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INTERNAL REPORT

APPLICATION OF THE METHOD OF THE AUXILIARY MATRIX IN EVALUATING VIRIAL COEFFICIENTS FROM PVT DATA

BY

B. J. Dalton

BRANCH Fundamental Research

PROJECT NO. 4335

DATE November 1964

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B. J. Dalton[1/]

ABSTRACT

An important application of the method of the auxiliary matrix is in the least squares evaluation of virial coefficients from PVT data. This analytical method for solving constants from general equations containing these coefficients is much shorter than a solution by determinents and is most desirable for desk calculation work as the only writing involved is that of writing the auxiliary matrix and the final results.

This report gives a brief summary of the method of the auxiliary matrix, previously published by Crout, and its application to rational, integral functions of one to four degrees together with formulas for evaluating the standard error in a single measurement, the standard error in each coefficient, and the standard error of these functions.

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The formulas presented in this report for evaluating the standard errors mentioned above are expressed in terms of the elements of the auxiliary matrix. These formulas were derived by expressing the constants in terms of the original data and applying the law for the "Propagation of Errors", unit weight being assigned to each of the observed measurements.

INTRODUCTION

In a previous publication (3)[2/], formulas were presented for evaluating the constants of rational integral functions of one to four degrees together with formulas for calculating the standard error of a single measurement, the standard error in each coefficient, and the standard error of the resulting function. The derivations for calculating the errors mentioned above were based on the law for the "Propagation of Errors" (1, 4), unit weight being given to each of the observed measurements.

After publication, this author became aware of the Crout Method (2), the method of the auxiliary matrix. This method is a modification of the elimination method and it is most desirable for desk calculation work. It is a fact that this analytical method for solving a set of normal equations is much shorter than a solution by determinents as

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

given previously (3). Therefore, it was decided to derive the equations for evaluating the above-mentioned errors. This author does not claim any originality with respect to this method for solving constants from general equations containing these coefficients.

The purpose of this report is to give, without proof, the Crout Method as applied to rational, integral functions of one to four degrees together with formulas which I have derived for evaluating the standard error in a single Y_i, in each coefficient, and in the resulting function. The formulas presented for evaluating these errors are expressed in terms of the elements of the auxiliary matrix and they were derived on the basis of the law for the "Propagation of Errors", each observation having unit weight.

CALCULATION OF THE STANDARD ERROR

An important application of the method of the auxiliary matrix is in the least squares evalation of the coefficients from a general equation containing these constants. For example, the PV product of a gas is represented as a function of either the pressure or the density by an equation such as

$$Y = A + Bx_1 + Cx_2 + Dx_3 + Ex_4 + \ldots$$

in which Y is the PV product; x_1, x_2, x_3, x_4, ... are forms of either the pressure or the density variable; and A, B, C, D, E, ... represent so-called virial coefficients to be determined by least squares solution using the Crout method.

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in which Y is the PV product; x_1, x_2, x_3, x_4, ... are forms of either the pressure or the density variable; and A, B, C, D, E, ... represent so-called virial coefficients to be determined by least squares solution using the Crout method.

The form of the general equation given above is desirable when considered from the standpoint of the independent variable. That is, the PV-dependent variable may or may not be expressed in terms of a power series expansion

$$x = x_1;\ x^2 = x_2;\ x^3 = x_3;\ x^4 = x_4;\ \ldots$$

of the independent variable.

The following symbolism has been used in the derivation of all equations for evaluating standard errors contained in this report: Y_i, x_{1_i}, x_{2_i}, ... designate observed values; Y refers to the function; s_A^2, s_B^2, ... are the variances in the coefficients; $S_{Y_i}^2$ and S_{Y_i} are the variance and the standard error in a single Y_i, respectively; S_Y^2 and S_Y are the variance and the standard error in the function, respectively; R and C represent the words row and column, respectively, and refer to those elements of the given coefficient matrix; and r and c represent the words row and column, respectively, and refer to those elements of the auxiliary matrix.

Now if one has a function, F, of a number of independently observed quantities, Y_1, Y_2, Y_3, ..., whose standard errors S_{Y_1}, S_{Y_2}, S_{Y_3}, ... are known, then the variance, S_F^2, in F is given by the formula (1, 4) for the "Propagation of Errors":

$$S_F^2 = \left(\frac{\partial F}{\partial Y_1} \cdot S_{Y_1}\right)^2 + \left(\frac{\partial F}{\partial Y_2} \cdot S_{Y_2}\right)^2 + \ldots + \left(\frac{\partial F}{\partial Y_n} \cdot S_{Y_n}\right)^2 \qquad (1)$$

Extracting the square root of the variance, one obtains a value on the same scale as the original measurements; this value is called the standard error or standard deviation.

