The criterion is shown to be valid for small ϵ and γ, which is common in practice. Given the constraints of a particular reactor, Eq. 9 allows one to optimize one or more free parameters to achieve a uniform radial flow distribution.

NOTATION

b^* = friction coefficient in bed
f = friction factor in flow channels
l = height of reactor
R_o = outer radius of outer annulus
r_2 = outer radius of catalyst basket
r_1 = inner radius of catalyst basket
v = dimensionless radial velocity
w = dimensionless axial velocity
ψ = catalyst porosity
ϕ_1 = fraction free surface area of screen of catalyst basket

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Method for Estimation of Second Virial Coefficients from Pressure Measurements Alone

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INTRODUCTION

The compressibility factor may be expressed in terms of the virial expansion

$$z = 1 + nB/V + n^2C/V^2 + \ldots \qquad (1)$$

In moderate pressure operations virial coefficients after the second may be neglected.

A procedure for estimation of the second virial coefficient described by Couldwell et al. (1978) has the advantage that three pressures only need be measured but requires quantitative transfer of material by condensation as well as requiring estimation of the number of moles of material. The procedure described here requires pressure measurement only and is not restricted to condensible substances.

EXPERIMENTAL METHOD

In Figure 1, schematic representation of the apparatus, the quantity of gas to be studied, n moles, is first loaded into volume V_1 at the selected pressure, p_1. This pressure is measured via the null differential pressure gauge using a manometer or dead weight gauge. The gas is then expanded into the previously evacuated vessel V_2, and the pressure p_{12} measured. Tap T_2 is closed and the gas remaining, n', is allowed to expand into previously evacuated vessel V_3. The pressure p_{13} is measured, and then tap T_2 opened allowing the total quantity of gas access to volume $V_1 + V_2 + V_3$ at a pressure of p_{123}.

Employing the pressure series virial expansion truncated after the third virial coefficient, we have for each of the four pressures the following relations:

$$\frac{V_1}{n} = \frac{RT}{p_1} + B + C'p_1 \qquad (2)$$

$$\frac{V_1 + V_2}{n} = \frac{RT}{p_{12}} + B + C'p_{12} \qquad (3)$$

$$\frac{V_1 + V_2 + V_3}{n} = \frac{RT}{p_{123}} + B + C'p_{123} \qquad (4)$$

$$\frac{V_1 + V_3}{n'} = \frac{RT}{p_{13}} + B + C'p_{13} \qquad (5)$$

Now since the ratio of the numbers of moles n' and n is equal to the ratios of the volumes V_1 and $V_1 + V_2$, we have

$$n' = n\frac{V_1}{V_1 + V_2} \qquad (6)$$

and Eq. 5 becomes

$$\frac{(V_1 + V_3)(V_1 + V_2)}{nV_1} = \frac{RT}{p_{13}} + B + C'p_{13} \qquad (7)$$

The relation which results from substitution of the volumes V_1, V_2 and V_3 in Eq. 7 with the volumes given by Eqs. 2, 3 and 4 may be arranged to give the following expression for B.

$$\frac{B}{RT} = \left\{ \frac{1}{p_{12}}\left(\frac{1}{p_{123}} - \frac{1}{p_{12}}\right) - \frac{1}{p_1}\left(\frac{1}{p_{13}} - \frac{1}{p_{12}}\right)\right\} \Bigg/ \left\{\frac{1}{p_{13}} - \frac{1}{p_{123}}\right\}$$
$$+ \frac{C'}{RT}\left\{ p_1\left(\frac{1}{p_{13}} - \frac{1}{p_{12}}\right) - p_{12}\left(\frac{1}{p_{123}} + \frac{1}{p_1}\right)\right.$$
$$\left. + \frac{p_{13}}{p_1} - \frac{p_{123}}{p_{12}} + 2\right\} \Bigg/ \left\{\frac{1}{p_{123}} - \frac{1}{p_{13}}\right\}$$
$$+ \frac{BC'}{(RT)^2}\{p_{13} - p_{123}\} + \text{a term in } \left(\frac{C'}{RT}\right)^2 \qquad (8)$$

