

# New Method for Conversion of Gas Sonic Velocities to Density Second Virial Coefficients

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*A new, numerical method was developed to calculate density second virial coefficients  $B(T)$  from sonic velocity measurements in gases at low pressures. Unlike existing methods, this procedure requires no model assumption as to the form of the temperature variation of  $B(T)$ . Rather, it differences the measured acoustic second virial coefficient according to a new mathematical identity. While two higher-ordered terms in the identity must be ignored to initiate the numerical calculations, the magnitude of these terms can later be found from the initial determination of  $B(T)$ . This article describes new equations developed, numerical procedures, calculations with Redlich-Kwong and Peng-Robinson gases and, with a Lennard-Jones model gas, to show the accuracy of the method and the magnitude of the two error terms, and the method applied to existing sets of sonic velocity data.*

## Introduction

Density second virial coefficients  $B(T)$  are very valuable in that they provide the first-order deviation from an ideal gas. For both pure components and mixtures, their experimental values find application in (1) testing molecular theories, (2) correcting pure and mixture gas densities and (3) phase equilibrium data corrections as in the case of the gamma-phi method (Smith et al., 1996). However, accurate measurement of  $B(T)$  with conventional P-V-T apparatus is expensive, tedious, and difficult, especially for polar gases that show strong molecular adsorption to the container walls. Nonpolar gases also show adsorption for subcritical temperatures where the vapor pressure limits the range of measurements and errors of  $\pm 0.03\%$  in the density propagate to  $\pm 3\%$  in  $B(T)$  (Eubank et al., 1994).

Sonic velocity experiments, on the other hand, are less expensive, faster, mostly void of adsorption errors and generally more accurate in that random errors at least can be reduced to  $\pm 5$  ppm (Ewing et al., 1988). It must also be acknowledged that the accuracy of sonic velocity measurements has improved by one or two orders of magnitude (Moldover et al., 1979; Ewing et al., 1987) in the past 20 years whereas that of P-V-T measurements has made only incremental gains. The problem is that the thermodynamic conversion of sonic velocity data to density second virial coefficients can easily yield

propagation factors of 500 (Eubank et al., 1994) so that errors of  $\pm 20$  ppm in sound speeds become  $\pm 1\%$  in  $B(T)$ . The major reason why this propagation factor is so high is that the connecting thermodynamic identity is a second-order, ordinary differential equation

$$\left(\beta_a/2\right) \equiv B + (\gamma^* - 1)T(dB/dT) \\ + \{[(\gamma^* - 1)T]^2/2\gamma^*\}(d^2B/dT^2) \quad (1)$$

where  $\gamma^*$  is the ratio of the isobaric to isochoric perfect gas heat capacities which also may be determined from the sonic first virial coefficient  $W_o^2 = (RT\gamma^*/M)$ , where  $M$  is the molecular weight. The acoustic virial equation of state, in terms of a power series with pressure as the independent variable is

$$W^2 = W_o^2 \left[ 1 + (\beta_a P/RT) + (\gamma_a P^2/RT) + \dots \right] \quad (2)$$

where  $W$  is the sound speed and  $\gamma_a$  is the acoustic third virial coefficient. In order to use Eq. 1 to calculate  $B(T)$  it is obvious that the form of the temperature dependency of  $B$  must be assumed. This is commonly taken from either a molecular model (such as Lennard-Jones) or an empirical equation of state (EoS) causing a model-bias in the calculated  $B(T)$  and

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additional uncertainty as reflected by the large propagation factor.

We present here a new method for conversion of  $\beta_a(T)$  into  $B(T)$  which differences the sonic  $\beta_a(T)$  results without the assumption of the temperature dependence of  $B(T)$  as in earlier methods (Riazi and Mansoori, 1993; Shabani et al., 1998). The new equations are presented. Sample calculations are provided with both Redlich-Kwong and Peng-Robinson gases to show the accuracy of the method and the magnitude of the two error terms created by the method. Similar calculations with a Lennard-Jones model gas are presented. Familiar numerical methods necessary for application of the method to real sonic data are presented. A noisy data set, obtained by superimposing random errors onto a known background model gas, is reduced by our new method and the  $B(T)$  results are compared with previous methods as previously published. The method is applied to literature sonic velocity data for n-butane.

### Derivation of the New Method

Define  $t \equiv \ln T$ ;  $B'_t \equiv (dB/dt)$ ,  $B' \equiv (dB/dT)$ ,  $B'' \equiv (d^2B/dt^2)$ , and so on. Also, define the ratio of perfect-gas heat capacities  $\gamma \equiv (C_p^*/C_v^*)$ ,  $C_p^* - C_v^* = R$ , where  $\gamma$  is a weak function of  $T$ . Equation 1 can then be written as

$$\beta_a = 2B + [(\gamma^2 - 1)/\gamma] B'_t + [(\gamma - 1)^2/\gamma] B''_t \quad (3)$$

or

$$\beta_a = 2(B + C_1 B'_t + C_2 B''_t) \quad (4)$$

where

$$C_1 \equiv [(\gamma^2 - 1)/\gamma]/2 \quad \text{and} \quad C_2 \equiv [(\gamma - 1)^2/\gamma]/2.$$

