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INTERNAL REPORT

DERIVATION OF FORMULAS FOR EVALUATING THE STANDARD ERRORS IN B, C, AND $N_{P=0}$ WHICH APPEAR IN THE EQUATION:

$$Z_r = (Z_o/P_o) f N^r_{P=0} P_r$$

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BRANCH Fundamental Research Branch

PROJECT NO. 4335

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B. J. Dalton[1/] and Robert E. Barieau[2/]

ABSTRACT

The method of treating a set of isothermally measured pressures P_o, P_1, P_2, ... , P_r, for a Burnett experiment, consists of expressing the compressibility factor isotherm of the gas in terms of a function of either P or ρ and evaluating the volume ratio, $N_{P=0}$, and the constants in the function by least squares solution. This report gives the method of least squares as applied to the fundamental equation for the Burnett experiment, taking into consideration the change in $N_{P=0}$ with pressure.

Formulas are given for evaluating the standard deviation of a single P_r, the standard deviation of each of the constants evaluated, and the standard deviation of the compressibility factor.

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INTRODUCTION

The method of treating Burnett type data consists of expressing the compressibility factor isotherm of the gas in terms of a function of P or ρ and evaluating the best values for the constants in the function by least squares solution.

In a previous report (6)[3/], we have given formulas for evaluating the best values for the constants appearing in the fundamental equation for the Burnett experiment: $Z_r = (Z_o/P_o)N^r P_r$, assuming N, the cell constant, to be independent of the pressure.

3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Canfield (5, 7) has pointed out that the volume ratio varies with pressure due to distortion of the bombs and a shift in the null point of the differential pressure indicator. This change in the cell constant, for a given expansion, was expressed by the equation

$$N_r = N_{P=0}\left(\frac{1 + \alpha P_r}{1 + \beta P_{r-1}}\right) \qquad (1)$$

where

$N_{P=0}$ = volume ratio at zero pressure

N_r = volume ratio for the r^{th} expansion

P_r = pressure after the r^{th} expansion

P_{r-1} = pressure before the r^{th} expansion

αP_r = change in the total volume, $(V_1 + V_2)_{P=P_r}$ divided by the total volume at zero pressure

βP_{r-1} = change in V_1 at $P=P_{r-1}$ divided V_1 at $P=0$

Therefore, representing the change in the volume ratio by equation (1), the fundamental equation for the Burnett experiment assumes the form

$$Z_r = (Z_o/P_o)N_1 \cdot N_2 \cdot \quad \ldots \quad N_r P_r \tag{2}$$

Since

$$N_1 = N_{P=0}\left(\frac{1 + \alpha P_1}{1 + \beta P_o}\right)$$

$$N_2 = N_{P=0}\left(\frac{1 + \alpha P_2}{1 + \beta P_1}\right)$$

$$\vdots$$

$$N_r = N_{P=0}\left(\frac{1 + \alpha P_r}{1 + \beta P_{r-1}}\right)$$

equation (2) is expressible as

$$Z_r = (Z_o/P_o) f \, N_{P=0}^{r} \, P_r \tag{3}$$

where

$$f = \frac{(1 + \alpha P_{1(obs)})(1 + \alpha P_{2(obs)}) \ \ldots \ (1 + \alpha P_{r(obs)})}{(1 + \beta P_{o(obs)})(1 + \beta P_{1(obs)}) \ \ldots \ (1 + \beta P_{r-1(obs)})} \qquad (4)$$

Associated with this function, equation (3), whose constants have been evaluated by least squares, the following errors are of interest: the standard deviation of a single $P_{r(obs)}$; the standard deviation of each of the constants; and the standard deviation of compressibility factors.

The method outlined in reference 1 served as the basis for evaluating the least squares solution for the constants appearing in equation (3). The methods outlined in reference 2 were used for evaluating the above-mentioned errors.

METHOD OF OBTAINING THE LEAST SQUARES SOLUTION FOR THE CONSTANTS APPEARING IN THE EQUATION: $Z_r = (Z_o/P_o) f N^r_{P=0} P_r$

The fundamental equation for the Burnett experiment, assuming the variation of the volume ratio with pressure to be expressible by equation (1), is of the form

$$Z_r = (Z_o/P_o) f N^r_{P=0} P_r \qquad (3)$$

where f is defined by equation (4).

Now there are two series expansion which can be employed for representing the compressibility factor isotherm: the Leiden expansion in powers of ρ and the Berlin expansion in powers of P. The Berlin expansion

$$Z_r = 1 + BP_r + CP_r^2 + \ldots \qquad (5)$$

$$Z_o = 1 + BP_o + CP_o^2 + \ldots \qquad (6)$$

was chosen because all of the parameters for which we seek a least squares solution can be expressed in terms of the original observations. It was assumed that the series expansion in powers of P could be truncated after the third virial coefficient.

