Optimum Mixture Compositions for Measurement of Cross Virial Coefficients

Random error propagation is examined to determine cross second and third virial coefficients from binary gas density measurements by both the indirect and direct methods. Determination of the cross second virial coefficient B_{12} from B_m at a single composition via the indirect method is optimized when $y_1^2 e_1 = y_2^2 e_2$, where e_1 and e_2 are the pure component uncertainties. When all errors are equal, the equimolar mixture is optimum as expected.

Corresponding analysis of the cross third virial coefficients, C_{112} and C_{122}, show that the optimum compositions are not (⅓, ⅔) as expected for equal error distribution, but rather (¼, ¾). Equations presented allow determination of the two optimum compositions, when e_m varies with composition. Minimization of the combined errors in B_{12}, C_{112}, and C_{122} via mixture measurements at two compositions provides results near (⅓, ⅔), when all errors are equal. Methods for direct measurement of B_{12} are reexamined. Optimal compositions are found using third virial coefficient correlations.

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Introduction

Gases and gas mixtures at low to moderate pressures are characterized by their departure from the perfect gas law by the virial equation of state

$$Z_m \equiv (P/\rho_m RT) = 1 + B_m\rho_m + C_m\rho_m^2 + \cdots \qquad (1)$$

where

B = second virial coefficient
C = third virial coefficient
ρ = density
P = pressure
T = temperature
Z = compressibility factor

We have written Eq. 1 for a mixture but note that for a pure gas i the subscript m becomes i—actually B_{ii} and C_{iii} for the virial coefficients. Indeed, the mixture virial coefficients are related exactly to the pure-component values by the statistical equations:

$$B_m = \sum_{j=1}^{N}\sum_{i=1}^{N} y_i y_j B_{ij} \qquad (2)$$

and

$$C_m = \sum_{k=1}^{N}\sum_{j=1}^{N}\sum_{i=1}^{N} y_i y_j y_k C_{ijk}. \qquad (3)$$

The cross virial coefficients $B_{ij}(i \neq j)$ and $C_{ijk}(i \neq j, k)$ are only functions of temperature, like B_{ii} and C_{iii}. For a binary mixture, Eq. 2 yields

$$B_{12} = (B_m - y_1^2 B_{11} - y_2^2 B_{22})/2y_1 y_2, \qquad (4)$$

where the mol fraction $y_2 = 1 - y_1$. At some temperature, B_m is measured at a composition y_1 to provide B_{12} from Eq. 4, which is termed the indirect method for determination of B_{12}.

Likewise, indirect determination of C_{112} and C_{122} for a binary mixture may be achieved from at least two independent measure-

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ments of the mixture third virial coefficient, C_m^a and C_m^b, at two compositions y_1^a and y_1^b. From Eq. 3,

$$C_m^a = (y_1^a)^3 C_{111} + (y_2^a)^3 C_{222} + 3(y_1^a)^2 y_2^a C_{112} + 3y_1^a (y_2^a)^2 C_{122} \qquad (5)$$

and a second equation results by replacing a with b. These two equations are solved simultaneously for C_{112} and C_{122}.

Second and third cross virial coefficients are widely used in phase equilibria calculations, especially in the so-called "gamma-phi method" (Smith and Van Ness, 1987). Selected literature values appear in the compilation by Dymond and Smith (1980), which is under revision.

The primary objective of this paper is to determine the optimum composition y_1 for minimization of the error in B_{12}, $e(B_{12})$, subject to known errors in B_{11}, B_{22}, and B_m, where $e(B_m)$ may vary with y_1. The second objective is determination of the optimum composition pair, y_1^a and y_1^b, for minimization of the sum of the square of $e(C_{112})$ and $e(C_{122})$ subject to known errors in C_{111}, C_{222}, and C_m, where $e(C_m)$ may vary with y_1. Our purpose in this exercise is to provide experimentalists with a method for estimating such optimum compositions prior to mixture preparation which, in turn, precedes the tedious task of data procurement. Modern gravimetric procedures allow gas mixtures to be prepared with compositions known to 10 ppm and mixture compositions duplicated to within 40 ppm.

While we believe this work to be the first formal attempt to meet these objectives, conventional wisdom has long told experimentalists that if the magnitude of the errors in B_{11}, B_{22}, and B_m are equal then the optimum value of y_1 is 0.5. Likewise, equality of the errors in C_{111}, C_{222}, and C_m should lead to the optimum composition set of $y_1^b = 1/3$ and $y_1^a = 2/3$, because C_{112} represents the interaction of two molecules of component 1 with one molecule of component 2 whereas the reverse is true for C_{122}. Our study shows our intuition to be correct for the cross second virial coefficient but incorrect for the cross third virial coefficients. Further, when the errors are not equally distributed, we would expect the optimum compositions to shift toward the pure component with lesser error. For example, in determining B_{12} for methane(1)/water(2) (Joffrion and Eubank, 1988), $B_{11} = -21.00 \pm 0.2$ at 373.15 K (Douslin et al., 1964) but $B_{22} = -452.7 \pm 8$ (Eubank et al., 1988) or $[e(B_{22})/e(B_{11})] = 40$. Assuming that $e(B_m)$ varies with y_1 as some continuous functionality between these pure end points, we will derive equations for the optimum composition y_1 to minimize $e(B_{12})$. Not surprisingly, $y_1(\text{opt}) = 0.86 > 0.5$.

The third objective is to find the optimum two compositions for simultaneous minimization of the combined errors in B_{12}, C_{112}, and C_{122} for binary mixtures.

