CRITICAL-REGION MODEL FOR BUBBLE CURVES OF AMMONIA-WATER WITH EXTRAPOLATION TO LOW PRESSURES*

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ABSTRACT

A modified Leung-Griffths correlation for the near-critical phase boundary of ammonia-water is extrapolated to low pressure. The extrapolation is based on the observation that, on a plot of logarithm of pressure versus inverse temperature, dew and bubble isopleths form straight lines below the critical region. The extrapolation is performed both directly and with additional optimization to a chosen low-pressure data set. On the bubble side, the method yields a useful baseline calculation against which different experimental measurements can be tested for mutual consistency, but the approach is considerably less successful on the dew side.

KEY WORDS

ammonia-water, critical state, Leung-Griffiths model, low-pressure extrapolation, mixture, vapor-liquid equilibria

1. Introduction

Vapor-liquid equilibrium of binary mixtures has in general been analyzed by two separate techniques over two distinct thermodynamic regions. At temperatures and pressures sufficiently removed from critical conditions, equations of state that represent pressure (P) as a function of temperature (T), density (ρ), and mole fraction (x) can yield accurate phase boundaries, except in some cases for coexisting liquid densities. Such equations range from a simple cubic EOS such as Redlich-Kwong [1] and Peng-Robinson [2] to many-parameter representations such as the 32-term modified Benedict-Webb-Rubin equation of state [3, 4]. On the other hand, in the critical region special scaling-law models such as the Leung-Griffiths model [5] in modified form [6,7] and related scaling-law models [8] can yield a superior correlation of the P-T-ρ-x phase boundary.

Each technique generally works well in its own regime but leads to difficulties in the opposite regime. Analytic equations of state yield classical and incorrect critical exponents, and thus must fail within some region close to the critical locus. On the other hand, scaling-law models are in some form an expansion of thermodynamic variables around the critical point, and that expansion has a limited range of validity. A useful guideline is that for the P-T-x surface, equations of state are reliable up to about three-fourths of the critical pressure and scaling-law models are reliable from the critical pressure down to about half that value.

In this work, we attempt to overcome in part the limitations of the scaling-law model by using it to construct a mathematical representation of the P-T-x surface of a particular mixture down to atmospheric pressure. That mixture is ammonia + water, which is of interest due to its use in the Kalina power cycle as an alternative to steam power plants [9]. Our work has been part of a larger project to develop an accurate correlation for this mixture [10-12].

2. Phase Equilibria Data for Ammonia-Water

The ammonia-water system has been studied in the critical region by Gillespie, et al. [13], Rizvi and Heidemann [14], Sassen, et al. [15], and Tsiklis, et al. [16], who presented data only in graphical form. There is considerable disagreement among these sources. As an example, for P-T critical locus Refs. [13] and [14] indicate a maximum in the pressure, but no such pressure was found in Refs. [15] and [16].

Low-pressure dew and bubble point measurements were presented by the cited authors as well as by Müller, et al. [17], Guillevic, et al. [18], and Smolen, et al. [19]. Some conclusions of Ref. 19 suggested that this mixture may be highly non-ideal and not easily described by standard equation-of-state methods. In particular, the authors attempted a correlation with the Peng-Robinson equation [2] and adjustable binary interaction parameters, but did so in two unusual ways. First, while in the customary usage of $(1-k_{ij})$ as a multiplicative factor the interaction parameter k_{ij} is in magnitude much less than one, they required values of $|k_{ij}|$ as large as 1.3. Second, they required separate values of k_{ij} on the liquid and vapor sides of the phase boundary, which is not the customary practice.

While equivalent difficulties were not found in the subsequent application of many-parameter equations of state to this mixture [11, 12], the conclusions of Smolen, et al. suggested that an alternative to the equation of state at low pressure might be useful. Also, since an important initial part of our project was to evaluate and to test the mutual consistency of low-pressure data, we felt it appropriate to establish a simple and fairly accurate representation of the phase boundary so that we could study deviations of the experimental data from that baseline representation.

