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Statistical Analysis of Material Balance of a Chemical Reactor

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A method is suggested for a complex statistical treatment of the material balance of a chemical reactor, based on the stoichiometric characteristics of reactions taking place in the reactor. Statistically adjusted values of the balance variables are obtained, and the hypothesis that the material balance data do not contain gross errors is tested. The calculation procedure is demonstrated by an illustrative example of the material balance of a fermentation process.

SCOPE

When carrying out the measurements necessary for the material balance of chemical reactors, one obtains data that contain certain errors, so that the measured values need not always comply with the stoichiometry of reactions taking place in the reactor. In such a case we say that the material balance data are not consistent. A question then arises: May the inconsistency be attributed to small random errors of the measurements or to some other effects (such as gross measuring errors, unknown side products, and the like) (Nogita, 1972)?

A method is suggested for a complex statistical analysis of inconsistency of a material balance. The purpose is to detect the possible gross and systematic errors. In the absence of errors of these types, statistically adjusted consistent values of the balance variables are obtained on the basis of the maximum likelihood principle.

CONCLUSIONS AND SIGNIFICANCE

A method for a complex statistical treatment of the material balance of a chemical reactor has been developed, enabling us to identify data which might contain gross errors (measuring errors, effluxes of materials, occurrence of unknown side products, and the like). It has been applied to the material balance of a process for the manufacture of single-cell protein from ethanol.

The suggested procedure is simple and can be readily programmed for a computer. In addition to the common cases of material balances of laboratory as well as plant scale reactors, the method may be advantageously applied for data collection and for computerized control of a manufacturing process, where the finding of errors in the material balance may give evidence of the malfunction of the automatic measuring systems (wrong calibration and the like).

Experimental data relating to the material balance of a chemical reactor are subjected to errors, and generally they need not satisfy the laws controlling the stoichiometry of the chemical process taking place in the reactor. The most frequently encountered errors are, in part, those of the measurements proper (for example, measuring of flow rates, volumes, concentrations) and partly those that are due to erroneous assumptions upon the reactor function (for example, unexpected effluxes of materials, unsteady state operation). Besides, there are errors occurring in the case of more complex reactions, such as microbial processes. These errors are due to the fact that one does not know all the substances taking part in the chemical reactions involved or to incomplete knowledge of the elementary composition of these substances.

A number of studies dealing with the statistical treatment of material balances have appeared in the literature (Kuehn and Davidson, 1961; Nogita, 1972; Ripps, 1965). Some of them are devoted directly to material balance of a chemical reactor (Madron and Vaněček, 1977; Murthy, 1973, 1974; Václavek, 1969).

If the application of the suggested methods is to be warranted, several assumptions must be fulfilled. They concern the magnitude and kind of errors that are made when we carry out the material balance. It is difficult, however, to verify the validity of such assumptions in advance, and, in most cases, the most reliable way of solving a particular problem is a thorough statistical analysis of the obtained experimental data (Nogita, 1972).

This paper presents a procedure for a complex statistical treatment of the material balance of a chemical reactor.

FORMULATION OF THE PROBLEM

Let us consider a system of I species $s_1 \ldots, s_I$ taking part in a chemical reaction. The changes in the amounts of these species within the reactor are brought about by two types of processes: convection (or diffusion) and chemical reactions. The material balance for the i^{th} species may be written in the following form:

$$\begin{array}{lcl} \text{accumulation of} & & \text{increases in its} & & \text{increase in its} \\ \text{the species in} & = & \text{amount due to} & + & \text{amount due to} \\ \text{the reactor} & & \text{convection} & & \text{chemical conversion} \end{array} \qquad (1)$$

The balance of a species in the further considerations is to be understood as an experimental determination of the first two terms in Equation (1), so that the increments due to chemical reactions can be found on the basis of this equation.

Let J chemical reactions proceed among the species

$$\sum_{i=1}^{I} a_{ji}s_i = 0; \quad j = 1 \ldots\ldots, J \quad \text{or} \quad \mathbf{A} \cdot \mathbf{s} = \mathbf{0} \quad (2)$$

where a_{ji} is the stoichiometric coefficient of the i^{th} species in the j^{th} stoichiometric equation, $\mathbf{A}$ is the matrix $\{a_{ji}\}$, and $\mathbf{s}$ the vector of the species s_i.