The last objective is to reexamine the methods of Knobler et al. (1959) and of Hall and Eubank (1973) for direct measurement of B_{12}. These direct methods avoid B_{11} and B_{22} in determination of B_{12} by manipulating the basic identities, such as Eq. 4. While they offer the advantage that errors in the pure virial coefficients do not propagate into B_{12}, the disadvantage is there in that the experiments must be performed under certain constraints upon the mixture compositions to meet the requirements of the manipulated identities. We show here that the method of Knobler et al. (1959) is so highly constrained that y_1 cannot be varied, once T, P, and the two pure gases are chosen. Attention turns to the direct method of Hall and Eubank (1973), developed for the Burnett PVT apparatus, which allows choice of y_1. Each direct measurement yields an apparent B^*_{12} so the error in B_{12} is minimized by $y_1(\text{opt})$ causing $B^*_{12} = B_{12}$, regardless of pressure. For each temperature, $y_1(\text{opt})$ is shown to be a function of the value of the third virial coefficients C_{111}, C_{222}, C_{112}, and C_{122}. Optimum values of y_1 cannot be close to zero nor unity but are seldom near 0.5 and may be double-valued, as when the above third virial coefficients are identical. The Knobler experiment must operate with a near equimolar mixture preventing errors in B_{12} as low as those in the Hall-Eubank method when the latter is performed at $y_1(\text{opt})$. Both experiments, however, remain more accurate than those of the indirect method.

The statistical equations presented here allow determination of the optimum compositions prior to measurements. This frees experimentalists from using their occasional poor intuition in the preparation of mixture samples for measurement of cross virial coefficients. In addition, the location of these optimum compositions $y_1(\text{opt})$ are shifted less than 0.01 by use of one of two popular statistical methods, sum of squared errors and sum of absolute errors. The results of this work do not apply to non-PVT methods, such as gas chromatography, excess enthalpy, and solubility.

State-of-the-Art in PVT Measurements

State-of-the-art PVT measurements can now provide second virial coefficients $B(T)$ to ± 0.2 cm^3/mol—0.2% if $B = -100$ cm^3/mol (Holste et al., 1987). Adsorption errors associated with a highly polar component, whether pure or in a mixture, cause uncertainty in $B(T)$ to rise by one or two orders of magnitude even after correction of the data for adsorption errors (Eubank et al., 1988). While polar effects cause $B(T)$ to be more negative, a modern apparatus with adsorption correction of the data can nevertheless provide $B(T)$ to ±1% for much of the temperature range. Neither absolute nor fractional uncertainty statements are entirely satisfactory for $B(T)$ over extended ranges of T. The former is unsatisfactory because $B(T)$ can range from roughly $-2{,}000$ to 30 cm^2/mol in practice, whereas the latter is obviously unsatisfactory near the Boyle temperature ($B = 0$).

These statements also apply to the third virial coefficient $C(T)$ except that the uncertainties are much higher. Modern measurements on nonadsorbing gases and gas mixtures can provide $C(T)$ to ±100 cm^6/mol^2—about ±3% for temperatures above critical, where $C(T)$ is usually positive and a weak function of T. Except for highly absorbing gases, leading laboratories have entered an era where duplication of $C(T)$ to within 10% is expected and routine. However, uncertainties in the fourth and higher virial coefficients are generally of equal or greater magnitude when compared to the value of the virial coefficient itself.

Thus, this paper is concerned only with $B(T)$ and $C(T)$. For pure components, B_{ii} and C_{iii} should be measured over a range of temperatures, as in the Burnett-isochoric experiment, and by duplicate samples, if possible, to check the precision (reproducibility) of B_{ii} and C_{iii} plus smoothness vs. temperature. Such random errors can be determined by the careful researcher. Uncertainty bands given in most experimental publications are precision bands at two or three times the standard deviation σ (95.5% and 99.7% probability levels, respectively). Systematic errors, which are usually not detected by the researchers, frequently cause differences between the values of two separate laboratories greater than the combined precision bands. Since this work is a statistical determination of optimum mixture composition for measurement of B_{ij} and C_{ijk}, all the present errors, e, are random with assumed normal distribution. While adsorption errors are systematic [$e(B_{ii}) < 0$, for example, with uncorrected data], measurements corrected for adsorption can be either undercorrected or overcorrected; so we assume for simplicity a random distribution of errors from such corrected data. The net result is that a polar, adsorbing gas will have an error band $\sqrt{\overline{e^2}} = 3\sigma$, which is one or sometimes two orders of magnitude greater than that for a nonpolar, nonadsorbing gas.

Indirect Methods

Second cross virial coefficient

Here we seek the optimum binary mixture composition y_1 to minimize the squared error $e^2(B_{12})$ when B_{12} is found from measurement of B_{11}, B_{22}, and B_m (at y_1) via Eq. 4. Assuming no error in the composition determination and zero covariance between the separate measurements of B_m, B_{11}, and B_{22},

$$e_{12}^2 = [e_m^2 + (y_1^2 e_1)^2 + (y_2^2 e_2)^2]/4y_1^2 y_2^2, \tag{6}$$

where $e_{12} = |e(B_{12})|$, $e_1 = |e(B_{11})|$ and $e_2 = |e(B_{22})|$. Differentiation of Eq. 6 followed by setting $(\partial e_{12}^2/\partial y_1)_T = 0$ results in

$$e_m(\partial e_m/\partial y_1)_T + 2y_1^3 e_1^2 - 2y_2^3 e_2^2 = [(1 - 2y_1)/y_1 y_2][e_m^2 + (y_1^2 e_1)^2 + (y_2^2 e_2)^2] \tag{7}$$

at the optimum value of y_1. Figure 1 provides five separate cases for how e_m might vary with y_1. If all measurements are made in the same apparatus $e_m = e_1$ when y_1 approaches unity and, likewise, e_m should approach e_2 at the other pure end point. However, if B_{11} is taken from another laboratory, we should be wary of a jump discontinuity in e_m as y_1 approaches unity as seen in Figure 1e.

