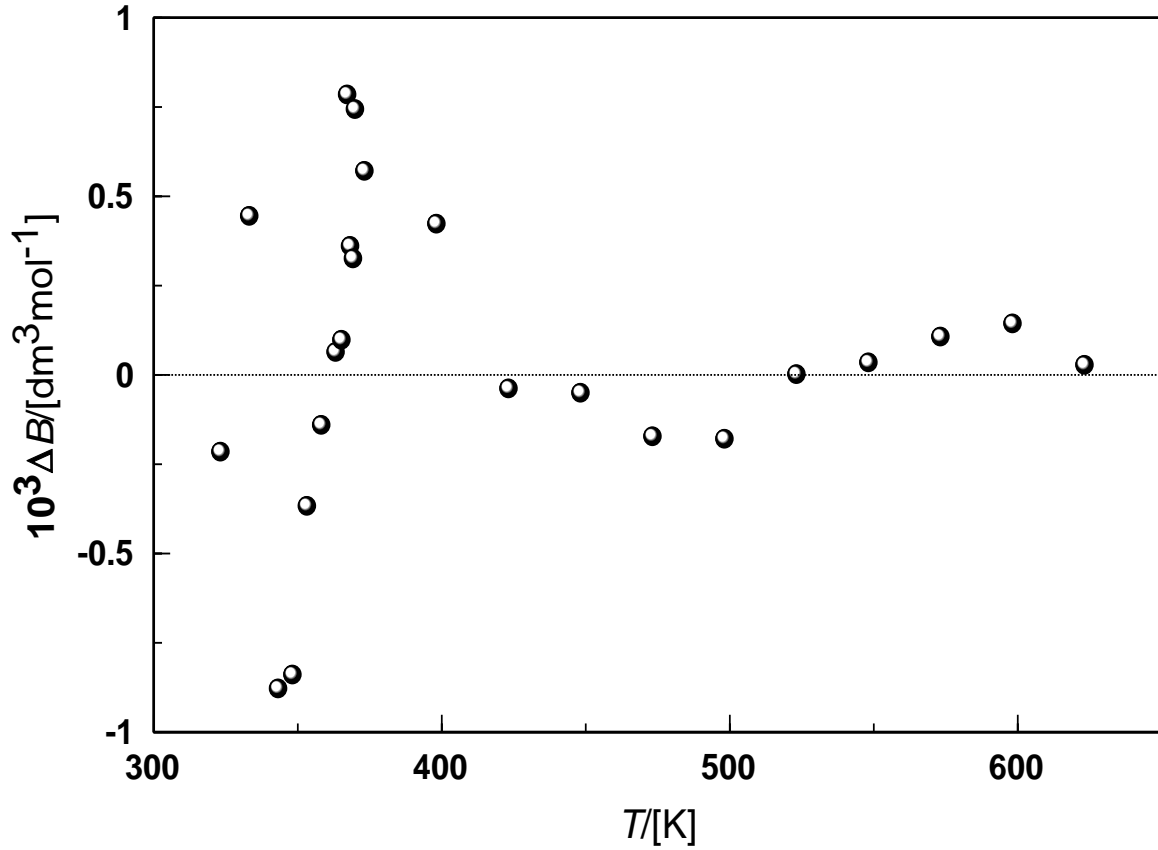


Fig 5: Deviations in experimental ordinary second virial coefficients of propane with respect to values predicted by Eq. (23).

Fig 5 is a deviation plot, $\Delta B = B_{\text{exp}} - B_{\text{cal}}$; where, B_{exp} are values from Thomas and Harrison(1982) and B_{cal} are those calculated from the present model. The estimated absolute errors in B , $|\Delta B|$, vary between 0.75cm^3 for $T/\text{K} \leq 450$ and $0.2\text{cm}^3 \text{mol}^{-1}$ for $T/\text{K} > 450$. When these values for $|\Delta B|$ are compared with analogous values for a three-term virial equation of state, they represent an increase in the uncertainties for B_{cal} of about 50 percent in the first temperature range and a decrease of some 20 percent in the second range.

The values for C predicted by the present model are compared with those of Thomas and Harrison in fig6; the corresponding deviation plot is displayed as fig7. The estimated absolute errors in C_{cal} are $1500\text{cm}^6 \text{mol}^{-2}$ in the range $T/\text{K} \leq 420$ and $300\text{cm}^6 \text{mol}^{-2}$ in the range $T/\text{K} > 420$.

These errors correspond to an increase of about 50 percent at $T/\text{K} \leq 420$ and a decrease of some 40 percent at $T/\text{K} > 420$ when they are compared with analogous results obtained with a three-term virial equation model.

