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# Linear Stoichiometry of Chemical Reactions

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The description of complex chemical reactions in terms of linear algebra (linear stoichiometry) is being increasingly employed in chemical and chemical engineering practice. The review deals with methods for the solution of the most frequently encountered problems in thermodynamics and kinetics involving linear combinations of stoichiometric equations.
The bibliography includes 61 references.

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## I. INTRODUCTION

Stoichiometry is defined as the "branch of chemistry including the laws of quantitative relations between the reactants, the derivation of chemical formulae, and the derivation of chemical reaction equations".[1] In a wider sense, stoichiometry includes also the application of the laws of conservation of matter and energy to systems in which physical and chemical changes take place[2]. These definitions are formulated regardless of the mathematical procedures for the solution of problems of the above class.

In the present review, linear stoichiometry is understood as the description of complex chemical reactions in terms of concepts of linear algebra. The employment of a unifying procedure involving vectors and matrices permits the maximum enhancement of a characteristic feature of stoichiometry—the derivation of general results without a detailed knowledge of all the characteristics of the phenomenon being investigated.

The language and methods of linear algebra[3-5] are widely employed in applied mathematics[6] and are becoming increasingly necessary in the development of a modern theory of contact and diffusion processes in chemical engineering[7-9]. This review deals with the rules involving linear combinations of stoichiometric chemical reaction equations for which linear or power functions, such as the enthalpy of reaction or reaction rate, have been determined. Topics requiring further research in the field of matrix theory, for example systems of first-order reactions[10] and the design of kinetic experiments[11], have been deliberately omitted.

The rules involving linear combinations of stoichiometric equations were already formulated to some extent by Hess (1840). They are widely employed in chemical thermodynamics albeit without a matrix formulation[12,13]. However, when the problem involves a large number of reactions, the application of linear algebra is both useful and necessary. Moreover, the matrix formulation of the

problem constitutes to some extent the formulation of the algorithm for its solution on a computer.

An interesting set of problems arises likewise in connection with linear combination of stoichiometric equations, which should be regarded also as molecular equations, if the chemical reactions described by them from a kinetic standpoint obey the law of mass action. The study of these problems was initiated by Horiuti [14,15]. A complete and large branch of kinetics—the kinetics of steady-state reactions—has now been established [16-18]. In the theory of steady-state reactions, the methods of linear algebra find the most direct application.

## II. ATOMS, MOLECULES, AND REACTIONS

Consider a closed system containing $N$ different substances in equilibrium. The molecular formula of the $i$th substance consisting of a finite number of $B_j$ atoms† can be expressed in the form

$$A_i = \sum_{j=1}^{n} \beta_{ij} B_j, \tag{1}$$

where $B_j$ is the symbol of an atom or a charge and $\beta_{ij}$ the number of atoms or charges of type $B_j$ in a molecule $A_i$. Then the set of molecules $A_1$, $A_2$, ..., $A_N$ consisting of atoms $B_1$, $B_2$, ..., $B_n$ can be formulated as a system of equations:

$$\begin{aligned} A_1 &= \sum_{j=1}^{n} \beta_{1j} B_j, \\ A_2 &= \sum_{j=1}^{n} \beta_{2j} B_j, \\ A_N &= \sum_{j=1}^{n} \beta_{Nj} B_j \end{aligned} \tag{2}$$

or in matrix form

$$\begin{Vmatrix} A_1 \\ A_2 \\ \vdots \\ A_3 \end{Vmatrix} = \begin{Vmatrix} \beta_{11}\beta_{12} \ldots \beta_{1n} \\ \beta_{21}\beta_{22} \ldots \beta_{2n} \\ \vdots \\ \beta_{N1}\beta_{N2} \ldots \beta_{Nn} \end{Vmatrix} \begin{Vmatrix} B_1 \\ B_2 \\ \vdots \\ B_n \end{Vmatrix} \tag{3}$$

$$A = \beta B \qquad B \tag{4}$$

The matrix $\beta$ comprising $\beta_{ij}$ coefficients with dimensions $N \times n$ is called the atomic matrix. It expresses the composition of a molecular mixture in terms of atomic components.

If one considers a reacting mixture of substances, then using the above concepts, each $i$th reactant $A_i$ may be associated with a row vector in the $\beta$ matrix:

$$\vec{\beta}_i = \| \beta_{i1}, \beta_{i2}, \ldots, \beta_{in} \| . \tag{5}$$

We shall suppose that the rank of the $\beta$ matrix is $r$ and therefore the number of independent $\vec{\beta}_i$ vectors is $r$. Suppose that these are the first $r$ vectors (i.e. the first $r$ rows of the $\beta$ matrix). Then each succeeding vector with the indices $r+1$, $r+2$, ..., $N$ can be expressed as a linear combination of the basis vectors

$$\beta_1, B_2, \ldots, \beta_r \tag{6}$$

$$\alpha_{r+1,r+1}\vec{\beta}_{r+1} = \alpha_{r+1,1}\vec{\beta}_1 + \ldots + \alpha_{r+1,r}\vec{\beta}_r \tag{7}$$

or

$$\alpha_{r+1,N}\vec{\beta}_N = \alpha_{N1}\vec{\beta}_1 + \ldots + \alpha_{Nr}\vec{\beta}_r$$

After transferring all the terms of these equations to one side, we obtain the following system:

$$\begin{aligned} &\sum_{i=1}^{r+1} \alpha_{r+1,i} A_i = 0, \\ &\sum_{i=1}^{r+1} \alpha_{r+2,i} A_i = 0, \\ &\vdots \\ &\sum_{i=1}^{r+1} \alpha_{Ni} A_i = 0. \end{aligned} \tag{8}$$

Eqns. (7) and (8) corresponds to chemical reaction equations.