Suppose we let the functional relationship between the variables, P_r and r, involving the three parameters, $N_{P=0}$, B, C, be

$$F = F(r, P_r, N_{P=0}, B, C) = 0 \qquad (7)$$

Now because of random errors in the observed pressures, when $P_{r(obs)}$ is substituted in the above expression, F will not be exactly zero. Let F_r be the value of F when the observed values of r and P_r are substituted in equation (7). Thus,

$$F_r = F(r, P_{r(obs)}, N_{P=0}, B, C) \qquad (8)$$

Now we assume that r, the expansion number, is accurately known. Therefore, equation (7) may be solved for $P_{r(calc)}$ so that equation (7) is exactly satisfied. Thus,

$$F = F(r, P_{r(calc)}, N_{P=0}, B, C) \equiv 0 \qquad (9)$$

and $P_{r(calc)}$ is the solution of equation (9).

Now ΔP_r, the residual of P_r, is the difference between the observed and calculated values. This is not the true random error in our observed P_r because we do not know the true value of P_r. However, we can maximize the probability that the ΔP_r's are equal

to the true random errors, and this is just what the principle of least squares does. The principle of least squares says that we maximize the probability that the ΔP_r's represent the true random errors by minimizing the sum of the squares of the weighted residuals. Thus, we should minimize the function

$$R = \sum_{r=1}^{r} W_{P_{r(obs)}} (\Delta P_r)^2 \tag{10}$$

and evaluate $N_{P=0}$, B, and C so that

$$\left(\frac{\partial R}{\partial B}\right)_{r, P_{r(obs)}, C, N_{P=0}} = 2 \sum_{r=1}^{r} W_{P_{r(obs)}} \Delta P_r \left(\frac{\partial \Delta P_r}{\partial B}\right) = 0 \tag{11}$$

$$\left(\frac{\partial R}{\partial C}\right)_{r, P_{r(obs)}, B, N_{P=0}} = 2 \sum_{r=1}^{r} W_{P_{r(obs)}} \Delta P_r \left(\frac{\partial \Delta P_r}{\partial C}\right) = 0 \tag{12}$$

$$\left(\frac{\partial R}{\partial N_{P=0}}\right)_{r, P_{r(obs)}, B, C} = 2 \sum_{r=1}^{r} W_{P_{r(obs)}} \Delta P_r \left(\frac{\partial \Delta P_r}{\partial N_{P=0}}\right) = 0 \tag{13}$$

In equation (10), $W_{P_{r(obs)}}$ is the weight ot be assigned to the observed P_r. If the P_r's all have the same precision index, then they will have the same weight and $W_{P_{r(obs)}} = 1$. If the P_r's do not all have the same precision index, then

$$W_{P_{r(obs)}} = \frac{L^2}{S^2_{P_{r(obs)}}}$$

where L is a constant and $S^2_{P_{r(obs)}}$ is the variance of $P_{r(obs)}$.

In a particular problem, it may be necessary to assume $W_{P_{r(obs)}} = 1$ in the beginning. However, if this is done the residuals, $Y_i = [P_{r(obs)} - P_{r(calc)}]$, should be examined to see if there is any statistical evidence for the residuals squared being a function of $P_{r(obs)}$. Any assumption as to the variance being a function of $P_{r(obs)}$ can always be checked by examining the residuals. In any event, $W_{P_{r(obs)}}$ is not a function of the constants to be evaluated.

In order to evaluate $N_{P=0}$, B, C, we need to linearize Y_i with respect to the undetermined constants. A truncated Taylor's series expansion was used to do this.

In a previous report (1), we show that the linearized normal equations are expressible as

$$a_1 \Delta B + b_1 \Delta C + c_1 \Delta N_{P=0} = m_1 \tag{14}$$

$$a_2 \Delta B + b_2 \Delta C + c_2 \Delta N_{P=0} = m_2 \tag{15}$$

$$a_3 \Delta B + b_3 \Delta C + c_3 \Delta N_{P=0} = m_3 \tag{16}$$

Equations (14), (15), and (16) result from expanding Y_i, $(\partial Y_i/\partial B)$, $(\partial Y_i/\partial C)$, and $(\partial Y_i/\partial N_{P=0})$ about an approximate solution Y_i^o, ignoring second and higher order derivatives. The linearized coefficients ΔB, ΔC, $\Delta N_{P=0}$ are defined as

$$\left.\begin{aligned} \Delta B &= B - B^{o} \\ \Delta C &= C - C^{o} \\ \Delta N_{P=0} &= N_{P=0} - N^{o}_{P=0} \end{aligned}\right\} \qquad (17)$$

where B, C, $N_{P=0}$ are the undetermined constants and B^{o}, C^{o}, $N^{o}_{P=0}$ are approximate values for these quantities.