3. Extrapolation of the Modified Leung-Griffiths Model

It is well known that, on a semilogarithmic plot of pressure versus inverse temperature, the vapor pressure curve of a pure fluid is approximately a straight line,

$$\ln P = A_1 + A_2 / T \qquad \textbf{(1)}$$

For constant-composition dew-bubble curves, Van Poolen and Graham [19], and Bloomer and Parent [20], have noted that the dew and bubble curves each obey Eq. (1) except in a region near the critical point over which they curve and join together, as shown schematically in Figure 1. Therefore, except close to the critical locus, the phase boundary can be represented by two surfaces of constant-composition loci given by Eq. (1) with A_1 and A_2 as functions of x, for $0 < x < 1$. There will be separate functions for the dew side and the bubble side, but they must join at the pure-fluid limits, $x = 0$ and $x = 1$.

The modified Leung-Griffiths model [6] has been found to be reliable over a range $-0.1 < t < 0$, where t is a reduced temperature distance such that $t = 0$ is the critical locus and $t = -0.1$ is approximately the locus of half the mixture critical pressure. The equations for this model have been presented elsewhere [6, 22] and will not be repeated here. On a semilogarithmic plot, dew-bubble curves generated from the model follow the pattern of Fig. 1.

An initial study of the various, mutually inconsistent sets of data in the critical region [12-15] suggested that the critical locus of Sassen, et al. [15] was the most credible. We used those data as input for the initial modified Leung-Griffiths correlation used in this work, and which was then compared against a preliminary equation of state by Friend, et al. [10]. Subsequently, Rainwater and Tillner-Roth [12] iteratively used the modified Leung-Griffiths model and a Helmholtz equation of state [11] to obtain an optimal overall correlation. That final model and the model of the present work differ somewhat in dew curve predictions, but

essentially yield the same bubble curves.

4. Results.

Our efforts to extrapolate to low pressure both the bubble and dew curves were found to be much more successful for the bubble curves, which we first discuss. Our initial approach was a direct extrapolation. Bubble curves were calculated from the modified Leung-Griffiths model over the interval $0 < x < 1$ in steps of 0.1, where $x = 1$ is pure ammonia. From the semilogarithmic plot, we located the limits of the linear regime of each bubble curve and fitted each linear segment to Eq. (1). We then fitted A_1 and A_2 to a fifth-order polynomial in x,

$$A_i = \sum_{j=1}^{5} A_{ij} x^j \quad . \qquad \textbf{(2)}$$

Our representation of the liquid phase boundary was then compared with data from various experimental sources [13, 15, 17-19] at pressures below 11.28 MPa, the critical pressure of pure ammonia.

The results are shown in Figure 2. For each experimental bubble point (P,T,x), we use Eqs. (1) and (2) first to calculate ρ given the experimental T, and then to calculate T given the experimental ρ. The calculated values of P and T are plotted in the figure. Lines have been drawn through the points as an aid to the eye, and the experimental temperature of each isotherm is indicated. Ideally, with both highly accurate data and a model, the points of each isotherm would lie on a vertical line at the temperature given by the horizontal axis. It is seen from Fig. 2 that the method works fairly well down to pressures of 3 MPa and temperatures of 400 K, but breaks down below those limits, with considerable spurious curvature at the lowest pressures and temperatures.

Our second technique was to analyze the bubble curves at each of the compositions measured by Smolen, et al. [19], as listed on Figure 3. Model bubble curves were calculated at these compositions, and Eq. (1) was fitted for each composition to both the linear region of the model curves and the data at lower pressure of Smolen, et al. simultaneously. Figure 3 shows the results for each isotherm. The resulting A_1 and A_2 were then again fitted to Eq. (2) as a function of x, and the resulting correlation was tested against the same set of data at lower pressures as in the previous case.