Suppose we have a function of the kind

$$Y = A + Bx_1 \tag{2}$$

where A and B are to be evaluated by least squares solution (using the method of the auxiliary matrix) along with the following errors: the standard error of a single measurement; the standard error in each coefficient; and the standard error of the resulting function. The estimated variance, $S^2_{Y_i}$, of a single Y_i is given as

$$S^2_{Y_i} = \frac{\Sigma(Y_{i_{obs}} - Y_{i_{cal}})^2}{n - 2} \tag{3}$$

Now in order to evaluate the standard error in both intercept and slope, we must express these quantities in terms of the original data. The residuals, W_i, are

$$W_i = (Y_i - A - Bx_{1_i}) \tag{4}$$

and the sum of the squares of the residuals is

$$\Sigma W_i^2 = \Sigma(Y_i - A - Bx_{1_i})^2 \tag{5}$$

the summation being over i for 1 to n for the n observations. Taking the partial derivative of equation (5) with respect to first A and

then B and setting each derivative equal to zero gives the normal equations

$$(Y_1 - A - Bx_{1_1}) + \ldots + (Y_n - A - Bx_{1_n}) = 0 \tag{6}$$

$$x_{1_1}(Y_1 - A - Bx_{1_1}) + \ldots + x_{1_n}(Y_n - A - Bx_{1_n}) = 0 \tag{7}$$

or their equivalents

$$An + B\Sigma x_{1_i} = \Sigma Y_i \tag{8}$$

$$A\,\Sigma x_{1_i} + B\Sigma x_{1_i}^2 = \Sigma x_{1_i} Y_i \tag{9}$$

Now equations (8) and (9) can be written as a general coefficient matrix as

$$\begin{vmatrix} n & \Sigma x_{1_i} & \Sigma Y_i \\ \Sigma x_{1_i} & \Sigma x_{1_i}^2 & \Sigma x_{1_i} Y_i \end{vmatrix} \qquad \text{(Matrix 10)}$$

or, abbreviating the above, using the letters R and C to represent the words row and column, respectively, as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 \\ R_2C_1 & R_2C_2 & R_2C_3 \end{vmatrix} \qquad \text{(Matrix 11)}$$

where $R_1C_1 = n$; $R_1C_2 = \Sigma x_{1_i}$; $R_1C_3 = \Sigma Y_i$; $R_2C_1 = \Sigma x_{1_i}$; $R_2C_2 = \Sigma x_{1_i}^2$; and $R_2C_3 = \Sigma x_{1_i} Y_i$. The solution of the constants of equation (2) requires

that we evaluate an auxiliary matrix and a final result. Now our auxiliary matrix is of the form

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 \\ R_2C_1 & r_2c_2 & r_2c_3 \end{vmatrix} \qquad \text{(Matrix 12)}$$

and our final results are

$$B = r_2c_3 \tag{13}$$

$$A = r_1c_3 - r_1c_2 \cdot B \tag{14}$$

The expressions derived by me for evaluating the variances in A and in B are of the form

$$s_A^2 = \left(\frac{r_2c_2}{R_1C_1}\right) \cdot s_B^2 - (r_1c_2) \cdot s_{AB}^2 \tag{15}$$

$$s_B^2 = S_{Y_i}^2 \left(\frac{1}{r_2c_2}\right) \tag{16}$$

where s_{AB}^2 is

$$s_{AB}^2 = (-r_1c_2) \cdot s_B^2 \tag{17}$$

From the variance in a single Y_i, in A, and in B, we can evaluate the variance in our function, equation (2). This is done by applying the general equation for the "Propagation of Errors", equation (1). To avoid repetition, familarity with the techniques given in reference 3 is assumed. The formula for evaluating the variance in our function, equation (2), can be determined from the equation (3):

$$s_Y^2 = s_A^2 + 2x_1 s_{AB}^2 + x_1^2 s_B^2 \tag{18}$$

1. Rules for obtaining the auxiliary matrix from the given coefficient matrix

The steps to follow in going from the given coefficient matrix, (Matrix 11), to the auxiliary matrix, (Matrix 12), are as follows:

(1) The first column of the auxiliary matrix is identical to the first column of the given coefficient matrix. Each element of the first row of the auxiliary matrix, except the first element, is obtained by dividing the corresponding element of the coefficient matrix by the first element of the coefficient matrix.

(2) "Each element on or below the principal diagonal (of the auxiliary matrix) is equal to the corresponding element of the given matrix (Matrix 11) minus the sum of those products of elements in its row and corresponding elements in its column (in the auxiliary matrix) which involve only previously computed elements" (2).

(3) "Each element to the right of the principal diagonal (of the auxiliary matrix) is given by a calculation which differs from rule 3 (rule 2 of this report) only in that there is a final division by its diagonal elment (in the auxiliary matrix)" (2).

Suppose we follow the above steps and proceed to go from our coefficient matrix to our auxiliary matrix. Now the coefficient matrix, in abbreviated form, is given as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 \\ R_2C_1 & R_2C_2 & R_2C_3 \end{vmatrix} \qquad \text{(Matrix 11)}$$

Now rule 1 says that the first column of the auxiliary matrix is identical to the first column of the coefficient matrix. Hence, R_1C_1 and R_2C_1 appear in the first column of the auxiliary matrix. Rule 1 also says that each element which lies in the first row of the auxiliary matrix, excluding R_1C_1, is equal to the corresponding element in the coefficient matrix divided by R_1C_1. Hence, R_1C_1, R_1C_2/R_1C_1, and R_1C_3/R_1C_1 appear in the first row of the auxiliary matrix.

