R & D NOTES

Mixture Compositions and Excess Volumes from the Burnett Apparatus

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The procedure for producing mixtures presented in this paper constitutes a technical improvement on the method published earlier by Kramer and Miller (1957). These mixtures with precisely known compositions can be used in the Burnett or one of the coupled experiments (Eubank and Kerns, 1973) to determine precisely the equation of state. The excess volume results from the same experiment used to produce the mixture with only the additional measurement of the mixture pressure.

Proposed Experiment

In Figure 1, we present a piping schematic for a Burnett apparatus which possesses some significant advantages over conventional diagrams. The most obvious feature is simplicity—valves and fittings inside the thermostat are minimal to reduce the possibility of leaks. Actually two valves are sufficient for Burnett measurements, but the three-valve arrangement offers greatly increased flexibility. A second feature is the capability of measuring pressure in either cell independently, that is, in $V_A + V_C$ or in $V_B + V_C$. Volume V_C is the composite volume of the tubing up to the valves and the lower cavity of the differential pressure cell. The final feature is the ability to open both sides of the differential pressure cell to vacuum which enables a null check after each Burnett expansion with negligible possibility of sample contamination.

The experiment we propose follows and utilizes standard Burnett-type measurements. First, charge volume $V_A + V_C$ with pure fluid a and measure the pressure P_a. Now evacuate V_C and V_B, then fill $V_B + V_C$ with pure fluid b and measure the pressure P_b. Finally, open the valves between V_A and V_B allowing the two pure fluids to mix in $V_A + V_B + V_C$. In practice, the latter process requires from one week to several months and should be aided by thermal or mechanical means. Upon pressure, temperature, and composition equilibrium, measure the pressure of the mixture P_m. From this experiment, precise compositions and excess volumes are calculable. In fact, if the fluids are at low enough densities, the interaction second virial coefficient is also calculable as shown by Hall and Eubank (1973).

For the calculations of the next section, it is assumed that additional data are available for the pure fluids. First, the Burnett cell constant,

$$N = \frac{V_A + V_B + V_C}{V_A} \tag{1}$$

must be known, normally from a He calibration (a standard procedure of the Burnett experiment). Second, the densities or compression factors Z for the two pure fluids must be known as a function of pressure, preferably from experiments in the same apparatus.

COMPOSITIONS FROM THE PROPOSED EXPERIMENT

At constant temperature, conservation of moles for nonreacting fluids provides the relationship

$$(P_m N/Z_m) = (P_a/Z_a) + (N-1)(P_b/Z_b) \tag{2}$$

where $Z_a = Z_a(P_a, T)$, $Z_b = Z_b(P_b, T)$, and $Z_m = Z_m(P_m, T, x_a)$. Equation (2) provides the initial Z factor for the mixture (in effect, the Burnett run constant) or, by rearrangement, the mole fraction

$$x_a = \frac{Z_m P_a}{N Z_a P_m} = \frac{(P_a/Z_a)}{(P_a/Z_a) + (N-1)(P_b/Z_b)} \tag{3}$$

Assuming precisions for pressure of 0.01% and for Z of 0.03% (which are reasonable in the Burnett method), the precision of x_a will be 0.05%.

Kramer and Miller (1957) prepared mixtures of He and N_2 for Burnett experiments by a method analogous to filling $V_A + V_C$ with pure fluid a, measuring P_a and then introducing pure fluid b also into $V_A + V_C$. Then they commenced a Burnett run at P_m. The Burnett analysis provided Z_m and Equation (3) yielded the composition. The present method has the advantage that none of fluid a can escape while charging fluid b. Further, the mixture density results directly from Equation (2) and

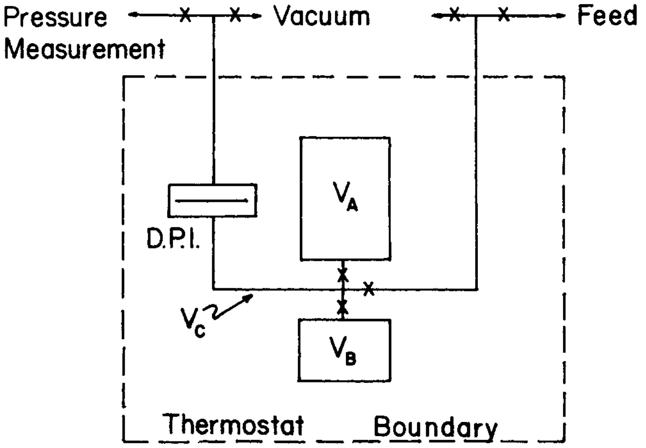

Fig. 1. A piping schematic for a Burnett apparatus.

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can be used to check the density from isothermal Burnett expansions. Better yet, Burnett-coupled isochoric measurements covering the (P, T, x_a) surface can be made conveniently without having to duplicate the composition. Because Equation (2) neglects adsorption, the mixing temperature should be high enough to negate sorption effects.