Differentiating with respect to  $t$

$$(\beta'_a)_t = 2(B'_t + C_1 B''_t + C_2 B'''_t), \quad \text{for } \gamma \neq \gamma(T) \quad (5)$$

and

$$(\beta''_a)_t = 2(B''_t + C_1 B'''_t + C_2 B''''_t) \quad (6)$$

Elimination of  $B'_t$  and  $B''_t$  from Eqs. 4–6 provides

$$\begin{aligned} \beta_a - C_1(\beta'_a)_t + (C_1^2 - C_2)(\beta''_a)_t \\ = 2[B + (C_1^2 - 2C_2)C_1 B'''_t + (C_1^2 - C_2)C_2 B''''_t] \end{aligned} \quad (7)$$

Truncation of Eq. 7 provides our working equation for the transformation of sonic second virial coefficients [ $\beta_a(T)$ ] to density second virial coefficients [ $B(T)$ ]

$$2B = \beta_a - C_1(\beta'_a)_t + (C_1^2 - C_2)(\beta''_a)_t \quad (8)$$

Equation 8 has neglected the terms involving the third and fourth temperature derivatives of  $B$ ; this together with neglect of the variation of heat capacities with temperature are

the only reasons for Eq. 8 to be inexact. For the numerical method proposed here, these contributions are regarded as error sources which can always be estimated once Eq. 8 has been used to find initial estimates of  $B(T)$  over a range of temperatures.

In performing numerical calculations, the following exact relations between derivatives of  $B$  with respect to  $t$  vs. those with respect to  $T$  are valuable

$$\begin{aligned} B'_t &= TB'; \quad B''_t = T(B' + TB''); \quad B'''_t = T(B' + 3TB'' + T^2B''') \\ B''''_t &= T(B' + 7TB'' + 6T^2B''' + T^3B''''') \end{aligned} \quad (9)$$

These equations will also be used with  $B$  replaced by  $\beta_a$ . Further, we define  $\Delta B$  as

$$-\Delta B \equiv (C_1^2 - 2C_2)C_1 B'''_t + (C_1^2 - C_2)C_2 B''''_t \quad (10)$$

so that

$$B_{\text{actual}} = B_{\text{approximated}}(\text{Eq. 8}) + \Delta B + e(B)_\gamma \quad (11)$$

where  $B_{\text{approximated}}(\text{Eq. 8}) + \Delta B$  provides  $B(T)$  according to Eq. 7 and  $e(B)_\gamma$  is the error in Eqs. 7 and 8 due to the assumption that  $\gamma$  is independent of temperature. In all examples and for each temperature studied here,  $e(B)$  was found to be negligible compared to  $\Delta B$  which explains why the [ $B_{\text{actual}} - B_{\text{approximated}}$ ] and  $\Delta B$  entries in the tables and graphs of results in Mossaad (1999) are always identical.

### Comparison to EoS Gases

Any closed-form equation of state (EoS) in the form  $P = P(T, \rho)$  can be used to generate  $B(T)$  and any of its derivatives with respect to  $T$  or  $t$ . With a separate equation to generate  $\gamma(T)$ , it can also provide values of  $\beta_a(T)$  as demonstrated by Eubank et al. (1994) for the Redlich-Kwong EoS with its parameters derived from the well-known critical constraints and the critical constants for n-butane. We again find  $\beta_a(T)$  and then find expressions for its temperature derivatives in Eq. 8 which allows calculation of  $B(T)$  from Eq. 8. We can also find the value of the terms involving  $B'''_t$  and  $B''''_t$  that we truncated from Eq. 7 to yield Eq. 8. We also know the actual value of  $B(T)$  from the EoS; for Redlich-Kwong,

$$\begin{aligned} B_{RK}(T) &= b - (a/RT^{1.5}); \quad a = 0.427848(R^2 T_c^{2.5}/P_c); \\ b &= 0.08664(RT_c/P_c). \end{aligned} \quad (12)$$

### Results from the Redlich-Kwong EoS

With Eq. 12, we used  $R = 83.144 \text{ cm}^3 \text{ -bar/mol-K}$  and  $T_c = 425.2 \text{ K}$  for n-butane (both in error in Eubank et al., 1994) plus  $P_c = 38.0 \text{ bar}$ ,  $b = 80.601 \text{ cm}^3/\text{mol}$ , and  $a = 2.9014 \times 10^8 \text{ cm}^6 \text{ -bar/K/mol}^2$  plus the heat capacity equation in Smith et al. (1996) for  $C_p^*$

$$(C_p^*/R) = 1.935 + 36.915 \times 10^{-3}(T/K) - 11.402 \times 10^{-6}(T/K)^2 \quad (13)$$

Further, for the Redlich-Kwong EoS,

$$2\beta_a = b - (a/RT^{1.5}) \left[ 1 - \frac{3(\gamma-1)}{2} + \frac{15(\gamma-1)^2}{8\gamma} \right], \quad (14)$$

so one can easily find two temperatures derivatives of  $\beta_a$  in Eq. 8 by also using Eq. 9 with  $B$  replaced by  $\beta_a$ . The result is that

$$B_{\text{approximated}} = b - \left[ 1 - \frac{3(\gamma-1)}{2} + \frac{15(\gamma-1)^2}{8\gamma} \right] \times \left[ 1 + (3C_1/2) + (21/4)(C_2 - C_1^2) \right] (a/RT^{1.5}) \quad (15)$$

