Prediction of Thermodynamic Properties for Binary, Ternary, and Quinary Gas Mixtures

LUIS RODRÍGUEZ, S.J.

Department of Mechanical Engineering
Marquette University
Milwaukee, Wisconsin 53235

OBJECTIVE

In analogy with Kay's rule for obtaining pseudo critical constants, a linear rule is proposed for estimating pseudo intermolecular force parameters of a mixture from those of its components. Then the reduced Bird-Spotz virial equation of state (1954) and the de Boer principle of corresponding states (1938) can be used to approximate the PVT behavior of mixtures. The form of the proposed mixture rule is

$$(\epsilon/k)_{\text{mix}} = \sum_{i=1}^{n} x_i(\epsilon/k)_i \tag{1}$$

$$(b_o)_{\text{mix}} = \sum_{i=1}^{n} x_i(b_o)_i \tag{2}$$

Mixture rules proposed in the past have focused on the prediction of either pseudo critical constants or pseudo intermolecular force parameters. Rules of the first type have been developed by Kay (1936), Joffe (1947), Guggenheim and McGlashan (1951), Prausnitz and Gunn (1958), Stewart, Burkhardt, and Voo (1959) and by Leland and Mueller (1959), among others. Most of them have been critically compared by Reid and Sherwood (1958). A summary and critical comparison of the second type of mixture rules has been presented by Good and Hope (1971). The aim of most of the rules of this second type has been the prediction of the contribution to the mixture parameters from interaction between pairs of unlike molecules, rather than a prediction of the mixture's pseudo parameters themselves. Lehman (1967) discusses the validity of rules proposed by various authors for the intermolecular force parameters reflecting interaction between pairs of unlike molecules in a binary mixture.

Two thermodynamic properties were used as a test of the rule proposed here: the compressibility factor z and the Joule-Thomson coefficient μ. The former offers the advantage of an abundance of compressibility data for binary and, to some extent, ternary mixtures; data for one quinary mixture were also available in the literature. Furthermore, the calculation of z having the simplest mathematical form, it serves as a minimum tolerance test for the accuracy of the rule. On the other hand, the formula to calculate the Joule-Thompson coefficient based on the reduced virial equation is mathematically most demanding, since it requires the use of first and second derivatives of the reduced virial coefficients, as well as an integral of a second derivative. Other thermodynamic properties can also be calculated using this rule, but these two properties represent the extremes of demands on the rule's applicability.

As mentioned above, the formula used for the calculation of the Joule-Thomson coefficient is quite complex. In order to simplify its appearance, the following equivalences will be established

$$L \equiv 1 + B_1^*\rho^* + C_1^*\rho^{*2} + D_1^*\rho^{*3} + E_1^*\rho^{*4} + \ldots \tag{3}$$

$$M \equiv 1 + 2B^*\rho^* + 3C^*\rho^{*2} + 4D^*\rho^{*3} + 5E^*\rho^{*4} + \ldots \tag{4}$$

$$N \equiv B_2^*\rho^* + \frac{1}{2}C_2^*\rho^{*2} + \frac{1}{3}D_2^*\rho^{*3} + \frac{1}{4}E_2^*\rho^{*4} + \ldots \tag{5}$$

where if any of the reduced virial coefficients is designated generically by V^*, the subscripts 1 and 2 have the meaning

$$V_1^* \equiv \frac{d(T^*V^*)}{dT^*} = T^*\frac{dV^*}{dT^*} + V^* \tag{6}$$

$$V_2^* \equiv \frac{d^2(T^*V^*)}{dT^{*2}} = T^*\frac{d^2V^*}{dT^{*2}} + 2\frac{dV^*}{dT^*} \tag{7}$$

Then, the resulting expression for the Joule-Thomson coefficient is

$$\mu(T^*, \rho^*) = \frac{\frac{b_o}{\rho^*}\left(\frac{L}{M} - 1\right)}{R\left(\frac{c_p^o}{R} - 1 - T^*N + \frac{L^2}{M}\right)} \tag{8}$$

Inspection of Equation (8) shows that once the parameters ϵ/k and b_o have been determined for a mixture, the property μ can be obtained for any given values of the temperature and density.

Compressibility data were obtained from the existing literature for twenty-nine binary, six ternary, and one quinary mixtures. Joule-Thomson coefficients were available for nine binary and four ternary mixtures. For the compositions of the binary mixtures see Rodríguez (1974). Ternary and quinary mixtures are listed in Tables 1 and 2; because specific reference will later be made to the results obtained in predicting the Joule-Thomson coefficient for binary mixtures, the pertinent binary compositions have also been included in Table 2.

