

constant. When applied to a quantity associated with Σ , the surface coordinates (Slattery, 1974) denoting position on Σ are fixed.

$d_{(v)}/dt$ = derivative with respect to time following a point within a phase that moves with the mass averaged velocity v

$d_{[v(\sigma)]}/dt$ = derivative with respect to time following a point in the interface that moves with the mass averaged velocity $v^{(\sigma)}$

∇ = gradient

$\nabla_{(\sigma)}$ = surface gradient operation (Slattery, 1974)

div = divergence

$\text{div}_{(\sigma)}$ = surface gradient operation (Slattery, 1974)

\det = determinant

[] = shorthand notation defined by Equation (3)

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The Relation Between the Reaction Mechanism and the Stoichiometric Behavior of Chemical Reactions

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The need to describe stoichiometric behavior of complex chemical reactions by independent reactions was first recognized by Gibbs (1876, 1961) in his work on heterogeneous chemical equilibria. Since then, several authors

have attacked the problem to find the independent reactions or the number of them from basic knowledge of the composition of the components and their reaction tendencies (Jouguet, 1921; Defay, 1931; Brinkley, 1946; Prigo-

gine and Defay, 1947; Peneloux, 1949; Denbigh, 1955; Schay and Pethö, 1962; Aris, 1963; Aris and Mah, 1963; Aris, 1965; Lielmezs, 1965; Pethö, 1965*a, b*; Amundson, 1966; Pethö, 1967; Aris, 1968; Bowen, 1968; Henley and Rosen, 1969; Whitwell and Dartt, 1973; Björnbom, 1974, 1975; Schneider and Reklaitis, 1975).

During a long period of time, the generally accepted meaning of independent reactions was a set of linearly independent reactions able to describe the composition changes of the system. Not until recently it has been demonstrated that such a definition is not strict but that also independence of the reaction extents must be considered (Björnbom, 1975).

A set of chemical reactions is a set of independent reactions if and only if the reactions are linearly independent, they can describe all the physically possible composition changes in the system, and all the extents of reaction can vary independently.

Thus, from the atomic matrix, one can always construct a set of linearly independent reactions which can describe the system. But the number of independent reactions according to the definition may be less, and in such a case the reaction extents for the reactions from the atomic matrix will vary with linear dependence. In a calculation of chemical equilibrium, such a dependence of the reaction extents will give an incorrect result.

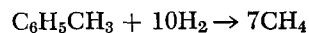
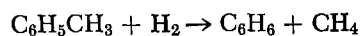
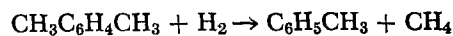
Empirically, the number of independent reactions can be determined by method described by Aris and Mah (1963). This method gives correct results, although a modified variation more firmly based on the definition above should be preferred (Björnbom, 1975). On the other hand, the independent reactions must be related to the reaction mechanism of the system. One difficulty in studying this relation is that the mechanism involves more species than the reactions describing the stoichiometry. In stoichiometric calculations, one is not concerned with such species which appear as intermediates in very small amounts, for example, free radicals, or species which do not change at all, like catalysts. However, in the reaction mechanism those species are very important.

Aris (1965, 1968) has discussed this relation, but his result cannot account for the case with fewer independent reactions than the maximum limit from the atomic matrix. The purpose of this work has been to perform such a study with the stricter definition of independent reactions in mind. Methods have been derived to determine the number and a set of independent reactions from a known or postulated reaction mechanism. The method provides a systematic means for testing various hypothetical reaction mechanisms. Given the species that occur in a proposed mechanism, the method generates independent reaction equations that are the basis for analysis using experimental kinetic data.

The concepts and the methods will be presented by application on two numerical examples. The detailed theoretical treatment is given in a separate supplement.* Some important theoretical points will be discussed in the concluding paragraph.