and

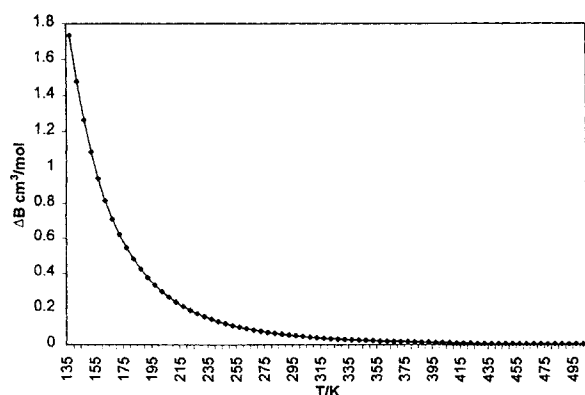
$$-\Delta B \equiv \left[ (27/8)(C_1^2 - 2C_2)C_1 - (81/16)(C_1^2 - C_2)C_2 \right] (a/RT^{1.5}), \quad (16)$$

using Eqs. 8, 10, and 12.

Figure 1 is a graph of  $\Delta B$  vs.  $T$  for the Redlich-Kwong EoS simulating *n*-butane from 135 (the triple point temperature)–500 K. Positive values of  $\Delta B$  mean that  $B(T)$  values from Eq. 8 are too negative. It is seen from Figure 1 that  $\Delta B$  is small, being less than 2 cm<sup>3</sup>/mol from 135–170 K, less than 1 cm<sup>3</sup>/mol above 170 K and less than 0.2 cm<sup>3</sup>/mol above 250 K. While an iterative procedure will be described later to correct experimental data for these truncation errors, it is not really necessary in this example as  $B_{RK} = -2,144$  cm<sup>3</sup>/mol at 135 K so the truncation error is less than 0.1%.

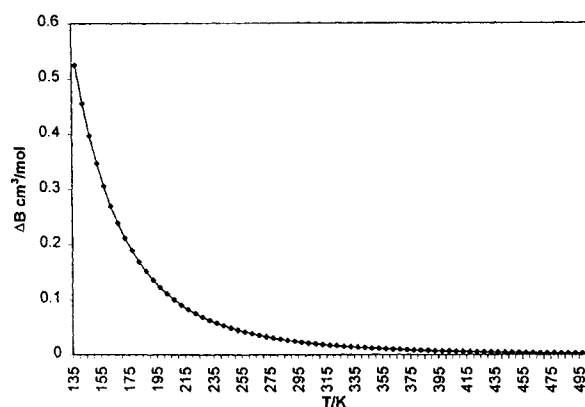
### Results from the Peng-Robinson EoS

We used the original Peng-Robinson formulation (Peng and Robinson, 1976), an acentric factor  $\omega$  of 0.193 and the above critical constants for *n*-butane. Following a procedure similar to that above for the Redlich-Kwong EoS, Mossaad (1999)



**Figure 1. Truncation error  $\Delta B$  from Eq. 10 for the Redlich-Kwong EoS simulating *n*-butane from 135–500 K.**

Positive values of  $\Delta B$  indicate that the  $B(T)$  values from Eq. 8 are too negative.



**Figure 2. Truncation error  $\Delta B$  from Eq. 10 for the Peng-Robinson EoS simulating *n*-butane from 135–500 K.**

Positive values of  $\Delta B$  indicate that the  $B(T)$  values from Eq. 8 are too negative.

found that  $b = 72.38$  cm<sup>3</sup>/mol

$$B_{PR} = -114.18 - (499,770/T) + (19,312/\sqrt{T}), \quad (17)$$

and

$$2\gamma\beta_a = -2.8422 \times 10^{14} - 144.18\gamma - (499,770/T) + (7,241.9 + 14,484\gamma - 2,414.0\gamma^2)/\sqrt{T} \quad (18)$$

Equation 13 was used again for the heat capacities,  $\gamma$ ,  $C_1$  and  $C_2$ . Mossaad (1999) then found  $B_{\text{approximated}}$  (Eq. 8) and the truncation error  $\Delta B$ . Figure 2 shows the values of  $\Delta B$  to be positive but less than (1/3) as high as for the Redlich-Kwong example. While we do not claim that a Redlich-Kwong gas or a Peng-Robinson gas represents nature (that is, all real gases), they are close enough to provide at least a rough idea of the errors generated by use of Eq. 8.

### Comparison to a Molecular Model

Here we repeat the above procedures for *n*-butane but with the well-known Lennard-Jones intermolecular potential model (Maitland et al., 1981). Following Hirshfelder et al., (1954), the equations are

$$B^* = (T^*/4) \left[ H_{12} - \frac{H_6}{2} \right],$$

where

$$B^* \equiv (3B/2\pi\tilde{N}\sigma^3); T^* \equiv [T/(\epsilon/k_B)] \equiv (4/Y^2) \quad (19)$$

and the spherical harmonic  $H_N(Y)$  is an infinite series involving gamma functions:

$$H_N(Y) \equiv Y^{\frac{27-N}{6}} \sum_{i=0}^{\infty} \left[ \frac{Y^i}{i!} \right] \Gamma \left\{ \frac{6i+N-3}{12} \right\} \quad (20)$$

The fundamental constants are Avogadro's number ( $\tilde{N} = 6.022 \times 10^{23} \text{ mol}^{-1}$ ) and the Boltzmann constant ( $k_B = 1.38066 \times 10^{-23} \text{ J/K}$ ). The force constants of  $(\epsilon/k_B) = 317 \text{ K}$  and  $\sigma = 0.577 \text{ nm}$  are from a fit of the experimental  $B(T)$  data of Gupta and Eubank (1997) taken in a Burnett-isochoric P-V-T apparatus from 265–450 K.