At moderate pressures, the terms containing the third virial coefficient may be neglected and the expression reduces to:

$$B = RT\left\{\frac{1}{p_{12}}\left(\frac{1}{p_{123}} - \frac{1}{p_{12}}\right) - \frac{1}{p_1}\left(\frac{1}{p_{13}} - \frac{1}{p_{12}}\right)\right\}\Bigg/\left\{\frac{1}{p_{13}} - \frac{1}{p_{123}}\right\} \qquad (9)$$
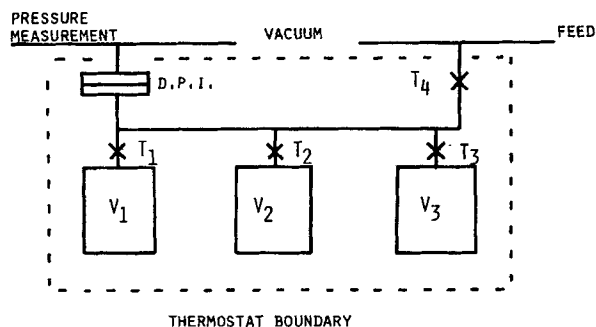
Figure 1. Piping diagram for virial coefficient measuring apparatus.

The second virial coefficient may thus be obtained for a given temperature from the measurement of four pressures alone.

The expression 9 may be simply analyzed to give the following relation for the possible error in B, δB, in terms of the uncertainties in the pressure measurements, δP_1, δP_{12}, etc.

$$\frac{1}{RT}\delta B = \left\{ \frac{1}{p_{12}^2}\left(\frac{1}{p_{123}} - \frac{2}{p_{12}} + \frac{1}{p_1}\right)\delta p_{12} \right.$$
$$+ \frac{1}{p_1^2}\left(\frac{1}{p_{13}} - \frac{1}{p_{12}}\right)\delta p_1 + \frac{1}{p_{13}^2 p_1}\delta p_{13}$$
$$\left. + \frac{1}{p_{123}^2 p_{12}}\delta p_{123}\right\} \left\{\frac{1}{p_{13}} - \frac{1}{p_{123}}\right\}^{-1} \quad (10)$$

A simple sum of positive values rather than a sum of squares was taken, since the difference in magnitude is generally small and a much more tractable relation is obtained.

If the pressure is measured on a device such as a dead-weight gauge, the fractional error $\delta p/p$ is approximately constant. For this case then we may write:

$$\frac{1}{RT}\delta B = \frac{\delta p}{p}\left\{\frac{1}{p_{12}p_{123}} - \frac{2}{p_{12}^2} + \frac{2}{p_1 p_{13}} + \frac{1}{p_{12}p_{123}}\right\}\left\{\frac{1}{p_{13}} - \frac{1}{p_{123}}\right\}^{-1} \quad (11)$$

Now we may approximate and let $1/p_i = V_i/nRT$ and also substitute $k_2 = V_2/V_1$ and $k_3 = V_3/V_1$ to obtain the following expressions:

$$\frac{1}{p_1} = \frac{V_1}{nRT}, \quad \frac{1}{p_{12}} = \frac{V_1}{nRT}(1 + k_2) = \frac{1}{p_1}(1 + k_2),$$

$$\times \frac{1}{p_{123}} = \frac{1}{p_1}(1 + k_2 + k_3), \quad \frac{1}{p_{13}} = \frac{1}{p_1}(1 + k_2 + k_3 + k_2 k_3) \quad (12)$$

Substitution gives

$$\frac{1}{RT}\delta B = \frac{\delta p}{p}\frac{2}{p_1}\left\{\frac{1}{k_2 k_3} + \frac{1}{k_3} + \frac{2}{k_2} + 2\right\} \quad (13)$$

Evidently the larger the magnitudes of k_2 and k_3 the smaller the error δB. Upper limits to k_2 and k_3 will be dictated, however, by the range of the pressure-measuring device used.