The formula used to predict the compressibility factor is the reduced virial equation of state truncated after five terms; namely

$$z(T^*, \rho^*) = 1 + B^*(T^*)\rho^* + C^*(T^*)\rho^{*2} + D^*(T^*)\rho^{*3} + E^*(T^*)\rho^{*4} \tag{9}$$

where

$$T^* \equiv kT/\epsilon \tag{10}$$

$$\rho^* \equiv b_o\rho \tag{11}$$

Virial coefficients at thirty-three different reduced temperatures from $T^* = 0.625$ to $T^* = 20.0$ have been published by Barker et al. (1966); the required interpolations for occurring intermediate temperatures have been performed using the cubic spline function described by Greville (1964). All calculations have been carried out on a Xerox Sigma-9 computer at Marquette University.

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Table 1. Ternary and Quinary Mixtures Tested for Z

System	Components	Mole fractions	Mixture number	Number of points
1	H_2-N_2-NH_3	0.6650, 0.2640, 0.0710	1	71
		0.6010, 0.2760, 0.1230	2	79
		0.5856, 0.2388, 0.1753	3	74
2	H_2-N_2-CO_2	0.3150, 0.3520, 0.3330	4	15
		0.5440, 0.2350, 0.2210	5	10
		0.2710, 0.5470, 0.3420	6	10
3	H_2-N_2-CO_2-CO-CH_4	0.6141, 0.1971, 0.1741 0.0108, 0.0039	7	45

Table 2. Mixtures Tested for μ

System	Components	Mole fractions	Mixture number	Number of points
4	CH_4-C_3H_8	0.4725, 0.5275	8	43
		0.7280, 0.2720	9	59
		0.8945, 0.1055	10	63
5	C_2H_6-CH_4	0.2362, 0.7638	11	36
		0.2496, 0.7504	12	36
		0.3995, 0.6005	13	36
		0.4999, 0.5001	14	35
		0.7340, 0.2660	15	25
		0.7500, 0.2500	16	23
6	C_2H_6-CH_4-N_2	0.3320, 0.3250, 0.3430	17	28
		0.0960, 0.4600, 0.4440	18	40
		0.2650, 0.2250, 0.5100	19	36
7	H_2-N_2-CH_4	0.3260, 0.3320, 0.3420	20	30

RESULTS

Comparison between experimental and calculated values of z for the six ternary and one quinary mixtures are given in Table 3. A detailed analysis and tables of the results obtained in predicting z for binary mixtures have been presented by this author in the above reference; they are not repeated here because, aside from their extensiveness, the parameter values used then for some of the pure substances have been slightly modified for use in the ternary and quinary mixtures, in the light of a more recent study by the same writer (1977). Although this circumstance prevents an unqualified comparison between the two, general reference will be made to the results obtained for binary mixtures.

Parameter values of repeatedly occurring pure components that are not identical in the last two references are listed below, each source being identified by the corresponding year.

Substance	ϵ/k (K)	b_o (dm³/gmole)	Source
Nitrogen	95.90	0.064	(1974)
	95.00	0.064	(1977)
Methane	149.23	0.067	(1974)
	149.00	0.067	(1977)
Ethane	230.86	0.108	(1974)
	231.00	0.103	(1977)
Propane	279.67	0.149	(1974)
	282.00	0.135	(1977)
Carbon dioxide	218.15	0.075	(1974)
	232.00	0.063	(1977)

Table 3. Percent Error in Predicting z

System	Mixture	Average error	Largest error
1	1	0.49%	+1.01%
	2	0.78%	+4.03%
	3	0.76%	+2.37%
2	4	3.26%	+6.48%
	5	3.47%	−9.19%
	6	1.98%	+3.47%
3	7	2.01%	−4.89%