The results are shown on Fig. 4, analogously to Fig. 2. With the inclusion of input from Ref. 19, the correlation is substantially improved, especially at the lower pressures and temperatures. Such a representation satisfies our objective for a reasonable baseline description of the phase boundary for an initial test of the mutual consistency of the various data sets. Figure 5 shows the deviation plot in temperature, with experimental temperature as the independent variable. Most of the predictions are within 4 K, and there is no evidence of significant bias. Furthermore, our results indicate that the five separate data sets, unlike those in the critical region, are for the most part mutually consistent.

The same two techniques were tried on the dew side, but with much less satisfactory results. The problem in part was that the critical-region data of Sassen, et al. [15] was much more thorough for bubble points than dew points. Consequently, the initial modified Leung-Griffiths correlation was much more uncertain on the dew side, as suggested by the work of Friend, et al. [10] and the subsequent iterative procedure of Rainwater and Tillner-Roth [12], and mismatches between the critical-region model and the data of Ref. 19 were found in our procedure for the dew, but not the bubble curves.

There were indications, however, that the problems on the vapor side have more

fundamental origins. While on the liquid side A_1 and A_2 were smooth functions of x, on the vapor side we found an abrupt peak in those values near x = 0.9, followed by a sharp drop to x = 1. Also, in general the curved region of a dew curve on our semilogarithmic plots is larger and thus the linear region smaller than for the corresponding bubble curve. In fact, over the usual range of the modified Leung-Griffiths model ($-0.1 < t < 0$), we did not find any linear regime for x = 0.1. The vapor phase boundary appears to be in general more irregular than the liquid phase boundary, which thereby makes the present methods harder to implement.

5. Conclusions.

By linearly extrapolating a critical-region model to lower pressure in the space of ln P and inverse temperature, we have constructed a useful approximate description of the liquid phase boundary of ammonia-water. Simple extrapolation yielded a good description down to 3 MPa for this mixture, for which the pure fluid critical pressures are 11.28 MPa and 22.09 MPa. With the inclusion of a chosen set of low-pressure data as input to the fitting procedure, the description became useful down to atmospheric pressure.

It should be understood that our description is a mathematical representation, not a thermodynamic model, of the phase boundary. Self-consistent equations of state yield phase boundaries that must satisfy thermodynamic consistency tests, and the modified Leung-Griffiths model, since it is derived from a potential function and the differential equations of thermodynamics, must also be thermodynamically consistent. However, thermodynamic consistency does not necessarily hold for Eqs. (1) and (2) as fitted to VLE data. The present technique could, however, be used to calculate phase boundary points that then could be used as input for an optimized equation of state that is thermodynamically consistent.

For many mixtures, equations of state (even cubic ones) should be preferable to the

present technique. However, the present methods are useful in situations where a nonideal mixture might not be describable by simple equations of state, as suggested by Smolen, et al. [19] for this mixture, and where a critical locus and critical-region VLE data are available. The present results are also not recommended as the best current values for the bubble surface of ammonia-water; for that one should use the Helmholtz equation of Tillner-Roth and Friend [11] or, near the critical locus, the iterated scaling-law model of Rainwater and Tillner-Roth [12]. Nevertheless, the present methods have proven useful for initial analysis in the development of those models and should be valuable for the study of other similar mixtures.

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FIGURE CAPTIONS

Figure 1. Constant-composition dew-bubble curve plotted as ln P versus 1/T (schematic), solid curve, and critical locus, dashed curve, with critical point (circle). Sufficiently below the critical pressure, both the dew and bubble curves become straight lines to a good approximation.

Figure 2. Comparison of experimental data below the critical region and temperature predictions from direct extrapolation of the modified Leung-Griffiths model for ammonia-water.

Figure 3. Extrapolated Leung-Griffiths model as optimized in part to the data of Smolen, et al. [19].

Figure 4. Comparison of experimental data below the critical region and temperature predictions from the optimized extrapolation of the Leung-Griffiths model in Fig. 3.

Figure 5. Deviation plot for the optimized extrapolation of the Leung-Griffiths model for ammonia-water.