The a's, b's, c's, and m's appearing in the normal equations are given as (1):

$$a_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^{o^2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B^2}\right)^{o} \right] \qquad (18)$$

$$a_2 = b_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^{o} \left(\frac{\partial Y_i}{\partial C}\right)^{o} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B \partial C}\right)^{o} \right] \qquad (19)$$

$$a_3 = c_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^{o} \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^{o} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B \partial N_{P=0}}\right)^{o} \right] \qquad (20)$$

$$b_2 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^{o^2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial C^2}\right)^{o} \right] \qquad (21)$$

$$b_3 = c_2 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^{o} \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^{o} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial C \partial N_{P=0}}\right)^{o} \right] \qquad (22)$$

$$c_3 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^{o^2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial N^2_{P=0}}\right)^{o} \right] \qquad (23)$$

$$m_1 = -\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i^o \left(\frac{\partial Y_i}{\partial B}\right)^o \quad (24)$$

$$m_2 = -\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i^o \left(\frac{\partial Y_i}{\partial C}\right)^o \quad (25)$$

$$m_3 = -\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \quad (26)$$

where

$$\left(\frac{\partial Y_i}{\partial B}\right)^o = \frac{(\partial F/\partial B)^o}{(\partial F/\partial P_{r(calc)})^o} \quad (27)$$

$$\left(\frac{\partial Y_i}{\partial C}\right)^o = \frac{(\partial F/\partial C)^o}{(\partial F/\partial P_{r(calc)})^o} \quad (28)$$

$$\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o = \frac{(\partial F/\partial N_{P=0})^o}{(\partial F/\partial P_{r(calc)})^o} \quad (29)$$

$$\left(\frac{\partial^2 Y_i}{\partial B^2}\right)^o = \left[\frac{(\partial^2 F/\partial B^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial B \partial P_{r(calc)})^o (\partial F/\partial B)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^{o^2} (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \quad (30)$$

$$\left(\frac{\partial^2 Y_i}{\partial C^2}\right)^o = \left[\frac{(\partial^2 F/\partial C^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial C\partial P_{r(calc)})^o(\partial F/\partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{\left.(\partial F/\partial C)^o\right.^2(\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \quad (31)$$

$$\left(\frac{\partial^2 Y_i}{\partial N_{P=0}\partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B\partial N_{P=0}}\right)^o = \left[\frac{(\partial^2 F/\partial N_{P=0}\partial B)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial B\partial P_{r(calc)})^o(\partial F/\partial N_{P=0})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial B)^o(\partial^2 F/\partial P_{r(calc)}\partial N_{P=0})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^o(\partial F/\partial N_{P=0})^o(\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \quad (32)$$

$$\left(\frac{\partial^2 Y_i}{\partial N_{P=0}\partial C}\right)^o = \left(\frac{\partial^2 Y_i}{\partial C\partial N_{P=0}}\right)^o = \left[\frac{(\partial^2 F/\partial N_{P=0}\partial C)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial C\partial P_{r(calc)})^o(\partial F/\partial N_{P=0})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial C)^o(\partial^2 F/\partial P_{r(calc)}\partial N_{P=0})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial C)^o(\partial F/\partial N_{P=0})^o(\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \quad (33)$$

$$\left(\frac{\partial^2 Y_i}{\partial N_{P=0}^2}\right)^o = \left[\frac{(\partial^2 F/\partial N_{P=0}^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial N_{P=0}\partial P_{r(calc)})^o(\partial F/\partial N_{P=0})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial N_{P=0})^{o^2}(\partial^2 F/\partial P_{r(calc)}^2)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3} \right] \quad (34)$$

$$\left(\frac{\partial^2 Y_i}{\partial C\partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B\partial C}\right)^o = \left[\frac{(\partial^2 F/\partial C\partial B)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial B\partial P_{r(calc)})^o(\partial F/\partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial B)^o(\partial^2 F/\partial P_{r(calc)}\partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^o(\partial F/\partial C)^o(\partial^2 F/\partial P_{r(calc)}^2)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3} \right] \quad (35)$$

$$Y_i^o = [P_{r(obs)} - P_{r(calc)}]^o \quad (36)$$

Now in order to evaluate the solutions of our linearized normal equations, we need values of first and second derivatives of the function, F,

$$F = F(r, P_{r(calc)}, N_{P=0}, B, C) \equiv 0 \quad (9)$$

and

$$F = Z_{r(calc)} - (Z_o/P_o)f_{(calc)} \; N^r_{P=0} \; P_{r(calc)} = 0$$

$$= 1 + BP_{r(calc)} + CP^2_{r(calc)} - \left(\frac{1 + BP_o + CP_o^2}{P_o}\right) f_{(calc)} N^r_{P=0} \; P_{r(calc)} \quad (37)$$

where $f_{(calc)}$ of equation (37) is given as

$$f_{(calc)} = \frac{(1 + \alpha P_{1(calc)})(1 + \alpha P_{2(calc)}) \ldots (1 + \alpha P_{r(calc)})}{(1 + \beta P_o)(1 + \beta P_{1(calc)}) \ldots (1 + \beta P_{r-1_{(calc)}})} \quad (38)$$