Mixtures of various compositions x_a can be produced by varying the relative magnitudes of P_a and P_b. Further, the charging sequence of fluids a and b can be reversed for low values of x_a to reduce the difference between P_a and P_b. Ternary mixtures may be prepared by evacuating $(V_B + V_C)$ after mixing the binary and charging component c into $(V_B + V_C)$ at a pressure P_c followed by mixing to produce pressure P_m. Equations analogous to (2) and (3) allow calculation of Z_m and the mole fractions. Such a procedure is easily extended to any number of components. The Kramer and Miller procedure requires $n - 1$ Burnett runs to produce an n-component mixture.

EXCESS VOLUMES FROM THE PROPOSED EXPERIMENT

Another important thermodynamic quantity is calculable from the information collected in the proposed experiment, the excess volume, v^E. By definition,

$$\frac{v}{RT} = \frac{Z}{P} \tag{4}$$

The excess volume is the mixture volume less the molar average of the pure component volumes all taken at the same pressure and temperature.

$$\frac{P_m v^E}{RT} = Z_m - [x_a Z_a{}^* + x_b Z_b{}^*] \tag{5}$$

where $Z_a{}^* = Z_a(P_m, T)$ and $Z_b{}^* = Z_b(P_m, T)$ for pure a and b. From the last section, Equation (3) allows substitution for x_a whereas

$$x_b = \frac{(N-1)(P_b/Z_b)}{(P_a/Z_a) + (N-1)(P_b/Z_b)} \tag{6}$$

The excess volume results from substitution of Equations (2), (3), and (6) into (5)

$$\frac{v^E}{RT} = \left[\frac{N}{(P_a/Z_a) + (N-1)(P_b/Z_b)}\right] - \left[\frac{(P_a/P_m)(Z_a{}^*/Z_a) + (N-1)(P_b/P_m)(Z_b{}^*/Z_b)}{(P_a/Z_a) + (N-1)(P_b/Z_b)}\right]$$

$$\frac{P_m v^E}{RT} = \frac{N Z_a (P_m Z_b - P_b Z_b{}^*) + P_b Z_b{}^* Z_a - P_a Z_a{}^* Z_b}{P_a Z_b + (N-1) P_b Z_a} \tag{7}$$

Equation (7) is the general expression for v^E. When the mixing experiment is conducted with $P_a = P_b$,

$$\frac{P_m v^E}{RT} = \frac{N Z_a [(P_m Z_b/P_b) - Z_b{}^*] + Z_b{}^* Z_a - Z_a{}^* Z_b}{Z_b + (N-1) Z_a} \tag{8}$$

Since v^E is zero for an ideal solution, Equation (8) yields $P_m = P_a = P_b$ for this special case.

Earlier, Hall and Eubank (1973) proposed a calculation which would produce the interaction second virial coefficient B_{ab} from the proposed experiment. In that paper, we presented a simulated experiment to illustrate the calculation of B_{ab}. Table 1 reproduces the simulated experiment to illustrate calculation of the excess volume.

TABLE 1. SIMULATED EXPERIMENT FOR CALCULATION OF B_{ab} AND v^E

Quantity	Value	Precision
Temperature/K	300.685	0.003%
Pressure/$MPa(P_a)$	3.8400	0.01%
Pressure/$MPa(P_b)$	4.7000	0.01%
Pressure/$MPa(P_m)$	4.1258	0.01%
Cell constant/N	1.5000	0.001%
Compression factor/(Z_a)	0.9600	0.03%
Compression factor/(Z_b)	0.9400	0.03%
Compression factor/(Z_m)	0.9521	0.04%
Compression factor/$(Z_a{}^*)$	0.9569	0.03%
Compression factor/$(Z_b{}^*)$	0.9478	0.03%
Interaction virial/m^3/mol(B_{ab})	-27.63×10^{-6}	1.0%
Excess volume/m^3/mol(v^E)	-7.677×10^{-7}	0.05%†
Composition/x_a	0.6154	0.05%

† Correct precision for this particular experiment. The % accuracy is much higher and is very sensitive to the particular experiment as $v^E = 0$ for an ideal solution.

We note that the precisions listed represent only the simulated experiment and will vary as the conditions of the experiment vary.

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NOTATION

B = second virial coefficient
B_{ab} = interaction second virial coefficient
N = Burnett cell constant
P = pressure
R = gas constant, 8.3143 MPa m^3/mol K
T = absolute temperature
V = cell volume
Z = compression factor
v = molar volume
v^E = excess volume
x = mole fraction

Superscript

$*$ = pure component value at mixture pressure and temperature

Subscripts

A = primary Burnett volume
a = pure component a
B = secondary Burnett volume
b = pure component b
C = volume associated with differential pressure cell (D.P.I.)
c = pure component c
m = mixture

LITERATURE CITED

Eubank, P. T., and W. J. Kerns, "Adsorption and Molecular Association in the Burnett Apparatus," *AIChE J.*, **19**, 711 (1973).

Hall, K. R., and P. T. Eubank, "Experimental Technique for Direct Measurement of Interaction Second Virial Coefficients," *J. Chem. Phys.*, **59**, 709, 6691 (1973).

Kramer, G. M., and J. F. Miller, "Compressibility of Gases. III. The Second and Third Virial Coefficients of Mixtures of Helium and Nitrogen at 30°," *J. Phys. Chem.*, **61**, 785 (1957).

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