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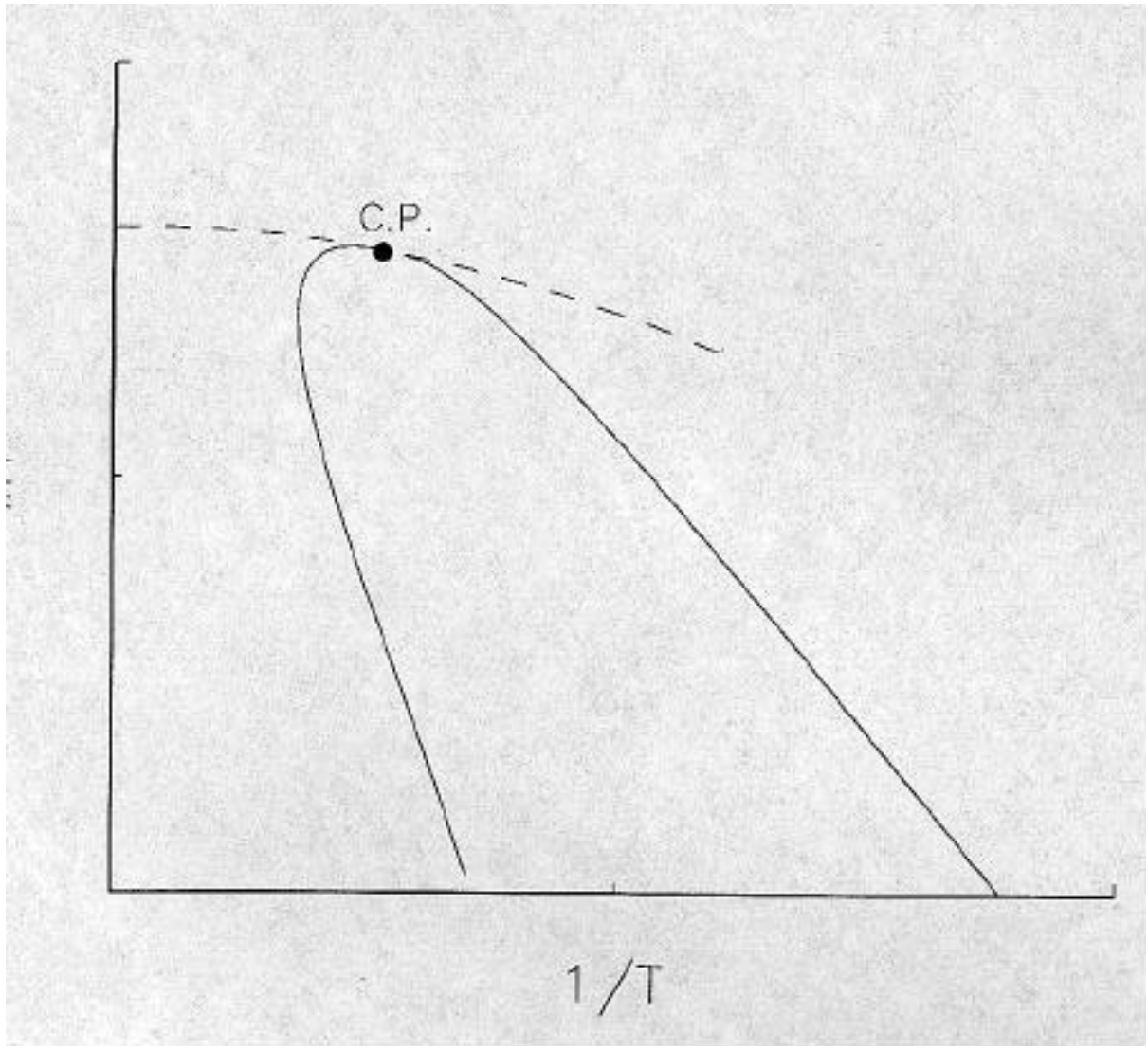