Therefore, from equations (37) and (38), the first and second derivatives of F are:

$$\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}} = P_{r(calc)}(1 - f_{(calc)} N^r_{P=0})$$

$$\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}} = P_{r(calc)}\left[P_{r(calc)} - f_{(calc)} N^r_{P=0} P_o\right]$$

$$\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}} = - r(Z_o/P_o) f_{(calc)} N^{r-1}_{P=0} \; P_{r(calc)}$$

$$\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N_{P=0}} = B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right]$$

$$\left(\frac{\partial^2 F}{\partial B^2}\right)_{r,C,N_{P=0},P_{r(calc)}} = 0$$

$$\left(\frac{\partial^2 F}{\partial C^2}\right)_{r,B,N_{P=0},P_{r(calc)}} = 0$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0}^2}\right)_{r,B,C,P_{r(calc)}} = -r(r-1)\left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-2} P_{r(calc)}$$

$$\left(\frac{\partial^2 F}{\partial P_{r(calc)}^2}\right)_{r,B,C,N_{P=0}} = 2C - 2\left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \left(\frac{\alpha}{1 + \alpha P_{r(calc)}}\right)$$

$$\left[\frac{\partial}{\partial C}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,N_{P=0},P_{r(calc)}} = 0$$

$$\left[\frac{\partial}{\partial N_{P=0}}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,C,P_{r(calc)}} = -r\ f_{(calc)} N_{P=0}^{r-1} P_{r(calc)}$$

$$\left[\frac{\partial}{\partial N_{P=0}}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]_{r,B,C,P_{r(calc)}} = -r\ P_o\ f_{(calc)} N_{P=0}^{r-1} P_{r(calc)}$$

$$\left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,C,N_{P=0}} = -f_{(calc)} N_{P=0}^{r} \left[1 + \frac{\alpha P_{r(calc)}}{1 + \alpha P_{r(calc)}}\right]$$

$$\left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]_{r,B,C,N_{P=0}} = 2P_{r(calc)} - f_{(calc)} N_{P=0}^{r} \alpha \left[1 + \frac{\alpha P_{r(calc)}}{1 + \alpha P_{r(calc)}}\right]$$

$$\left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]_{r,B,C,N_{P=0}} = -r\left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-1} \left[1 + \frac{\alpha P_{r(calc)}}{1 + \alpha P_{r(calc)}}\right]$$

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]_{r,C,N_{P=0},P_{r(calc)}} = \left[\frac{\partial}{\partial C}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,N_{P=0},P_{r(calc)}}$$

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]_{r,C,N_{P=0},P_{r(calc)}} = \left[\frac{\partial}{\partial N_{P=0}}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,C,P_{r(calc)}}$$

$$\left[\frac{\partial}{\partial C}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]_{r,B,N_{P=0},P_{r(calc)}} = \left[\frac{\partial}{\partial N_{P=0}}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]_{r,B,C,P_{r(calc)}}$$

$$\left[\frac{\partial}{\partial N_{P=0}}\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N_{P=0}}\right]_{r,B,C,P_{r(calc)}} = \left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]_{r,B,C,N_{P=0}}$$

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N_{P=0}}\right]_{r,C,N_{P=0},P_{r(calc)}} = \left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\right]_{r,B,C,N_{P=0}}$$

$$\left[\frac{\partial}{\partial C}\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N_{P=0}}\right]_{r,B,N_{P=0},P_{r(calc)}} = \left[\frac{\partial}{\partial P_{r(calc)}}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]_{r,B,C,N_{P=0}}$$

Therefore, equations (27) - (35) can be expressed in terms of the original observations by the following expressions:

$$\left(\frac{\partial Y_i}{\partial B}\right)^o = \frac{P_{r(calc)}\left[1 - f_{(calc)}N^r_{P=0}\right]}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]}$$

$$\left(\frac{\partial Y_i}{\partial C}\right)^o = \frac{P_{r(calc)}\left[P_{r(calc)} - f_{(calc)} N^r_{P=0}\, P_o\right]}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right]}$$

$$\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o = \frac{-r(Z_o/P_o)\, f_{(calc)} N^{r-1}_{P=0}\, P_{r(calc)}}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right]}$$

$$\left(\frac{\partial^2 Y_i}{\partial B^2}\right)^o = \left[\frac{-2P_{r(calc)}\left(1 - f_{(calc)} N^r_{P=0}\right)\left[1 - f_{(calc)} N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right]\right]^2} + \frac{2P^2_{r(calc)}\left(1 - f_{(calc)} N^r_{P=0}\right)^2\left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\frac{\alpha}{(1 + \alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right]\right]^3}\right]$$

$$\left(\frac{\partial^2 Y_i}{\partial C^2}\right)^o = \left[\frac{-2P_{r(calc)}\left[P_{r(calc)} - f_{(calc)} N^r_{P=0}\, P_o\right]\left[2P_{r(calc)} - f_{(calc)} N^r_{P=0}\, P_o\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2} + \frac{2P^2_{r(calc)}\left[P_{r(calc)} - f_{(calc)}\, N^r_{P=0}\, P_o\right]^2\left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\, \frac{\alpha}{(1 + \alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^3} \right]$$

$$\left(\frac{\partial^2 Y_i}{\partial N_{P=0}^2}\right)^o = \left[\frac{-\,r(r-1)\left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r-2}\, P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]} - \frac{2\left[r\left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r-1}\right]^2 P_{r(calc)}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2} + \frac{2\left[r\left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r-1}\, P_{r(calc)}\right]^2 \left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r} \frac{\alpha}{(1 + \alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^3} \right]$$

