A Simple Procedure for Estimating Virial Coefficients from Burnett PVT Data

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The popular method of Burnett (1936) ranks as one of the most precise methods for taking PVT data that produce accurate compressibility factors without the need for direct mass or volume measurements. The Burnett method consists of making a series of isothermal expansions of the experimental fluid from a primary volume into a previously evacuated secondary volume with the pressure being measured after each expansion. A series of such measurements makes up a run, and an analysis of the pressure sequence for each isotherm yields the densities, compressibility factors, and virial coefficients.

The method has been utilized by numerous investigators over a wide range of temperatures and pressures. Recent experimental investigations are those reported by Scheloske (1981), Patel (1986), and Holste *et al.* (1987).

Data reduction techniques to determine compressibility factors and virial coefficients from Burnett PVT data range from simple graphical techniques to more elaborate computer techniques. Among the latter are the parameter optimization methods of Hall and Canfield (1967, 1970a) and the maximum likelihood algorithm of Britt and Luecke (1973), which has been adapted by Embry (1980). Both these methods, although accurate, require extensive iterative computer calculations in their minimization procedures. In addition, Ewing and Marsh (1979) performed a series inversion on the Berlin (pressure) virial form of the compressibility factors to obtain a polynomial expression for the Burnett pressure ratios.

Here, we present a simple and elegant method that provides accurate estimates of the second and third virial coefficients directly from an experimental Burnett pressure sequence. The method is fast, requires no extensive calculations, and makes use of the pressure-ratio graphs routinely prepared during such experiments.

Development of the Method

For an apparatus configuration of the type shown in Figure 1, the general equations of state prior to and at the *i*th expansion are:

$$P_{i-1}(V_A)_{i-1} = (n_A)_{i-1}Z_{i-1}RT \tag{1}$$

and

$$P_i(V_A + V_B)_i = (n_{AB})_i Z_i RT \tag{2}$$

$$\frac{P_{i-1}}{P_i} = N_i \frac{Z_{i-1}}{Z_i} \tag{3}$$

For nonadsorbing gases, as the number of moles before and after the expansion are conserved, $(n_A)_{i-1} = (n_{AB})_i$. The equation for the pressure ratio for pressures before and after an expansion is thus obtained by dividing Eq. 2 by Eq. 1 as

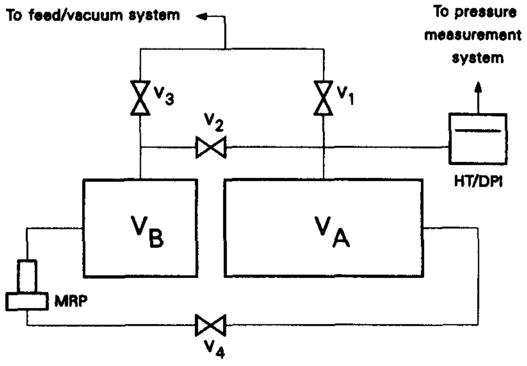

Figure 1. Burnett apparatus.

V_1–V_4, Valves
V_A, Primary cell volume
V_B, Secondary cell volume
HT/DPI, High-temperature differential pressure indicator
MRP, Magnetic recirculation pump

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where $N_i = (V_A + V_B)_i/(V_A)_{i-1}$ is termed the cell constant at the ith expansion. As P_i approaches zero, the Z_i's approach unity, and the zero pressure limit of this pressure ratio is defined as the true cell constant, or

$$N_0 \equiv \lim_{P_i \to 0} \frac{P_{i-1}}{P_i} \tag{4}$$

Furthermore, this true cell constant is related to N_i, as

$$N_i = \eta_i N_0 \tag{5}$$

where η_i, the cell distortion correction along the isotherm, is given by

$$\eta_i = \frac{1 + \gamma_{AB} P_i}{1 + \gamma_A P_{i-1}} \tag{6}$$

Here γ_A and γ_{AB} are the pressure distortion coefficients for cell volumes V_A and V_{AB}, respectively, for that isotherm. The working equation for the pressure ratio is therefore