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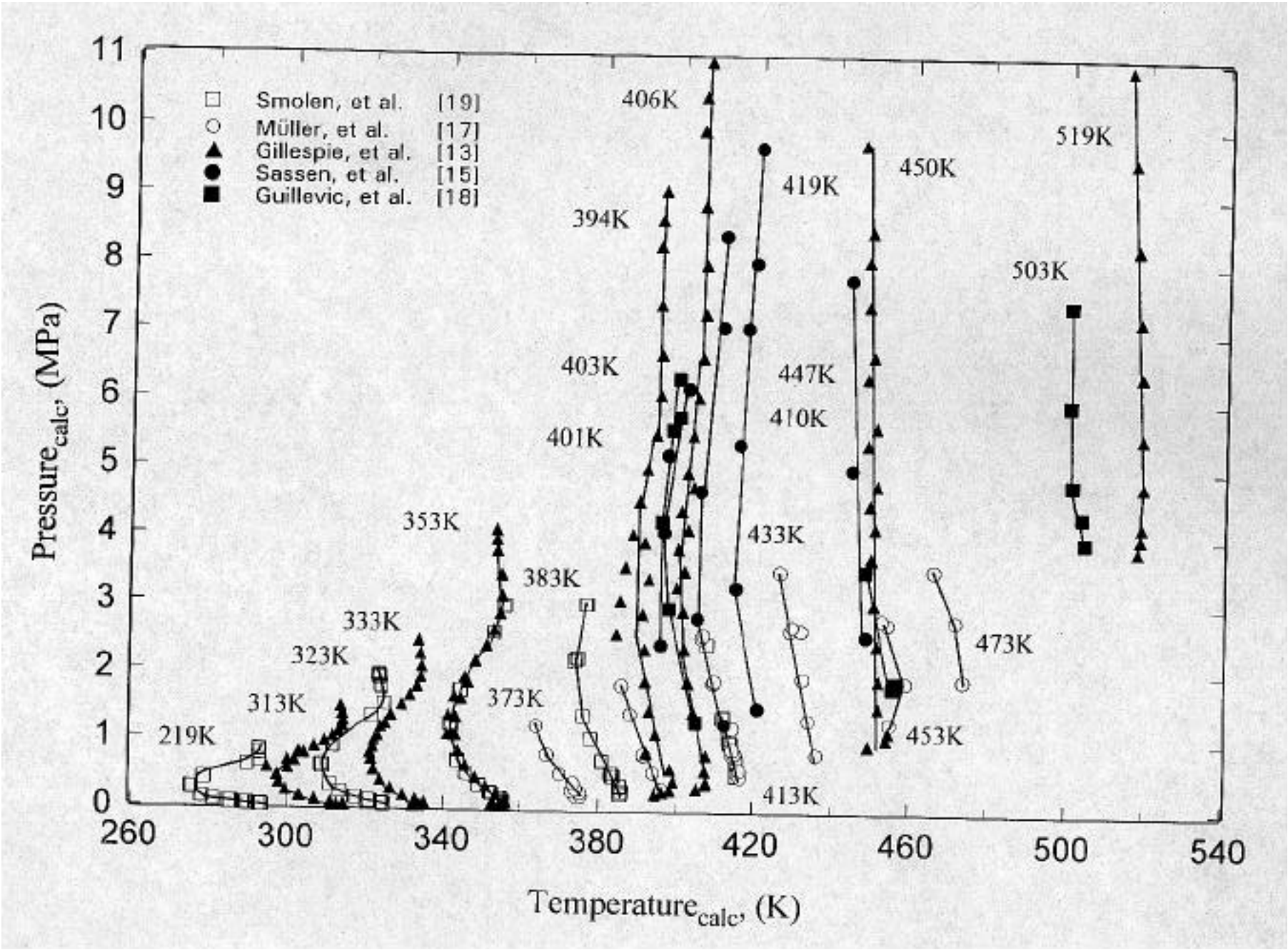
