

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231390735>

Reply to “Comments on ‘Joule–Thomson Inversion Curves and Third Virial Coefficients for Pure Fluids from Molecular–Based Models’ and ‘Predicted Inversion Curve and Third Virial Coe...

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JUNE 2009

Impact Factor: 2.59 · DOI: 10.1021/ie9008315

CITATIONS

2

READS

173

2 AUTHORS:



Coray M Colina

University of Florida

85 PUBLICATIONS 699 CITATIONS

SEE PROFILE



Claudio Olivera-Fuentes

Simon Bolívar University

60 PUBLICATIONS 256 CITATIONS

SEE PROFILE

Reply to “Comments on ‘Joule–Thomson Inversion Curves and Third Virial Coefficients for Pure Fluids from Molecular-Based Models’ and ‘Predicted Inversion Curve and Third Virial Coefficients of Carbon Dioxide at High Temperatures’”

Coray M. Colina^{*,†} and Claudio Olivera-Fuentes^{*,‡}

Materials Science and Engineering Department, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Thermodynamics and Transport Phenomena, Simón Bolívar University, Caracas 1080, Venezuela

Sir: From a thermodynamic analysis based on the Gibbs energy function, Espinoza et al.¹ develop their eq 18 for the limiting slope and curvature of the Joule–Thomson inversion curve (JTIC) at high temperatures. These results are not new to us; we derived equivalent formulas early in our work, in reply to a suggestion by one reviewer of our 2002 paper² that the virial expansion could be used to settle the question of physically acceptable curvatures of JTICs. We wrote at that time the following:⁶

Analytical expressions for the slope and curvature of the Joule–Thomson inversion curve in the P–T and v–T projections are readily derived from the appropriate virial expansions, but their interpretation requires a deeper knowledge of the temperature dependence of virial coefficients than is currently available. To fix ideas, consider the P–T inversion curve; this is more easily treated in terms of the volume-explicit virial expansion,

$$Z = 1 + bP + cP^2 + dP^3 + \dots \quad (1)$$

The convenient inversion criterion with T and P as independent variables

$$\left(\frac{\partial Z}{\partial T}\right)_P = 0 \quad (2)$$

leads to the following implicit equation for nontrivial inversion points P = P(T),

$$b' + c'P + d'P^2 + \dots = 0 \quad (3)$$

Implicit differentiation with respect to temperature now yields equations from which the slope dP/dT and curvature d²P/dT² can be obtained

$$[b'' + c''P + d''P^2 + \dots] + [c' + 2d'P + \dots]\frac{dP}{dT} = 0 \quad (4)$$

$$[b''' + c'''P + d'''P^2 + \dots] + 2[c'' + 2d''P + \dots]\frac{dP}{dT} + [2d' + \dots]\left(\frac{dP}{dT}\right)^2 + [c' + 2c'P + \dots]\frac{d^2P}{dT^2} = 0 \quad (5)$$

In these equations, b, c, d, etc. are the Berlin virial coefficients,

* To whom correspondence should be addressed. E-mail: colina@matse.psu.edu; claudio@usb.ve.

[†] The Pennsylvania State University.

[‡] Simón Bolívar University.

$$b \equiv \frac{B}{RT}, \quad c \equiv \frac{C - B^2}{(RT)^2}, \quad d \equiv \frac{D - 3BC + 2B^3}{(RT)^3}, \dots \quad (6)$$

different from (but directly related to) the more usual (Leiden) virial coefficients B, C, D, etc. of the pressure-explicit expansion in powers of density or volume. Primes, double primes, etc. denote first, second, etc. derivatives with respect to temperature.

In keeping with our purpose, consider the limiting values obtained at the high-temperature end of the Joule–Thomson inversion curve, where P = 0. From (3)–(5) these are

$$b' = 0 \quad (7)$$

$$\frac{dP}{dT} = -\frac{b''}{c'} \quad (8)$$

$$\frac{d^2P}{dT^2} = -\frac{b''' + 2c''\left(\frac{dP}{dT}\right) + 2d'\left(\frac{dP}{dT}\right)^2}{c'} \quad (9)$$

Thus, even in this simplest of cases, we see that the terminal temperature (solution of (7) depends only on b' [B and B'], the terminal slope depends on b'' and c' [B, B', B'', C and C'], and the terminal curvature follows from the slope, b''', c'', c', and d' [B, B', B'', B''', C, C', C'', D and D']. We believe that not enough is known on the higher coefficients and derivatives for real fluids to allow universal conclusions from these relations.