The increase in the number of moles of a species due to a chemical conversion (n_i) then may be described by a system of equations

$$n_i = \sum_{j=1}^{J} a_{ji}x_j; \quad i = 1 \ldots\ldots, I \quad \text{or} \quad \mathbf{n} = \mathbf{A}^T \cdot \mathbf{x} \quad (3)$$

where $\mathbf{x}$ is the column vector of the extents of reactions corresponding to Equation (2).

The chemical conversion can be expressed by Equation (3) by means of the largest system of linearly independent reactions selected from Equation (2); it will be assumed that Equation (2) contains only linearly independent equations (Aris, 1965).

Equation (3) represents I linearly independent relations among $I + J$ quantities (n_i and x_j), and, consequently, there are J degrees of freedom in the system. Let us see how these degrees of freedom are used when the material balance is carried out. Assuming that the balance is made for r species $s_1 \ldots s_r$, that is, that quantities $n_1 \ldots n_r$ are measured, Equation (3) for the balanced species may be written

$$n_i = \sum_{j=1}^{J} a_{ji}x_j; \quad i = 1 \ldots, r \quad \text{or} \quad \mathbf{n}_r = \mathbf{A}_r^T \cdot \mathbf{x} \quad (4)$$

The following relations exist between the measured values of the variables (n_i^+) and their actual values (n_i):

$$n_i^+ = n_i + \epsilon_i; \quad i = 1, \ldots, r \quad \text{or} \quad \mathbf{n}_r^+ = \mathbf{n}_r + \boldsymbol{\varepsilon}_r \quad (5)$$

where ϵ_i are the measuring errors. Since these errors are, to a certain extent, of a random character, the values n_i^+ may be considered to be independent variables, and thus one degree of freedom is used by each of the balanced species. As $I > J$, a situation may arise that more degrees of freedom than available are exhausted, and Equation (3) is then not satisfied for any vector $\mathbf{x}$. In such a case, we state that the material balance data are not consistent with the assumed model of chemical conversion (3).

Next, we shall deal with the case when the material balance data are not consistent, and their selection and number are sufficient for determining the stoichiometry of the chemical conversion (that is, quantities $n_i \ldots n_I$) from the Equation (3).

These assumptions are satisfied if it holds at the same time that (Madron, 1975)

$$\rho(\mathbf{A}_r) = J \quad (6)$$

and

$$r > J \quad (7)$$

In the case when redundant measurements are available, it is possible to carry out a statistical analysis of inconsistency of the material balance. This makes it possible to decide whether the inconsistency of data can be attributed to known errors only, or whether there are certain additional factors such as gross errors of measurements, side reactions, and the like.

STATISTICAL TREATMENT OF MATERIAL BALANCE

Equation (4) represents a mathematical model of a chemical conversion whose parameters are the quantities $\mathbf{x}$. It may be also written as

$$\mathbf{n}_r^+ = \mathbf{A}_r^T \cdot \mathbf{x} + \boldsymbol{\varepsilon}_r \quad (8)$$

Let us assume that the unknown errors $\boldsymbol{\varepsilon}_r$ are random variables with r variate normal probability distribution with zero mean values and with covariance matrix $\mathbf{F}$; that is

$$E(\boldsymbol{\varepsilon}_r) = \mathbf{0} \quad (9)$$

$$\mathbf{F} = \text{Covar}\ (\boldsymbol{\varepsilon}_r) = E\ \{\boldsymbol{\varepsilon}_r\ \boldsymbol{\varepsilon}_r^T\} \quad (10)$$

The probability density function of r variate normal distribution of the quantities $\boldsymbol{\varepsilon}_r$ is

$$p(\boldsymbol{\varepsilon}_r \mid \mathbf{x}, \mathbf{F}) = k\ e^{-q/2} \quad (11)$$

where

$$k = (2\pi)^{-r/2} \det{}^{-1/2}\ \mathbf{F}$$

and

$$q = \boldsymbol{\varepsilon}_r^T \cdot \mathbf{F}^{-1} \cdot \boldsymbol{\varepsilon}_r$$

