New Reference Equation of State for Carbon Dioxide

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ABSTRACT

For carbon dioxide, the current reference for thermodynamic properties is the equation of state (EOS) of Span and Wagner published in 1996. While the Span-Wagner EOS provides accurate properties at most conditions of industrial interest, some deficiencies have been identified since it was developed. NIST has developed a replacement for the Span-Wagner EOS. The new EOS makes use of state-of-the-art molecular calculations for the ideal-gas heat capacity and for the thermal virial coefficients, improving accuracy for the gas phase and allowing extrapolation to temperatures above the range of experimental data. The functional form of the EOS has been optimized to prevent spurious near-critical behavior and to avoid problems with mixture calculations. The new EOS represents the available experimental data as well as or better than the Span-Wagner EOS. The behavior is greatly improved outside the region where extensive measurements exist, and calculational speed has been improved by roughly a factor of 1.5–2. The new EOS will be made available for use in NIST's REFPROP software.

INTRODUCTION

Design of machinery for power cycles requires accurate thermophysical properties of the working fluid. In the case of carbon dioxide (CO$_2$), the equation of state (EOS) of Span and Wagner (1996) has served as an accurate source of thermodynamic properties for many years, and is implemented in common databases such as REFPROP (Lemmon *et al.*, 2018). While the Span-Wagner EOS is highly accurate in its region of validity (at least for the main thermodynamic properties such as density and enthalpy) and is adequate for many purposes, shortcomings have been identified over the years that make development of a new EOS desirable.

One issue with the Span-Wagner EOS arises from the fact that EOS developers in the 1990s did not have the tools to ensure smooth, physical behavior of derivative properties such as the isothermal compressibility. The Span-Wagner EOS exhibits oscillations in some of these derivative properties near the critical point. This unphysical thermodynamic behavior also distorts calculated thermal conductivities (Huber *et al.*, 2016). It is conceivable that irregular behavior in derivative properties could cause problems in process control algorithms that depend on derivatives, although we are not aware of any reports of such problems.

Advances in equation-of-state technology are also now able to produce better extrapolation behavior; the Span-Wagner EOS begins to exhibit unphysical behavior when extrapolated to low temperatures. This can produce problems in modeling CO_2-containing mixtures, where typical mixture models may require evaluating the EOS at conditions outside the range of pure-component conditions to which it was fitted. At high temperatures (above about 800 K), the uncertainty of the Span-Wagner EOS is larger than one might hope, due to the lack of available experimental information.

Finally, the Span-Wagner EOS is computationally complex, containing 42 terms of different types. This makes it inconveniently slow in applications that require many computations of thermodynamic properties. Modern EOS fitting technology can reduce the number of terms, and hence the computation time, by roughly a factor of two.

In the following, we provide a preliminary description of our new equation of state, including selected comparisons with data. The new reference EOS, which may still undergo some minor fine-tuning, will be fully documented in a forthcoming journal article.

DEVELOPMENT OF THE EQUATION OF STATE

The database of experimental measurements for fitting the equation of state for CO_2 began with that used by Span and Wagner (1996), but was augmented by several additional data sources that helped to reduce the uncertainty of the EOS and/or extend its range of applicability. Particularly helpful sources for constraining the EOS included a high-accuracy measurement of the saturation pressure at 273.16 K (Bignell and Bean, 1988), four studies of the speed of sound over a wide range of fluid conditions (Giordano *et al.*, 2006; Lin and Trusler, 2014; Liu *et al.*, 2014; Rivas *et al.*, 2016;), and three studies of the fluid density that cover the region near the critical point (Deering *et al.*, 2016; Bazile *et al.*, 2018; Sanchez-Vicente *et al.*, 2018). While not the main focus of the project, new experimental data at pressures up to 10 GPa extend the range of application to much higher pressures.

We were also able to take advantage of advances in molecular theory. The ideal-gas heat capacity c_p^0 determines the caloric behavior for the vapor at low densities, and is especially important for extrapolation to high temperatures. Previously, c_p^0 was obtained from a relatively simple model that took into account molecular rotations and vibrations in a first-order way. It is now possible to use the abundant spectroscopic information available for the CO_2 molecule (Tashkun and Perevalov, 2011), supplemented by additional calculations, to generate highly accurate ideal-gas thermochemistry for CO_2 at temperatures up to at least 3000 K, by direct calculation of the partition function similar to recently published work for oxygen (Furtenbacher *et al.*, 2019). These directly calculated values have very small relative uncertainties, less than 0.001 % below 1200 K and less than 0.02 % up to 2100 K. This improves the high-temperature behavior of the EOS, particularly the enthalpy.