When the errors are equal ($e_m = e_1 = e_2$) as in Figure 1a, Eq. 7 provides $y_1 = ½$, as expected. Equation 6 provides the following values of $e_{12}(y_1)$ when $e_m = e_1 = e_2 = 1$: 2.1213(0.5), 2.2392(0.6), 2.6601(0.7), 3.7123(0.8), and 7.1496(0.9).

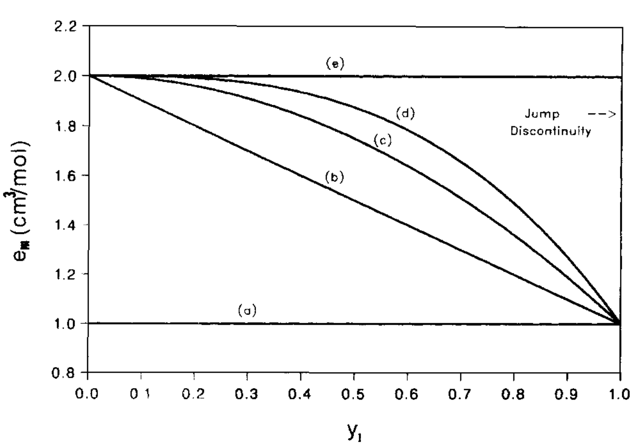

Figure 1. Variation of the error in the second virial coefficient of a binary mixture with composition.

With $e_1 = 1$: (a) $e_1 = e_2 = e_m$; (b) $e_2 = 2$ and e_m linear ($n = 1$); (c) $e_2 = 2$ and e_m quadratic ($n = 2$); (d) $e_2 = 2$ and e_m cubic ($n = 3$); (e) $e_2 = e_m = 2$ with a jump discontinuity at $y_1 = 1$.

However, even simple variations of e_m with y_1 [e.g., linear variations of $e_m = (e_1 - e_2)y_1 + e_2$] provide the optimum y_1 through complex equations. More simple, but approximate, equations result from minimizing the sum of the absolute errors or

$$e_{12} = [(e_m + y_1^2 e_1 + y_2^2 e_2)/2y_1 y_2]. \tag{8}$$

Whether one uses squared errors. Eq. 6, or absolute errors, Eq. 8, is somewhat a matter of choice. Squared errors are statistically correct, but absolute errors have two practical advantages. First, they provide simpler expressions following differentiation with only slight dislocation of the optimum composition. Second, the resultant error (here, e_{12}) is always greater when adding the absolute values of the component errors (here, e_m, e_1, and e_2) than when taking their vector sum for the same value of the independent variable (here, y_1). Experimentalists using absolute errors are thus more likely to avoid underestimation of the resultant error. Such underestimation leads to long-term chaos and disagreements in the literature.

Setting $(\partial e_{12}/\partial y_1)_T$ to zero in Eq. 8 yields

$$(\partial e_m/\partial y_1)_T + 2y_1 e_1 - 2y_2 e_2 = [(1 - 2y_1)/y_1 y_2][e_m + y_1^2 e_1 + y_2^2 e_2]. \tag{9}$$

Again, equal errors provides $y_1 = ½$ with the following corresponding values of $e_{12}(y_1)$: 3.0(0.5), 3.1667(0.6), 3.7619(0.7), 5.25(0.8), and 10.1111(0.9) as shown on Figure 2a. When e_m varies linearly between e_2 and e_1, as shown by Figure 1b, $(\partial e_m/\partial y_1)_T = e_1 - e_2$ and Eq. 9 reduces to

$$y_1^2 e_1 = y_2^2 e_2. \tag{10}$$

or

$$y_1 = [\sqrt{e_2}/(\sqrt{e_1} + \sqrt{e_2})]. \tag{11}$$

Equations 10 and 11 also follow from quadratic behavior of e_m with y_1 but not from cubic behavior. The general polynomial result for

$$e_m = (e_1 - e_2)y_1^n + e_2 \tag{12}$$

is

$$[(n - 1)y_1^n - (n - 2)y_1^{n+1} + y_1^2]e_1 = [(n - 1)y_1^n - (n - 2)y_1^{n+1} + y_1^2 + 2 - 4y_1]e_2. \tag{13}$$

For adsorption examples (2 = polar, adsorbing gas; 1 = nonpolar gas), the cubic behavior (Figure 1) is close to the observation (Mansoorian et al., 1981) that the dominant adsorption errors for an equimolar binary mixture are roughly (1/7) of those of the pure polar compound.

The results of several numerical examples are as follows. First, the methane (1)/water(2) case at 373.15 K noted in the Introduction section has $(e_2/e_1) = 40$ so Eq. 11 yields $y_1 = 0.8635$, whereas Eq. 13 with $n = 3$ yields $y_1 = 0.8369$. Second,

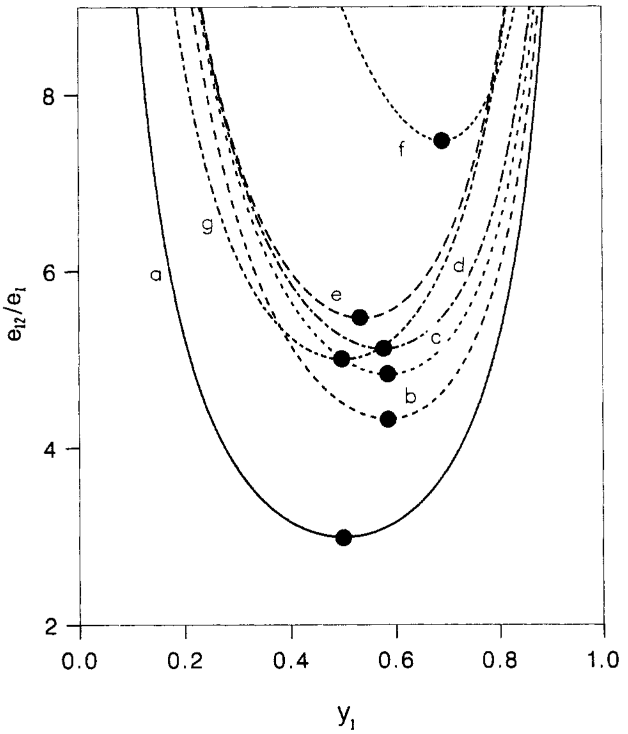

Figure 2. Variation of the error in the second cross virial coefficient with composition by minimization of the sum of absolute errors.