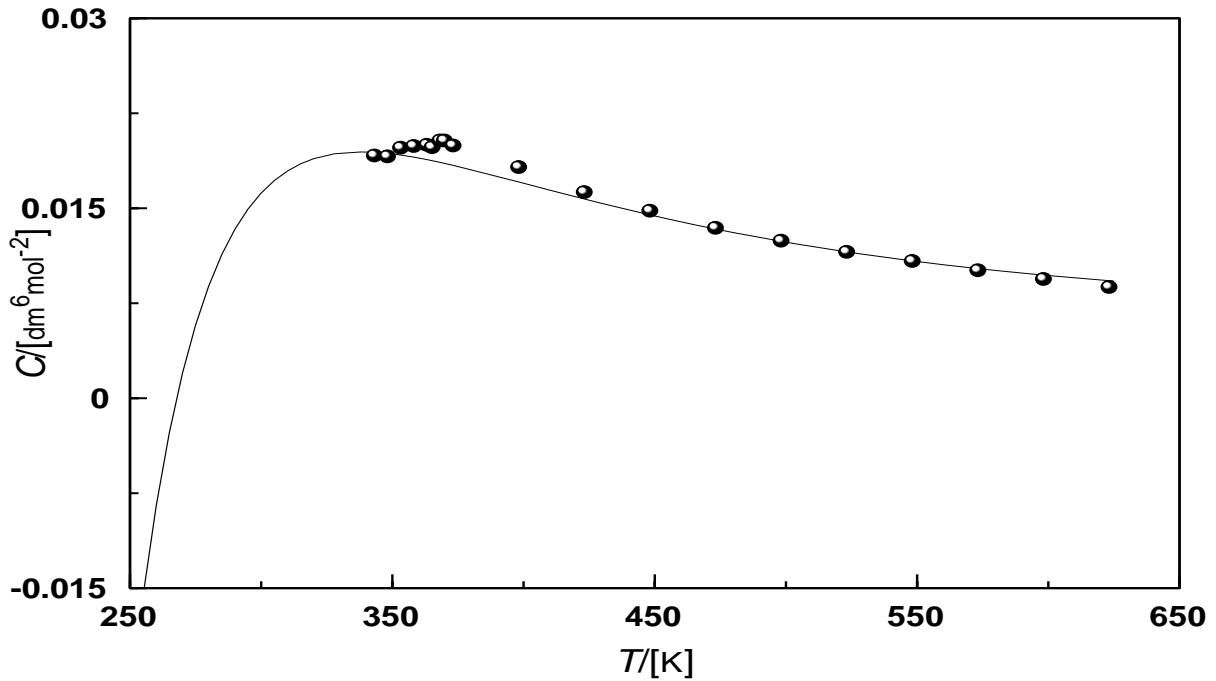


Fig 6: Experimental and predicted ordinary third virial coefficient of propane as a function of temperature. —, this work; •, Thomas and Harrison (1982).

The values for the fourth virial coefficient obtained from the present equation of state are compared with the data of Thomas and Harison(1982) in fig8. In interpreting this diagram it may be useful to recall that non-

additive interactions account for 30 percent of the values of C near the critical point of argon; therefore, it is possible that inclusion of the neglected graphs in D will improve agreement between experiment and theory.

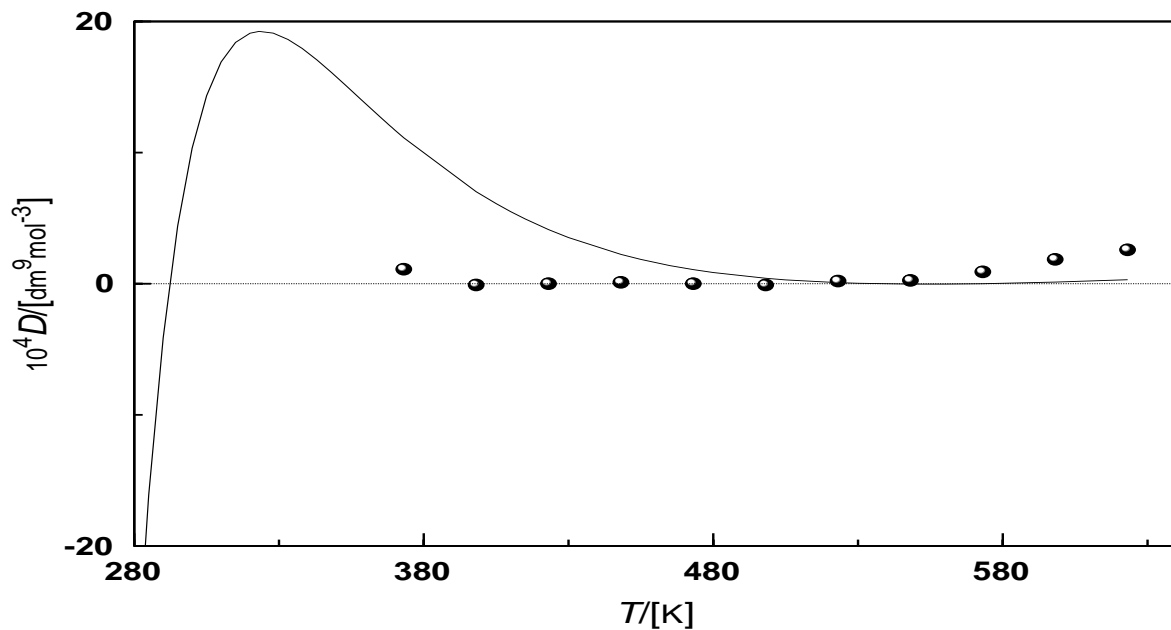


Fig 7: Experimental and predicted ordinary fourth virial coefficient of propane as a function of temperature. —, this work; •, Thomas and Harrison (1982).

At present we cannot calculate the 4th virial coefficient with exactness and it is reasonable to substitute a linear approximation in three-body non-additive forces to D for the unknown value. However, does this approach necessarily lead to a more useful theory?

When a linear approximation to D is employed, the resulting equation of state for propane is less accurate at sub-critical temperatures than if D is neglected altogether. This is demonstrated by the calculated values for B and C which exhibited greater discrepancies with experimental values; also, the resulting equation of state predicted experimental orthobaric vapour density only at $T/K < 323.15$, whereas the three-coefficient analogue agreed with experiment up to $T/K < 333.15$.

Conversely, the equation of state for propane constructed with the linear approximation performed better at supercritical temperatures. The calculated values of B and C for this temperature range are in closer agreement with those determined from volumetric data than comparable virial coefficients from a three-coefficient equation of state. Furthermore, the maximum density at which the equation of state agree with experimental volumetric data increased to 2mol/dm^3 , or $2\rho_c/5$; this may be compared with the three-coefficient equation of state that predicted experimental volumetric data up to $\rho_c/5$.

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