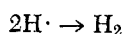
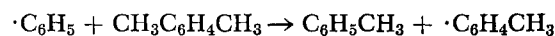
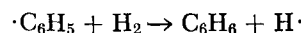
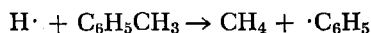
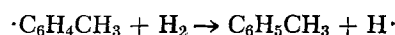
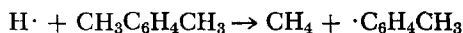
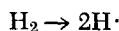
EXAMPLE 1

We will consider the dehydroalkylation of a xylene isomer to obtain benzene as the final product and toluene as an intermediate. Atomic matrix analysis states that the maximum number of linearly independent reactions equals 3. Thus, three linearly independent reactions can describe this system; for example



We will demonstrate how a postulated mechanism indicates that the number of independent reactions are not more than two. We will also, by a matrix method, construct two independent reactions

According to Silsby and Sawyer (1956, 1957), the following reaction mechanism can be postulated:



The elementary steps in the reaction mechanism define the columns of the mechanistic matrix **M**:

$$\mathbf{M} = \begin{bmatrix} 0 & -1 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & -1 & 0 & -1 & 0 & 1 \\ 0 & 1 & -1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & -1 & -1 & 0 \\ 2 & -1 & 1 & -1 & 1 & 0 & -2 \end{bmatrix} \begin{matrix} \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 \\ \text{C}_6\text{H}_5\text{CH}_3 \\ \text{C}_6\text{H}_6 \\ \text{CH}_4 \\ \text{H}_2 \\ \cdot\text{C}_6\text{H}_4\text{CH}_3 \\ \cdot\text{C}_6\text{H}_5 \\ \cdot\text{H} \end{matrix}$$

The three radical species represent the Bodenstein products (Frank-Kamenetsky, 1940) in the mechanism, that is products that can be neglected in stoichiometric calculations.

The three rows in **M** corresponding to the Bodenstein products form the matrix **M'**. From the rank of **M** and **M'**, the number of independent reactions are calculated by

$$R(\mathbf{M}) - R(\mathbf{M}') \quad (1)$$

(A condition for the validity of this formula will be discussed in the concluding paragraph.) For our example, we find $R(\mathbf{M}) = 5$ and $R(\mathbf{M}') = 3$. Thus, the number of independent reactions equals 2.

To construct two independent reactions we proceed as follows.

1. Find five linearly independent columns in **M**. They form the matrix **S'**; for example

$$\mathbf{S}' = \begin{bmatrix} 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 0 & -1 & 0 & -1 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ 2 & -1 & 1 & -1 & 1 \end{bmatrix}$$

2. The submatrix of **S'** corresponding to the Bodenstein products is

$$\mathbf{S}'' = \begin{bmatrix} 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ 2 & -1 & 1 & -1 & 1 \end{bmatrix}$$

From this matrix a basis of the linear space of solutions of the system of linear equations

* Supplementary material has been deposited as Document No. 03000 with the National Auxiliary Publications Service (NAPS), c/o Microfilm Publications, 440 Park Ave. South, New York, N. Y. 10016 and may be obtained for \$3.00 for microfiche or \$5.00 for photocopies.

$$S''x = \begin{pmatrix} 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ 2 & -1 & 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{pmatrix} = 0 \quad (2)$$

is constructed (that is, a basis of the null space of S''). One of the fundamental sets of solutions (Shilov, 1961) is such a basis. In our case, such a set is obtained by, for example, solving

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 2 & -1 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_4 \end{pmatrix} = - \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix} x_3 - \begin{pmatrix} 0 \\ -1 \\ 1 \end{pmatrix} x_5$$

for the following two sets of values of x_3 and x_5

$$x_3 = 1, \quad x_5 = 0$$

$$x_3 = 0, \quad x_5 = 1$$

In numerical practice, these solutions can be neatly obtained at the same time by a combined Gauss elimination procedure on the following augmented matrix:

$$\begin{pmatrix} 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 2 & -1 & -1 & -1 & -1 \end{pmatrix}$$

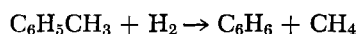
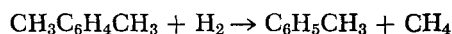
3. The matrix Z formed by the fundamental set of solutions gives the stoichiometric matrix of the independent reactions according to the formula

$$S = S'Z \quad (3)$$

that is

$$S = \begin{pmatrix} 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 0 & -1 & 0 & -1 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ 2 & -1 & 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 1 & 0 \\ 1 & 0 \\ 0 & 1 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \\ 1 & 1 \\ -1 & -1 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{matrix} \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 \\ \text{C}_6\text{H}_5\text{CH}_3 \\ \text{C}_6\text{H}_6 \\ \text{CH}_4 \\ \text{H}_2 \\ \cdot\text{C}_6\text{H}_4\text{CH}_3 \\ \cdot\text{C}_6\text{H}_5 \\ \cdot\text{H} \end{matrix}$$

Thus, we find the following independent reactions



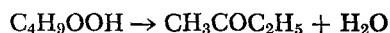
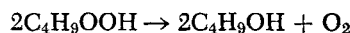
which are supported by experimental data.

