Failure of the Element-by-Species Method to Calculate the Number of Independent Reactions

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In a recent paper Whitwell and Dartt (1973) discussed the concept of independent reactions in the presence of isomers. They showed that the method of finding the number of independent reactions by use of the standard rank-determining method (Amundson, 1966) might fail in the presence of isomers. This is important in process design since the accurate number of independent reactions is required in order to calculate the degree of freedom of the process. The purpose of the present note is to show that the standard rank-determining method might also fail without any isomers at all. A formula will also be presented, which can be used in the general case to calculate the number of independent reactions.

The failure of the above-mentioned method is best shown by means of an example. Consider the liquid-phase oxidation of propane by means of molecular oxygen as described by Bulygin et al. (1972). In this reaction the products are acetone, isopropanol acetic acid, acetaldehyde, methanol, carbon dioxide, formic acid, and water. The element-by-species matrix has the rank $R = 3$ in this case. Since the number of species $NSP = 10$, the standard rank method indicates that the number of independent reactions would be equal to $10 - 3 = 7$. Such a set of reactions would be the following:

$$C_3H_8 + O_2 \rightarrow (CH_3)_2CO + H_2O \tag{1}$$

$$C_3H_8 + \tfrac{1}{2}O_2 \rightarrow C_3H_7OH \tag{2}$$

$$C_3H_8 + O_2 \rightarrow CH_3CHO + CH_3OH \tag{3}$$

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH \tag{4}$$

$$CH_3OH + 1\tfrac{1}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{5}$$

$$CH_3OH + O_2 \rightarrow HCOOH + H_2O \tag{6}$$

$$2C_3H_8 + 2\tfrac{1}{2}O_2 \rightarrow 3CH_3CHO + 2H_2O \tag{7}$$

According to these reactions the following equations are obtained for the changes of the numbers of moles for acetaldehyde, acetic acid, methanol, carbon dioxide, and formic acid:

$$\Delta N_{al} = x_3 + 3x_7 - x_4 \tag{8}$$

$$\Delta N_{ac} = x_4 \tag{9}$$

$$\Delta N_m = x_3 - x_5 - x_6 \tag{10}$$

$$\Delta N_c = x_5 \tag{11}$$

$$\Delta N_f = x_6 \tag{12}$$

where ΔN_{al}, ΔN_{ac}, etc. refer to changes of the number of moles of acetaldehyde, acetic acid, methanol, carbon dioxide, and formic acid, x_1, x_2, etc. refer to the molar extents of reaction 1, 2, etc.

Bulygin et al. showed experimentally that the total formation of products with two carbon atoms is equal to the total formation of products with one carbon atom. (This is explained as due to the splitting of a radical, participating in the reaction mechanism, into two parts, one giving products with two carbon atoms, the other products with one carbon atom.) This means that the following equation is satisfied:

$$\Delta N_{al} + \Delta N_{ac} = \Delta N_m + \Delta N_c + \Delta N_f \tag{13}$$

By inserting Equations (8) to (12) into (13), it is found that

$$x_7 = 0$$

Thus reaction (7) does not work, but in this system there are only 6 independent reactions going on.

The failure of the rank method to calculate the number of independent reactions in the above example obviously is connected with the Equation (13). This is a linear combination of ΔN-values which is equal to zero.

As shown by Aris (1963) the number of linear combinations in ΔN-values, which remain equal to zero during a reaction, can be calculated from the number of independent reactions and equals

$$NSP - NRX$$

where NRX is the number of independent reactions.

Now the material balances over the elements obviously define R such independent linear combinations. Therefore, the total number of linear combinations equals

$$NLCE + R = NSP - NRX \tag{14}$$

where $NLCE$ refers to the number of independent linear combinations in excess over those derived from the material balances over the elements. Thus the number of independent reactions can be calculated

$$NRX = NSP - R - NLCE \tag{15}$$

In the example above Equation (13) constitutes one linear combination, which cannot be obtained from the material balances over the elements. Therefore $NLCE = 1$ and Equation (15) gives the right result.