—Colina and Olivera-Fuentes

Consequently, we have never claimed, in the papers^{2,3} considered above by Espinoza et al. or elsewhere, that the second and third virial coefficients are enough for determining the ending curvature of the JTIC. If they have regrettably misread our work in this respect, we may point out that the opening paragraph of their letter displays a much better understanding of our true contention, that the third virial coefficient affects (not fixes) the prediction of the upper branch of the JTIC. Thus, in the two papers under discussion we variously state for example the following:

“any EOS that fails to predict third virial coefficients accurately will yield a correspondingly inaccurate inversion curve, at least at the higher temperatures”²

“third virial coefficients are also instrumental in predicting a correctly shaped inversion curve in the vicinity of the upper inversion temperature”²

“deviations from the correct shape of the JTIC at high temperatures directly reflect the inadequacies in the predicted third virial coefficients”³

“the predicted behavior of the third virial coefficient has a definite impact on the shape of the JTIC at high temperatures”³

and so on. Put in simple terms, for a *correct* prediction of the limiting curvature it is *necessary* that *B*, *C*, and *D* be correctly predicted. On the other hand, for an *incorrect* prediction of the limiting curvature it is *sufficient* that *B*, *C*, or *D* is incorrectly predicted. Our work has centered on exploring cases where an imperfect prediction of the JTIC can be clearly and definitely tied to a correspondingly imperfect prediction of *C*. Even if *C* alone does not define the end curvature of the JTIC, it does (together with *B*) determine the end slope, and if this is incorrect, then surely the curvature will be affected to some extent. An extreme example of this was shown in Figure 4 of our 2002 paper,² where because of a demonstrably wrong *C*, the Sterner–Pitzer equation of state for CO₂ predicts a *positive* terminal slope dP/dT of the JTIC. As the slope changes to a correct *negative* value at higher pressures, this at once gives rise to a faulty curvature characterized by a “hump” no matter what *D* may do.

Since most modern equations of state already give a fairly accurate representation of *B*, we have suggested that the next logical step in developing and testing equations of state is to include available information on *C*, scarce and fragmentary though that may be. The fact that in many cases we find that both *C* and the JTIC deviate from the expected behavior over exactly the same temperature range indicates that the contribution of the terms involving *D* in eq 9 may not be substantial. In such cases, the JTIC computed from a virial expansion truncated at *C* coincides with that obtained from the complete equation of state over a wide stretch, as shown for instance in Figure 1 of our 2002 paper.²

As a final point, we agree with Espinoza et al.’s closing remark on the unreliability of experimental data and empirical correlations in the high temperature branch of the JTIC. We have said as much in our articles, e.g. “experimental inversion curve data are rather scarce and often unreliable.”³ We have also brought the fact that “an alternative method to circumvent

the difficulties associated with the experimental determination of the inversion points has been the use of molecular simulations”³ to attention. In the papers under discussion, however, we have not resorted to experimental, interpolated, or simulated data for JTIC but have in fact used the state-of-the-art reference equations of the NIST Chemistry WebBook⁴ as a source of “pseudo-experimental” JTIC data. For example, the Span–Wagner equation of state for CO₂⁵ is the current standard for this fluid. We thus fail to perceive the relevance of Espinoza et al.’s last remark to the issues being discussed.

We still believe that not enough is known on the fourth virial coefficient *D* from an experimental or theoretical point of view to make our eq 9 or the equivalent eq 18 by Espinoza et al. of much practical value. We recognize however that these formulas may be of academic interest and thank Espinoza et al. for this chance to publish and discuss them.

Literature Cited

- (1) Espinoza, D.; Segura, H.; Wisniak, J.; Polishuk, I. Comments on “Joule–Thomson Inversion Curves and Third Virial Coefficients for Pure Fluids from Molecular-Based Models” and “Predicted Inversion Curve and Third Virial Coefficients of Carbon Dioxide at High Temperatures”. *Ind. Eng. Chem. Res.*, <http://dx.doi.org/10.1021/ie900275w>.
- (2) Colina, C. M.; Olivera-Fuentes, C. G. Predicted Inversion Curve and Third Virial Coefficients of Carbon Dioxide at High Temperatures. *Ind. Eng. Chem. Res.* **2002**, *41*, 1064.
- (3) Castro-Marciano, F.; Olivera-Fuentes, C. G.; Colina, C. M. Joule–Thomson Inversion Curves and Third Virial Coefficients for Pure Fluids from Molecular-Based Models. *Ind. Eng. Chem. Res.* **2008**, *47*, 8894.
- (4) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. Thermophysical properties of fluid systems. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 2005; available at <http://webbook.nist.gov/chemistry/> (accessed June 2007).
- (5) Span, R.; Wagner, W. 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. Chem. Ref. Data* **1996**, *25* (6), 1509.
- (6) Colina, C. M.; Olivera-Fuentes, C. Private Communication to the Editor, Industrial and Engineering Chemistry Research, 2002.

IE9008315