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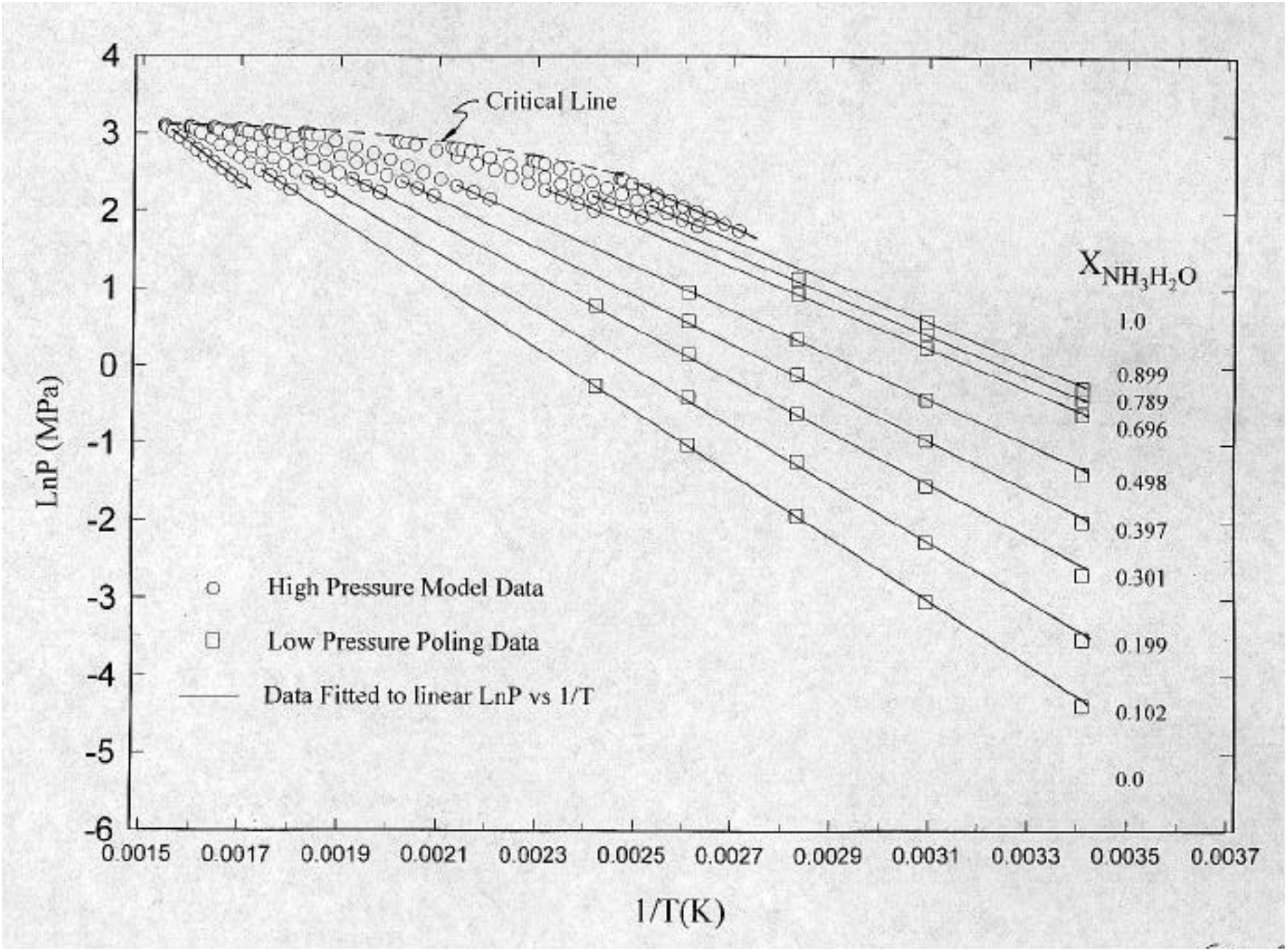
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