Table 4. Percent Error in Predicting μ for Binary Mixtures

System	Mixture	Isotherm (°K)	Average error	Largest error
4	8	360.93	10.16%	−22.02%
		377.59	9.70%	−19.85%
		427.59	11.16%	−17.35%
	9	310.93	7.88%	−14.76%
		360.93	6.85%	−14.74%
		427.59	7.30%	−12.46%
	10	294.26	10.15%	−12.77%
		360.93	7.88%	−11.72%
		427.59	6.88%	−11.53%
5	11	294.26	1.87%	+4.65%
		310.93	1.72%	+4.63%
		344.26	2.25%	+3.29%
		377.59	2.38%	+4.71%
	12	294.26	2.90%	+4.96%
		310.93	2.38%	+4.66%
		344.26	1.67%	+3.12%
		377.59	1.83%	−4.57%
	13	294.26	2.72%	−5.24%
		310.93	1.72%	−4.31%
		344.26	1.26%	−3.55%
		377.59	1.72%	−3.31%
	14	294.26	4.46%	+7.12%
		310.93	3.90%	+5.87%
		344.26	2.45%	−4.08%
		377.59	2.01%	−4.06%
	15	310.93	5.86%	−9.31%
		344.26	2.41%	−5.62%
		377.59	2.35%	−4.76%
	16	327.59	4.51%	−5.94%
		344.26	3.78%	−6.41%
		377.59	2.56%	−4.42%

Given the margins of variation established in the last reference, the differences observed above are more apparent than real, except in the case of carbon dioxide. As explained there, the values recommended in 1977 are considered to be more reliable for the purpose of predicting thermodynamic properties.

The results obtained with binary mixtures are summarized in Table 4; comparison with experimental values is made separately for the various isotherms. Because published values of μ for ternary and quinary mixtures used pressure as the independent variable, their tabulation does not lend itself to the same format. The corresponding results are presented in Table 5.

In Tables 3 to 5, the entry average error represents the average of the absolute value of percent errors over all experimental points of the mixture. The entry largest error reflects the largest magnitude of the percent error; its sign indicates whether the prediction errs by excess (+) or by defect (−).

Table 5. Percent Error in Predicting μ for Ternary Mixtures

System	Mixture	Average error	Largest error
6	17	5.83%	−21.27%
	18	3.36%	−12.36%
	19	3.46%	−9.76%
7	20	8.85%	−14.60%

Table 6. Percentage of Total Points within Given Error Range in System 6

Mixture	Error $< 5.0\%$	Error $< 7.0\%$
17	57.14%	67.86%
18	72.50%	90.00%
19	72.22%	97.22%

The prediction of z values is considered to be excellent for ternary system 1 and quite acceptable for system 2. In the second system, only two points of mixture 4 have an absolute deviation larger than 5.0% and only one point in mixture 5; the latter, however, is large enough (−9.19%) to affect unfavorably the mixture's average value. Although the quinary system 3 exhibits less accuracy than ternary system 1, it is considered to be a very good result for a mixture of five components. All mixtures in Table 3 have compressibility factors between 0.9 and 1.0 at any experimental point. The accuracy observed for binary mixtures over points in the same z range is very nearly the same as in ternary system 1; at lower values of the compressibility factor, the results resemble those of systems 2 and 3. At very low values ($z \leq 0.7$), the use of this rule as a prognostic tool is not always satisfactory. This may reflect the inadequacy of Equation (9), truncated after only five terms, to account for the contribution of higher-order virials at lower values of the compressibility factor.

As Table 4 shows, the Joule-Thomson coefficient is quite accurately predicted for binary system 5 having methane and ethane as its components, especially at compositions richer in methane. Predictions for the methane-propane mixtures (system 4), on the other hand, can only be considered approximations. Results for the ternary systems 6 and 7 show a degree of accuracy intermediate between those of systems 4 and 5. However, the largest percent deviations listed for system 6 could be misleading. Table 6 shows the percentage of the total number of experimental points of each mixture in this system that are predicted within a given margin of per cent absolute error. The distribution in mixture 20 (system 7) is less favorable, as only 56.67% of the thirty points involved exhibit less than 10.0% absolute error.

A question may arise as to why the value of μ would be more accurately predicted for systems 5 and 6 than for the binary system 4 made up of methane and propane. In this context it should first be stressed here that no strict physical meaning can be attached to a given pair of pseudo parameters assigned to a mixture; a single ϵ cannot represent the minimum of the various potential functions for the various types of molecular interactions, and the same must be said of b_o. Each parameter pair can only be understood as a proper, though not unique, set of values to be used in the pertinent prediction equation; it is the observation of this author that a change in the value of one of the parameters can be compensated for by some appropriate change in the value of the other parameter without significantly altering the accuracy of the predictions. Thus, the pseudo parameters resulting from the linear mixture rule proposed here have to be understood strictly as one set of mathematically adequate values that can be systematically obtained from those of the pure components. Having said this, and returning to the question posed above, the difference in accuracy may well be associated with the degree of accuracy in the experimental data used in this study. System 4 data are reported by Budenholzer et al. (1942) with an uncertainty margin as large as 2.0%, whereas those of system 5 published by Budenholzer et al. (1939) are assigned a maximum uncertainty of 1.5%. Ahlert and Wenzel (1969) do not assign an overall uncertainty margin to the μ data themselves for system 7; they only estimate the composite error in T values at 0.03° to 0.2°K in the μ range of 0.1 to 1.0°K/atm. Experimental data for all other mixtures analyzed are discussed and referenced in the two studies by this author listed at the end of this writing.