EXAMPLE 2

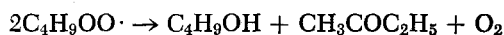
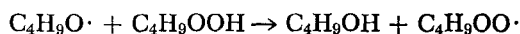
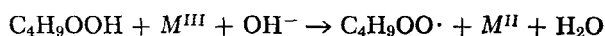
This example will illustrate how the independent reactions can be obtained by trial and error combination of the elementary reaction steps. It will also demonstrate an important theoretical point which will be discussed in the concluding paragraph.

Consider the metal catalyzed decomposition of secondary butyl hydroperoxide in *n*-pentane solution to give secondary butyl alcohol, methyl butyl ketone, water and oxygen, as described by Hiatt and co-workers (1968). Atomic matrix analysis shows that the maximum number of linearly independent reactions equals 2. The following

two reactions, for example, can describe this system:



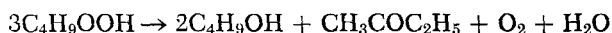
The following reaction mechanism was postulated by Hiatt and co-workers:



M^{II} and M^{III} refer to the metal catalyst in di and trivalent state.

From the matrices M and M'' it is found that the number of independent reaction equals 1. This is less than the maximum number of linearly independent reactions.

The trial and error method is based on linear combination of the elementary reactions such that the Bodenstein products disappear. Trying different linear combinations, one can find $R(M) - R(M'')$ linearly independent reactions without Bodenstein products which constitute a set of independent reactions. In our example this means that we seek one such combination. Addition of the four reaction steps in the mechanism fulfills the condition giving the following result:



This stoichiometry was supported by Hiatt and co-workers' experiments.

CONCLUDING REMARKS

The methods presented give the independent reactions and the number of them if one condition is fulfilled, that the rate functions for the elementary steps must be linearly independent functions. In the supplementary part, this condition is discussed and found unlikely not to be fulfilled in a real case. However, if it is not fulfilled, the number of independent reactions is less than $R(M) - R(M'')$, and the set of reactions obtained by the present methods must be further reduced to get independent reaction extent variations.

The examples demonstrate that different postulated reaction mechanisms can result in different stoichiometric behavior and consequently in possibilities to obtain some mechanistic information. In example 1 a reaction mechanism completed with reaction steps resulting in the breakdown of the aromatic nucleus would give three independent reactions rather than two. Thus, if experiments indicate two independent reactions, the reaction mechanism with breakdown must be rejected.

Use of radioactive labeling in the experiments should increase the possibilities of getting some mechanistic information by use of the present method. This topic remains to be investigated.

In example 1, it is obviously possible to obtain the same result as by the present method by an atomic matrix analysis considering also the aromatic nucleus as an element. An interesting question is does this represent a general case. The answer is no. Example 2 is counter evidence.

NOTATION

M = mechanistic matrix

M'' = submatrix of M corresponding to Bodenstein products

$R(\)$ = rank of matrix inside parenthesis

S = stoichiometric matrix

S' = stoichiometric matrix formed by deleting dependent columns in M
 S'' = submatrix of S' corresponding to Bodenstein products
 x_j = molar extent of reaction to j
 x = vector of x_j values
 Z = matrix the columns of which constitute a basis of the null space of S''

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Analysis of Heat Transfer for Laminar Power Law Pseudoplastic Fluids in a Tube With an Arbitrary Circumferential Wall Heat Flux

An analysis is performed to obtain an exact solution to the problem of thermal entry region heat transfer in a circular tube with an arbitrary circumferential wall heat flux for pseudoplastic fluids using the power law constitutive model. The solution is expanded in a power series form, with expansion coefficients and related constants obtained numerically. A simple result is presented for a cosine heat flux distribution around the periphery of the tube which illustrates the simultaneous influence of circumferential wall heat flux variation and non-Newtonian fluid behavior on heat transfer.

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SCOPE

The problem of laminar, forced convection flow of a fluid through a pipe with a heated wall is classic in the heat transfer literature. Analytical and experimental studies

have been reported with various flow and wall conditions for both Newtonian and non-Newtonian fluids.

The motivation for the present work arose from the