$$\left(\frac{\partial^2 Y_i}{\partial C \partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B \partial C}\right)^o = \left[\frac{- P_{r(calc)}\left(P_{r(calc)} - f_{(calc)}\, N^r_{P=0}\, P_o\right)\left[1 - f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2} \right.$$

$$\frac{- P_{r(calc)}\left(1 - f_{(calc)}\, N^r_{P=0}\right)\left[2P_{r(calc)} - f_{(calc)}\, N^r_{P=0}\, P_o\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2}$$

$$\left. + \frac{2P^2_{r(calc)}\left(1 - f_{(calc)}\, N^r_{P=0}\right)\left(P_{r(calc)} - f_{(calc)}\, N^r_{P=0}\, P_o\right)\left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\, \frac{\alpha}{(1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^3} \right]$$

$$
\left(\frac{\partial^2 Y_i}{\partial N_{P=0}\,\partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B\,\partial N_{P=0}}\right)^o = \Bigg[\frac{-\, r\, f_{(calc)}\, N_{P=0}^{r-1}\, P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}
$$

$$
+ \frac{r\left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r-1}\, P_{r(calc)}\left[1 - f_{(calc)}\, N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2}
$$

$$
+ \frac{P_{r(calc)}\left(1 - f_{(calc)}\, N_{P=0}^{r}\right) r\left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r-1}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2}
$$

$$
- \frac{2P_{r(calc)}^2\left(1 - f_{(calc)} N_{P=0}^{r}\right) r\left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-1}\left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r}\, \frac{\alpha}{(1 + \alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)}\, N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^3} \Bigg]
$$

$$\left(\frac{\partial^2 Y_i}{\partial N_{P=0}\partial C}\right)^o = \left(\frac{\partial^2 Y_i}{\partial C \partial N_{P=0}}\right)^o = \left[\frac{- r P_o f_{(calc)} N_{P=0}^{r-1} P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]} \right.$$

$$+ \frac{r\left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-1} P_{r(calc)} \left[2P_{r(calc)} - f_{(calc)} N_{P=0}^{r} P_o \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2}$$

$$+ \frac{P_{r(calc)}\left(P_{r(calc)} - f_{(calc)} N_{P=0}^{r} P_o\right) r \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-1} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^2}$$

$$\left. - \frac{2P_{r(calc)}^2\left(P_{r(calc)} - f_{(calc)} N_{P=0}^{r} P_o\right) r \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r-1} \left[C - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \frac{\alpha}{(1 + \alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right)\right]^3} \right]$$

Now in evaluating the best values for B, C, and $N_{P=0}$, we solve the linearized normal equations by an iterative procedure. Even though it is necessary to solve equations (14), (15), and (16) by a series of approximations, it is important to realize that the best values for the constants are determined such that the normal equations are exactly satisfied.

The solutions to equations (14), (15), and (16) are (1):

$$D_o \Delta B = D_1 m_1 + D_2 m_2 + D_3 m_3 \tag{39}$$

$$D_o \Delta C = D_4 m_1 + D_5 m_2 + D_6 m_3 \tag{40}$$

$$D_o \Delta N_{P=0} = D_7 m_1 + D_8 m_2 + D_9 m_3 \tag{41}$$

where

$$D_1 = b_2 c_3 - b_3 c_2 \tag{42}$$

$$D_4 = D_2 = b_3 c_1 - b_1 c_3 \tag{43}$$

$$D_7 = D_3 = b_1 c_2 - b_2 c_1 \tag{44}$$

$$D_5 = a_1 c_3 - a_3 c_1 \tag{45}$$

$$D_8 = D_6 = a_2 c_1 - a_1 c_2 \tag{46}$$

$$D_9 = a_1 b_2 - a_2 b_1 \tag{47}$$

$$D_o = D_1 a_1 + D_2 a_2 + D_3 a_3 \tag{48}$$

[illegible]

[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
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[illegible]	[illegible]
[illegible]	[illegible]

EXPRESSIONS FOR DETERMINING VARIANCES AND COVARIANCES OF THE CONSTANTS EVALUATED

We now proceed to evaluate the variances and covariances of the constants evaluated. To do this, we apply the law for the "Propagation of Errors" (3, 8). This law states that if we have a function or quantity, say Q, that is a function of the independently observed quantities $y_1, y_2, \ldots$, then the variance of the quantity Q is given as

$$S_Q^2 = \sum_{i=1}^{n} \left(\frac{\partial Q}{\partial y_{i(obs)}} \right)^2 S_{y_{i(obs)}}^2 \qquad (49)$$

where S_Q^2 is the variance of Q and $S_{y_{i(obs)}}^2$ is the variance of $y_{i(obs)}$. Extracting the square root of the variance, we obtain a value on the same scale as the original measurements. This value, S_Q, is called the standard error or the standard deviation of Q.