Figure 3 again provides  $\Delta B$  vs.  $T$  simulating n-butane from 135–500 K. However, for this Lennard-Jones gas,  $\Delta B$  is significantly positive below about 220 K and rises to nearly 120  $\text{cm}^3/\text{mol}$  at 135 K. Again, the difference between  $[B_{\text{actual}} - B_{\text{approximated}}]$  and  $\Delta B$  is insignificant so that all of the error lies in  $\Delta B$  and none in the variation of the heat capacity ratio with temperature. While Figure 3 supplies an important warning about the use of Eq. 8 without correction, several points should be kept in mind: (1) at 135 K, the L-J model value of  $B$  is near  $-3,400 \text{ cm}^3/\text{mol}$  so that the error represented by  $\Delta B$  is 3.5%; (2)  $\Delta B$  drops strongly with increasing temperature to be only 0.81 at 250 K and 0.14 at 320 K, the range of sonic velocity data of Ewing et al. (1988), considered later. The effected temperature range of 135–220 K corresponds to a reduced temperature range of 0.32–0.52, which is often too low to take gas measurements, whether sonic or density, due to the low vapor pressures. Indeed, a search of Dymond and Smith (1980) found only a single measurement of  $B$  below a reduced temperature of 0.32 (for  $^4\text{He}$ ) and few are below 0.5 as seen in Pitzer (1995).

## Numerical Methods and Iterative Correction

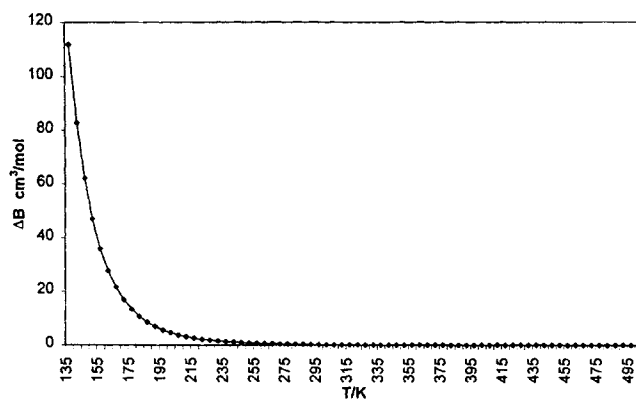
As a prelude to the application of the new method to real sonic velocity data, we here provide a review of common numerical methods plus an iterative procedure for correction of the error  $\Delta B$ .

The acoustic second virial coefficients  $\beta_a(T)$  are first placed in a difference table (see *Numerical Analysis*, Burden and Faires (1989), or *CRC Handbook of Mathematical Tables* (1964). With the divided-difference notation in the *CRC Handbook*, we used (1) Newton's forward formula (NF), (2) Newton's backward formula (NB), and (3) Stirling's central-difference formula (SCD)

$$\text{NF: } f(T) = f(T_0, p) = f_0 + p\Delta_0 + (p/2)(p-1)\Delta_0^2 + (p/6)(p-1)(p-2)\Delta_0^3 + \dots (p/n!)[(p-1) \dots (p-n+1)]\Delta_0^n, \quad (21)$$

where  $p \equiv (T - T_0)/h$ ,  $h$  is the uniform temperature interval,  $f \equiv [\beta_a(T)]/2$ ,  $f_0 \equiv [\beta_a(T_0)]/2$ ,  $\Delta_0$  is the first forward difference,  $\Delta_0^2$  is the second difference and in the general term for  $n \geq 2$ ,  $\Delta_0^n$  is the  $n^{\text{th}}$  difference, all with units of  $\text{cm}^3/\text{mol-K}$ . If there are a total of  $m$  data, then  $n$  cannot exceed  $(m-1)$  when the first datum is  $T_0$ . Equation 21 can also be applied starting from the second datum  $T_1$  using the divided differences  $\Delta_1^n$ , but now  $n$  cannot exceed  $(m-2)$ .

Equation 21 can be differentiated easily using  $(df/dp) = h(df/dT) = (h\beta_a/2)$ , and so on, for the higher derivatives of  $\beta_a$ . These derivatives can then be used in Eq. 9 to find the derivatives of  $\beta_a$  with respect to  $t$  followed by use in Eq. 8 to get  $B(T_0)$  or Eq. 10 to get  $\Delta B$  at  $T_0$ . Equation 8 requires only the first two temperature derivatives or  $m \geq 3$ , whereas



**Figure 3. Truncation error  $\Delta B$  from Eq. 10 for the Lennard-Jones intermolecular potential model simulating n-butane from 135–500 K.**

Positive values of  $\Delta B$  indicate that  $B(T)$  values from Eq. 8 are too negative.

estimation of  $\Delta B$  requires two additional derivatives of  $m \geq 5$ . Of course, if we start NF at  $T_1$ , then the minimum number of data are increased by unity.

In the example used in the next section, Ewing et al. (1988) took eight data points at equally spaced temperatures, so we can only use NF for  $B(T)$  for the first six data with  $p = 0$  and only for the first four data can we estimate  $\Delta B$ . We later use the first six data of Ewing to find  $B(T)$  by Eq. 8 and find  $\Delta B$  to be unimportant for all temperatures.

