Prediction of the Joule-Thomson Coefficients of a Gas Mixture from a Generalized Equation of State: The Nitrogen-Ethane System

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Using a thermodynamically consistent form of equation of state proposed by Foulkes, one can determine the virial coefficients of the pressure expansion from Joule-Thomson coefficient data. A modification of the method has been applied for nitrogen and ethane within the temperature range from 50°C. to the normal boiling point. Mixture rules are proposed that allow reproduction of experimental data on μ for nitrogen-ethane mixtures at pressures below the critical pressure of ethane.

The measurement of Joule-Thomson coefficients for the nitrogen-ethane system has been previously reported (*14*) and the experimental results were compared with literature values for the pure components. Zero pressure Joule-Thomson coefficients (μ°) for the mixtures were compared with predictions based on the reduced parameters correlation of McGlashan and Potter (*10*).

This paper reports a reexamination of these data in terms of a generalized equation of state. It shows how virial coefficients can be obtained from the measured values of μ, and gives expressions for the virial coefficients of the pure components and their mixtures.

A GENERALIZED EQUATION OF STATE

Foulkes (*4*) showed that a general equation of state could be obtained from thermodynamic stipulations alone. Imposing the conditions that $P > 0$, $V > 0$, $T \geqq 0$, $(\partial P/\partial V)_T < 0$, $\lim\limits_{T\to 0} S = 0$, and that equilibrium requires extremal properties of E and S, he showed that an equation of state must have the form

$$V = \frac{T}{P}\phi\left(\frac{P}{T^{n+1}}\right) + \psi(P) \tag{1}$$

in order to ensure thermodynamic consistency. No assumptions as to molecular or intermolecular characteristics were involved. He also showed that Equation (1) reduced to the virial expansion of Kamerlingh Onnes

$$PV = RT + A_1(T)P + A_2(T)P^2 + \ldots \tag{2}$$

if the functions of Equation (1) are chosen as

$$\phi\left(\frac{P}{T^{n+1}}\right) = R + \sum_{i=1}^{\infty} \alpha_i \left(\frac{P}{T^{n+1}}\right)^i \tag{3}$$

$$\psi(P) = \frac{1}{P}\sum_{i=1}^{\infty} \beta_i P^i \tag{4}$$

where n, α_i, and β_i are constants. Replacing Equations (3) and (4) into Equation (1) and comparing with Equation (2), we get a general form for the virial coefficients:

$$A_i(T) = \frac{\alpha_i}{T^{i(n+1)-1}} + \beta_i \tag{5}$$

The Kamerlingh Onnes virial coefficients are related to the coefficients of the density virial expansion (*6*):

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \ldots \tag{6}$$

The second virial coefficients are equal and from Equation (5)

$$A_1(T) = B(T) = \frac{\alpha_1}{T^n} + \beta_1 \tag{7}$$

The second virial coefficient can be used to calculate Joule-Thomson coefficients at zero pressure, but it has previously been assumed that the reverse calculation could not be done because a constant of integration was lacking (*9*). Using the virial expansion with coefficients of the form required by the Foulkes equation, it can readily be shown that the reverse calculation can be carried through. Making use of the equation relating zero pressure Joule-Thomson coefficient and second virial coefficient (*4*):

$$(\mu\, Cp)^o = T^2\frac{\partial(B/T)}{\partial T} \tag{8}$$

and combining it with Equation (5), we get

$$(\mu\, Cp)^o = -(n+1)\frac{\alpha_1}{T^n} - \beta_1 \tag{9}$$

Again using Equation (8) and substituting Equation (9), we get

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$$\frac{B}{T} = \int \frac{(\mu\, Cp)^o}{T^2}\, dT = \frac{\alpha_1}{T^{n+1}} + \frac{\beta_1}{T} + K \qquad (10)$$

where K is the constant of integration. Solving for B

$$B = \frac{\alpha_1}{T^n} + \beta_1 + KT \qquad (11)$$

we find that by comparison with Equation (7), K must be zero.