Molecular theory is also able to supply accurate values for the second (Hellmann, 2014) and third (Hellmann, 2017) virial coefficients, which represent the first- and second-order deviations from the ideal-gas law, constraining the gas-phase behavior at low and moderate pressures. These virial coefficients are known with good accuracy from experiment between roughly 250 K and 400 K, but the theoretical calculations (which agree with experimental data where they exist) can give values at any temperature, greatly expanding the range in which the nonideal gas-phase behavior can be known with confidence.

The structure of the EOS is the Helmholtz-energy form that is typically used for reference equations of state (Span and Wagner, 1996; Herrig *et al.*, 2018). The molar Helmholtz energy *a* (reduced by *RT*, where *R* is the molar gas constant and *T* is the absolute temperature) is written as a function of temperature *T* and density ρ as the sum of an ideal-gas term *a*° and a residual term *a*ʳ, where the residual term accounts for all intermolecular interactions:

$$\alpha(\tau,\delta) = \frac{a(T,\rho)}{RT} = \frac{a°(T,\rho) + a^r(T,\rho)}{RT} = \alpha°(\tau,\delta) + \alpha^r(\tau,\delta), \qquad (1)$$

In Eq. (1), τ is the reciprocal reduced temperature T_c/T while δ is the reduced density ρ/ρ_c, where the subscript c denotes the value at the vapor-liquid critical point (T_c = 304.1282 K, ρ_c = 10.6249 mol dm⁻³).

The structure of the residual contribution is optimized so that the primary data are reproduced within their uncertainties with a minimal number of terms. In this case, the residual contribution has 24 terms (compared to the 42 terms required by Span and Wagner).

RESULTS AND DISCUSSION

We begin our review of the performance of the new equation of state by examining the ideal-gas heat capacity, which determines the caloric behavior at low densities. Figure 1 compares the values of c_p^0 determined in this project with those calculated from the *a*° term in our EOS. Some older, less accurate sources of c_p^0 values are also shown, along with those from the previous reference EOS of Span and Wagner (1996). While the older, simpler calculations for c_p^0 are reasonably good (within about 0.05 %) below about 800 K, their temperature trend is clearly not correct at higher temperatures. This is probably due to higher-order effects of phenomena like anharmonicity and rotation-vibration coupling that could only be considered in approximate ways in previous calculations. The new equation will therefore provide more accurate enthalpies for the gas phase at high temperatures.

Second, we examine the second virial coefficient *B* and third virial coefficient *C*, where molecular theory has produced values of high accuracy over a wide temperature range (Hellmann, 2014; Hellmann, 2017). These coefficients constrain the fluid behavior at moderate densities in the gas and supercritical regions. Figure 2 shows the deviations in *B*(*T*) of different data sets (and of the Span-Wagner EOS) from those calculated with our new EOS. The calculated data of Hellmann (2014) should be accurate to within roughly 0.2 cm³/mol in the range plotted, and we fit those data well within that uncertainty, including at higher temperatures not shown in the plot. The highest-quality experimental data (Holste *et al.*, 1987; Duschek *et al.*, 1990) are fitted within their uncertainties. *B*(*T*) from the Span-Wagner EOS becomes increasingly inaccurate at high temperatures, which implies a corresponding inaccuracy in properties for high-temperature gases. Figure 3, for *C*(*T*) where the experimental database is more sparse, shows similar results, with the high-accuracy calculations of Hellmann (2017) reproduced well. These results allow us to describe gas-phase thermodynamics with higher confidence in the range (above about 500 K) where few reliable experimental data exist.

One of the most important quantities calculated from the equation of state is the vapor pressure. Figure 4 shows the relative deviations of selected data sources, and of the Span-Wagner EOS, from our equation of state. The scatter in the best experimental vapor-pressure data is on the order of 0.002 % to 0.005 % over most of the temperature range; the performance of our new

equation is of similar quality to that of Span and Wagner (1996).