For Newton's backward formula (NB),

$$\text{NB: } f(T) = f(T_0, p) = f_0 + p\nabla_0 + (p/2)(p+1)\nabla_0^2 + (p/6)(p+1)(p+2)\nabla_0^3 + \dots (p/n!)[(p+1) \dots (p+n+1)]\nabla_0^n, \quad (22)$$

where Eq. 22 is similar to Eq. 21 except that  $\nabla_0^n$  is the  $n^{\text{th}}$  backward difference starting from the last datum (highest temperature) and working backwards. We can again differentiate Eq. 22 to find the higher temperature derivatives of  $\beta_a$  followed by use in Eq. 8 to get  $B(T_0)$  or Eq. 10 to get  $\Delta B$  at  $T_0$ . In the next section with Ewing's n-butane data, we use NB to find  $B(T)$  for the last six datum, but later also use NB for the first two datum using  $p = -2$  and  $p = -1$ , respectively.

Finally, we use Stirling's central-difference formula (SCD)

$$\text{SCD: } f(T) = f(T_0, p) = f_0 + (p/2)(\delta_{1/2} + \delta_{-1/2}) + (p^2/2)\delta_0^2 + (p/2)(p^2-1)(\delta_{1/2}^3 + \delta_{-1/2}^3) + \dots \quad (23)$$

where one starts in the middle of the divided difference table with a base datum  $T_0$  with  $\delta_{1/2}$  being the divided difference between the datum  $f_1$  and  $f_0$ , whereas  $\delta_{-1/2}$  is the divided difference between the datum  $f_0$  and  $f_{-1}$ , the latter being the entry above  $T_0$ .  $\delta_0^2$  is the second divided difference that aligns horizontally with  $T_0$  in the table. The reader is reminded that the superscript on  $\delta$  is not a power, but rather the divided difference number. The general term of Eq. 23 is

not difficult to decipher but cumbersome to express mathematically (Burden and Faires, 1989).

We can again differentiate Eq. 23 to find the higher temperature derivatives of  $\beta_a$  followed by use in Eq. 8 to get  $B(T_0)$  or Eq. 10 to get  $\Delta B$  at  $T_0$ . Here we see an important difference between central difference approximations and forward/backward type approximations; the second derivative,  $(d^2f/dp^2)$  of Eqs. 21 and 22 at the base  $T_0$  receives contributions not only from the second divided difference, but also higher divided difference terms because they all have a quadratic component. This is not true with Eq. 23 where  $(d^2f/dp^2)$  at  $T_0$  is exactly estimated as  $\delta_0^2$ . As Eq. 8 requires the second derivative and thus only the  $\delta_0^2$  term of Eq. 23, our chosen  $T_0$  base datum must have at least a datum above the below it in the tables. However, Eq. 8 also contains the first derivative  $(df/dp)$  which at the base  $T_0$  receives contributions from the second, fourth, and other terms of Eq. 23. Thus, we get reasonable estimates of  $(df/dp)$  and thus  $B(T_0)$  for **SCD** with at least one data point above  $T_0$  and one below; this is the criteria chosen in the next section where **SCD** is applied to the center six of Ewing's eight data points. This is consistent with our taking the first six data points for **NF** in that both first and second derivative terms have at least *one numerical contribution*. The same arguments can be applied to  $\Delta B$  except the highest derivative is now the fourth and everything above must be reduced by two. While  $\Delta B$  is unimportant with Ewing's data, we could evaluate it by the above criterion for the first four data points by **NF**, the last four by **NB** and the center four by **SCD**.

## Comparison to Previous Methods

Real sonic data contain systematic and random errors as studied in detail by Eubank et al. (1994). In one of their tests, random errors were added to a Redlich-Kwong (RK) gas at  $W^2$  levels of 5 ppm and 50 ppm. The lower level is sometimes claimed by modern experimentalists, while the upper level is more realistic for much of the older literature mea-

surements. We select here the two 50 ppm data sets labeled *LNM-50* and *HPM-50* in Table 5 of Eubank et al. (1994). The first set has a square mean of  $-0.0020$ , whereas the second set has a square mean of  $0.0082$  causing the designations *low negative mean (LNM)* and *high positive mean (HPM)*, respectively. Despite these averages over temperatures from 250–420 K simulating n-butane, the *LNM-50* set was more difficult to reduce back to the known  $B(T)$  for the RK gas due to the presence of a number of strong outliers in the  $W^2$  data causing strong scatter in  $f \equiv [\beta_a(T)]/2$ , as seen in Table 1. Eubank et al. (1994) found that reducing  $f$  to  $B(T)$  using the traditional exponential model, labeled (exp-M) in Table 1, (based on a square-well potential)

$$B = \beta_0 + \beta_1 \exp(\beta_2/T), \quad (24)$$

or the Lennard-Jones (m,6) model, labeled (*L-J; m,6*) in Table 1, made little difference as also seen in Table 1. The root-mean-squared error (RMSE) for the 18 temperatures ranging from 250–420 K at 10 degree intervals was about 6.4 for *LNM-50* and 1.7 for *HPM-50* using these traditional methods.