The likelihood function is then

$$L(\mathbf{x}|\mathbf{n}_r^+, \mathbf{F}, \mathbf{A}_r) = k \cdot \exp[-1/2(\mathbf{n}_r^+ - \mathbf{A}_r^T \cdot \mathbf{x})^T \cdot \mathbf{F}^{-1} \cdot (\mathbf{n}_r^+ - \mathbf{A}_r^T \cdot \mathbf{x})] \tag{12}$$

The maximum likelihood estimates of parameters **x** are parameters which satisfy the following condition:

$$(\mathbf{n}_r^+ - \mathbf{A}_r^T \cdot \mathbf{x})^T \cdot \mathbf{F}^{-1} \cdot (\mathbf{n}_r^+ - \mathbf{A}_r^T \cdot \mathbf{x}) = \min \tag{13}$$

The solution of this problem (Madron and Vaněček, 1977) is

$$\hat{\mathbf{x}} = (\mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{n}_r^+ \tag{14}$$

In this case it is assumed that the matrix $(\mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{A}_r^T)$ is regular. The sufficient conditions for regularity of this matrix are the validity of the previously accepted assumption $J = \rho(\mathbf{A}_r)$ and the positive-definite character of the matrix **F** (see Appendix).

Substituting $\hat{\mathbf{x}}$ into Equation (3), we get the vector of smoothed values $\hat{\mathbf{n}}$:

$$\hat{\mathbf{n}} = \mathbf{A}^T \cdot (\mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{n}_r^+ \tag{15}$$

The terms $\hat{\mathbf{n}}$ and $\hat{\mathbf{x}}$ are linear forms of random variables with normal distribution, and they themselves are random variables with normal distribution. It is possible to prove easily that

$$E(\hat{\mathbf{n}}) = \mathbf{n} \tag{16}$$

$$E(\hat{\mathbf{x}}) = \mathbf{x} \tag{17}$$

$$\mathbf{P} = \mathrm{Covar}\,(\hat{\mathbf{x}}) = E\,[(\hat{\mathbf{x}} - \mathbf{x}) \cdot (\hat{\mathbf{x}} - \mathbf{x})^T] = (\mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{A}_r^T)^{-1} \tag{18}$$

$$\mathbf{Q} = \mathrm{Covar}\,(\hat{\mathbf{n}}) = E\,[(\hat{\mathbf{n}} - \mathbf{n}) \cdot (\hat{\mathbf{n}} - \mathbf{n})^T] = \mathbf{A}^T \cdot (\mathbf{A}_r \cdot \mathbf{F}^{-1} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A} \tag{19}$$

Obviously

$$p_{jj} = \mathrm{Var}\,(\hat{x}_j) = \sigma^2_{\hat{x}j}$$

$$q_{ii} = \mathrm{Var}\,(\hat{n}_j) = \sigma^2_{\hat{n}i}$$

ANALYSIS OF INCONSISTENCY OF MATERIAL BALANCE

The actual errors $\boldsymbol{\varepsilon}_r$ are estimated by residuals $\mathbf{n}_r^+ - \hat{\mathbf{n}}_r$, that is

$$\hat{\boldsymbol{\varepsilon}}_r = \mathbf{n}_r^+ - \mathbf{n}_r = \mathbf{M}\mathbf{n}_r^+ \tag{20}$$

where

$$\mathbf{M} = \mathbf{I} - \mathbf{A}_r^T\,(\mathbf{A}_r\,\mathbf{F}^{-1}\,\mathbf{A}_r^T)^{-1}\mathbf{A}_r\,\mathbf{F}^{-1} \tag{21}$$

The analysis of inconsistency of material balance, which is represented by the vector $\hat{\boldsymbol{\varepsilon}}_r$, can be executed on the basis of the quadratic form $\psi_{\min}$ (13):

$$\psi_{\min} = \hat{\boldsymbol{\varepsilon}}_r^T\,\mathbf{F}^{-1}\,\hat{\boldsymbol{\varepsilon}}_r = \mathbf{n}_r^{+T}\mathbf{M}^T\mathbf{F}^{-1}\,\mathbf{M}\,\mathbf{n}_r^+ \tag{22}$$

$\psi_{\min}$ is a random variable with χ^2 probability distribution function with $r - J$ degrees of freedom $\chi^2(r - J)$. This assertion, however, holds true only if all the preliminarily accepted assumptions are satisfied:

1. All the species taking part in the chemical conversion are known.
2. No reaction proceeds among these species, whose stoichiometric equation would be linearly independent on Equation (2).
3. The obtained data are subjected only to random errors with r variate normal probability distribution with zero mean value.