The value of the constant B, which we have evaluated is a function of all of the observed r's and of all of the observed P_r's. Since we have assumed that r is accurately known, then the expression for the variance in B is given by the equation

$$S_B^2 = \sum_{r=1}^{r} \left(\frac{\partial B}{\partial P_{r(obs)}} \right)^2 S_{P_{r(obs)}}^2 \qquad (50)$$

and there will be an equation similar to equation (50) for determining the variance of C and the variance of $N_{P=0}$.

[illegible]

[illegible]

[illegible]

$$[illegible]$$

[illegible]

[illegible]

$$[illegible]$$

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In order to evaluate equation (50), we must evaluate $(\partial B/\partial P_{r(obs)})$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the product, and then sum the product over all of the observed P_r's.

In a previous report (2), we have outlined the details for evaluating the variances and all of the covariances of the constants evaluated.

For our particular problem, these variances and covariances are determined from the following relations (2):

$$S_B^2 = \frac{L^2}{D_o^2}\left[D_1^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_2^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 + D_3^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 + 2D_1D_2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o + 2D_1D_3 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o + 2D_2D_3 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \right] \quad (51)$$

$$S_C^2 = \frac{L^2}{D_o^2}\left[D_4^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_5^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 + D_6^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 + 2D_4D_5 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o + 2D_4D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o + 2D_5D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \right] \quad (52)$$

$$S^2_{N_{P=0}} = \frac{L^2}{D_o^2} \left[D_7^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_8^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 + D_9^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 + 2D_7D_8 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o + 2D_7D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o + 2D_8D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \right] \quad (53)$$

$$S^2_{BC} = \frac{L^2}{D_o^2} \left[D_1D_4 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_2D_5 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 + D_3D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 + (D_2D_4 + D_1D_5) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o + (D_1D_6 + D_3D_4) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o + (D_2D_6 + D_3D_5) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \right] \quad (54)$$

$$S^2_{BN_{P=0}} = \frac{L^2}{D_o^2}\left[\begin{array}{l} D_1D_7 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_2D_8 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 \\ + D_3D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 \\ + (D_1D_8 + D_2D_7) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o \\ + (D_1D_9 + D_3D_7) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \\ + (D_2D_9 + D_3D_8) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \end{array}\right] \quad (55)$$

$$S^2_{CN_{P=0}} = \frac{L^2}{D_o^2}\left[\begin{array}{l} D_4D_7 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o\right]^2 + D_5D_8 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o\right]^2 \\ + D_6D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o\right]^2 \\ + (D_4D_8 + D_5D_7) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o \\ + (D_4D_9 + D_6D_7) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \\ + (D_5D_9 + D_6D_8) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N_{P=0}}\right)^o \end{array}\right] \quad (56)$$

We have indicated that the solutions to equations (14), (15), and (16) are solved by an iterative procedure. When we have the correct solutions, our linearized normal equations will be satisfied exactly. Therefore, once the best values for the constants have been determined, the remaining questions to be answered are: (1) what is the variance of the calculated P's and any other calculated P that reduces F to zero?; and (2) what is the variance of the compressibility factor?

EVALUATION OF THE VARIANCE OF THE $P_{r(calc)}$'S AND ANY OTHER CALCULATED P THAT REDUCES F TO ZERO

The variance of a calculated P_r which reduces F to zero for a given observed r value is obtained in the following way: $P_{r(calc)}$ is a function of the observed r's and, through the constants evaluated, is a function of all of the $P_{r(obs)}$'s. When we apply the law for the "Propagation of Errors" to obtain an expression for determining the variance of $P_{r(calc)}$, we see from equation (49) that this involves evaluation of the quantity

$$S^2_{P_{r(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \qquad (57)$$

In order to evaluate the variance of the calculated P_r's, we need an expression for $[\partial P_{r(calc)}/\partial P_{r(obs)}]$. This quantity can be determined from equation (9)

$$F = F(r, P_{r(calc)}, N_{P=0}, B, C) \equiv 0 \qquad (9)$$

Suppose we differentiate equation (9) with regard to $P_{r(obs)}$, holding r constant. This gives us

$$\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial B}\right)_{C,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial C}\right)_{B,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial N_{P=0}}\right)_{B,C,r,P_{r(calc)}}\left(\frac{\partial N_{P=0}}{\partial P_{r(obs)}}\right)\right]=0 \quad (58)$$

Solving equation (58) for $[\partial P_{r(calc)}/\partial P_{r(obs)}]$, we get

$$\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right) = -\frac{\left[\left(\frac{\partial F}{\partial B}\right)_{C,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial C}\right)_{B,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial N_{P=0}}\right)_{B,C,r,P_{r(calc)}}\left(\frac{\partial N_{P=0}}{\partial P_{r(obs)}}\right)\right]}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}} \quad (59)$$

Multiplying equation (59) by $S_{P_{r(obs)}}$, squaring the product, and then summing over all of the observed P_r's, we get

$$S^2_{P_{r(calc)}} = \frac{\begin{aligned}&S_B^2\left(\frac{\partial F}{\partial B}\right)^2_{r,C,N_{P=0},P_{r(calc)}} + S_C^2\left(\frac{\partial F}{\partial C}\right)^2_{r,B,N_{P=0},P_{r(calc)}} \\ &+ S^2_{N_{P=0}}\left(\frac{\partial F}{\partial N_{P=0}}\right)^2_{r,B,C,P_{r(calc)}} \\ &+ 2S^2_{BC}\left[\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right] \\ &+ 2S^2_{BN_{P=0}}\left[\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right] \\ &+ 2S^2_{CN_{P=0}}\left[\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]\end{aligned}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}} \quad (60)$$

from which we can evaluate the (n-1) values of $S^2_{P_{r(calc)}}$ corresponding to the observed r's.