Rule 2 states that any element in the auxiliary matrix which lies on or below the principal diagonal[3/] of the auxiliary matrix

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3/ The principal diagonal is composed of those elements which have the same row and column index—i.e.: R_1C_1, R_2C_2, ...R_nC_n. The principal diagonal starts with that element in the upper left hand corner and slopes down to the right. In our coefficient matrix, the principal diagonal is made up of R_1C_1 and R_2C_2.

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is equal to the corresponding element in the given matrix, R_2C_2, minus the sum of those products of elements in its row and corresponding elements in its column, $R_2C_1.r_1c_2$. Therefore, from our auxiliary

matrix

$$\left|\begin{matrix} R_1C_1 & r_1c_2 & r_1c_3 \\ R_2C_1 & r_2c_2 & r_2c_3 \end{matrix}\right| \qquad \text{(Matrix 12)}$$

we see from rule 2 that $r_2c_2 = R_2C_2 - R_2C_1 \cdot r_1c_2$.

Finally, rule 3 says that in evaluating an element which lies to the right of the principal diagonal of the auxiliary matrix, we follow step 2 and then divide by the diagonal element. That is, r_2c_3 is equal to the corresponding element in our coefficient matrix, R_2C_3, minus the sum of those products of elements in its row and corresponding elements in its column of the auxiliary matrix, $R_2C_1 \cdot r_1c_3$, and then all of this is to be divided by the diagonal element of the auxiliary matrix which lies in the same row as r_2c_3. Therefore,

$$r_2c_3 = \frac{R_2C_3 - R_2C_1 \cdot r_1c_3}{r_2c_2}$$

Now all of the elements which make up our auxiliary matrix have been defined and we proceed to outline the procedure for going from our auxiliary matrix to a set of final results.

2. <u>Rules for obtaining the final results from the auxiliary matrix</u>

In going from the auxiliary matrix, (Matrix 12), to the final result, equations (13) and (14), we proceed as follows:

(1) We evaluate our coefficients of equation (2) in reverse order; for example, we evaluate first B and then A.

(2) The last coefficient, B, is numerically equal to the corresponding element in the last column of our auxiliary matrix.

(3) Each of the other coefficients is "...equal to the corresponding element of the last column of the auxiliary matrix minus the sum of those products of elements in its row in the auxiliary matrix and corresponding elements in its column in the final matrix which involve only previously computed elements" (2).

Now suppose we follow the above steps in going from our auxiliary matrix to our final solution. Now the auxiliary matrix, in abbreviated form, is given as

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 \\ R_2C_1 & r_2c_2 & r_2c_3 \end{vmatrix} \qquad \text{(Matrix 12)}$$

Rule 1 says that the first constant we evaluate is B and the second constant we evaluate is A. Rule 2 says that B is numerically equal to the last element in the last column of the auxiliary matrix. Therefore, $B = r_2c_3$. Rule 3 then says that A is equal to the next to the last element in the last column of the auxiliary matrix (r_1c_3) minus the sum of those products of elements in its row in the auxiliary matrix and corresponding elements in the last column of our final results. Therefore, $A = r_1c_3 - r_1c_2 \cdot B$.

For curves of higher degree, the following formulas for evaluating coefficients are given along with formulas derived by me for evaluating the above-mentioned errors.

For a function of the kind

$$Y = A + Bx_1 + Cx_2 \qquad (19)$$

the method of the auxiliary matrix can be used for the solution of the set of normal equations. The normal equations are:

$$An + B\Sigma x_{1_i} + C\Sigma x_{2_i} = \Sigma Y_i \tag{19a}$$

$$A\Sigma x_{1_i} + B\Sigma x_{1_i}^2 + C\Sigma x_{1_i} x_{2_i} = \Sigma x_{1_i} Y_i \tag{19b}$$

$$A\Sigma x_{2_i} + B\Sigma x_{1_i} x_{2_i} + C\Sigma x_{2_i}^2 = \Sigma x_{2_i} Y_i \tag{19c}$$

Therefore, our coefficient matrix is of the form

$$\begin{vmatrix} n & \Sigma x_{1_i} & \Sigma x_{2_i} & \Sigma Y_i \\ \Sigma x_{1_i} & \Sigma x_{1_i}^2 & \Sigma x_{1_i} x_{2_i} & \Sigma x_{1_i} Y_i \\ \Sigma x_{2_i} & \Sigma x_{1_i} x_{2_i} & \Sigma x_{2_i}^2 & \Sigma x_{2_i} Y_i \end{vmatrix} \qquad \text{(Matrix 19d)}$$

or, if we use the symbolism R and C to represent the words row and column, respectively, we can abbreviate (Matrix 19d) as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 \end{vmatrix} \qquad \text{(Matrix 19e)}$$

and from the rules cited for obtaining the auxiliary matrix from the given coefficient matrix, we have as our auxiliary matrix[4/]

4/ The relations for obtaining each element of the auxiliary matrix from the given coefficient matrix for third and fourth order matrices, respectively, are given in the appendix of this report.