Equation (15) is valid also in the presence of isomers provided NSP is calculated in the way proposed by Whitwell and Dartt. It might be said that this equation should not be applicable in the presence of class b isomers (see Whitwell's and Dartt's classification of isomers) when isomeric forms react in parallel forming new isomeric forms and the relative proportions between the new forms are the same as between the ultimate forms. However, in this case the value of $NLCE$ will be influenced such that the right number of independent reactions is obtained from Equation (15). The following example on sulfonation of cresols, given by Whitwell and Dartt, will illustrate this and also how to determine $NLCE$:

In the sulfonation of a mixture of ortho- and metha-cresol, the two cresols react in parallel

$$OC + \text{acid} \rightarrow OCS + H_2O \tag{16}$$

$$MC + \text{acid} \rightarrow MCS + H_2O \tag{17}$$

where OC and MC refer to ortho- and metha-cresol and OCS and MCS to the respective sulfonates. The acid is sulfuric acid. Isomerizations between the cresols or the sulfonates are forbidden. The number of species NSP calculated according to Whitwell and Dartt equals 6, and the rank $R = 3$. By use of the material balances for carbon, sulfur, and oxygen, the following three independent linear combinations are found:

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{MC}} + \Delta N_{\mathrm{OCS}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (18)$$

$$\Delta N_{\mathrm{acid}} + \Delta N_{\mathrm{OCS}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (19)$$

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{MC}} + 4\Delta N_{\mathrm{acid}} + 4\Delta N_{\mathrm{OCS}} + 4\Delta N_{\mathrm{MCS}} + \Delta N_{\mathrm{water}} = 0 \qquad (20)$$

The material balance over hydrogen is dependent of these three equations since the rank $R = 3$. However, since only the two reactions (16) and (17) occur, the following equations, which cannot be obtained from the material balances over the elements, must be satisfied

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{OCS}} = 0 \qquad (21)$$

$$\Delta N_{\mathrm{MC}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (22)$$

Thus there are two linear combinations in excess. However, only four of the Equations (18) to (22) are independent equations. Equation (22), for example, can be obtained by combining (18) and (21). Therefore, the number of independent linear combinations in excess, $NLCE = 1$. This means that Equation (15) gives the right number of independent reactions also in this case.

NOTATION

$\Delta N_{al}, \Delta N_{ac} \ldots \Delta N_{\mathrm{OC}}$ etc. = change in number of moles
$NLCE$ = the number of independent linear combinations of ΔN-values, which remain zero during reaction, in excess over those derived from material balances over the elements.
NRX = number of independent reactions
NSP = number of species
R = rank of the elements-by-species matrix
x_i = molar extent of the ith reaction

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Manuscript received March 26, 1974 and accepted May 31, 1974.

Reply to Björnbom's Note

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The case described by Björnbom, where the number of independent reactions exceeds the difference between the numbers of species and the rank of the element-by-species matrix, contains kinetic constraints on ratio of product species. The equality

$$NRX = NSP - NC$$

should be replaced by

$$NRX \leq NSP - NC$$

as noted by Aris (1963).

In our original paper (1973) we did not consider compositional constraints in cases that did not involve isomeric species. These constraints can, however, easily be added to the program by defining a new variable (for example, CONSTR), which takes on integer values equal in number to the constraints of the type described by Björnbom. This variable would be subtracted from Equation (3) in our original paper.

We wish to thank Dr. Björnbom for bringing this interesting case to our attention.

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Mass Transfer to the Free Interface in a Stirred Vessel

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A turbulent, free interface occurs at the liquid surface with liquid and gas phases in a mechanically stirred vessel. At low stirring speeds in baffled vessels, the interface is not broken by gas entrapment and the turbulence at the interface appears to correspond to the turbulence in the stream generated by the impeller. This note presents an analysis of the mechanism of liquid phase mass transport at this free interface by comparison of the impeller stream turbulence to that for turbulent flow in a circular pipe.

PIPE FLOW

Transition region turbulence in pipe flow appears similar to that for a free interface because both show a penetration model response. Hughmark (1973) has shown that the

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