Now we ask ourselves the question: how do we calculate the variance of any other calculated P that exactly satisfies equation (9)? In order to answer this question, we must find a value of r, say r_P, and we must find a value of f, say f_P, which exactly satisfy the equation

$$Z_{P_{(calc)}} \equiv (Z_o/P_o) f_P \, N_{P=0}^{r_P} \, P_{(calc)} \quad (61)$$

where

$$Z_{P_{(calc)}} = 1 + BP_{(calc)} + CP^2_{(calc)} \tag{62}$$

Now suppose we have previously evaluated B, C, and $N_{P=0}$ by some means or other. We now proceed to evaluate an f, say f_P, which will exactly satisfy equation (61). We do this as follows: from equation (38), f is given to be

$$f_{(calc)} = \frac{(1 + \alpha P_{1(calc)})(1 + \alpha P_{2(calc)}) \cdots (1 + \alpha P_{r(calc)})}{(1 + \beta P_o)(1 + \beta P_{1(calc)}) \cdots (1 + \beta P_{r-1(calc)})} \tag{38}$$

Briggs (4) has indicated that the constants α and β which are ..." dependent on the dimensions of V_1^o and V_2^o, Poisson's ratio for V_1 and V_2, and Young's modulus for V_1 and V_2" ... have the following values at 30° C:

$$\left.\begin{aligned} \alpha &= 1.1463 \times 10^{-7}, \text{ psi}^{-1} \\ \beta &= 1.1457 \times 10^{-7}, \text{ psi}^{-1} \end{aligned}\right\} \text{ at } 30^\circ \text{ C}$$

for the Burnett apparatus located in room 211A of the Helium Research Center. Now assuming $\alpha = \beta$, then f of equation (38) can be written as

$$f_{(calc)} = \frac{(1 + \alpha P_{r(calc)})}{(1 + \alpha P_o)} \tag{63}$$

or,

$$f_{(calc)} = 1 + \alpha(P_{r(calc)} - P_o)[1 - \alpha P_o + \alpha^2 P_o^2 - \ldots]$$

For $P_o = 1 \times 10^4$ psi, $\alpha P_o \cong 1.1 \times 10^{-3}$. Therefore,

$$f_{(calc)} \cong 1 + \alpha(P_{r(calc)} - P_o)(1 - \alpha P_o) \qquad (64)$$

which is accurate to about 1 part in 10^9. Representing the correction to $N_{P=0}$ as a function of $P_{(calc)}$ by f_P, then the value of f_P which satisfies equation (61) to about 1 part in 10^9 is

$$f_P = 1 + \alpha(P_{(calc)} - P_o)(1 - \alpha P_o) \qquad (65)$$

Now r_P, the expansion number corresponding to $P_{(calc)}$ and f_P, can be determined from the equation

$$r_P = \left[\frac{\ln Z_{P(calc)} - \ln(Z_o/P_o) - \ln P_{(calc)} - \ln f_P}{\ln N_{P=0}}\right] \qquad (66)$$

Equation (66) results from our taking natural logarithms of equation (61) and solving for r_P. Now that we have determined values of r and f for $P_{(calc)}$, we can proceed to evaluate $S^2_{P_{(calc)}}$, the variance of a calculated P that exactly satisfies equation (9).

To evaluate the variance of $P_{(calc)}$, we employ equation (60) where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, r_P, f_P. The expression for $[\partial F/\partial P_{(calc)}]_{B,C,r_P,N_{P=0}}$ is

given as

$$\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{B,C,r_P,N_{P=0}} = B + 2CP_{(calc)} - \left(\frac{Z_o}{P_o}\right) N_{P=0}^{(r_P)} \left[\frac{2f_P P_{(calc)} - f_P P_o - P_{(calc)}}{P_{(calc)} - P_o}\right] \quad (67)$$

EXPRESSION FOR EVALUATING THE VARIANCE OF THE COMPRESSIBILITY FACTOR

To evaluate the variance of $Z_{P_{(calc)}}$, where $Z_{P_{(calc)}}$ is given by

$$Z_{P_{(calc)}} = 1 + BP_{(calc)} + CP^2_{(calc)} \quad (62)$$

and $P_{(calc)}$ is any calculated P which exactly satisfies equation (9), we apply the law for the "Propagation of Errors." This law says that since Z is a function of r_P and, through the constants evaluated, is a function of all of the original observed P_r's, then the variance of $Z_{P_{(calc)}}$ is given as

$$S^2_{Z_{P_{(calc)}}} = \sum_{r=1}^{r} \left(\frac{\partial Z_{P_{(calc)}}}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \quad (68)$$

where $S^2_{Z_{P_{(calc)}}}$ is the variance of $Z_{P_{(calc)}}$ and $S^2_{P_{r(obs)}}$ is the variance of $P_{r(obs)}$.