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 \end{vmatrix} \qquad \text{(Matrix 19f)}$$

and our final result is of the form

$$C = r_3c_4 \tag{19g}$$

$$B = r_2c_4 - r_2c_3C \tag{19h}$$

$$A = r_1c_4 - r_1c_3 \cdot C - r_1c_2 \cdot B \tag{19i}$$

The variance in a single Y_i is given as

$$S^2_{Y_i} = \frac{\Sigma(Y_{i\,obs} - Y_{i\,cal})^2}{n - 3} \tag{19j}$$

The error in our function, equation (19), can be evaluated from the expression (3)

$$S^2_Y = s^2_A + 2x_1s^2_{AB} + x^2_1s^2_B + 2x_1x_2s^2_{BC} + 2x_2s^2_{AC} + x^2_2s^2_C \tag{19k}$$

where

$$s^2_A = (r_3c_3/R_1C_1) \cdot s^2_C - (r_1c_3) \cdot s^2_{AC} - (r_1c_2) \cdot s^2_{AB} \tag{19m}$$

$$s^2_{AB} = -(r_1c_3) \cdot s^2_{BC} - (r_1c_2) \cdot s^2_B$$

$$s^2_{AC} = -(r_1c_3) \cdot s^2_C - (r_1c_2) \cdot s^2_{BC} \tag{19o}$$

$$s^2_B = (r_3c_3/r_2c_2) \cdot s^2_C - (r_2c_3) \cdot s^2_{BC} \tag{19p}$$

$$s^2_{BC} = -(r_2c_3) \cdot s^2_C \tag{19q}$$

$$s^2_C = S^2_{Y_i} (1/r_3c_3) \tag{19r}$$

For an equation of the form

$$Y = A + Bx_1 + Cx_2 + Dx_3 \tag{20}$$

our normal equations are

$$An + B\Sigma x_{1_i} + C\Sigma x_{2_i} + D\Sigma x_{3_i} = \Sigma Y_i \tag{20a}$$

$$A\Sigma x_{1_i} + B\Sigma x^2_{1_i} + C\Sigma x_{1_i}x_{2_i} + D\Sigma x_{1_i}x_{3_i} = \Sigma x_{1_i}Y_i \tag{20b}$$

$$A\Sigma x_{2_i} + B\Sigma x_{1_i}x_{2_i} + C\Sigma x^2_{2_i} + D\Sigma x_{2_i}x_{3_i} = \Sigma x_{2_i}Y_i \tag{20c}$$

$$A\Sigma x_{3_i} + B\Sigma x_{1_i}x_{3_i} + C\Sigma x_{2_i}x_{3_i} + D\Sigma x^2_{3_i} = \Sigma x_{3_i}Y_i \tag{20d}$$

Hence, our coefficient matrix is of the form

$$\begin{vmatrix} n & \Sigma x_{1_i} & \Sigma x_{2_i} & \Sigma x_{3_i} & \Sigma Y_i \\ \Sigma x_{1_i} & \Sigma x^2_{1_i} & \Sigma x_{1_i}x_{2_i} & \Sigma x_{1_i}x_{3_i} & \Sigma x_{1_i}Y_i \\ \Sigma x_{2_i} & \Sigma x_{1_i}x_{2_i} & \Sigma x^2_{2_i} & \Sigma x_{2_i}x_{3_i} & \Sigma x_{2_i}Y_i \\ \Sigma x_{3_i} & \Sigma x_{1_i}x_{3_i} & \Sigma x_{2_i}x_{3_i} & \Sigma x^2_{3_i} & \Sigma x_{3_i}Y_i \end{vmatrix} \quad \text{(Matrix 20e)}$$

We can write (Matrix 20e) in abbreviated form as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 & R_1C_5 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 & R_2C_5 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 & R_3C_5 \\ R_4C_1 & R_4C_2 & R_4C_3 & R_4C_4 & R_4C_5 \end{vmatrix} \qquad \text{(Matrix 20f)}$$

Proceeding from (Matrix 20f), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 & r_1c_5 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 & r_2c_5 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 & r_3c_5 \\ R_4C_1 & r_4c_2 & r_4c_3 & r_4c_4 & r_4c_5 \end{vmatrix} \qquad \text{(Matrix 20g)}$$

and our final result is of the form

$$D = r_4c_5 \tag{20h}$$

$$C = r_3c_5 - (r_3c_4) \cdot D \tag{20i}$$

$$B = r_2c_5 - (r_2c_4) \cdot D - (r_2c_3) \cdot C \tag{20j}$$

$$A = r_1c_5 - (r_1c_4) \cdot D - (r_1c_3) \cdot C - (r_1c_2) \cdot B \tag{20k}$$