$$\frac{P_{i-1}}{P_i} = \eta_i N_0 \frac{Z_{i-1}}{Z_i} \tag{7}$$

We now derive the equations for our proposed method as follows. First, with the pressure ratio denoted by u_i, Eq. 7 becomes

$$u_i = \frac{P_{i-1}}{P_i} = \eta_i N_0 \frac{Z_{i-1}}{Z_i} \tag{8}$$

Next, differentiation of this equation with respect to P_i, at constant T, leads to

$$\left(\frac{\partial u_i}{\partial P_i}\right)_T = \frac{N_0 \eta_i \left[\frac{u_i}{Z_i} x_{i-1} - \frac{Z_{i-1}}{Z_i^2} x_i + \frac{Z_{i-1}}{Z_i} \frac{1}{(1 + \gamma_A P_{i-1})} \left(\frac{\gamma_{AB}}{\eta_i} - \gamma_A u_i\right)\right]}{\left[1 - N_0 \eta_i P_i \left(\frac{x_{i-1}}{Z_i} - \frac{Z_{i-1}}{Z_i} \frac{\gamma_A}{(1 + \gamma_A P_{i-1})}\right)\right]} \tag{9}$$

where

$$x_k \equiv \left(\frac{\partial Z_k}{\partial P_k}\right)_T = \left(\frac{Z_k RT}{B + 2C\rho_k} + \frac{P_k}{Z_k}\right)^{-1} \tag{10}$$

and the virial coefficients are introduced via the truncated Leiden expansion

$$Z = 1 + B\rho + C\rho^2 \tag{11}$$

In the limit as P_i approaches zero, $Z_i \to 1$, $\rho_i \to 0$, $\eta_i \to 1$, $u_i \to N_0$, and $x_i \to B/RT$. Hence,

$$u_0' \equiv \lim_{P_i \to 0} \left(\frac{\partial u_i}{\partial P_i}\right)_T = N_0(N_0 - 1)\frac{B}{RT} + y_1 \tag{12}$$

where

$$y_1 = N_0(\gamma_{AB} - N_0 \gamma_A) \tag{13}$$

Furthermore, differentiation of Eq. 9 once more with respect to P_i and evaluating the limit as $P_i \to 0$, (with some rearrangement) leads to the following expression:

$$u_0'' \equiv \lim_{P_i \to 0} \left(\frac{\partial^2 u_i}{\partial P_i^2}\right)_T = \frac{2N_0(N_0^2 - 1)C - 4N_0(N_0 - 1)B^2}{R^2 T^2} + y_2 \tag{14}$$

where

$$y_2 = 2N_0^2(\gamma_{AB} - N_0\gamma_A)\left(\frac{B}{RT} - 2\gamma_A\right) + (\gamma_{AB} - 2N_0\gamma_A)\frac{2BN_0(N_0 - 1)}{RT} \tag{15}$$

Note that Eqs. 12 and 14 represent the limiting slope and curvature of a curve on the u vs. P plot.

In the expressions above, the terms y_1 and y_2 are two to four orders of magnitude smaller than u_0' and u_0'', respectively, and may be effectively neglected without any significant loss in accuracy in the estimated virial coefficients. Therefore, if u_0' and u_0'' can be determined, the virial coefficients may be calculated from the following equations:

$$B = \frac{u_0' RT}{N_0(N_0 - 1)} \tag{16}$$

and

$$C = \frac{2B^2}{N_0 + 1} + \frac{R^2 T^2 u_0''}{2N_0(N_0^2 - 1)} \tag{17}$$

The above approach is also valid in the analysis of Burnett-isochoric (B-I) data because for nonadsorbing gases the iso-

Table 1. Cell Constants and Virial Coefficients Estimated by Present Method and Reported in Literature

