

STATISTICAL ADJUSTMENT OF MATERIAL BALANCE OF A CHEMICAL REACTOR

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Received November 27th, 1975

The material balance of a chemical reactor is adjusted statistically by a newly proposed method based on stoichiometric properties of a system of reactions taking place in the reactor. Uncomplete balancing is considered in which not all reacting compounds are balanced. The method is simple and easy for programming on the computer. The procedure is illustrated by a simple example.

In balancing of chemical reactors individual measurements are affected by experimental and other errors so that the material balance could be in contradiction with the laws governing stoichiometry of chemical reactions taking place in the system¹. Recently, methods have been developed which enable statistical treatment of balance data of chemical reactors²⁻⁵. Here a new method of smoothing of the material balance is proposed based on stoichiometric properties of reactions taking place in the chemical reactor.

THEORETICAL

Let us consider the system of I compounds A_1, \dots, A_I taking part in the chemical reactions. Amounts of these components in the reactor are changing in two ways: by convection (or diffusion) and by chemical reactions. The material balance of the i -th compound can be written as

$$\begin{array}{l} \text{accumulation of compound} \\ \text{in the reactor} \end{array} = \begin{array}{l} \text{increment due to} \\ \text{convection} \end{array} + \begin{array}{l} \text{increment due to} \\ \text{chem. reactions} \end{array} \quad (1)$$

Under balancing of the i -th compound is further on considered the experimental determination of the first two terms in Eq. (1) so that from this equation the increments resulting from the chemical reactions can be calculated. Let between the compounds A_i J chemical reactions take place then

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

where a_{ji} is the stoichiometric coefficient of the i -th compound in the j -th reaction, \mathbf{A} is the matrix $\{a_{ji}\}$ and \mathbf{A} is the vector of compounds A_i . We assume that the law of conservation of elements is in Eqs (2) preserved during the reaction.

The increase in the number of mol of the compound due to chemical reactions can be expressed by the system (2). As long as the system (1) is in the differential form, the increment can be expressed by use of reaction rates corresponding to the system (2). Extents of individual reactions for the material balance of the reactor written for a longer time interval appear in the considered terms. For the last case, which is in the material balance most frequent, the increments of number of moles resulting from the chemical reactions (n_i) can be expressed by the system (3)

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

where \mathbf{X} is the vector of extents of chemical reactions corresponding to the system (2).

It is important that the chemical conversion can be expressed by the system (3) by use of the largest system of linearly independent reactions selected from the system¹ (2). Therefore it will be assumed further on that the system (2) includes only linearly independent equations.

Let us assume that in total r compounds have been balanced. Without any effect on generality we can assume that they are compounds A_1, \dots, A_r . For balanced compounds, the system (3) can be written in the form

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

where \mathbf{n}_r and \mathbf{A}_r^T have originated from \mathbf{n} and \mathbf{A}^T by eliminating the terms or rows corresponding to the non-balanced compounds A_{r+1}, \dots, A_I . The system (4) holds for actual values of quantities n_i . Let us denote the measured values n_i^+ . The actual and experimental values are related by the relation

$$n_i = n_i^+ - \varepsilon_i; \quad i = 1, \dots, r, \quad (5)$$

where ε_i are errors. If we substitute the values n_i^+ into (4) it does not need to hold any more *i.e.* the vector \mathbf{X} which would be the solution of the system (4) does not need to exist. The experimental data are in this case considered to be inconsistent with the proposed model of the chemical conversion (3).

Let us now consider the following case when: 1) The data are not consistent (and adjustment of data has a sense only in such case); 2) Information included in the data suffices for identification of \mathbf{X} from the system (4) (*e.g.* a system forms by dropping off the suitable equations which is uniquely solvable with respect to \mathbf{X}). It can be proved^{6,7} that the above given assumptions are valid only when the rank of matrix $\mathbf{A}_r - \varrho(\mathbf{A}_r) = J$ and simultaneously when $r > J$.

New Method of Smoothing the Data

The basic idea of the proposed data adjustment method is the assumption that the material balance of the reactor can be always expressed by the system (3) and thus the vector \mathbf{X} defined by the system (4) must exist.