The variance in our function, equation (20), can be determined from the expression (3)

$$s_Y^2 = \begin{aligned} & s_A^2 + 2x_1 s_{AB}^2 + 2x_2 s_{AC}^2 + 2x_3 s_{AD}^2 \\ & + x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + 2x_1 x_3 s_{BD}^2 \\ & + x_2^2 s_C^2 + 2x_2 x_3 s_{CD}^2 + x_3^2 s_D^2 \end{aligned} \tag{20m}$$

where

$$S_{Y_i}^2 = \frac{\Sigma(Y_{i_{obs}} - Y_{i_{cal}})^2}{n - 4} \tag{20n}$$

$$s_A^2 = (r_4 c_4 / R_1 C_1) \cdot s_D^2 - (r_1 c_4) \cdot s_{AD}^2 - (r_1 c_3) \cdot s_{AC}^2 - (r_1 c_2) \cdot s_{AB}^2 \tag{20o}$$

$$s_{AB}^2 = - (r_1 c_4) \cdot s_{BD}^2 - (r_1 c_3) \cdot s_{BC}^2 - (r_1 c_2) \cdot s_B^2 \tag{20p}$$

$$s_{AC}^2 = - (r_1 c_4) \cdot s_{CD}^2 - (r_1 c_3) \cdot s_C^2 - (r_1 c_2) \cdot s_{BC}^2 \tag{20q}$$

$$s_{AD}^2 = - (r_1 c_4) \cdot s_D^2 - (r_1 c_3) \cdot s_{CD}^2 - (r_1 c_2) \cdot s_{BD}^2 \tag{20r}$$

$$s_B^2 = (r_4 c_4 / r_2 c_2) \cdot s_D^2 - (r_2 c_4) \cdot s_{BD}^2 - (r_2 c_3) \cdot s_{BC}^2 \tag{20s}$$

$$s_{BC}^2 = - (r_2 c_4) \cdot s_{CD}^2 - (r_2 c_3) \cdot s_C^2 \tag{20t}$$

$$s_{BD}^2 = - (r_2 c_4) \cdot s_D^2 - (r_2 c_3) \cdot s_{CD}^2 \tag{20u}$$

$$s_C^2 = (r_4 c_4 / r_3 c_3) \cdot s_D^2 - (r_3 c_4) \cdot s_{CD}^2 \tag{20v}$$

$$s_{CD}^2 = - (r_3 c_4) \cdot s_D^2 \tag{20w}$$

$$s_D^2 = s_{Y_i}^2 \quad (1/r_4c_4) \qquad (20x)$$

Attention has been given to functions of the kind

$$Y = 1 + Bx_1 + Cx_2 \qquad (21)$$

and of higher degree and to the standard error associated with each coefficient. The normal equations for equation (21) are

$$B\Sigma x_{1_i}^2 + C\Sigma x_{1_i} x_{2_i} = (\Sigma x_{1_i} Y_i - \Sigma x_{1_i}) \qquad (21a)$$

$$B\Sigma x_{1_i} x_{2_i} + C\Sigma x_{2_i}^2 = (\Sigma x_{2_i} Y_i - \Sigma x_{2_i}) \qquad (21b)$$

and our coefficient matrix is of the form

$$\begin{vmatrix} \Sigma x_{1_i}^2 & \Sigma x_{1_i} x_{2_i} & (\Sigma x_{1_i} Y_{1_i} - \Sigma x_{1_i}) \\ \Sigma x_{1_i} x_{2_i} & \Sigma x_{2_i}^2 & (\Sigma x_{2_i} Y_i - \Sigma x_{2_i}) \end{vmatrix} \qquad \text{(Matrix 21c)}$$

Writing (Matrix 21c) in abbreviated form, we have

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 \\ R_2C_1 & R_2C_2 & R_2C_3 \end{vmatrix} \qquad \text{(Matrix 21d)}$$

as our given coefficient matrix. The auxiliary matrix is given by

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 \\ R_2C_1 & r_2c_2 & r_2c_3 \end{vmatrix} \qquad \text{(Matrix 21e)}$$

Thus, our final result is

$$C = r_2c_3 \tag{21f}$$

$$B = r_1c_3 - (r_1c_2) \cdot C \tag{21g}$$

The variance in our function, equation (21), is given by (3)

$$S_Y^2 = x_1^2 s_B^2 + 2x_1x_2 s_{BC}^2 + x_2^2 s_C^2 \tag{21h}$$

where

$$s_B^2 = (r_2c_2/R_1C_1) \cdot s_C^2 - (r_1c_2) \cdot s_{BC}^2 \tag{21i}$$

$$s_{BC}^2 = -(r_1c_2) \cdot s_C^2 \tag{21j}$$

$$s_C^2 = S_{Y_i}^2 \; (1/r_2c_2) \tag{21k}$$

and

$$S_{Y_i}^2 = \frac{\Sigma(Y_{i_{obs}} - Y_{i_{cal}})^2}{n - 2} \tag{21m}$$

For the function

$$Y = 1 + Bx_1 + Cx_2 + Dx_3 \tag{22}$$

our normal equations are

$$B\Sigma x_{1_i}^2 + C\Sigma x_{1_i}x_{2_i} + D\Sigma x_{1_i}x_{3_i} = (\Sigma x_{1_i}Y_i - \Sigma x_{1_i}) \tag{22a}$$

$$B\Sigma x_{1_i}x_{2_i} + C\Sigma x_{2_i}^2 + D\Sigma x_{2_i}x_{3_i} = (\Sigma x_{2_i}Y_i - \Sigma x_{2_i}) \tag{22b}$$

$$B\Sigma x_{1_i}x_{3_i} + C\Sigma x_{2_i}x_{3_i} + D\Sigma x_{3_i}^2 = (\Sigma x_{3_i}Y_i - \Sigma x_{3_i}) \tag{22c}$$