With $e_1 = 1$: (a)-(e) correspond to the legend of Figure 1; (f) $(e_2/e_1) = 5$ and e_m linear; (g) $(e_2/e_1) = 1$ and $e_m = 2$. The optimum composition for each case (denoted by • is (a) 0.5, (b) 0.588, (c) 0.588, (d) 0.575, (e) 0.536, (f) 0.691, and (g) 0.5.

when $(e_2/e_1) = 2$, Eq. 11 yields $y_1 = 0.5878$ (Figures 2b and 2c), whereas Eq. 13 with $n = 3$ yields ■$_1 = 0.5753$ (Figure 2d). Third, suppose $e_2 = e_m$ from an in-house apparatus but $(e_2/e_1) = 2$ with e_1 from a more precise literature measurement, as shown in Figure 1e. Equation 9 remains valid, but not Eqs. 10–13. Solving Eq. 9 we find $y_1 = 0.5359$ (Figure 2e). Fourth, e_1 and e_2 are taken from the literature, but two mixture measurements from the in-house apparatus provide a linear fit of $e_m = ay_1 + b$. The optimum value of y_1 is:

$$y_1 = [(e_2 + b)/(e_1 - e_2 + a)] \cdot [-1 + \sqrt{1 + (e_1 - e_2 + a)/(e_2 + b)}]. \quad (14)$$

When $(e_1 - e_2 + a)$ is zero, Eq. 14 becomes indeterminate, but L'Hospital's rule provides an optimum value of y_1 of $(^1/_2)$.

As Figure 2 shows, the minimum in e_{12} is not sharp in general, so it is not necessary to make the mixture measurement of B_m exactly at the optimum compositions in the figure. The case of $e_1 = e_2 = e_m$ provides a particularly shallow curve (Figure 2a); measurement of y_1 at 0.4 (or 0.6) provides B_{12} with an error only 5.6% greater than that at the optimum y_1 of 0.5. When y_1 is 0.3 (or 0.7), however, this figure rises to over 25%. When $(e_2/e_1) = 5$ and e_m linear, Figure 2f shows that increasing the optimum y_1 of 0.691 to 0.791 provides an 8.5% increase, whereas decreasing y_1 to 0.591 provides a 5.8% increase. While these percentages are not high, there is no reason to suffer these additional errors in B_{12} when y_1 can be easily set near its optimum value.

Figure 2 provides further insight on how two or more measurements of $B_m(y_1)$ should be made to check for constancy of B_{12} from Eq. 4. In dealing with the random errors considered here, we should repeat the B_m measurements at compositions near the optimum. For example, with Figure 2a, we should measure within the band of 0.4–0.6 for y_1. The frequent practice of this and other laboratories to measure at even intervals across the entire band of y_1 is seen to be often ineffective—values obtained for compositions far removed from the optimum carry uncertainties too large to make them useful. However, this practice remains effective in the detection of systematic errors when they are larger than the random errors considered here.

Cross third virial coefficients-binary mixtures

In the above analysis for B_{12}, we could have minimized the error in the difference function

$$\delta_{12} \equiv 2B_{12} - B_{11} - B_{22} \quad (15)$$

and obtained the same results with slight economy in notation. Because of the algebraic complexities, it is almost imperative to work with the corresponding difference functions for cross third virial coefficients:

$$\Delta_1 \equiv \Delta_{112} \equiv 3C_{112} - 2C_{111} - C_{222} \quad (16)$$

and

$$\Delta_2 \equiv \Delta_{122} \equiv 3C_{122} - C_{111} - 2C_{222}. \quad (17)$$

Here we seek the composition pair (y_1^a, y_1^b) to minimize $[e_{\Delta_1}^2 + e_{\Delta_2}^2]$, where $e_{\Delta_1}(y_1^a, y_1^b)$ and $e_{\Delta_2}(y_1^a, y_1^b)$. At this global minimum,

$$\frac{\partial}{\partial y_1^a}[e_{\Delta_1}^2 + e_{\Delta_2}^2]_{y_1^b} = 0 \quad (18)$$

and

$$\frac{\partial}{\partial y_1^b}[e_{\Delta_1}^2 + e_{\Delta_2}^2]_{y_1^a} = 0. \quad (19)$$

It is further convenient to replace the two mixture third virial coefficients of Eq. 5 by

$$C^a \equiv [C_m^a - y_1^a C_1 - y_2^a C_2]/y_1^a y_2^a \quad (20)$$

and

$$C^b \equiv [C_m^b - y_1^b C_1 - y_2^b C_2]/y_1^b y_2^b. \quad (21)$$

Then the following equations result in progression:

$$\Delta_1 = [(y_2^b C^a - y_2^a C^b)/(y_1^a y_2^b - y_1^b y_2^a)], \quad (22)$$

$$\Delta_2 = [(y_1^b C^a - y_1^a C^b)/(y_1^b y_2^a - y_1^a y_2^b)], \quad (23)$$

$$e(C^a) = [(e_m^a - y_1^a e_1 - y_2^a e_2)/y_1^a y_2^a], \quad (24)$$

and

$$e(C^b) = [(e_m^b - y_1^b e_1 - y_2^b e_2)/y_1^b y_2^b]. \tag{25}$$

Assuming no errors in the compositions themselves, two further equations result for e_{Δ_1} and e_{Δ_2} as functions of $e(C^a)$ and $e(C^b)$; these equations are analogous to Eqs. 22 and 23. Combination of these equations with Eqs. 24 and 25 provide the working equations