In conclusion, it appears justified to state that the proposed mixture rule successfully predicts values of the compressibility factor for mixtures of gases in the higher ranges of z, but it loses accuracy as the value of z decreases. The mathematically most demanding prediction of the Joule-Thomson coefficient, on the other hand, represents a reasonable approximation to the experimental values. It is surmised that the predictive accuracy of the rule for other thermodynamic properties, such as enthalpy or entropy, the complexity of whose calculations falls between the two extremes used here, will lie between the degrees of closeness observed in these cases.

Without comparing the merits of this approach against those of other proposed methods individually, the following remarks can be made here by way of comparison. In general, it can be said that the combination of great simplicity in formulation and an acceptable degree of accuracy is a favorable feature of the rule used here. Existing rules with comparable simplicity (say, Kay's rule) are far less accurate, while rules with a similar level of accuracy are less straightforward in their mathematical formulation. On the other hand, equations for the prediction of thermodynamic properties based on the generalized virial Equation (9) tend to be more complex.

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NOTATION

B^* = reduced second virial coefficient
b_o = $2\pi N_O \sigma^3/3$
C^* = reduced third virial coefficient
c_p^o = ideal gas specific heat at constant pressure
D^* = reduced fourth virial coefficient
E^* = reduced fifth virial coefficient
i = subscript for i^{th} component
k = Boltzmann's constant
L = defined by Equation (3)
M = defined by Equation (4)
N = defined by Equation (5)
n = number of components
N_O = Avogadro's number
R = gas constant
T = temperature
T^* = defined by Equation (10)
V^* = any of the reduced virial coefficients
V_1^* = defined by Equation (6)
V_2^* = defined by Equation (7)

x = mole fraction
z = compressibility factor

Greek Letters

ϵ = minimum of potential function
μ = Joule-Thomson coefficient
ρ = density
ρ^* = defined by Equation (11)
σ = intermolecular distance at minimum potential

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BOOKS

Fluid Phase Equilibria, edited by H. Renon, Elsevier Scientific Publishing Company, Amsterdam and New York, $57.75 for Volume I (in four issues).

There are a number of important characteristics of Fluid Phase Equilibria to justify the appearance of this new journal. First, is that it (unlike Industrial and Engineering Chemistry Fundamentals or the AIChE Journal) is devoted solely to applied thermodynamics, statistical mechanics and phase equilibria. This whole area is one of renewed engineering interest due to the need for physical properties and phase equilibrium data and prediction methods as a result of more stringent pollution standards, tighter design requirements necessary for energy conservation, and the development of synthetic fuels processing and other new technologies. It is also an area in which rapid progress is being made. Second, the editorial policy of this new journal, unlike that of the Journal of Chemical Thermodynamics, is such as to encourage a juxtaposition of the results of experimental and theoretical research, which may lead to more theorists reading about experiments, and more experimentalists reading theory. Next, Fluid Phase Equilibria, unlike Molecular Physics and the Journal of Physical Chemistry, publishes review articles, which should be of interest and value to those concerned with physical properties. The first two such articles, on statistical thermodynamics by T. Boublik and the start of a series on high pressure phase equilibria by I. Wichterle, indicate the diversity of subjects that the editorial policy of this journal permits. Finally, the two issues of Fluid Phase Equilibria which have appeared suggest that it will be a truly international journal, with authors from many countries.

Fluid Phase Equilibria is likely to attract readers and authors from all of the other journals mentioned above, and promises to be a necessary addition to the reading list of physical properties practitioners in industry and at universities. It is unfortunate that the subscription price of Fluid Phase Equilibria will also make it a rather expensive addition.

STANLEY I. SANDLER
Professor of Chemical Engineering
University of Delaware

Vapor-Liquid Equilibria using UNIFAC, Aage Fredenslund, Jurgen Gmehling and Peter Rasmussen, Elsevier Scientific Publishing Company, Amsterdam and New York, 1977. 380 pages. $59.75.

This monograph treats thoroughly the application of a method for prediction of activity coefficients in multicomponent liquid mixtures of nonelectrolytes at low to moderate pressures. Word of the success of the UNIFAC method has spread rapidly through the chemical-engineering community, and prospective users will find here complete descriptions which readily allow its implementation. All avail-