From equations (22a), (22b), and (22c), we can write our coefficient matrix as

$$\begin{vmatrix} \Sigma x_{1_i}^2 & \Sigma x_{1_i} x_{2_i} & \Sigma x_{1_i} x_{3_i} & (\Sigma x_{1_i} Y_i - \Sigma x_{1_i}) \\ \Sigma x_{1_i} x_{2_i} & \Sigma x_{2_i}^2 & \Sigma x_{2_i} x_{3_i} & (\Sigma x_{2_i} Y_i - \Sigma x_{2_i}) \\ \Sigma x_{1_i} x_{3_i} & \Sigma x_{2_i} x_{3_i} & \Sigma x_{3_i}^2 & (\Sigma x_{3_i} Y_i - \Sigma x_{3_i}) \end{vmatrix} \qquad \text{(Matrix 22d)}$$

In abbreviated form, (Matrix 22d) is given as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 \end{vmatrix} \qquad \text{(Matrix 22e)}$$

and from (Matrix 22e), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 \end{vmatrix} \qquad \text{(Matrix 22f)}$$

Hence, our final result is given to be

$$D = r_3c_4 \qquad \text{(22g)}$$

$$C = r_2c_4 - (r_2c_3) \cdot D \qquad \text{(22h)}$$

$$B = r_1c_4 - (r_1c_3) \cdot D - (r_1c_2) \cdot C \qquad \text{(22i)}$$

We can determine the error in our function, equation (22), from the expression (3)

$$S_Y^2 = x_1^2 s_B^2 + 2x_1x_2 s_{BC}^2 + 2x_1x_3 s_{BD}^2 + x_2^2 s_C^2 + 2x_2x_3 s_{CD}^2 + x_3^2 s_D^2 \qquad (22j)$$

where

$$s_B^2 = (r_3c_3/R_1C_1) \cdot s_D^2 - (r_1c_3) \cdot s_{BD}^2 - (r_1c_2) \cdot s_{BC}^2 \qquad (22k)$$

$$s_{BC}^2 = -(r_1c_3) \cdot s_{CD}^2 - (r_1c_2) \cdot s_C^2 \qquad (22m)$$

$$s_{BD}^2 = -(r_1c_3) \cdot s_D^2 - (r_1c_2) \cdot s_{CD}^2 \qquad (22n)$$

$$s_C^2 = (r_3c_3/r_2c_2) \cdot s_D^2 - (r_2c_3) \cdot s_{CD}^2 \qquad (22o)$$

$$s_{CD}^2 = -(r_2c_3) \cdot s_D^2 \qquad (22p)$$

$$s_D^2 = S_{Y_i}^2 \,(1/r_3c_3) \qquad (22q)$$

and

$$S_{Y_i}^2 = \frac{\Sigma(Y_{i\,obs} - Y_{i\,cal})^2}{n - 3} \qquad (22r)$$

Finally, for the function

$$Y = 1 + Bx_1 + Cx_2 + Dx_3 + Ex_4 \qquad (23)$$

we have the set of normal equations

$$B\Sigma x_{1_i}^2 + C\Sigma x_{1_i} x_{2_i} + D\Sigma x_{1_i} x_{3_i} + E\Sigma x_{1_i} x_{4_i} = (\Sigma x_{1_i} Y_i - \Sigma x_{1_i}) \qquad (23a)$$

$$B\Sigma x_{1_i} x_{2_i} + C\Sigma x_{2_i}^2 + D\Sigma x_{2_i} x_{3_i} + E\Sigma x_{2_i} x_{4_i} = (\Sigma x_{2_i} Y_i - \Sigma x_{2_i}) \tag{23b}$$

$$B\Sigma x_{1_i} x_{3_i} + C\Sigma x_{2_i} x_{3_i} + D\Sigma x_{3_i}^2 + E\Sigma x_{3_i} x_{4_i} = (\Sigma x_{3_i} Y_i - \Sigma x_{3_i}) \tag{23c}$$

$$B\Sigma x_{1_i} x_{4_i} + C\Sigma x_{2_i} x_{4_i} + D\Sigma x_{3_i} x_{4_i} + E\Sigma x_{4_i}^2 = (\Sigma x_{4_i} Y_i - \Sigma x_{4_i}) \tag{23d}$$

from which we can evaluate B, C, D, and E. Our given coefficient matrix, written in abbreviated form, is given as

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 & R_1C_5 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 & R_2C_5 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 & R_3C_5 \\ R_4C_1 & R_4C_2 & R_4C_3 & R_4C_4 & R_4C_5 \end{vmatrix} \qquad \text{(Matrix 23e)}$$