$$e_{\Delta_1} = \left[\frac{(y_2^b/y_1^a y_2^a)e_m^a - (y_2^a/y_1^b y_2^b)e_m^b}{y_1^a - y_1^b}\right] - \left(\frac{y_2^a + y_2^b}{y_2^b y_2^a}\right)e_1 + \left(\frac{y_2^a - y_1^b}{y_1^a y_1^b}\right)e_2 \tag{26}$$

and

$$e_{\Delta_2} = \left[\frac{(y_1^a/y_1^b y_2^b)e_m^b - (y_1^b/y_1^a y_2^a)e_m^a}{y_1^a - y_1^b}\right] + \left(\frac{y_1^a - y_2^b}{y_2^b y_2^b}\right)e_1 - \left(\frac{y_1^a + y_1^b}{y_1^a y_1^b}\right)e_2, \tag{27}$$

where arbitrarily $y_1^a > y_1^b$.

With the assumption of zero covariance between the separate measurements of C_m^a, C_m^b, C_{111}, and C_{222}, above terms are individually squared to provide

$$e_{\Delta_1}^2 = \left[\frac{y_2^b e_m^a}{y_1^a y_2^a(y_1^a - y_1^b)}\right]^2 + \left[\frac{y_2^a e_m^b}{y_1^b y_2^b(y_1^a - y_1^b)}\right]^2 + \left[\frac{(y_2^a + y_2^b)e_1}{y_2^a y_2^b}\right]^2 + \left[\frac{(y_2^a - y_1^b)e_2}{y_1^a y_1^b}\right]^2 \tag{28}$$

and

$$e_{\Delta_2}^2 = \left[\frac{y_1^a e_m^b}{y_1^b y_2^b(y_1^a - y_1^b)}\right]^2 + \left[\frac{y_1^b e_m^a}{y_1^a y_2^a(y_1^a - y_1^b)}\right]^2 + \left[\frac{(y_1^a - y_2^b)e_1}{y_2^a y_2^b}\right]^2 + \left[\frac{(y_1^a + y_1^b)e_2}{y_1^a y_1^b}\right]^2. \tag{29}$$

The minimization of $[e_{\Delta_1}^2 + e_{\Delta_2}^2]$ is most complex in general. When all errors are equal in magnitude ($e = e_1 = e_2 = e_m^a = e_m^b$), the result should be symmetric ($y_1^a = y_2^b, y_2^a = y_1^b$). Then,

$$e_{\Delta_1}^2 = e_{\Delta_2}^2 = [(y_1^a)^2 + (y_1^b)^2 + (2y_1^a - 1)^2] \cdot e^2/[y_1^a y_1^b(y_1^a - y_1^b)]^2. \tag{30}$$

Here, $(\partial e_{\Delta_1}^2/\partial y_1^a) = 0$ provides

$$(3/2)\, y_1^a y_2^a(2y_1^a - 1)^2 = [3(y_1^a)^2 - 3y_1^a + 1][6y_1^a - 6(y_1^a)^2 - 1] \tag{31}$$

or

$$24x^2 - 15x + 2 = 0; \quad x \equiv y_1^a y_1^b; \quad 2y_1^a = 1 - \sqrt{1 - 4x} \tag{32}$$

Solution of this quadratic equation in x provides $x = 0.19282$ or $y_1^b = 0.26088$, $y_1^a = 0.73912$. The sensitivity of $e_{\Delta_1}(y_1^a)$ near this minimum for $e = 1$ is: 29.00(0.55), 15.59(0.6), 11.68(0.65), 11.02(⅔), 10.24(0.7), 9.96(0.739), 9.98(0.75), 10.62(0.8), 12.45(0.85), and 16.78(0.9).

As with the cross second virial coefficient, a simpler result is obtained by minimization of $[e_{\Delta_1} + e_{\Delta_2}]$ using Eqs. 26 and 27 with all error terms made positive on the righthand side. When all the errors are equal,

$$e_{\Delta_1} = e_{\Delta_2} = [(1 + y_1^a - y_1^b)/y_1^a y_1^b(y_1^a - y_1^b)]e, \tag{33}$$

resulting in minimization at $y_1^b = (1/4)$ and $y_1^a = (3/4)$. Note that whether we minimize the squared errors or the absolute sum, the results for equal error distribution are similar ($y_1^a = 0.73912$ vs. 0.75000) but fail to equal $y_1^b = (1/3)$, $y_1^a = (2/3)$, as expected by intuition. The values of $e_{\Delta_1}(y_1^a)$ from Eq. 33 are: 44.44(0.55), 25.00(0.6), 19.05(0.65), 18.00(⅔), 16.67(0.7), 16.00(0.75), 16.67(0.8), 19.05(0.85), and 25.00(0.9).

The following two examples use the simpler minimization of the above statements but with linear variation of the error e_m with y_1 as $e_m = (e_1 - e_2)y_1 + e_2$. Then Eqs. 26 and 27, with all error terms positive, provide

$$e_{\Delta_1} + e_{\Delta_2} = 2[(e_1/y_2^a) + (e_2/y_1^b)]/(y_1^a - y_1^b) \tag{34}$$

for minimization at (y_1^a, y_1^b). In the first example, let $e_1 = 2$ and $e_2 = 1$. Equation 34 can be differentiated first with respect to y_1^a and then with respect to y_1^b to provide equations which are zeroed to yield $y_1^b = 0.2071$ and $y_1^a = 0.7071$. As expected, y_1^b plus $y_1^a \neq 1$ and both y_1^b and y_1^a are less than their corresponding values for the case of equal errors. For the second example, let $e_1 = 10$ and $e_2 = 1$. Then $y_1^b = 0.1201$ and $y_1^a = 0.6201$. As (e_1/e_2) increases further, y_1^a is driven into 0.5 and y_1^b is driven to zero. In the methane(1)/water(2) data of Joffrion and Eubank (1988), C_m was measured at $y_1^a = 0.5$, $y_1^b = 0.75$ and $y_1^c = 0.90$. Systematically at each T, $C_{112}(a, b) < C_{111}(a, c) < C_{112}(b, c)$ and $C_{122}(a, b) > C_{122}(a, c) > C_{122}(b, c)$. The above analysis, with $e_2 \simeq 300\, e_1$, shows why our final recommended values are weighted heavily on those from (y_1^a, y_1^c).