The value of $\psi_{\min}$ enables us to draw conclusions as to how the above assumptions are met. The procedure is as follows.

Let us assume that all these conditions are satisfied. In this case we may expect that the random variable $\psi_{\min}$ will occur within the interval $<0;\ \chi^2_{1-\alpha}\,(r - J)>$ with probability $1 - \alpha$. When this condition is not met, the hypothesis concerning the validity of the accepted assumptions is rejected. Such a case may indicate the occurrence of uncontrolled effects in the material balance, for example, gross measuring errors, side reactions, and the like. In the opposite case, however, we may claim that, based upon the measured data, it is not possible to prove that the above assumptions are not satisfied.

MATERIAL BALANCE OF A CHEMICAL REACTOR

The discussed method of material balance analysis anticipates the normal distribution of random variables n_i^+ and the knowledge of the covariance matrix **F**.

Usually the quantities n_i are not measured directly. They are obtained by calculating from the directly measured so-called prime variables, for example, concentrations, flow rates, and the like. Let us assume that the prime variables are subjected to errors which are random variables with zero mean values with normal distribution and, further, the errors are statistically independent.

Now, let us deal with expressing of the covariance matrix **F** by means of variances of the measured prime variables. Two cases of expressing the variables n_i^+ will be considered. The values of n_i^+ in the material balance are frequently calculated from the relations

$$n_i^+ = \sum_k v_k^+\,c^+_{ki}; \quad i = 1, \ldots, r \tag{23}$$

where v_k^+ are the measured volumes (or flow rates) and c^+_{ki} concentrations of the i^{th} species in k^{th} volume (or stream).

The relations between the measured and actual values are

$$v_k^+ = v_k + \epsilon_{vk} \quad k = 1, \ldots, K \tag{24}$$

$$c^+_{ki} = c_{ki} + \epsilon_{cki} \quad k = 1, \ldots, K; \quad i = 1, \ldots, r \tag{25}$$

A combination of Equations (5), (23), (24), and (25) enables us to express the errors ϵ_i by means of prime variables errors

$$\epsilon_i = \sum_{k=1}^{K} (v_k\,\epsilon_{cki} + c_{ki}\,\epsilon_{vk} + \epsilon_{vk}\,\epsilon_{cki}) \tag{26}$$

It is then possible to prove readily that it holds

$$\mathrm{Var}(\epsilon_i) = f_{ii} = \sum_{k=1}^{K} (v_k^2\,\sigma^2_{cki} + c_{ki}\,\sigma^2_{vk} + \sigma^2_{vk}\,\sigma^2_{cki}) \tag{27}$$

$$\mathrm{Covar}\,(\epsilon_i, \epsilon_{i'}) = f_{ii'} = \sum_{k=1}^{K} c_{ki}c_{ki'}\,\sigma^2_{vk}$$

for $i \neq i'$.

Thus, expressed values of ϵ_i have their distribution close to normal. This is due to the fact that the greater part of ϵ_i values, as given by the sum of the first two terms of the right-hand side of Equation (26), is a linear function of independent random variables with normal distribution. An approximation of the distribution of ϵ_i values by normal distribution will be better the smaller are the errors ϵ_{vk} and ϵ_{cki} when compared with the true values v_k and c_{ki}.