This argument simply demonstrates a unique characteristic of Equation (7). Intuitively, one can grasp the significance of the result by noting that the same parameters are involved in the expressions for B [Equation (7)] and $(\mu\, Cp)^o$ [Equation (9)]. Thus, all the required parameters can be estimated from $(\mu\, Cp)^o$ data.

ZERO PRESSURE JOULE-THOMSON COEFFICIENTS AND THE SECOND VIRIAL COEFFICIENT

The paper of McGlashan and Potter (*10*) provided values of the second virial coefficients for nitrogen and ethane. The least squares procedure described by Box and Tidwell (*1*) was initially used to evaluate the parameters in Equation (7) for nitrogen and ethane with these data used. The results suggested that a value for n of about 1.5 would be suitable for both the nitrogen and ethane data. After setting $n = 1.5$, the constants α_1 and β_1 were estimated from the McGlashan and Potter values by linear regression; they are listed in Table 1. In all calculations T = °K./100, P = atm./100, and Equation (7) has been scaled to give $B(T)/100$.

The second virial coefficients calculated from Equation (7) reproduced the McGlashan and Potter values to better than 0.1% for nitrogen between 293° and 173°K. For ethane these calculations gave results showing a root mean square deviation of 3% between 395° and 235°K. when compared with the McGlashan and Potter values (*10*). For ethane these second virial coefficients are from 5 to 12% lower than those reported by Hoover (*7*) at temperatures from 273° to 215°K. For nitrogen, values obtained from Equation (9) agree with those reported by Gyorog and Obert (*5*) to within 1 cc./g.-mole between 260° and 100°K., but show deviations increasing up to 6 cc./g.-mole as temperature increases to 600°K. Within the range of the data used to obtain the constants of Equation (9) for nitrogen, the maximum discrepancy in $B(T)$ is 1.4 cc./mole.

The internal consistency of these relations can be further demonstrated by calculating the isothermal zero pressure Joule-Thomson coefficients from Equation (9) and by comparing these with values taken from the literature. The average deviation between Equation (9) and the data of Roebuck (*11*) for nitrogen is about 1% with a maximum deviation of 1.4%, whereas the deviation between Equation (9) and the data of Stockett (*13*) for ethane averages 4% with a maximum deviation of 8%. These comparisons are within the experimental errors associated with the measured values.

Since it is usually desired to calculate the properties of a mixture from those of the pure components from which the mixture was made, mixture rules were evaluated in terms of zero pressure coefficients. The study was limited to the class of mixture rules defined by

$$Z_m = (x_a Z_a{}^k + x_b Z_b{}^k)^{1/k} \qquad (12)$$

where $1/k$ is an integer. This class contains many of the common mixture rules, including linear ($k = 1$), geometric ($k = 0$), and harmonic ($k = -1$) (*16*).

Computations were made for integer values of $1/k$, considering the possibility that k for α_1, might be different from k for β_1. Table 2 shows the comparison between zero pressure Joule-Thomson coefficients calculated from the pure component values with the use of the mixture rule indicated and the coefficients obtained directly by experiment (*14*). Thirty-six experimental values were available for mixtures of 27.9, 56.9, 77.5, 85.7, and 94.9% of nitrogen in ethane at temperatures from 198° to 286°K.

Obviously the choice of $1/k = 3$ for α_1 is critical, whereas the data show little sensitivity to $1/k$ for β_1. This is true whether absolute average deviations are used as criteria or whether maximum deviations, shown in Table 2 only for mixture rules with $k = 1/3$, are used. Thus it is recommended that $k = 1/3$ be used both for α_1 and β_1.