For other properties, such as densities, heat capacities, and sound speeds, the new EOS has uncertainties at least as small as those of the Span-Wagner EOS. In some cases, such as sound speeds for dense phases at supercritical conditions, we are able to achieve smaller uncertainties because of the availability of new experimental data. More thorough examination of these additional properties and comparison with the Span-Wagner EOS will be provided in an upcoming archival paper (Harvey *et al.*, 2022).

One motivation for this work was to derive a more efficient form for the equation of state. While the computational savings depend on the calculation, preliminary timings indicate that the new EOS improves the calculational speed by a factor of 1.5–2 compared to the Span-Wagner EOS.

CONCLUSIONS

We have taken advantage of new experimental data, new data from molecular theory, and state-of-the art techniques for fitting equations of state to produce a new reference equation of state for carbon dioxide. The improvement in accuracy compared to the previous reference EOS of Span and Wagner (1996) is modest in regions where the previous equation was valid, but the new formulation covers a wider range of conditions and exhibits better extrapolation behavior, particularly for the gas phase at high temperatures. It is also incrementally faster.

Once the EOS is finalized, the remaining step in this project is to examine the existing reference correlations for the viscosity (Laesecke and Muzny, 2017) and thermal conductivity (Huber *et al.*, 2016). These correlations are based on using the EOS of Span and Wagner (1996) to convert experimental data measured as a function of temperature and pressure into the combination of temperature and density used by the correlations. While we expect the effect of updating the EOS to be small, if it turns out to be significant compared to the experimental uncertainties some minor refitting of these transport property correlations may be required.

It is expected that the new EOS will be made available (along with new transport property correlations if required) in a fluid file for use in the NIST REFPROP software (Lemmon *et al.*, 2018) sometime in 2022. An archival paper fully documenting the EOS and its performance will be submitted to the *Journal of Physical and Chemical Reference Data* (Harvey *et al.*, 2022).

REFERENCES

Bazile, J.-P., D. Nasri, A.W.S. Hamani, G. Galliero, and J.-L. Daridon (2018), "Excess volume, isothermal compressibility, isentropic compressibility and speed of sound of carbon dioxide + n-heptane binary mixture under pressure up to 70 MPa. I. Experimental measurements," *J. Supercrit. Fluids* **140**, 218.

Bignell, N., and V.E. Bean (1988), "A Fixed Point on the Pressure Scale: Carbon Dioxide Vapor Pressure at 273.16 K," *Metrologia* **25**, 141.

Deering, C.E., E.C. Cairns, J.D. McIsaac, A.S. Read, and R.A. Marriott (2016), "The partial molar volumes for water dissolved in high-pressure carbon dioxide from T = (318.28 to 369.40) K and pressures to p = 35 MPa," *J. Chem. Thermodyn.* **93**, 337.

Duschek, W., R. Kleinrahm, and W. Wagner (1990), "Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide I. The homogeneous gas and liquid regions in the temperature range from 217 K to 340 K at pressures up to 9 MPa," *J. Chem. Thermodyn.* **22**, 827.

Furtenbacher, T., M. Horváth, D. Koller, P. Sólyom, A. Balogh, I. Balogh, and A.G. Császár (2019), "MARVEL Analysis of the Measured High-Resolution Rovibronic Spectra and Definitive Ideal-Gas Thermochemistry of the $^{16}O_2$ Molecule," *J. Phys. Chem. Ref. Data* **48**, 023101.

Giordano, V.M., F. Datchi, and A. Dewaele (2006), "Melting curve and fluid equation of state of carbon dioxide at high pressure and high temperature," *J. Chem. Phys.* **125**, 054504.

Harvey, A.H., S.A. Tashkun, and E.W. Lemmon (2022), "New Reference Equation of State for Fluid Carbon Dioxide," *J. Phys. Chem. Ref. Data*, in preparation.

Hellmann, R. (2014), "*Ab initio* potential energy surface for the carbon dioxide molecule pair and thermophysical properties of dilute carbon dioxide gas," *Chem. Phys. Lett.* **613**, 133.

Hellmann, R. (2017), "Nonadditive three-body potential and third to eighth virial coefficients of carbon dioxide," *J. Chem. Phys.* **146**, 054302.

Herrig, S., M. Thol., A.H. Harvey, and E.W. Lemmon (2018), "A Reference Equation of State for Heavy Water," *J. Phys. Chem. Ref. Data* **47**, 043102.