Let us look for smoothed values n'_r which would satisfy the conditions of solvability of the system (4). Let us also assume that the data are affected only by random errors and let us require from n'_r that the values n_r^+ differ from it as little as possible. A quite general characteristics of closeness of experimental and smoothed data is given by Box and Draper⁸ which is given by Eq. (7).

Let us require that simultaneously hold the relations

$$n'_r = \mathbf{A}_r^T \cdot \mathbf{X} \quad (6)$$

and

$$\sum_{i=1}^r \sum_{k=1}^r w_{ik} (n'_i - n_i^+) (n'_k - n_k^+) = \min. \quad (7)$$

It is assumed that the matrix $\mathbf{W} = \{w_{ik}\}$ is symmetrical. The statistical significance of coefficients w_{ik} can be found in the above mentioned study⁸. In the case when \mathbf{W} is diagonal, relation (7) is simplified to the usual weighed sum of squared deviations where w_{ii} are statistical weights corresponding to individual quantities n_i^+ .

So the minimum of the relation (7) is being looked for with the conditions of Eq. (6) satisfied. Solution of this problem results in the relation (8)

$$n'_r = \mathbf{A}_r^T \cdot (\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{W} \cdot n_r^+ \quad (8)$$

Derivation of this relation is demonstrated in the appendix. The inversion of the matrix $(\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)$ is to be performed, the matrix must be regular. The necessary condition for regularity of this matrix is the already mentioned assumption $\varrho(\mathbf{A}_r) = J$.

It remains to mention that, as an additional product of adjustment, the smoothed vector of extents of chemical reactions is obtained

$$\mathbf{X} = (\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{W} \cdot n_r^+ \quad (9)$$

By substitution for \mathbf{X} into (3) the smoothed values are obtained not only for the balanced but also for the non-balanced compounds

$$n' = \mathbf{A}^T \cdot (\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{W} \cdot n_r^+ \quad (10)$$

DISCUSSION

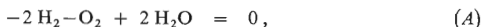
The proposed method enables an easy and quick smoothing of the material balance of the chemical reactor on the basis of relation (8). Greatest doubts experimentally difficult to overcome concern the assumption that no reaction takes place between the compounds whose stoichiometric equation would be linearly independent of the system (2). Substantial is that the number of linearly independent equations is considerably limited in the given system of compounds. The maximum number of linearly independent reactions in the given system of compounds was in detail studied by Whitwell and Dartt⁹. Actually, this upper boundary does not need to be reached. The method of experimental determination of the largest system of linearly independent reactions which actually take place among the compounds are given by Aris and Mah¹⁰.

The data smoothed according to relation (8) are obviously satisfying the condition of conservation of elements during the chemical reaction. This results from the fact that also individual reactions in the system (2) have this property. But the reversed statement does not hold. The system (2) can supply more information on stoichiometry of chemical changes than the simple balance of chemical elements. Though from another point of view this question has been in detail studied by Schneider and Reklaitis¹¹. Only in case when the system (2) is the largest possible system of linearly independent reactions in the given system of compounds, the proposed method as well as methods based on conservation of elements during the reaction^{2,3} are equivalent. If information are lacking on the system (2) the smoothing can be performed by use of the maximum system of linearly independent reactions in the given system of compounds. There has been published a number of methods for determination of such a system^{6,9}. But it is necessary to realize that so obtained results can be worse than those obtained by smoothing on basis of the system (2).

The method of smoothing which is proposed here is related to earlier studies on the smoothing of material balance of the chemical reactor²⁻⁵. The principles in which this study differs from the previous ones are: The non-complete balancing is studied systematically, no assumption is made on the type of the balanced reactor, more general criterion of the agreement of experimental and smoothed values (7) is considered which can form the basis for a detailed statistical analysis of the material balance; solution of the problem of smoothing in the form of relation (8) is more compact and simpler than in the up-to-now used methods; at the time when sub-routines for the matrix operations are a part of the software even of small computers the computation procedure according to relation (8) is very easy for programming on the computer.