Table 1. Constants for the Second Virial Coefficient

	[Equation (7)] Nitrogen	Ethane
n	1.5	1.5
α_1	−1.89	−15.21
β_1	0.30	1.02

Table 2. Average Percent Deviation in Zero Pressure Joule-Thomson Coefficients for Mixture Rules of the Class

$$Z_m = (x_a Z_a{}^k + x_b Z_b{}^k)^{1/k}$$

		$1/k$ for β_1			
		1	2	3	4
$1/k$ for α_1	1	36.0	37.6	38.0	38.3
	2	6.9	8.2	8.7	8.9
	3	4.4 (13.2 max.)	4.0 (11.9 max.)	4.0 (12.4 max.)	4.0 (12.6 max.)
	4	6.5	5.5	5.2	5.1

JOULE-THOMSON COEFFICIENTS AT FINITE PRESSURES

A consideration of Joule-Thomson coefficient data in general can start with the relation (*2*)

$$\mu C_p = T\left(\frac{\partial V}{\partial T}\right)_P - V \qquad (13)$$

If the general equation of state, Equation (1), is inserted, Equation (13) becomes

$$\mu C_p = \frac{T}{P} \sum_{i=1}^{\infty} - i(n+1)\alpha_i \left(\frac{P}{T^{n+1}}\right)^i - \frac{1}{P} \sum_{i=1}^{\infty} \beta_i P^i \qquad (14)$$

A similar substitution in the heat capacity relation

$$C_p - C_p{}^o = - T \int_o^p \left(\frac{\partial^2 V}{\partial T^2}\right) dP \qquad (15)$$

gives an expression for C_p in terms of the general constants

$$C_p = C_p{}^o + \sum_{i=1}^{\infty} [(n+1) - i\,(n+1)^2]\, \alpha_i \left(\frac{P}{T^{n+1}}\right)^i \qquad (16)$$

Combination of Equations (14) and (16) gives a general expression for the Joule-Thomson coefficient in terms of virial coefficient parameters:

$$\mu = \frac{\dfrac{T}{P} \displaystyle\sum_{i=1}^{\infty} - i(n+1)\, \alpha_i \left(\frac{P}{T^{n+1}}\right)^i - \frac{1}{P} \sum_{i=1}^{\infty} \beta_i P^i}{C_p{}^o + \displaystyle\sum_{i=1}^{\infty} [(n+1) - i\,(n+1)^2]\, \alpha_i \left(\frac{P}{T^{n+1}}\right)^i} \qquad (17)$$

Thus the Joule-Thomson coefficient may be obtained at any point in the fluid phase continuum if the α_i and β_i parameters can be evaluated, and provided Foulke's equation of state pertains.

As with the zero pressure Joule-Thomson coefficients, it was desired to use data for the pure components to evaluate the respective α_i and β_i parameters. Mixture rules for each parameter were then investigated and the results were compared with the experimental mixture data.

For nitrogen corresponding values of μ and of C_p were taken from Roebuck (*11*) at temperatures from 50° to −50°C. and pressures up to 2,000 lb./sq.in.abs. Equation (17) was expanded with additional terms added until a satisfactory fit was obtained. Truncation of the equation after the third virial coefficient showed that significantly large deviations between calculated and observed values began to occur at about 1,500 lb./sq.in.abs. At 2,000 lb./sq.in.abs. the deviations were in excess of 10%, so it was concluded that the additional terms were needed. Therefore the terms corresponding to the fourth virial coefficient were permitted, and Equation (17) took the form

$$\frac{(\mu C_p)^\circ - \mu C_p}{P} = \frac{2(n+1)\alpha_2}{T^{2n+1}} + \beta_2 + P\left[\frac{3(n+1)\alpha_3}{T^{3n+2}} + \beta_3\right] \qquad (18)$$

Nitrogen parameters obtained with Equation (18) are presented in Table 3. With these parameters used the calculated Joule-Thomson coefficients agreed with the measured values to an average absolute deviation of 2.8%.

As indicated earlier for Equation (7), it was necessary to scale Equation (5) to obtain adequate sensitivity in calculating the virial coefficients. The scaling system used gave $A_1(T) \times 10^{-2}$, $A_2(T) \times 10^0$, $A_3(T) \times 10^2$, $A_4(T) \times 10^4$, and $A_5(T) \times 10^6$ when these values are calculated from the appropriate α_i and β_i values. Third virial coefficients calculated from these parameters agree only qualitatively with those reported by Gyorog and Obert, giving an average absolute deviation of 30% within the range of 200° to 400°K. No attempt was made to calculate fourth virial coefficients.