Holste, J.C., K.R. Hall, P.T. Eubank, G. Esper, M.Q. Watson, W. Warowny, D.M. Bailey, J.G. Young, and M.T. Bellomy (1987), "Experimental (p, V_m, T) for pure CO_2 between 220 and 450 K," *J. Chem. Thermodyn.* **19**, 1233.

Huber, M.L., E.A. Sykioti, M.J. Assael, and R.A. Perkins (2016), "Reference Correlation of the Thermal Conductivity of Carbon Dioxide from the Triple Point to 1100 K and up to 200 MPa," *J. Phys. Chem. Ref. Data* **45**, 013102.

Laesecke, A., and C.D. Muzny (2017), "Reference Correlation for the Viscosity of Carbon Dioxide," *J. Phys. Chem. Ref. Data* **46**, 013107.

Lemmon, E.W., I.H. Bell, M.L. Huber, and M.O. McLinden (2018), *Reference Fluid Thermodynamic and Transport Properties – REFPROP*, NIST Standard Reference Database 23, Version 10.0 (National Institute of Standards and Technology).

Lin, C.-W., and J.P.M. Trusler (2014), "Speed of Sound in (Carbon Dioxide + Propane) and Derived Sound Speed of Pure Carbon Dioxide at Temperatures between (248 and 373) K and at Pressures up to 200 MPa," *J. Chem. Eng. Data* **59**, 4099.

Liu, Q., X. Feng, B. An, and Y. Dan (2014). "Speed of Sound Measurements Using a Cylindrical Resonator for Gaseous Carbon Dioxide and Propene," *J. Chem. Eng. Data* **59**, 2788.

Rivas, C., B. Gimeno, M. Artal, S.T. Blanco, J. Fernández, and I. Velasco (2016), "High-pressure speed of sound in pure CO_2 and in CO_2 with SO_2 as an impurity using methanol as a doping agent," *Int. J. Greenhouse Gas Cont.* **54**, 737.

Sanchez-Vicente, Y., W.J. Tay, S.Z. Al Ghafri, and J.P.M. Trusler (2018), "Thermodynamics of carbon dioxide-hydrocarbon systems," *Appl. Energy* **220**, 629.

Span, R., and W. Wagner (1996), "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa," *J. Phys. Chem. Ref. Data* **25**, 1509.

Tashkun, S.A., and V.I. Perevalov (2011), "CDSD-4000: High-resolution, high-temperature carbon dioxide spectroscopic databank," *J. Quant. Spectrosc. Rad. Trans.* **112**, 1403.
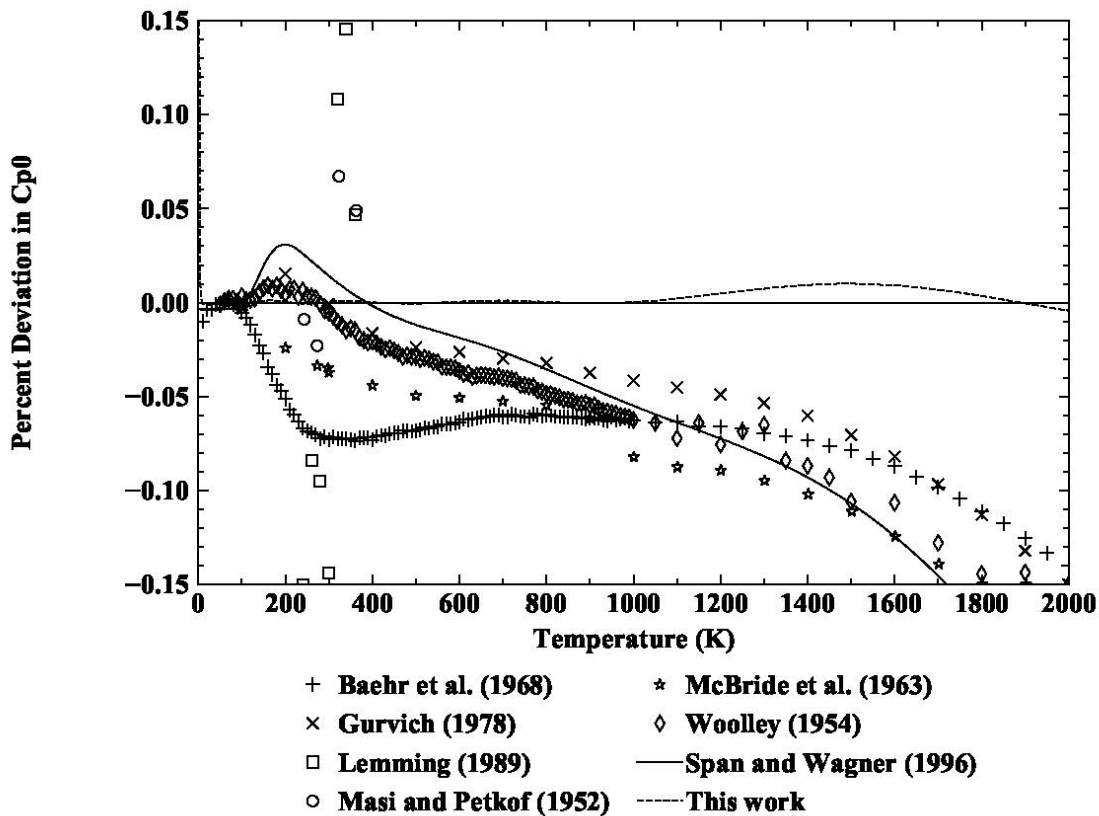
ACKNOWLEDGEMENTS