Simultaneous optimization of second and third cross virial coefficients for binary mixtures

An appropriate question is what are the optimum values (y_1^a, y_1^b) for a binary mixture to provide the "best" results for B_{12}, C_{112}, and C_{122}, as a combination. The function to be optimized is somewhat arbitrary because we must first decide the relative importance of the errors in B_{12} vs. those in C_{112} and C_{122}. For simplicity, we use only the sum of absolute errors and examine the case where $e_B = e_{B_{11}} = e_{B_{22}} = e_{B_m}$ and $e_C = e_{C_{111}} = e_{C_{222}} = e_{C_m}$. Then,

$$e_\delta = (2e_B/y_1 y_2), \tag{35}$$

where $\delta \equiv \delta_{12} \equiv 2B_{12} - B_{11} - B_{22}$. Further, e_{Δ_1} and e_{Δ_2} are equal as given by Eq. 33 with $e \equiv e_C$. Considering that (1) e_C has units of e_B^2 and (2) that e_B is at best ± 0.2 cm^3/mol whereas e_C is ±100 cm^6/mol^2, we arbitrarily chose to optimize the combined function

$$e_{BC} \equiv [100/(0.2)^2][e_{\delta^a}^{-2} + e_{\delta^b}^{-2}]^{-1} + e_{\Delta_1} \tag{36}$$

as an example which places roughly equal weight on the cross second and combined third virial coefficients consistent with the present state-of-the-art in determination of pure B and pure C. Here e_{δ^a} is given by Eq. 35 with $y_1 = y_1^a$. Equation 36 becomes

$$(e_{BC}/100) = [2/(y_1^a y_1^b)^2] + [2/y_1^b(2y_1^a - 1)] \tag{37}$$

which provides the symmetric result of $y_1^b = 0.3620$ and $y_1^a = 0.6380$. This result is closer to the (1/3, 2/3) combination expected originally to optimize cross third virial coefficients alone. Changing the above analysis only in giving each of the three cross coefficients equal weight results in $y_1^b = 0.3375$ and $y_1^a = 0.6625$.

Direct Methods for Measurement of the Second Cross Virial Coefficient

The inherently better accuracy of direct methods over indirect ones has diminished in recent years due to significant improvements in the preparation of gas mixtures to ±10 ppm by gravimetric procedures. The indirect method uses these mixtures for determination of B_m and C_m, whereas the direct methods make the mixture in the PVT apparatus with composition, dependent on density, no better than ±200 ppm. Possible compositions are often constrained by the particular direct method with less freedom to optimize B_{12}. We provide here an overview of what is possible to optimize for several direct methods and how the resultant errors in B_{12} compare with those from the indirect method.

The original direct method of Knobler et al. (1959) determined B_{12} by pressure change upon mixing of two pure fluids originally contained in two identical volumes at the same pressure ($P_1 = P_2$). The exact relation between the second cross virial coefficient and the pressure change ΔP is

$$\delta_{12} = (4Z_1/\rho_2)\left[\left(\frac{\Delta P}{P_1}\right) + 1 - (4y_1y_2)^{-1}\right]. \tag{38}$$

The last two terms inside the bracket cancel for an equimolar mixture and are sometimes omitted from the relation (Holste et al., 1980). Because of the highly constrained nature of the experiment,

$$y_1Z_1 = y_2Z_2$$
$$\rho_1Z_1 = \rho_2Z_2$$
$$y_1\rho_2 = y_2\rho_1$$

and

$$\rho_m = (\rho_1 + \rho_2)/2. \tag{39}$$

A useful approximation (second virial Berlin gases),

$$2y_1 = 1 + (P/2RT)(B_{22} - B_{11}), \tag{40}$$

shows that y_1 cannot be varied in this experiment once T, P, and the two gases are chosen. Because fractional errors in B_{ii} are typically 10–40 times those in Z_i or ρ_i, Eq. 38 provides fractional errors in δ_{12} similar to those in ΔP for near equimolar mixtures:

$$[e(\delta_{12})/\delta_{12}] \simeq [e(Z_1)/Z_1] + [e(\rho_2)/\rho_2] + [e(\Delta P)/\Delta P] \tag{41}$$

When $[e(\Delta P)/\Delta P]$ is as high as 1% but $[e(Z_1)/Z_1]$ and $[e(\rho_2)/\rho_2]$ are each 0.05%, then $e(\delta_{12})$ is 1.1 cm^3/mol when $\delta_{12} = 100$ cm^3/mol leading to $e(B_{12}) = 1.55$ cm^3/mol when $e(B_{11}) = 1$ cm^3/mol $= e(B_{22})$. Equation 8 for the corresponding indirect measurement yields $e(B_{12}) = 3$ cm^3/mol when $e(B_m)$ is also unity, y_1 is optimum and errors in the composition are negligible.