A more general case is the expression of $\mathbf{n}_r^+$ by the relations

$$n_i^+ = f_i\,(\mathbf{t}^+), \quad i = 1, \ldots, r \tag{28}$$

where $\mathbf{t}^+$ is the vector of measured prime variables, and f_i are generally nonlinear functions of quantities $\mathbf{t}^+$. A method for an approximate calculation of the matrix **F** from the variances of quantities $\mathbf{t}^+$ has been suggested by Box (1970). The method consists of linearizing the functions f_i according to prime variables. It is then possible to approximate ϵ_i by the expressions

$$\epsilon_i = \sum_k \left(\frac{\partial f_i}{\partial t_k^+}\right) \epsilon_{tk} = \sum_k b_{ik}\, \epsilon_{tk}; \quad i = 1, \ldots, r \tag{29}$$

where

$$b_{ik} = \left(\frac{\partial f_i}{\partial t_k^+}\right)$$

and ϵ_{tk} are the prime variables errors.

Then, it holds for the covariance matrix **F** that

$$\mathbf{F} = \mathbf{B} \cdot \mathbf{F}' \cdot \mathbf{B}^T \tag{30}$$

where $\mathbf{F}'$ is the diagonal matrix of variances of the prime variables.

The results obtained by this method will be better the more justified is the linearization according to Equation (29).

It is necessary to state that in most cases neither the variances of the prime variables nor their actual values, appearing in Equations (27) and (30), are known. They are, therefore, replaced by estimates of these values, for example, by sample variances in the case of variances and by measured values in the case of actual values of prime variables.

EXAMPLE: MATERIAL BALANCE OF FERMENTATION

Let us consider the balance of a reactor, in which biomass is formed from ethanol (Madron, 1975). It has been established by previous studies that essentially, eight species are taking part in the process of fermentation: biomass (general formula: $C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00}$, where Ah is a fictive element representing the inorganic component of the biomass), ethanol, acetic acid, oxygen, carbon dioxide, ammonia, water, and mineral nutrients (also designated as Ah).

The biomass formation can be described by three linearly independent stoichiometric equations:

Synthesis of biomass

$$1.917\ \mathrm{C_2H_5OH} + 1.618\ \mathrm{O_2} + 0.643\ \mathrm{NH_3} + 7\,Ah \rightarrow C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00} + 3.214\ \mathrm{H_2O} \tag{31}$$

Oxidation of ethanol

$$\mathrm{C_2H_5OH} + 3\mathrm{O_2} \rightarrow 2\mathrm{CO_2} + 3\mathrm{H_2O}$$

Formation of by-product acetic acid

$$\mathrm{C_2H_5OH} + \mathrm{O_2} \rightarrow \mathrm{CH_3COOH} + \mathrm{H_2O}$$

Other reactions need not be considered, since the three above reactions represent the largest possible linearly independent system for the given set of substances (Madron, 1975). The corresponding matrix of stoichiometric coefficients is

$$\mathbf{A} = \begin{bmatrix} 1 & -1.917 & 0 & -1.618 & 0 & -0.643 & 3.214 & -7 \\ 0 & -1 & 0 & -3 & 2 & 0 & 3 & 0 \\ 0 & -1 & 1 & -1 & 0 & 0 & 1 & 0 \end{bmatrix}$$

The description of the process of fermentation by Equation (31) is only approximate, and it is appropriate to verify whether this model is adequate to the description of the microbial conversion under consideration.

Five species were balanced, that is, the biomass, ethanol, acetic acid, oxygen, and carbon dioxide. This system contains two more species then necessarily needed for the determination of stoichiometry. It is, therefore, possible to carry out the analysis of inconsistency of the material balance $[J = 3,\ r = 5,\ \rho(\mathbf{A}_r) = 3]$.

The following relations, enabling us to compute the values of n_i^+ from the prime variables t_k^+, were established on the basis of the fermentor material balance:

$$\begin{aligned} n_1^+ &= t_2^+ t_4^+ / 100 \\ n_2^+ &= -\,t_1^+ t_3^+ / 46 \\ n_3^+ &= t_2^+ t_5^+ / 60 \\ n_4^+ &= A(t_{12}^+ B - 20.87) \\ n_5^+ &= A(t_{11}^+ B - 0.03) \end{aligned} \tag{32}$$

where

$$A = (t_6^+ - t_7^+ t_8^+) t_9^+ / (831.4\, t_{10}^+)$$

$$B = 79.1 / (100 - t_{11}^+ - t_{12}^+)$$

According to the adopted system of notation, for example, the symbol t_4^+ represents the biomass concentration in the liquid stream leaving the fermentor, t_7^+ stands for the temperature of air entering the fermentor and the like. The vector $\mathbf{t}^+$ was measured:

$$\mathbf{t}^+ = (3.285;\ 3.241;\ 15.25;\ 10.8;\ 0.06;\ 99\,400;\ 298;\ 0.8;\ 0.83;\ 297;\ 2.48;\ 16.03)^T$$