Figure 1: Relative deviations of previous experimental and calculated results for the ideal-gas heat capacity from those calculated with the new equation of state. State-of-the-art c_p^0 calculations from Tashkun (labeled "This work") were used as input.
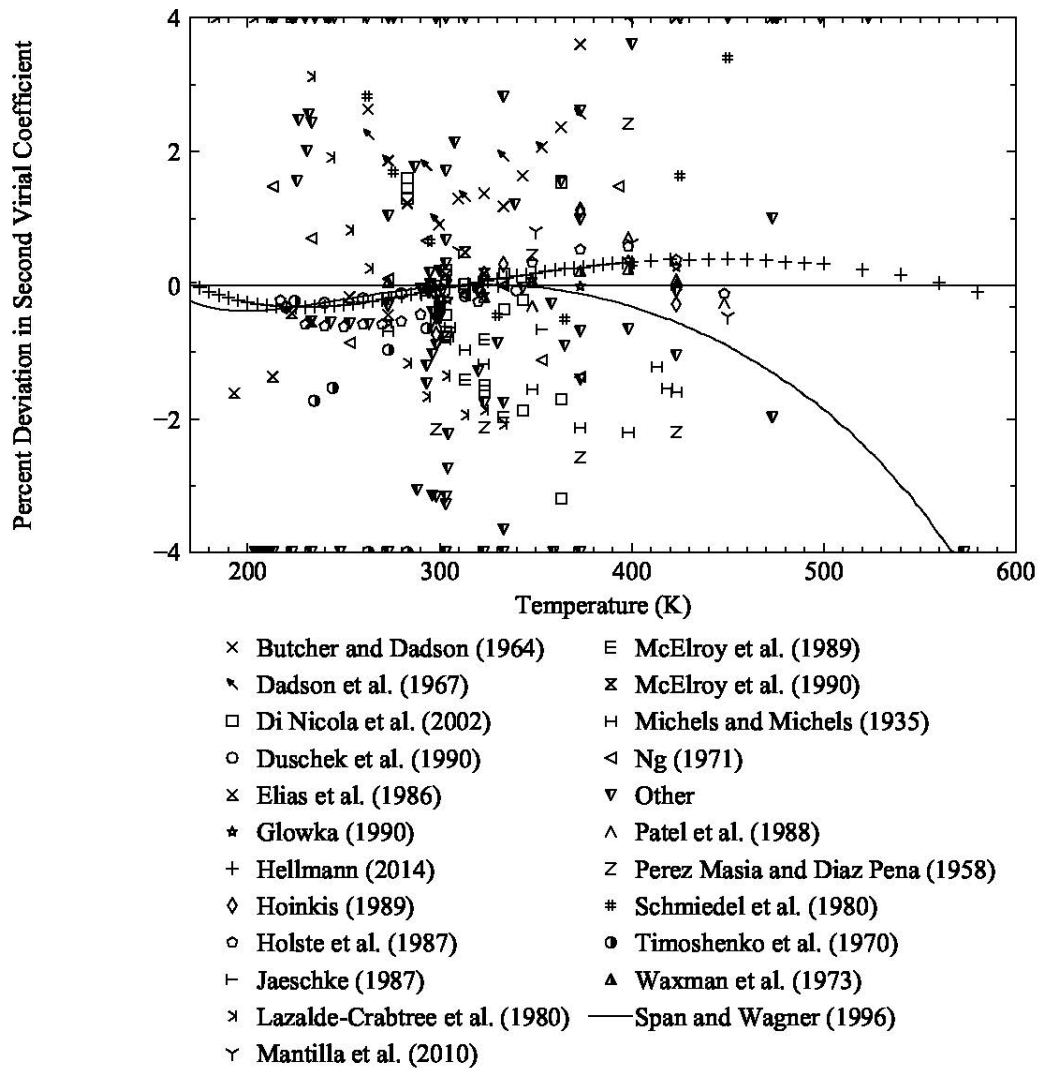
Percent Deviation in Second Virial Coefficient