Inasmuch as corresponding Joule-Thomson coefficient and heat capacity data were not readily available for ethane, a different approach was used. From Equation (16) the α_i parameters were evaluated by fitting heat capacity data (*15*) from 230° to 350°K. up to 150 atm. To describe the behavior which occurs in the neighborhood of the critical region, it was found that terms up to the sixth virial coefficient were necessary. The resulting expression thus provided calculated heat capacity values with an average deviation over the range of interest of approximately 2%.

Using the estimates of α_i and fourteen experimental Joule-Thomson coefficients of Stockett and Wenzel (*11*) and four of Sage et al. (9), we used Equation (17) to evaluate the β_i parameters. The ethane parameter values thus obtained are presented in Table 4.

The average absolute deviation between observed and calculated Joule-Thomson coefficients below the critical pressure is 3.7%. Again only qualitative agreement was found between third virial coefficients calculated from these parameters and experimental values (*7*) and no attempt was made to calculate higher virial coefficients.

TABLE 4. ETHANE PARAMETER VALUES

$n = 1.5$

$\alpha_1 = -15.2$	$\beta_1 = 1.02$
$\alpha_2 = 132$	$\beta_2 = 4.02$
$\alpha_3 = -37{,}200$	$\beta_3 = 88.0$
$\alpha_4 = 715{,}000$	$\beta_4 = -126$
$\alpha_5 = -3{,}830{,}000$	$\beta_5 = 46.2$

All others equal zero

This method of approaching the estimation problem is similar to one discussed by Huang (*8*). Huang used isothermal Joule coefficients $\lambda = (\partial E/\partial P)_T$ to estimate a portion of the parameters and isothermal Joule-Thomson coefficients to estimate another portion. He showed how virial coefficients could be obtained, and he developed virial coefficients and their first derivatives with respect to temperature for nitrogen at 0° and 100°C.

With values for the parameters of each pure gas estimated, it was possible to study mixture rules as done before with zero pressure data. The mixture rules of interest were again to be in accordance with Equation (12). Two hundred and eleven Joule-Thomson coefficients estimated from the experimental data were available for the analysis. Equation (17) was used to calculate values of μ corresponding to the temperature and pressure conditions of the experimental Joule-Thomson coefficients.

Based on the earlier experience with zero pressure data, the first mixture rule to be tested had $1/k = 3$ for both sets of α and β parameters. This test indicated that there simply was no correspondence between the observed and calculated values at high pressures. This situation suggested that each parameter was subject to its own mixture rule. With five α parameters and five β parameters to be considered, there existed a rather large number of possible combinations. A significant number of evaluations were made, although all possible combinations were not explored, and all produced essentially the same poor results. The conclusion was reached that no mixture rule within the scope of this study would be satisfactory for estimating Joule-Thomson coefficients over the entire region covered by the experimental values.

It became clear that major discrepancies between observed and calculated values occurred at temperature and pressure conditions corresponding to the condensed phase region of pure ethane. The cause of such results is probably due to divergence of the finite series equation. Hirschfelder (*6*) has already pointed out that divergence occurs at about the density of the liquid, and the range of validity of the virial expansion is therefore limited.

For the final analysis, therefore, only those Joule-Thomson coefficients in the region corresponding to the gas phase of pure ethane up to 25°C. and 400 lb./sq.in.abs.

TABLE 3. NITROGEN PARAMETER VALUES

$n = 1.5$

$\alpha_1 = -1.89$	$\beta_1 = 0.30$
$\alpha_2 = 0.72$	$\beta_2 = 0.03$
$\alpha_3 = 1.55$	$\beta_3 = 0.05$

All others equal zero

TABLE 5. PERCENT DEVIATION IN JOULE-THOMSON COEFFICIENTS FOR MIXTURES WITH THE USE OF MIXTURE RULES OF THE CLASS

$$Z_m = (x_a Z_a{}^k + x_b Z_b{}^k)^{1/k}$$

		$1/k$ for β_i		
		3	4	5
$1/k$	2	10.4	11.4	11.9
for	3	4.6	4.0	4.1
α_i	4	9.1	8.2	7.7

were considered. Various combinations of mixing rules were evaluated for each set of α and β parameters. The results of these computations are summarized in Table 5 in terms of the average absolute percent deviation between one hundred and twenty-six experimental and calculated values.