The corresponding vector of standard deviations was

$$\boldsymbol{\sigma}_t = (0.008;\ 0.016;\ 0.08;\ 0.16;\ 0.0006;\ 100;\ 0.5;\ 0.1;\ 0.002;\ 0.5;\ 0.12;\ 0.25)^T$$

The vector $\mathbf{n}_r^+$ was then calculated from (32):

$$\mathbf{n}_r^+ = (0.3500;\ -1.0890;\ 0.0032;\ -1.7712;\ 0.7857)^T$$

with the covariance matrix

$$\mathbf{F} = \begin{bmatrix} 2.99 \times 10^{-5} & 0 & 2.77 \times 10^{-8} & 0 & 0 \\ 0 & 3.97 \times 10^{-5} & 0 & 0 & 0 \\ 2.77 \times 10^{-8} & 0 & 1.31 \times 10^{-9} & 0 & 0 \\ 0 & 0 & 0 & 9.60 \times 10^{-3} & 5.30 \times 10^{-4} \\ 0 & 0 & 0 & 5.30 \times 10^{-4} & 1.61 \times 10^{-3} \end{bmatrix}$$

Substitution into Equations (14) and (15) yielded

$$\hat{\mathbf{x}} = (0.3527;\ 0.4076;\ 0.0032)^T$$

$$\hat{\mathbf{n}} = (0.3527;\ -1.0870;\ 0.0032;\ -1.7968;$$

$$0.8152; -0.2268; 2.3598; -2.4691)^T$$

The variances of adjusted variables $\hat{\mathbf{n}}$ (diagonal of matrix $\mathbf{Q}$) were

$$\boldsymbol{\sigma}_n^2 = (2.2 \times 10^{-5}; 3.6 \times 10^{-5}; 1.3 \times 10^{-9}; 5.8 \times 10^{-4};$$
$$3.9 \times 10^{-4}; 9.4 \times 10^{-6}; 3.8 \times 10^{-4}; 1.1 \times 10^{-3})^T$$

A comparison of these data with the diagonal of matrix $\mathbf{F}$ shows that the adjusted values are more accurate than the measured ones.

Finally, the value of the term $\psi_{\min} = 1.019$ was calculated. In the case that the selected confidence level is 95%, $\chi^2_{0.95}(2) = 5.991$. At the confidence level 95%, the model of stoichiometry of the fermentation process as described by Equations (3) and (31) is adequate (that is, no statistically significant product of fermentation was omitted), and the measured data do not contain gross errors.

NOTATION

$\mathbf{A}$ = $J \times I$ matrix of stoichiometric coefficients
a_{ji} = element in the matrix $\mathbf{A}$
$\mathbf{B}$ = $I \times K'$ matrix of partial derivatives used in Equation (30)
b_{ik} = element in the matrix $\mathbf{B}$
c_{ki} = concentration of i^{th} species in k^{th} volume (stream)
Covar = covariance
Det = determinant
$E()$ = expectation
$\mathbf{F}$ = $r \times r$ covariance matrix of $\boldsymbol{\varepsilon}$
$f_{ii'}$ = element in matrix $\mathbf{F}$
$\mathbf{I}$ = identity matrix
I = number of species
J = number of reactions
K = number of streams
K' = number of measured prime variables
$\mathbf{M}$ = $r \times r$ matrix defined by Equation (21)
$\mathbf{n}$ = column vector of number of moles produced by chemical reactions
n_i = element of vector $\mathbf{n}$
$\mathbf{P}$ = $J \times J$ covariance matrix of $\hat{\mathbf{x}}$
$P_{jj'}$ = element in matrix $\mathbf{P}$
$\mathbf{Q}$ = $I \times I$ covariance matrix of $\hat{\mathbf{n}}$
$q_{ii'}$ = element in matrix $\mathbf{Q}$
r = number of the balanced species
$\mathbf{s}$ = column vector of species
s_i = element of vector $\mathbf{s}$
$\mathbf{t}$ = column vector of prime variables
t_k = element in vector $\mathbf{t}$
u = standardized normal random variable
Var = variance
v_k = molar flow rate of k^{th} stream
$\mathbf{x}$ = column vector of extents of reactions
x_i = element of vector $\mathbf{x}$
$\mathbf{O}$ = column null vector