4

2

0

−2

−4

200   300   400   500   600

Temperature (K)

× Butcher and Dadson (1964)   E McElroy et al. (1989)
↖ Dadson et al. (1967)   ⋈ McElroy et al. (1990)
□ Di Nicola et al. (2002)   ⊢ Michels and Michels (1935)
○ Duschek et al. (1990)   ◁ Ng (1971)
× Elias et al. (1986)   ▽ Other
★ Glowka (1990)   ∧ Patel et al. (1988)
+ Hellmann (2014)   Z Perez Masia and Diaz Pena (1958)
◊ Hoinkis (1989)   # Schmiedel et al. (1980)
○ Holste et al. (1987)   ⊙ Timoshenko et al. (1970)
⊢ Jaeschke (1987)   ▲ Waxman et al. (1973)
⋊ Lazalde-Crabtree et al. (1980)   ——Span and Wagner (1996)
Y Mantilla et al. (2010)

Figure 2: Relative deviations of second virial coefficient *B*(*T*) from those calculated with the new equation of state. Calculated values from Hellmann (2014) were used as part of the input.
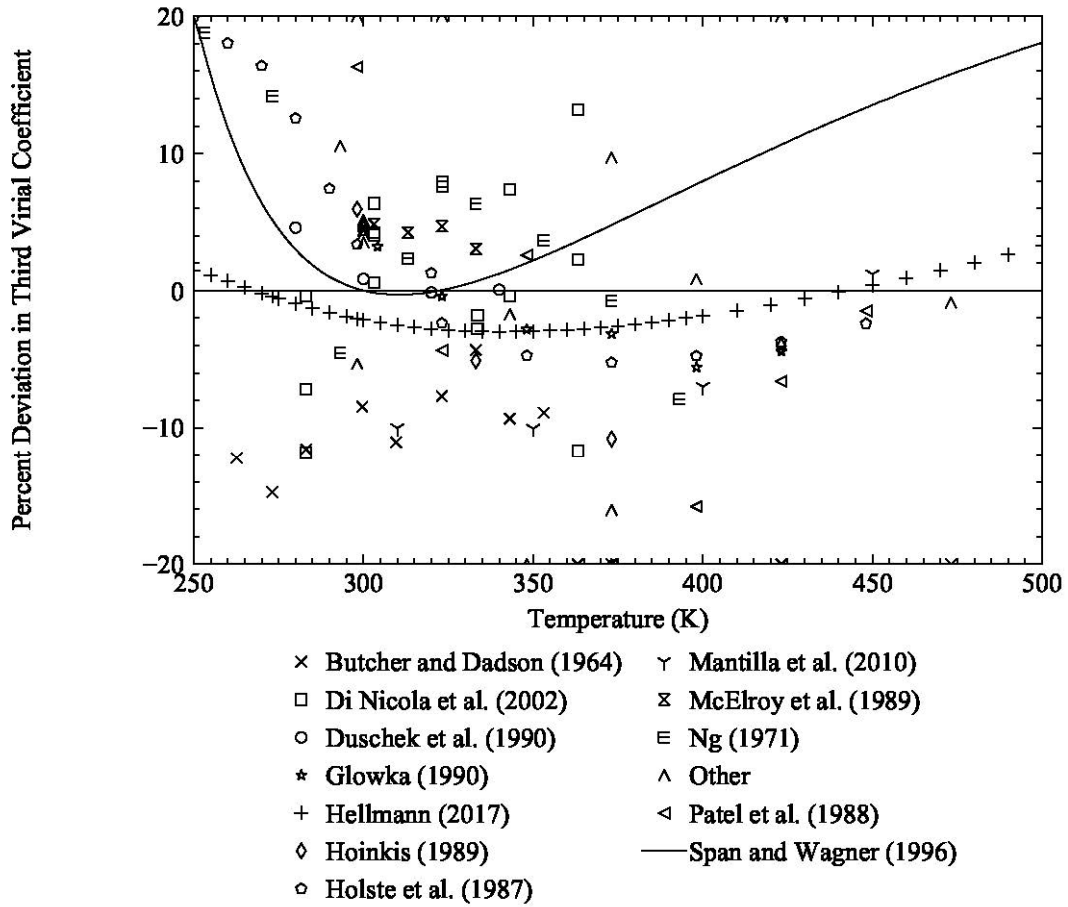
Figure 3: Relative deviations of third virial coefficient $C(T)$ from those calculated with the new equation of state. Calculated values from Hellmann (2017) were used as part of the input.
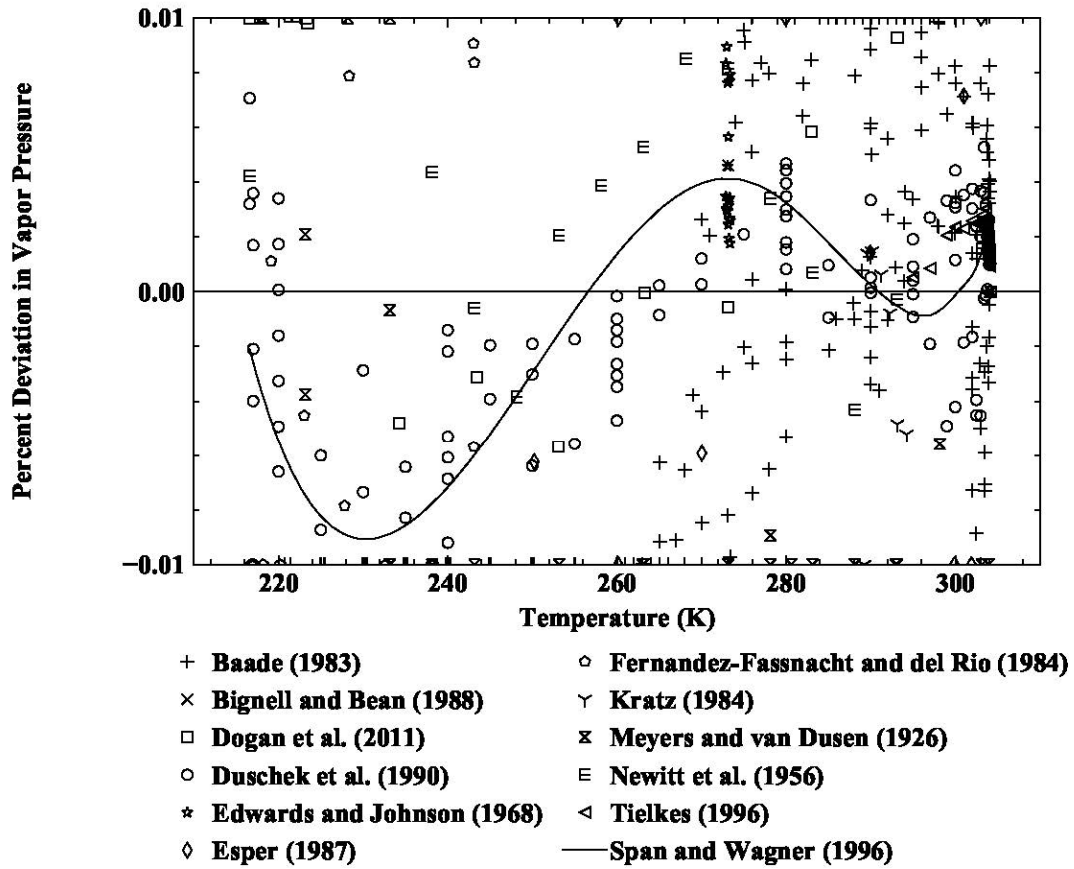
Figure 4: Relative deviations of experimental vapor-pressure data, and vapor pressure calculated from the Span-Wagner equation of state, from those calculated with the new equation of state.