Proceeding from (Matrix 23e), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 & r_1c_5 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 & r_2c_5 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 & r_3c_5 \\ R_4C_1 & r_4c_2 & r_4c_3 & r_4c_4 & r_4c_5 \end{vmatrix} \qquad \text{(Matrix 23f)}$$

Hence, from our auxiliary matrix, (Matrix 23f), we have as our final result

$$E = r_4c_5 \tag{23g}$$

$$D = r_3c_5 - (r_3c_4) \cdot E \tag{23h}$$

$$C = r_2c_5 - (r_2c_4) \cdot E - (r_2c_3) \cdot D \tag{23i}$$

$$B = r_1c_5 - (r_1c_4) \cdot E - (r_1c_3) \cdot D - (r_1c_2) \cdot C \tag{23j}$$

The variance in our function, equation (23), can be determined from the equation (3)

$$\begin{aligned} S_Y^2 = & \; x_1^2 s_B^2 + 2x_1x_2s_{BC}^2 + 2x_1x_3s_{BD}^2 \\ & + 2x_1x_4s_{BE}^2 + x_2^2s_C^2 + 2x_2x_3s_{CD}^2 \\ & + 2x_2x_4s_{CE}^2 + x_3^2s_D^2 + 2x_3x_4s_{DE}^2 \\ & + x_4^2s_E^2 \end{aligned} \tag{23k}$$

where

$$s_B^2 = (r_4c_4/R_1C_1) \cdot s_E^2 - (r_1c_4) \cdot s_{BE}^2 - (r_1c_3) \cdot s_{BD}^2 - (r_1c_2) \cdot s_{BC}^2 \tag{23m}$$

$$s_{BC}^2 = - (r_1c_4) \cdot s_{CE}^2 - (r_1c_3) \cdot s_{CD}^2 - (r_1c_2) \cdot s_C^2 \tag{23n}$$

$$s_{BD}^2 = - (r_1c_4) \cdot s_{DE}^2 - (r_1c_3) \cdot s_D^2 - (r_1c_2) \cdot s_{CD}^2 \tag{23o}$$

$$s_{BE}^2 = - (r_1c_4) \cdot s_E^2 - (r_1c_3) \cdot s_{DE}^2 - (r_1c_2) \cdot s_{CE}^2 \tag{23p}$$

$$s_C^2 = (r_4c_4/r_2c_2) \cdot s_E^2 - (r_2c_4) \cdot s_{CE}^2 - (r_2c_3) \cdot s_{CD}^2 \tag{23q}$$

$$s_{CD}^2 = - (r_2c_4) \cdot s_{DE}^2 - (r_2c_3) \cdot s_D^2 \tag{23r}$$

$$s_{CE}^2 = - (r_2c_4) \cdot s_E^2 - (r_2c_3) \cdot s_{DE}^2 \tag{23s}$$

$$s_D^2 = (r_4c_4/r_3c_3) \cdot s_E^2 - (r_3c_4) \cdot s_{DE}^2 \tag{23t}$$

$$s_{DE}^2 = -(r_3c_4) \cdot s_D^2 \tag{23u}$$

$$s_E^2 = S_{Y_i}^2 \; (1/r_4c_4) \tag{23v}$$

and

$$S_{Y_i}^2 = \frac{\Sigma(Y_{i\,obs} - Y_{i\,cal})^2}{n - 4} \tag{23w}$$

CONCLUSIONS

The method of treating PVT data on gases consists of expressing the isothermal variation of the PV product of a gas in terms of a power series in either the pressure or the density and of evaluating so-called virial coefficients by least squares solution. This report gives a brief summary of the method of the auxiliary matrix, previously published by Crout, and its application to rational integral functions of one to four degrees, without going into any details of the mathematical background of statistics or into the various approaches to the problem of curve fitting.

Formulas for calculating the standard error in a single measurement, the standard error in each coefficient, and the standard error of the respective functions are given, without proof, and are presented on the basis of unit weight being given to each observed measurement.

APPENDIX

In evaluating the elements of the auxiliary matrix, it is most convenient to determine these elements in the following order: First, we evaluate all elements which lie in the first column of our auxiliary matrix. We then evaluate all elements which lie in the first row of our auxiliary matrix. Next we evaluate all elements in the second column and then all elements in the second row and so on until all elements of our auxiliary matrix are defined.

Now suppose we have a third order coefficient matrix of the form

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 \end{vmatrix} \qquad \text{(Matrix 19d)}$$

and a third order auxiliary matrix of the form

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 \end{vmatrix} \qquad \text{(Matrix 19e)}$$

From the rules given on page 10 of this report, the elements of our third order matrix, (Matrix 19e), can be determined from the following relations

$$r_1c_2 = R_1C_2 \div R_1C_1$$

$$r_1c_3 = R_1C_3 \div R_1C_1$$

$$r_3c_3 = R_3C_3 - R_3C_1 \bullet r_1c_3 - r_3c_2 \bullet r_2c_3$$

$$r_1c_4 = R_1C_4 \div R_1C_1$$

$$r_2c_2 = R_2C_2 - R_2C_1 \cdot r_1c_2$$

$$r_3c_2 = R_3C_2 - R_3C_1 \cdot r_1c_2$$

$$r_2c_3{}^{5/} = [R_2C_3 - R_2C_1 \cdot r_1c_3] \div r_2c_2$$

$$r_2c_4 = [R_2C_4 - R_2C_1 \cdot r_1c_4] \div r_2c_2$$

$$r_3c_4 = [R_3C_4 - R_3C_1 \cdot r_1c_4 - r_3c_2 \cdot r_2c_4] \div r_3c_3$$

It is to be noted that (Matrix 19e) and (Matrix 22f) are third order auxiliary matrices. Therefore, the elements of (Matrix 22f) are determined as outlined above.