Test of the Method

The feasibility of the method may be tested by considering a particular system with pressures measured on a particular dead weight gauge. For example, the second virial coefficient of carbon dioxide has been found to be -104 cm^3 mol^{-1} at 322.87 K by Butcher and Dadson (1964).

Pressures may be measured using, for example, a "Ruska Corporation" model 2465 air dead weight gauge with a range of 0.013 to 1 bar (1.3 to 100 kPa) and a claimed uncertainty of either 0.01% or 3 × 10^{-6} bar (0.3 Pa) whichever is the larger. If $k_2 = k_3$, the range of pressure dictates $k_2 = k_3 < 7.5$.

Consider 0.018 mol of carbon dioxide and vessel volumes $V_1 = 500$ cm^3, $V_2 = 2,500$ cm^3 and $V_3 = 2,500$ cm^3 (i.e., $k_2 = k_3 = 5$). Using Eq. 1 (neglecting C, D, etc.) and the known second virial coefficient the pressures at each stage of the experiment may be calculated as follows:

$$p_1 = 0.9638 \pm 1 \times 10^{-4}\text{ bar} \quad p_{12} = 0.16907 \pm 2 \times 10^{-5}\text{ bar}$$
$$p_{123} = 0.08791 \pm 1 \times 10^{-5}\text{ bar} \quad p_{13} = 0.026866 \pm 3 \times 10^{-6}\text{ bar}$$

These pressures employed in Eq. 9 gives $B = -99.7$ cm^3 mol^{-1} to $B = -108.7$ cm^3 mol^{-1} when the extremes of error are applied to p_{13}. Equation 12 indicates a worst possible combination of errors ± 14.0 cm^3 mol^{-1}.

The proof that the method is feasible as well as being simple to execute is thus demonstrated. The error estimate though already better than that associated with many other methods will be an overestimate for the fol-

lowing reasons. Of the pressure measurement error of 0.01%, 0.008% arises from systematic error largely in the estimated area of the dead weight gauge piston. A feature of this method and of other methods of obtaining virial coefficients from pressure measurement alone is that errors due to systematic errors in pressures effectively cancel and result in negligible errors in the virial coefficient.

Systematic errors will always be in the same sense (e.g., always positive) and so we may write:

$$p_i\text{ (actual)} = p_i\text{ (observed)}(1 + \delta p/p)$$

Substitution in Eq. 9 gives:

$$B\text{ (observed)} = B\text{ (actual)}/(1 + \delta p/p)$$

For systematic error in pressure then the contribution to the error in B is simply the percentage error in p itself, i.e., in this case 0.01% or in the example of CO_2 considered here ± 0.01 cm^3 mol^{-1}. This is negligible compared to errors from other sources and may be ignored.

Considering only a random pressure error of $\pm 0.002\%$ in Eq. 13 gives an error from this the major source of error

$$\delta B = \pm 3\text{ cm}^3\text{ mol}^{-1}.$$

CONCLUSION

The method here described and "pressures only" methods in general enable advantage to be taken first of the high accuracy at low pressures (a result of constant percentage error) of air dead weight gauges and secondly of the fact that the error is largely systematic.

Since after loading the apparatus, four valve operations and four pressure measurements are all that are required, the method is particularly simple and the true accuracy should therefore not be highly dependent on operator skill.

The particular arrangement of gas vessels and the sequence of expansions described here for obtaining second virial coefficients from four pressures alone is not the only possible procedure and we are proceeding with measurements in a similar fashion on an existing apparatus.

NOTATION

B	= second virial coefficient
δB	= uncertainty in B
C'	= third pressure series virial coefficient
k	= ratio of volume to V_1
n	= number of moles
p	= pressure
δp	= uncertainty in p
R	= gas constant
T	= absolute temperature
V	= cell volume
z	= compressibility factor

Subscripts

1	= primary volume
2	= secondary volume
3	= tertiary volume
12	= referring to volume $V_1 + V_2$
13	= referring to volume $V_1 + V_3$
123	= referring to volume $V_1 + V_2 + V_3$

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