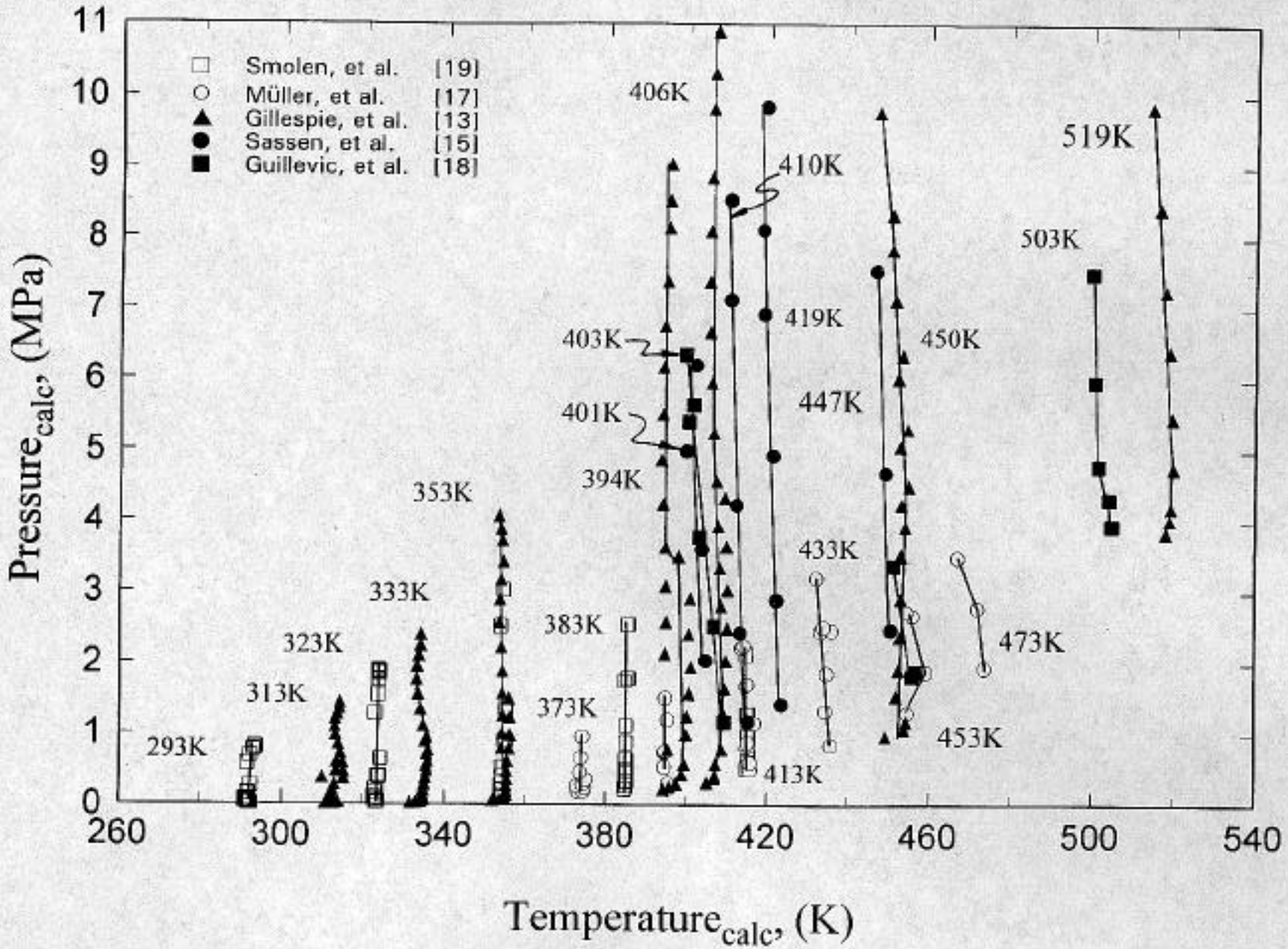
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