Greek Letters

$\boldsymbol{\varepsilon}$ = column vector of errors
$\hat{\boldsymbol{\varepsilon}}$ = column vector of residuals
$\rho()$ = rank of matrix
σ = standard deviation of random variable
$\chi^2(r - J)$ = chi square random variable with $(r - J)$ degrees of freedom
$\chi^2_{1-\alpha}(r - J)$ = chi square for a significance level of $1 - \alpha$
$\psi_{\min}$ = quadratic form defined in Equation (22)

Subscripts

i = i^{th} species
j = j^{th} equation
k = k^{th} stream or prime variable
r = vector or matrix concerning balanced species

Other

$\mathbf{n}^+$ = measured value of $\mathbf{n}$
$\hat{\mathbf{n}}$ = estimated value of $\mathbf{n}$
$\mathbf{A}^T$ = transposed matrix $\mathbf{A}$
$\mathbf{F}^{-1}$ = inverse of matrix $\mathbf{F}$

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APPENDIX: REGULARITY OF MATRIX $\mathbf{A}_r\mathbf{F}^{-1}\mathbf{A}_r^T$

Let us consider r random variables $\epsilon_1, \ldots., \epsilon_r$ and r arbitrary scalars $x_1 \ldots., x_r$. Then

$$(x_1\epsilon_1 + \ldots + x_r\epsilon_r)^2 = \sum_{i=1}^{r}\sum_{i'=1}^{r} x_i x_{i'}\ \epsilon_i\epsilon_{i'} \geq 0$$

It holds for the mean value that

$$E(x_1\epsilon_1 + \ldots + x_r\epsilon_r)^2 = \sum_{i=1}^{r}\sum_{i'=1}^{r} x_i x_{i'}\ E(\epsilon_i\epsilon_{i'}) \geq 0$$

The quadratic form $q(\mathbf{x}) = \mathbf{x}^T\mathbf{F}\,\mathbf{x}$, where $\mathbf{F} = E(\epsilon_i\,\epsilon_{i'})$, is then generally positive semidefinite. Except for cases when ϵ_i are algebraically dependent (that is, when it holds identically that $a_1\epsilon_1 + \ldots + a_r\epsilon_r = 0$ for a nonnull vector $\mathbf{a}$), the quadratic form $q(\mathbf{x})$ is positive definite. It can be proved readily that the same is true also for $q(\mathbf{x}) = \mathbf{x}^T\mathbf{F}^{-1}\mathbf{x}$.

Let us further consider the matrix $\mathbf{A}_r\mathbf{F}^{-1}\mathbf{A}_r^T = \mathbf{C}$, where $\mathbf{F}^{-1}$ is positive definite, and the rank of matrix $\mathbf{A}_r$ is J. If it is true for the quadratic form

$$q(\mathbf{x}) = \mathbf{x}^T\mathbf{C}\mathbf{x} = (\mathbf{A}_r^T\mathbf{x})^T\,\mathbf{F}^{-1}(\mathbf{A}_r^T\,\mathbf{x}) = 0,$$

it follows from the positive definite character of $\mathbf{F}^{-1}$ that also $\mathbf{A}_r^T\,\mathbf{x} = \mathbf{0}$. Since $\rho(\mathbf{A}_r) = J$, such a case is possible only when $\mathbf{x} = \mathbf{0}$; consequently, $\mathbf{C}$ is positive definite and thus regular.

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