The new method with Eq. 8 and the Newton-Backward (**NB**) interpolation formula (Eq. 22) were applied to the  $f(\text{LNM-50})$  and  $f(\text{HPM-50})$  data sets of Table 1. Equation 13 supplied the heat capacities. Because of the considerable scatter, it was first necessary to smooth these sets. The first procedure employed was simple graphing (of fairing) labeled **NB-g** in Table 1 for the *LNM-50* set. The second procedure was to use a standard spline/least-squares program (Klaus and Van Ness, 1967) labeled **NB-s** in Table 1 for both data sets. Once the sets were smoothed, first and second difference could be taken numerically and Eq. 8 used to estimate  $B(T)$ . For *LNM-50*, Table 1 shows that both **NB-g** and **NB-s** provide a RMSE of 1.8, although at selected temperatures the two different smoothing procedures can provide differences in  $B(T)$  of up to  $3 \text{ cm}^3/\text{mol}$ . Regardless, the RMSE is

Table 1. Tests of New vs. Old Methods with Two Sets of Sonic Data with High Random Errors\*

$T/K$	$-f(\text{RK})$	$-f(\text{LNM-50})$	$-B(\text{exp-M})$	$-B(\text{L-J;m,6})$	$-B(\text{NB-g})$	$-B(\text{NB-s})$	$-f(\text{HPM-50})$	$-B(\text{exp-M})$	$-B(\text{L-J;m,6})$	$-B(\text{NB-s})$	$-B(\text{RK})$
250	678.3	683.9	821.3	821.7	799.5	799.9	677.9	800.3	800.3	801.0	801.5
260	638.2	641.9	764.4	764.5	750.4	751.4	632.9	749.0	749.0	750.9	751.1
270	601.5	602.8	713.8	713.7	705.9	706.1	598.5	702.8	702.7	704.8	705.6
280	567.9	566.2	668.5	668.4	664.3	665.1	563.4	660.9	660.9	662.8	663.6
290	536.9	535.7	627.7	627.6	626.6	627.6	538.3	622.8	622.8	624.5	625.5
300	508.4	512.2	590.9	590.7	590.6	592.9	504.1	588.0	588.0	589.3	590.5
310	482.0	477.8	557.4	557.3	557.8	560.7	484.4	556.1	556.1	556.9	558.2
320	457.5	461.5	526.9	526.8	527.3	530.1	456.9	526.7	526.7	527.0	528.5
330	434.7	429.5	499.0	498.9	498.8	502.0	441.4	499.6	499.6	499.4	501.1
340	413.5	418.0	473.3	473.3	472.9	474.1	412.9	474.5	474.5	473.9	475.6
350	393.8	383.4	449.7	449.7	448.9	450.5	393.9	451.2	451.2	450.1	451.9
360	375.3	375.9	427.9	427.9	426.8	427.9	370.7	429.5	429.5	428.1	429.9
370	358.0	355.2	407.6	407.7	406.5	407.1	351.9	409.2	409.2	407.5	409.3
380	341.7	341.4	388.9	388.9	387.7	387.7	344.6	390.3	390.3	388.5	390.1
390	326.5	320.6	371.4	371.4	370.4	369.5	320.8	372.6	372.6	370.7	372.1
400	312.1	301.6	355.0	355.1	354.4	352.8	318.7	355.9	355.9	354.0	355.3
410	298.6	310.0	339.8	339.8	339.3	337.4	306.6	340.3	340.3	338.4	339.4
420	285.8	291.6	325.4	325.4	325.5	323.1	284.4	325.5	325.5	323.7	324.5
RMSE	—	—	6.4	6.5	1.8	1.8	—	1.7	1.7	1.3	Basis

\*All entries are in  $\text{cm}^3/\text{mol}$ .

**Table 2. Difference Table for the Sonic Velocity Data of Ewing, et al. (1988) for *n*-Butane**

<i>T</i> /K	$-f$	$\Delta$	$-\Delta^2$	$\Delta^3$
250	844.85 ± 0.65			
260	774.0 ± 0.35	70.85 ± 1.00	9.25 ± 1.55	
270	712.4 ± 0.20	61.60 ± 0.55	9.00 ± 0.90	0.25 ± 2.45:2.0
280	659.8 ± 0.15	52.60 ± 0.35	5.70 ± 0.70	3.30 ± 1.60:1.6
290	612.9 ± 0.2	46.90 ± 0.35	5.60 ± 0.65	0.10 ± 1.35:1.2
300	571.6 ± 0.1	41.30 ± 0.30	4.45 ± 0.50	1.15 ± 0.70:0.8
310	534.75 ± 0.1	36.85 ± 0.20	4.30 ± 0.65	0.15 ± 1.15:0.5
320	502.2 ± 0.35	32.55 ± 0.20		

over 3.5 times better than for the two traditional methods. For *HPM*-50, Table 1 shows the **NB**-s procedure to provide a RMSE of 1.3 compared to 1.7 for the two traditional methods. While still superior, the advantage of the new method is not as much with a less problematic data set.

Whether the base model used here was RK or L-J, for example, is immaterial. Both can be shown to represent  $f(T)$  and  $B(T)$  well in this temperature region for *n*-butane. What would be unfair in this test is to start with L-J as the base model and then use the same model for smoothing the noisy  $f(T)$  with a standard least-squares fit. The advantage of the new method is that it is purely based on the  $f(T)$  measured and does not assume the temperature-dependent form of  $B(T)$ . All agree that we do not know this form, especially at temperatures below critical and for complex molecules such as water. Even if the new method were not shown superior in the tests of Table 1, it would remain valuable as an independent check of the traditional methods—that is, an alternate data reduction method allowing estimate of final uncertainties in  $B(T)$ .