Example: A reactor is balanced in which hydrogen reacts with oxygen to form water. Hydrogen and oxygen are balanced and the following data are obtained $n_1^+ = n_{H_2}^+ = -7$ mol; $n_2^+ = n_{O_2}^+ = -3$ mol. A single stoichiometric equation can be

written between the both reactants entering the reaction



while any other must be linearly dependent on (A). Then $\mathbf{A} = (-2, -1, 2)$, $\mathbf{A}_r = (-2, -1)$, $J = 1$, $\rho(\mathbf{A}_r) = 1$, $r = 2$. The smoothing can be made according to relations (8) or (10). For simplicity, let us assume $w_{11} = w_{22} = 1$ and $w_{12} = w_{21} = 0$. The matrix \mathbf{W} is then a unit matrix and after substitution into (10) we have

$$\mathbf{n}' = \begin{pmatrix} -2 \\ -1 \\ 2 \end{pmatrix} \cdot \left((-2, -1) \cdot \begin{pmatrix} -2 \\ -1 \end{pmatrix} \right)^{-1} \cdot (-2, -1) \cdot \begin{pmatrix} -7 \\ -3 \end{pmatrix} = \begin{pmatrix} -6.8 \\ -3.4 \\ 6.8 \end{pmatrix}$$

The smoothed values are thus: $n'_1 = n'_{\text{H}_2} = -6.8$ mol; $n'_2 = n'_{\text{O}_2} = -3.4$ mol
 $n'_3 = n'_{\text{H}_2\text{O}} = 6.8$ mol.

LIST OF SYMBOLS

- a* stoichiometric coefficient
- A* compound
- \mathbf{A} vector of compounds
- \mathbf{A} matrix of stoichiometric coefficients
- I* number of compounds
- J* number of reactions
- n* increment of number of mol of compound due to chemical reactions
- n* vector of quantities *n*
- r* number of balanced components
- X* extent of reaction
- \mathbf{X} vector of extents of reactions
- w* coefficient in Eq. (7)
- \mathbf{W} matrix of coefficients *w*
- ρ rank of matrix
- $\mathbf{0}$ null vector

Subscripts

- i* related to the *i*-th compound
- j* related to the *j*-th reaction
- k* related to the *k*-th compound
- r* vector or matrix concerning the balanced compounds

Superscripts

- ± experimental value
- ' smoothed value
- T transposed matrix

APPENDIX

Derivation of relation (8). Abbreviated writing of summations is used. For summation over i or k , the summation is performed from 1 to r , over j , from 1 to J .

Equation (6) written for individual components is

$$n_i' = \sum_j a_{ji} X_j \quad i = 1, \dots, r \quad (D-1)$$

n_i' can be substituted into (7)

$$\psi(\mathbf{X}) = \sum_i \sum_k w_{ik} \left(\sum_j a_{ji} X_j - n_j^+ \right) \left(\sum_j a_{jk} X_j - n_k^+ \right). \quad (D-2)$$

The necessary condition for the existence of minimum of function (D-2) is the zero value of partial derivatives according to individual X_j .

$$\frac{\partial \psi}{\partial X_s} = \sum_i \sum_k w_{ik} \left[a_{si} \left(\sum_j X_j a_{jk} - n_k^+ \right) + a_{sk} \left(\sum_j X_j a_{ji} - n_i^+ \right) \right] = 0; \quad s = 1, \dots, J. \quad (D-3)$$

After rewriting Eq. (D-3) and after arrangement of summations the system of normal equations (D-4) is obtained

$$\begin{aligned} & \sum_j X_j \sum_i \sum_k (w_{ik} a_{si} a_{jk} + w_{ik} a_{sk} a_{ji}) = \\ & = \sum_i \sum_k w_{ik} (a_{si} n_k^+ + a_{sk} n_i^+); \quad s = 1, \dots, J. \end{aligned} \quad (D-4)$$

It can be easily proved that this system of normal equations can be written for symmetrical \mathbf{W} in the matrix form as

$$(\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T) \cdot \mathbf{X} = \mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{n}_r^+ \quad (D-5)$$

The system (D-5) can be solved with respect to \mathbf{X} e.g. by multiplication from the left side by the inverse matrix to $(\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)$

$$\mathbf{X} = (\mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{A}_r^T)^{-1} \cdot \mathbf{A}_r \cdot \mathbf{W} \cdot \mathbf{n}_r^+ \quad (D-6)$$

By substitution of \mathbf{X} into Eq. (6) the relation (8) is obtained.

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Translated by M. Rylek.