Hall and Eubank (1973) developed a direct method for use with the Burnett apparatus where neither the initial volumes nor pressures of the pure components need to equal prior to mixing. Later, Ewing and Marsh (1979) developed a differential Burnett apparatus and substantiated the earlier equations of both Knobler et al. (1959) and Hall and Eubank (1973). Holste et al. (1980) simplified the main equation of Hall and Eubank to yield

$$B^*_{12} = \left[\frac{N^2}{2(N-1)\rho_1\rho_2}\right] \cdot \left[\frac{P_m}{RT} - \frac{\rho_1(Z_1 + N - 1)}{N^2} - \frac{\rho_2(N-1)^2\left(Z_2 - 1 + \dfrac{N}{N-1}\right)}{N^2}\right], \tag{42}$$

where B^*_{12} is the apparent cross second virial coefficient, $N = 1 + (V_B/V_A)$ is the Burnett apparatus constant, V_A is the primary cell volume and V_B is the secondary cell volume. B^*_{12} is related to the true B_{12} by

$$B^*_{12} = B_{12} + A_1RT\rho_2 + A_2(RT\rho_2)^2 + \cdots, \tag{43}$$

where A_i depends upon temperature and composition. B_{12} is given by the intercept of B^*_{12} vs. $RT\rho_2$ for a series of experiments performed at constant temperature and composition. The slope of these nearly straight lines is

$$A_1 = [(N-1)/2RTN][(1-N)C_{111}\nu^2 + 3C_{112}\nu + 3C_{122} - C_{222}/(N-1)\nu], \tag{44}$$

where

$$\nu \equiv (y_1/y_2) = [\rho_1/\rho_2(N-1)], \tag{45}$$

and it is assumed that pure component 1 originally occupies V_A. The density of the mixture of

$$\rho_m = [\rho_2(N-1)(\nu + 1)/N] \tag{46}$$

allowing Eq. 42 to be written more simply as

$$2\rho_1B^*_{12} = Z_mN(\nu + 1) - \nu(N + Z_1 - 1) - Z_2(N-1) - 1. \tag{47}$$

Unlike the experiment of Knobler et al. (1959), the direct method of Hall and Eubank (1973) allows choice of the composition. Here we seek the optimum composition for a binary mixture to minimize $e(B_{12})$. Because of the complexity of this method, we fail to find exact answers, unlike the results of the indirect experiment analysis, but hopefully provide the reader considerable insight as to which compositions are best. First, we can operate with $P_1 = P_2$, as in the Knobler et al. experiment, causing

$$\nu = [Z_2/Z_1(N-1)] \tag{48}$$

or

$$\nu \simeq [1 + (B_{22} - B_{11})P/RT]/(N-1). \tag{49}$$

For a Burnett apparatus with $N \simeq 1.5$, then y_1 will be near (2/3) whereas in the Knobler et al. experiment ($N = 2$) y_1 will be near (1/2). Second, if pure component densities are set equal, then y_1 is exactly the inverse of N. Lastly, we examine strategies to reduce $e(B_{12})$ below that of the Knobler et al. method (Hall and Eubank, 1973).

Figure 3 (Holste et al., 1980) illustrates the variation of B^*_{12} with ρ_2 at 300 K for several mixtures of $CO_2(1)/He(2)$ with $N \simeq 1.61$. The slope of these isotherms, A_1, is given by Eq. 44. With $C_{111} = 4{,}927$ cm^6/mol^2 and $C_{222} = 72$, we estimate $C_{112} = 1{,}354$ and $C_{122} = 331$ from the correlation of Orbey and Vera (1983) with slight quantum corrections. For $y_1 = 0.413$, 0.5, and 0.608, A_1RT is 416, 366 and -2.4 cm^6/mol^2, respectively, in agreement with the general trend of B^*_{12} to be lowered by increasing y_1. With this information, our selected value of B_{12} should be fine-tuned from 19.6 to about 19.3 cm^3/mol; and such a change is well within our claimed error band of ± 1 cm^3/mol.

Holste et al. (1980) also showed that systematic errors produce marked curvature in such graphs as Figure 3, so both random and systematic errors are easily detected unlike most experiments in which systematic errors are impossible to detect.

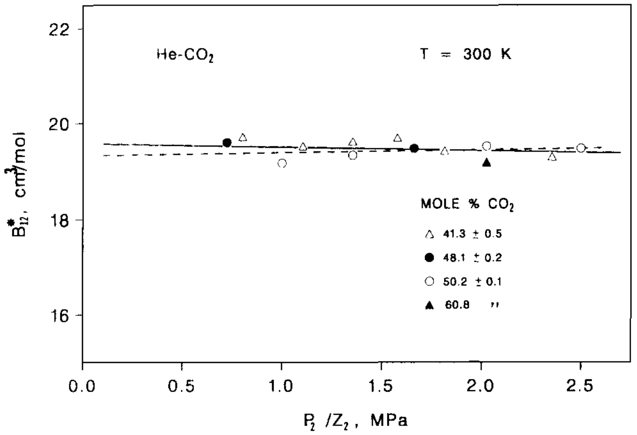

Figure 3. Experimental B_{12} data at 300 K.

———, best fit of a linear function to all data; ----, best fit to all circles.

Experimental value of B_{12} is determined from the lefthand intercept. Uncertainties listed with the compositions represent the extreme variation in composition over the entire set of samples with that symbol.

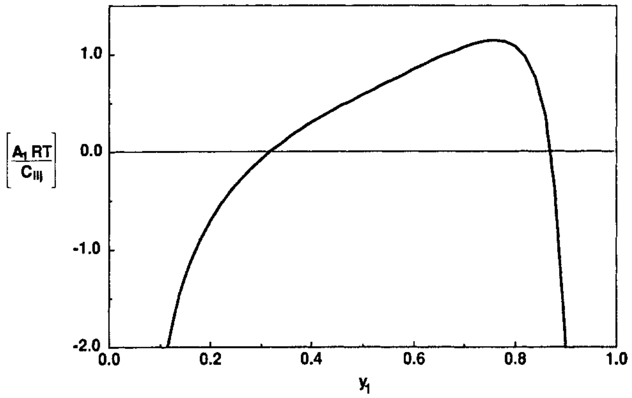

Figure 4. Dimensionless slope of the apparent second cross virial coefficient B^*_{12} vs. density ρ_2 (or P_2/Z_2RT) as a function of composition for equal values of C_{iij} and $N = 1.5$.