### Application to Literature Sonic Velocity Data

Staying with *n*-butane, we select the data of Ewing et al. (1988) with which we have worked before and know to be of high quality. Table 2 provides the published data points with the authors' uncertainty estimates. We calculate the differ-

ences in **NF** notation, but these values may also be used for **NB** and **SCD**. We have also propagated the authors' uncertainties into the higher derivatives assuming no error compensation—that is, the worse possible scenario. This approach seems advised when we arrive at the third divided difference in Table 2 where the data show significant scatter. This scatter proves that this is real data not smoothed by the authors prior to publication. Few sets of real thermophysical property measurements can withstand a third difference without the appearance of some chaos. Our general numerical procedure is different here from that of the previous section with particularly noisy data, because Table 2 shows immediately that even  $\Delta^2$  is monotonic, while  $\Delta$  is not monotonic for either *LN*M-50 or *HPM*-50. Roughly each successive derivative increases errors by at least a factor of ten, so we may conclude that the data of Ewing et al. (1988) has random errors no more than 5 ppm, as claimed by the authors.

While these data are conveniently every ten degrees, we have not included errors in the temperatures themselves. Although Ewing et al. (1988) used platinum resistance thermometry and appear to have measured to within a few mK, an error of ±1 mK in each temperature reading can cause an error of (2/10,000) in the first temperature derivative, which can easily propagate to 2% or more in the third derivative.

Table 3 provides our results using Eq. 8 and the three different numerical procedures. Here we have used the smoothed values of  $\Delta^3$  that are shown *underlined* in Table 2, but we have not smoothed  $\Delta$  nor  $\Delta^2$ . At the four highest temperatures, the agreement in  $B(T)$  among the third numerical procedures is excellent. From a general mathematical viewpoint, we expect **NF** to be superior at the top of the table, **NB** at the bottom of the table and **SCD** in the center of the table. However, the physical situation is that  $(B'/B)$  increases sharply with falling temperature as does  $-(B''/B')$ , so that the higher derivatives gain importance at the lower temperatures as we have seen in the simulations. Because it is the two derivative terms in Eq. 1 that cause  $B(T)$  to vary from  $f \equiv [\beta_a(T)]/2$ , it seems logical to start at the high temperature and work downwards as suggested by Trusler and Zarari (1992); this is precisely what the **NB** procedure does and why we believe that the best values in Table 3 are from that method. For this reason, we also calculate  $B(T)$  at 250 K from **NB** where  $p = -2$  coming from a base temperature of 270 K and at 260 K where  $p = -1$  coming from the same base.

**Table 3. Second Virial Coefficient of *n*-Butane from the Sonic Velocity Data of Ewing et al. (1988)**

<i>T</i> /K	$-B/\text{cm}^3 \cdot \text{mol}^{-1}$					
	Ewing et al.*	Eq. 8/NF	Eq. 8/NB	Eq. 8/SCD	Eq. 8/GB	$\Delta B$ (NB)
250	1081.5	1066.3 ± 9.2	1067.5 <sup>†</sup> ± 8.0	--	1068.7 <sup>‡</sup> ± 8.0	0.98
260	979.5	973.3 ± 5.4	967.2 <sup>‡</sup> ± 7.0	963.2 ± 6.2	966.0 ± 7.0	0.81
270	892.4	873.5 ± 4.0	880.3 ± 6.0	878.6 ± 4.4	884.9 ± 6.0	0.67
280	817.6	807.9 ± 3.7	807.1 ± 5.1	803.3 ± 3.5	804.4 ± 5.1	0.56
290	752.6	741.0 ± 3.2	741.6 ± 4.2	741.3 ± 3.3	744.0 ± 4.2	0.45
300	695.9	686.8 ± 3.5	686.9 ± 3.7	686.6 ± 2.5	687.3 ± 3.7	0.39
310	646.0	—	639.3 ± 2.9	639.1 ± 2.1	640.0 ± 2.9	0.36
320	601.8	—	596.0 ± 4.4	—	596.0 <sup>§</sup> ± 4.4	0.33

\* From a square-well model that yields  $B(T)$  according to Eq. 24.

<sup>†</sup> With  $T_0 = 270$  K so  $p = -2$ ; <sup>‡</sup> With  $T_0 = 270$  K so  $p = -1$ ; <sup>§</sup> With  $T_0 = 260$  K so  $p = -1$ .

<sup>||</sup> With  $T_0 = 310$  K so  $p = 1$ .

One test for consistency is to form difference tables for  $B(T)$  from the various columns of Table 3. The values of Ewing et al. (1988) are smooth, of course, being from an equation regressed with the raw acoustic data. However, the lack of smoothness in the two higher differences of Table 2 cause  $B(T)$  from Eq. 8 to be subject to a lack of smoothness itself. Both  $B(T)$  from **NB** and from **SCD** hold up reasonably well in this regard with their second differences being 13.4, 14.8, 5.5, 11.9, 7.1, and 4.3 for **NB** and 11.2, 11.5, 8.2, and 7.2 for **SCD**, whereas we find a dismal -6.8, 25.2, -3.3, and 13.7 for **NF**.