Now suppose we have a fourth order coefficient of the form

$$\begin{vmatrix} R_1C_1 & R_1C_2 & R_1C_3 & R_1C_4 & R_1C_5 \\ R_2C_1 & R_2C_2 & R_2C_3 & R_2C_4 & R_2C_5 \\ R_3C_1 & R_3C_2 & R_3C_3 & R_3C_4 & R_3C_5 \\ R_4C_1 & R_4C_2 & R_4C_3 & R_4C_4 & R_4C_5 \end{vmatrix} \qquad \text{(Matrix 20f)}$$

and a fourth order auxiliary matrix of the form

5/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this particular element can be evaluated by dividing its symmetrically opposite element below the principal diagonal, r_3c_2, by the diagonal element which lies in the same row as r_2c_3. That is, $r_2c_3 = r_3c_2 \div r_2c_2$.

$$\begin{vmatrix} R_1C_1 & r_1c_2 & r_1c_3 & r_1c_4 & r_1c_5 \\ R_2C_1 & r_2c_2 & r_2c_3 & r_2c_4 & r_2c_5 \\ R_3C_1 & r_3c_2 & r_3c_3 & r_3c_4 & r_3c_5 \\ R_4C_1 & r_4c_2 & r_4c_3 & r_4c_4 & r_4c_5 \end{vmatrix} \quad \text{(Matrix 20g)}$$

Now we determine the elements of our auxiliary matrix in the same order as cited above — i.e., first column and then first row ; second column and then second row, and so on until all of the elements are defined.

Now from the rules given on page 10 of this report, we see that the elements of (Matrix 20g) can be evaluated from the following relations

$$r_1c_2 = R_1C_2 \div R_1C_1$$

$$r_1c_3 = R_1C_3 \div R_1C_1$$

$$r_1c_4 = R_1C_4 \div R_1C_1$$

$$r_1c_5 = R_1C_5 \div R_1C_1$$

$$r_2c_2 = R_2C_2 - R_2C_1 \cdot r_1c_2$$

$$r_3c_2 = R_3C_2 - R_3C_1 \cdot r_1c_2$$

$$r_4c_2 = R_4C_2 - R_4C_1 \cdot r_1c_2$$

$$r_2c_3\underline{^{6/}} = [R_2C_3 - R_2C_1 \cdot r_1c_3] \div r_2c_2$$

6/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this particular element can be evaluated by dividing its symmetrically opposite element below the principal diagonal, r_3c_2, by the diagonal element which lies in the same row as r_2c_3. That is, $r_2c_3 = r_3c_2 \div r_2c_2$.

$$r_2c_4^{7/} = [R_2C_4 - R_2C_1 \cdot r_1c_4] \div r_2c_2$$

$$r_2c_5 = [R_2C_5 - R_2C_1 \cdot r_1c_5] \div r_2c_2$$

$$r_3c_3 = R_3C_3 - R_3C_1 \cdot r_1c_3 - r_3c_2 \cdot r_2c_3$$

$$r_4c_3 = R_4C_3 - R_4C_1 \cdot r_1c_3 - r_4c_2 \cdot r_2c_3$$

$$r_3c_4^{8/} = [R_3C_4 - R_3C_1 \cdot r_1c_4 - r_3c_2 \cdot r_2c_4] \div r_3c_3$$

$$r_3c_5 = [R_3C_5 - R_3C_1 \cdot r_1c_5 - r_3c_2 \cdot r_2c_5] \div r_3c_3$$

$$r_4c_4 = R_4C_4 - R_4C_1 \cdot r_1c_4 - r_4c_2 \cdot r_2c_4 - r_4c_3 \cdot r_3c_4$$

$$r_4c_5 = [R_4C_5 - R_4C_1 \cdot r_1c_5 - r_4c_2 \cdot r_2c_5 - r_4c_3 \cdot r_3c_5] \div r_4c_4$$

It is to be noted that (Matrix 20g) and (Matrix 23f) are fourth order auxiliary matrices. Therefore, the elements of (Matrix 23f) are determined as outlined above.

7/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this element can be determined by dividing its symmetrically opposite element below the principal diagonal, r_4c_2, by the diagonal element which lies in the same row as r_2c_4. That is, $r_2c_4 = r_4c_2 \div r_2c_2$.

8/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this element can be determined by dividing its symmetrically opposite element below the principal diagonal, r_4c_3, by the diagonal element which lies in the same row as r_3c_4. That is, $r_3c_4 = r_4c_3 \div r_3c_3$.

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