An obvious strategy is to make the mixture composition in such a way that A_1 is nearly zero for each temperature thereby reducing $e(B_{12})$. When all values of C_{iij} are equal, A_1 is zeroed at $y_1 = 0.318$ and 0.872 for $N = 1.5$, whereas for $N = 2$ the values are symmetric at 0.212 and 0.788. The general nature of A_1 is to diverge at both pure end points. Negative divergence is the result of a positive third virial coefficient of the appropriate pure component, whereas positive divergence results from negative third virial coefficients. For nonpolar compounds, the third virial coefficient is negative below a reduced temperature of about 0.74, but otherwise positive. A variety of interesting variations of A_1 with y_1 result depending primarily on the pure-component third virial coefficients. Figure 4 is (A_1RT/C_{iij}) vs. y_1 when all the C_{iij} are equal (and positive) with $N = 1.5$; and the maximum value of A_1 is obtained when $y_1 = 0.762$ with all the positive values of A_1 low enough for excellent determination of B_{12} by the method of Hall and Eubank. Figure 5 is a similar graph but for $CO_2(1)/H_2O(2)$ at 448.15 K where $C_{111} = 2{,}444$, $C_{222} = -56{,}200$, $C_{112} = 2{,}811$ and $C_{122} = 1{,}775$ cm^6/mol^2 from previous measurements. Here A_1 is zero only near $y_1 = 0.9$; and the magnitudes of A_1RT are roughly 100 times those of the $CO_2(1)/He(2)$ mixture at 300 K. Unless fortunate enough to

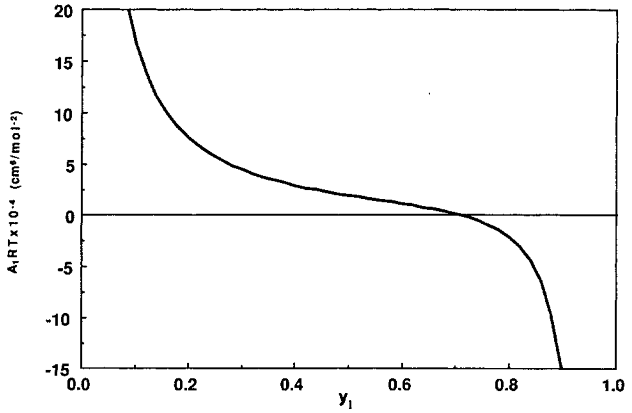

Figure 5. Slope of the apparent second cross virial coefficient B^*_{12} vs. density ρ_2 as a function of composition for $CO_2(1)/H_2O(2)$ at 448.15 K and $N = 1.5$.

measure exactly at the optimum composition, one should expect steep slopes (on the scale of Figure 3) for the CO_2/H_2O system. It is further obvious as to why water should always be placed in the smaller of the two Burnett cells.

We conclude that graphs such as Figures 4 and 5 are invaluable in setting the composition for direct determination of B_{12}. Values of A_1RT are fortunately more sensitive to the pure third virial coefficients than to the cross third virial coefficients allowing rough estimate of the latter to be sufficient.

Conclusions

We have shown that the accuracy of measurements of cross virial coefficients are often sensitive to the composition of the mixture. Indirect method measurements require knowledge of how the errors in B_m (or C_m) vary with composition, particularly how the errors in B_{11} (or C_{111}) compare with those in B_{22} (or C_{222}). When these errors are unaffected by composition, B_{12} is best found from B_m at $y_1 = 0.5$, whereas surprisingly C_{112} and C_{122} are best found from C_m at $y_1^b = 0.25$ and $y_1^a = 0.75$. Direct measurement of B_{12} benefits from prior knowledge of C_{111} and C_{222} although B_{11} and B_{22} are not used in this method.

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Notation

a = slope for linear functions in Figure 1
A_i = power-series constants for apparent second cross virial coefficient
b = intercept for linear functions in Figure 1
B_{ij} = second virial coefficient, cm^3/mol
B_m = mixture second virial coefficient
B_{12}^* = apparent second cross virial coefficient
C_{iij} = third virial coefficient (binary) cm^6/mol^2
C_m = mixture third virial coefficient
e_i = absolute error in B_{ii}
e_{12} = absolute error in B_{12}
e_m = absolute error in B_m or in C_m
e_{Δ_i} = absolute error in Δ_{iij}
$e(X)$ = general notation for absolute error in the quantity X
n = degree of polynomial, Eq. 12
N = Burnett apparatus constant, $(V_A + V_B)/V_A$
P = pressure, MPa
R = gas constant, $8.3144\ cm^3 \cdot MPa/mol \cdot K$
T = temperature, K
V = total volume, cm^3
$x = y_1^a y_1^b$
y_i^j = mol fraction of component i at location j
Z_i = compressibility factor of pure gas i
Z_m = compressibility factor of gas mixture

Greek letters

$\delta_{12} = 2B_{12} - B_{11} - B_{22}$
$\Delta_1 = \Delta_{112} = 3C_{112} - 2C_{111} - C_{222}$
$\Delta_2 = \Delta_{122} = 3C_{122} - C_{111} - 2C_{222}$
$\nu_1 = (y_1/y_2)$
ρ_i = density of pure gas i, mol/cm^3
ρ_m = density of gas mixture, mol/cm^3
σ = standard deviation

Subscripts

B = second cross virial coefficient
BC = combined optimization of second and third cross virial coefficients
C = third cross virial coefficient
i = species i
m = mixture

Superscripts

a, b = different values of the mol fraction

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