T	N_0		B, cm^3 · mol^{-1}		C, cm^6 · mol^{-2}		
K	PM	LR	PM	LR	PM	LR	Ref.
			Argon				
223.15	1.565005	1.564987	−37.44	−37.30	1,510	1,401	Blancett et al. (1970)
273.15	1.564875	1.564860	−20.95	−20.90	1,067	1,029	
323.15	1.564796	1.564837	−10.79	−10.82	1,029	974	
			Helium				
83.15	1.563153	1.563299	11.16	10.97	175.1	193.0	Hall & Canfield (1970b)
103.15	1.563247	1.563236	11.56	11.57	167.9	171.3	
113.15	1.563076	1.563176	11.85	11.77	159.0	166.3	
348.15	1.474462	1.474480	11.44	11.45	105.8	134.3	Patel (1986)
423.15	1.474418	1.474431	11.12	11.11	100.0	126.1	
498.15	1.474457	1.474483	10.75	10.83	93.4	112.2	
			Nitrogen				
103.15	1.563113	1.5632	−148.64	−148.46	—	—	Hall & Canfield (1970b)
113.15	1.559757	1.5632	−118.52	−117.78	—	—	
303.15	1.467052	1.467078	−4.21	−4.14	1,520	1,500	Pfefferle et al. (1955)
			Propane				
373.15	1.569028	1.569646	−244.39	−244.18	24,777	21,404	Warowny et al. (1978)
393.19	1.393353	1.393499	−212.63	−214.76	16,215	18,604	
407.50	1.394502	1.393674	−197.58	−197.89	12,577	17,290	
422.97	1.392797	1.392725	−179.47	−180.88	12,133	16,097	
			Carbon Dioxide				
298.15	1.481473	1.481466	−123.70	−123.15	5,664	4,905	Holste et al. (1987)
323.15	1.481430	1.481466	−101.87	−102.00	4,128	4,208	
348.15	1.481509	1.481466	−85.75	−85.19	3,948	3,672	
373.15	1.481422	1.481466	−71.20	−71.62	2,720	3,254	
398.15	1.481412	1.481466	−60.41	−60.49	2,644	2,923	
423.15	1.481492	1.481466	−51.45	−51.26	2,586	2,658	
448.15	1.481499	1.481466	−43.57	−43.51	2,466	2,444	
			Krypton				
223.15	1.587748	1.58813	−90.86	−93.05	3,709	3,075	Dillard et al. (1978)
273.15	1.588263	1.58821	−61.23	−61.53	2,928	2,544	
323.15	1.588634	1.58850	−41.59	−41.72	2,258	2,126	

PM, Present method; LR, Literature reported

therms on a B-I grid correspond to true Burnett runs. An analysis on an isotherm by isotherm basis is therefore possible.

Test of the Method

In Table 1 we provide the results of calculations performed on six representative gases: argon, helium, nitrogen, propane, carbon dioxide, and krypton, for which raw experimental data were available in the literature. In order to estimate the limiting slope and curvature, we fitted u as a polynomial in P and subsequently differentiated the fitting equation to obtain u_0' and u_0''. N_0, as defined by Eq. 4, is simply the intercept of the u vs. P curve. For the sake of comparison, and as examples of the validity of our method, we also provide the reported literature values for the cell constant and second and third virial coefficients. Using our values of the pressure distortion coefficients, we estimate the average error in B as a result of neglecting γ_1 to be 0.15%, and the error in C as a result of neglecting γ_2 to be less than 1 cm^6/mol^2.

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Notation

B = second virial coefficient
C = third virial coefficient
N = cell constant
n = number of moles
P = pressure
R = universal gas constant, 8.31448 J/mol · K
T = absolute temperature
u = pressure ratio
V = volume
Z = compressibility factor, $P/\rho RT$

Greek letters

γ = pressure distortion coefficient
η = cell distortion correction factor
ρ = density

Superscripts

$'$ = first derivative
$''$ = second derivative

Subscripts

A, B = respective cells
i = isotherm value
0 = zero pressure limiting value

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