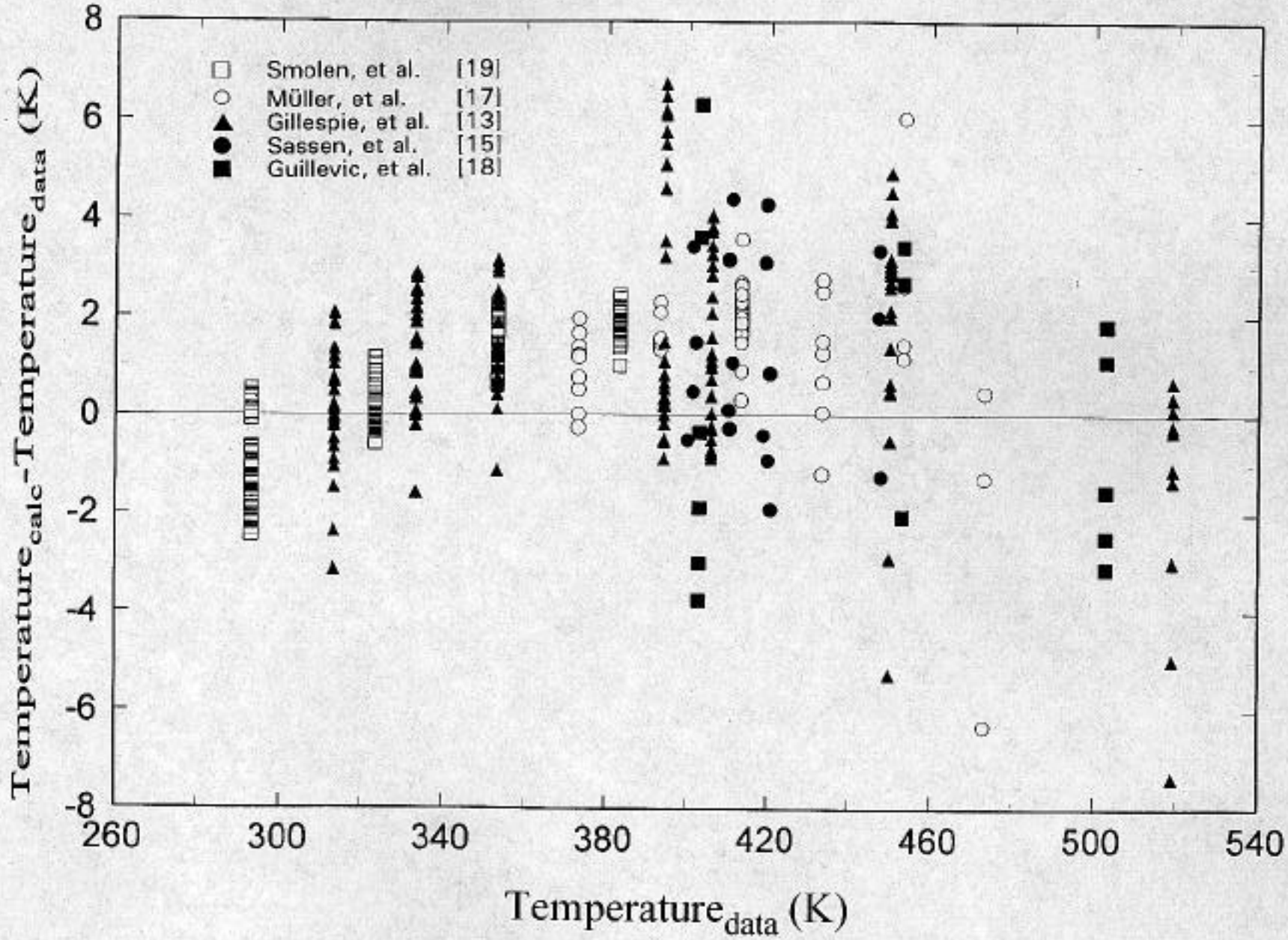
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