With this success for **NB**, we decided to add another backward-type numerical procedure and chose the Gauss-backward formula **GB** (CRC *Handbook of Mathematical Tables*, 1964)

$$\text{GB: } f(T) = f(T_0, p) = f_0 + p\delta_{-1/2} + (p/2)(p+1)\delta_0^2 + (p/6)(p^2-1)\delta_{-1/2}^3 + \dots, \quad (25)$$

where the notation is the same as for **SCD**. The results for **GB** are also shown in Table 3 and are seen to agree well with those from **NB**. The disagreements of  $\sim \pm 3\text{--}5 \text{ cm}^3/\text{gmol}$  at the lower temperatures is due to the second derivative term which for  $p=0$  is found from contributions due to both  $\Delta^2$  and  $\Delta^3$  in **NB** but only  $\Delta^2$  in **GB**. As we did not smooth  $\Delta^2$  in Table 2, there appear to be more variations in  $B(T)$  from Eq. 8 with **GB** as seen by their second differences of 21.6, 1.4, 18.5, 4.5, 9.4, and 3.3, which shows a distinct up-down repetitive quality.

For this reason, the preferred values for  $B(T)$  from Eq. 8 in Table 3 are those from **NB**. These values are seen to be in good agreement with those published by Ewing et al. (1988), but with our values being 6–15 units higher and increasing as we move to the lower temperatures. Our previous suspicion (see Gupta and Eubank, 1997, for details) that Ewing's determination of  $B(T)$  was faulty, although the sonic data were accurate is seen to be incorrect. Because we believe the values of  $B(T)$  given here via **NB** are superior to those of Ewing, we are left with an even larger disagreement with the more negative P-V-T values (Gupta and Eubank, 1997) in this lower temperature range. We are then left with experimental errors, likely systematic, in the sonic and/or density measurements with the latter particularly suspect due to adsorption, although Gupta and Eubank (1997) corrected their data for this error.

Finally, Table 3 shows the error  $\Delta B$  to be small over the present temperature range. These values are calculated from the smoothing equation

$$B(T) = -825.217 + (551,164/T) - (1.529 \times 10^8/T^2), \quad (26)$$

which fits all the **NB** values in Table 2 to within 1.1 units allowing then for the third and fourth temperature derivatives to be estimated for use in Eqs. 9 and 10. In this example, the values of  $\Delta B$  are too small to warrant use in Eq. 11 for correction of Eq. 25 and the **NB** values in Table 3.

Even at very low reduced temperatures when the  $\Delta B$  correction is important, one follows the above numerical procedure to estimate initially  $B(T)$ , then numerically differentiates those values to get the third and fourth temperature

derivatives for use in Eq. 10 and, finally, uses Eq. 11 to get an improved set of  $B(T)$ . This procedure can then be repeated to convergence. In all but a few cases it appears that  $\Delta B$  is so small that this correction is unnecessary.

## Conclusions

We have derived a new, numerical method for the reduction of gas sonic velocity data to second density virial coefficients  $B(T)$ . By numerically differencing the data, it is quickly determined if the data are of the internal consistency to merit reduction. The procedure is simplified when the data are at even temperature intervals, but this is not required. The results are always improved when the data have been taken over a wide range of temperature with many data points.

The new method has been shown to be highly accurate for three simulated gas models: (1) the Redlich-Kwong EoS, (2) the Peng-Robinson EoS, and (3) the Lennard-Jones intermolecular potential energy model. For reduced temperatures above about 0.5, the error  $\Delta B$ , introduced in the derivation by truncation of the third and fourth derivative terms, was found to be negligible. For reduced temperatures from 0.5 to unity, our experience is that derivatives with respect to  $t$  alternate in sign, out to at least the fifth derivative; the third derivative term in Eq. 10 is usually small due to the multiplier ( $C_1^2 - 2C_2$ ) being very small so that the error  $\Delta B$  is dominated by the fourth derivative term. In Table 2 at 280 K, for example,  $\Delta B = -0.0255 + 0.5866 \approx 0.56$ , following the order of Eq. 10. The fortuitous near cancellation of  $C_1^2$  with  $2C_2$  is one of the reasons that Eq. 8 succeeds so well without the  $\Delta B$  correction.

The second error source, caused by neglect of the temperature dependency of the heat capacity ratio  $\gamma$ , was found to be negligible under all conditions.

A simple iterative procedure was presented which allows correction for the primary error source  $\Delta B$ . The new method was found to be superior to existing procedures in the conversion of noisy sonic measurements to  $B(T)$ . This improvement was shown to reduce conversion error by over three times in a particular noisy set of sonic data termed *LNM-50*, whereas the reduction was only about 24% in a less noisy set termed *HPM-50*.

The new method was used to convert the sonic measurements of Ewing et al. (1988) for n-butane to density second virial coefficients for 250–320 K. The results appear very consistent, especially when *Backward-type* numerical differentiation formulas are used with the sonic data. The final results for  $B(T)$  are not perfectly smooth with temperature as they reflect random errors in the raw sonic data. This feature differs from previous methods that assume a model for the dependency of  $B$  upon  $T$  and thus have a smoothed equation as the final result. We leave it to others to convert the literature sonic data for other compounds, and we hope that this method will be used in the future by sonic velocity experimentalists to evaluate and convert their measurements free of an assumed model.

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