Thus, it is evident from Table 5 that the best mixture rules are $k = 1/3$ for α parameters and $k = 1/4$ for β parameters. Again, $1/k$ for α parameters is much more critical than that for β parameters. Furthermore, the average deviation of 4.0 (max. = 15.7) for the calculated values is consistent with the level desired, within 5%.

The parameters listed in Tables 3 and 4 for the pure components were thus obtainable from pure component Joule-Thomson data. Rules have been selected that allow the use of these parameters for the prediction of Joule-Thomson coefficients of mixtures of the pure components, and the results compare satisfactorily with experimental Joule-Thomson coefficients of mixtures. These parameters have not been used to predict PVT or phase equilibria data for hydrogen-ethane mixtures because of a lack of available data. The data of Eakin et al. (3) are limited to pressures above 400 lb./sq.in.abs., and hence do not fall within the scope of this study.

The evaluation of the virial coefficient parameters would best be approached directly from Equation (17) with the use of nonlinear estimation methods. Here the large number of coefficients that were required would have made this approach expensive, both in computing time and effort. It is suggested that a simpler system, where the complexities associated with the critical region do not appear, would allow testing this more general approach. Until this is done, the optimization of the parameter n must be considered as an approximation. It is conceivable that different values of n might be needed for different pure components. If this occurs, mixture rules would be needed for this parameter also. With the system examined here, the limited validity of the equation of state and the large number of coefficients needed for adequate data fit make a critical examination of the n parameter impossible.

Since the comparison of virial coefficients from Joule-Thomson data with those obtained from PVT measurements would represent a powerful test of the consistency of both sets of data, virial coefficients were calculated from the equation of state proposed by Eakin. Despite the long pressure extrapolation required of the Eakin data, second virial coefficients for both pure components and mixtures showed fair agreement with those reported here. Higher virial coefficients could not be readily calculated from the Eakin equation, and since the pressure ranges did not overlap those correlated here, no comparisons were made of higher virial coefficients.

CONCLUSIONS

Parameters for the Kamerlingh Onnes virial coefficients, and hence for the coefficients of the density virial expansion, have been obtained for nitrogen and for ethane with the use of Joule-Thomson coefficients and heat capacity data. Using the temperature function of these virial coefficients suggested by Foulkes (4), one can reproduce experimental Joule-Thomson coefficients for pressures below 2,000 lb./sq.in.abs. and for temperatures between 50° and −50°C. for nitrogen and for pressures below 400 lb./sq.in.abs. and for temperatures between 35° and −40° for ethane.

Joule-Thomson coefficients for mixtures of nitrogen and ethane can be predicted for pressures below 400 lb./sq.in.abs. from the pure component parameters by using a mixture rule of the type presented by Equation (12). In this study mixture rules which are independent of the virial coefficient being determined were found to be acceptable.

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NOTATION

A = virial coefficient of the Kamerlingh Onnes expansion
B, C = virial coefficients of the density expansion
Cp = heat capacity at constant pressure
E = internal energy
K = constant of integration
k = exponent in the mixture relation, Equation (12)
n = parameter of Equation (1)
P = pressure, atm.
R = universal gas constant, (cc.)(atm.)/(g.-mole)(°K.)
S = entropy
T = temperature, °K.
V = volume, cc./g.-mole
x = mole fraction
Z = any of the parameters of the virial coefficients
α, β = parameters of the virial coefficients
μ = Joule-Thomson coefficient, °K./atm.
ϕ = function of P/T^{n+1}, see Equation (1)
ψ = function of P, see Equation (1)

Subscripts

i = integer referring to the Kamerlingh Onnes virial coefficient
m = property of a mixture
a, b = components of a mixture
1, 2, 3 = one less than the virial coefficient

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