Now in order to evaluate equation (68), we must evaluate $[\partial Z_{P_{(calc)}}/\partial P_{r(obs)}]$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the product, and then sum the product over all of the observed P_r's. When we do this, we get

$$S^2_{Z_{P_{(calc)}}} = \Big[B^2 S^2_{P_{(calc)}} + 4C^2 P^2_{(calc)} S^2_{P_{(calc)}} + P^2_{(calc)} S^2_B + P^4_{(calc)} S^2_C + 4BCP_{(calc)} S^2_{P_{(calc)}} + 2BP_{(calc)} S^2_{B,P_{(calc)}} + 2BP^2_{(calc)} S^2_{C,P_{(calc)}} + 4CP^2_{(calc)} S^2_{B,P_{(calc)}} + 4CP^3_{(calc)} S^2_{C,P_{(calc)}} + 2P^3_{(calc)} S^2_{BC} \Big] \tag{69}$$

The terms $S^2_{B,P_{(calc)}}$ and $S^2_{C,P_{(calc)}}$, which appear in equation (69), are defined as

$$S^2_{B,P_{(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} \tag{70}$$

$$S^2_{C,P_{(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} \tag{71}$$

and these quantities are to be evaluated from equations (70) and (71), which we proceed to do.

$[\partial P_{(calc)}/\partial P_{r(obs)}]$ can be determined from equation (59), where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, r_P, f_P, and $[\partial F/\partial P_{(calc)}]$ is defined by equation (67). Multiplying equation (59) by $(\partial B/\partial P_{r(obs)})S^2_{P_{r(obs)}}$ and summing the product over all of the observed P_r's, we get

$$\sum_{r=1}^{r}\left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right)S^2_{P_{r(obs)}} = S^2_{B,P_{(calc)}} = -\frac{\left[S^2_B\left(\frac{\partial F}{\partial B}\right)_{r_P,C,N_{P=0},P_{(calc)}} + S^2_{BC}\left(\frac{\partial F}{\partial C}\right)_{r_P,B,N_{P=0},P_{(calc)}} + S^2_{BN_{P=0}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r_P,B,C,P_{(calc)}}\right]}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N_{P=0}}} \quad (72)$$

If we multiply equation (59) by $(\partial C/\partial P_{r(obs)})S^2_{P_{r(obs)}}$ and then sum the product over all of the observed P_r's, we get

$$\sum_{r=1}^{r}\left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right)S^2_{P_{r(obs)}} = S^2_{C,P_{(calc)}} = -\frac{\left[S^2_{BC}\left(\frac{\partial F}{\partial B}\right)_{r_P,C,N_{P=0},P_{(calc)}} + S^2_C\left(\frac{\partial F}{\partial C}\right)_{r_P,B,N_{P=0},P_{(calc)}} + S^2_{CN_{P=0}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r_P,B,C,P_{(calc)}}\right]}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N_{P=0}}} \quad (73)$$

Therefore, the use of equations (72) and (73) in equation (69) will enable the variance of a calculated Z_P, $S^2_{Z_{P(calc)}}$, to be determined.

REFERENCES

1. Barieau, Robert E., and B. J. Dalton. Method of Solving Non-Linear Least Squares Problems. Helium Research Center Memorandum Report No. 63, March 1965, 17 pp.

2. _____. Non-Linear Regression and the Principle of Least Squares. Helium Research Center Memorandum Report No. 62, March 1965, 59 pp.

3. Birge, Raymond T. The Calculation of Errors by the Method of Least Squares. The Phys. Rev., v. 40, Apr. 15, 1932, pp. 207-227.

4. Briggs, Ted C. Elastic Distortion of the High Pressure Compressibility Bombs at 30° C. Helium Research Center Internal Report No. 77, June 1965, 23 pp.

5. Canfield, Frank B., Jr. The Compressibility Factors and Second Virial Coefficients for Helium-Nitrogen Mixtures at Low Temperatures and High Pressure. Dissertation submitted in May 1962, Rice University.

6. Dalton, B. J., and Robert E. Barieau. Derivation of Formulas for Evaluating the Standard Errors in B, C, and N Which Appear In the Fundamental Equation for the Burnett Experiment: $Z_r = (Z_o/P_o)N^r P_r$. Helium Research Center Internal Report No. 66 (Rev.), July 1965, 28 pp.

7. Hoover, Alan E., Frank B. Canfield, Jr., Riki Kobayashi, and Thomas W. Leland, Jr. Determination of Virial Coefficients by the Burnett Method. J. of Chem. and Eng. Data, v. 9, No. 4, October 1964, pp. 568-573.

REFERENCES (Con.)

8. Merriman, Mansfield. A Textbook on the Method of Least Squares. John Wiley and Sons, Inc., New York, N. Y., 8th ed., 1911, pp. 75-79.