The numbers $\alpha_{ki}$ are called the stoichiometric coefficients of the substance $A_i$ in the reaction ($k = r+1, \ldots, N$; $i = 1, \ldots, r+1$). They are negative if the $i$th substance is the starting material in the $k$th reaction and positive for the products. The set of stoichiometric coefficients for the given set of reactions gives rise to the stoichiometric $\alpha$ matrix. In this matrix, each reaction corresponds to a row vector $\vec{\alpha}_k = \| \alpha_{k1}, \ldots, \alpha_{k,r+1} \|$.

Thus the minimum number of reactions required to describe the chemical processes in a system of $N$ reactants is $N - r$, where $N$ is the number of reactants $A_i$ in the given system and $r$ is the rank of its atomic $\beta$ matrix.

The rank of the atomic matrix determines the number of independent components of the reaction mixture. This concept is used successfully in the study of equilibria. Thus for an equilibrium system in which $N - r$ reactions takes place, one can formulate a system of equations describing the chemical equilibrium conditions (the law of mass action):

$$\begin{aligned} K_1 &= f_1(\eta_1, \eta_2, \ldots, \eta_N), \\ K_2 &= f_2(\eta_1, \eta_2, \ldots, \eta_N), \\ &\vdots \\ K_{N-r} &= f_{N-r}(\eta_1, \eta_2, \ldots, \eta_N), \end{aligned} \tag{9}$$

where $\eta_i$ are the numbers of models of the $A_i$ reactants. These $N - r$ equations can be solved simultaneously with $r$ conservation equations:

$$\sum_{i=1}^{N} \beta_{ij}\eta_i = 0 \quad (j = 1, \ldots, r) \tag{10}$$

in order to obtain the composition of the equilibrium mixture on the basis of the initial composition. It is then evident that $N - r$ relations (10) are used to determine $N - r$ values of $\eta_i$ in terms of $r$ values of independent $\eta_i$. If these $r$ values of independent $\eta_i$ are known, the composition of any equilibrium mixture is fully defined.

Key substances, the number of which is equal to the number of independent reactions, i.e. to the rank $R$ of the stoichiometric matrix, should be distinguished from the independent components. Key substances are used as independent variables for an unambiguous description of the kinetics in systems where several reactions take place simultaneously.

The relation between the ranks of the atomic and stoichiometric matrices has been given, for example, by Aris and Mah [22]:

$$R + r \leqslant N. \tag{11}$$

Eqn. (11) is called the Gibbs stoichiometric rule.

The first application of linear algebra to stoichiometric problems involved in fact the theorems of the ranks of the

†Atoms can be understood not only as atoms in the usual sense but also various groups of atoms [19,20] and other structural fragments of the molecule, for example $CH_3$, $\diagdown CH_2$, and $\diagdown\!\!>CH$ in alkanes [21].

atomic $\beta$ matrix and the stoichiometric coefficient $\alpha$ matrix: Jouguet (1921),[23] Brinkley[24], and Pshezhetskii and Rubinshtein[25]. A convenient numerical method for finding the rank of the atomic matrix was recently described by Hanson[26]. The use of the procedures of linear algebra to give a formalised formulation of the problems arising in the study of equilibria and chemical reaction kinetics was considered by Aris[27].

Since it is frequently difficult to formulate *a priori* a system of reactants $\{A_j\}$ for the chemical reaction under investigation, the problem naturally arises of the experimental determination of the number of independent reactants and hence of the rank of the stoichiometric coefficient matrix[22]. In this case, all the $N$ reactants in the system are determined quantitatively for the chosen initial conditions at $N + 1$ different instants $t_0$, $t_1$, ..., $t_N$, i.e. the composition matrix is obtained. Such analysis makes it possible to reduce the problem of the determination of the rank of the stoichiometric matrix to the determination of the rank of the composition matrix. Here the necessity to take into account the accuracy of the determination of the composition constitutes a complication.

We may note that a related problem arises also in the interpretation of the results of spectrophotometric analysis of multicomponent systems in solution[28,29].

According to Eqn. (8), any reaction can be formulated thus:

$$R_k \equiv \sum_i \alpha_{ki} A_i = 0, \tag{12}$$

where $k$ is the number of the reaction and $i$ the number of the substance. Here the reactions $\sum_i \alpha_{ki} A_i = 0$ and $\sum_i (\gamma \alpha_{ki}) A_i = 0$ are identical and therefore only the ratios of the stoichiometric coefficients are important. These ratios are rational numbers and for the $\alpha_{ki}$ it is always possible to select integral values. Different conditions which the $\alpha_{ki}$ must obey have been formulated[30-32] but none of these formulations has been adopted. Usually the values of $\alpha_{ki}$ are chosen as the smallest integral numbers compatible with Eqn. (12).

If one remembers that $\alpha$ is the matrix of the stoichiometric coefficients $\alpha_{ki}$ and the column vector of the substances ($A_1$, $A_2$, ..., $A_N$) is denoted by A, Eqn. (12) can be written in the form

$$\alpha A = 0. \tag{13}$$

Since according to Eqn. (1)

$$A_i = \sum_{j=1}^{n} \beta_{ij} B_j,$$

the chemical reaction equation can be rewritten in the form

$$\sum_{i=1}^{N} \alpha_{ki} \sum_{j=1}^{n} \beta_{ij} B_j = 0. \tag{14}$$
$$(k = 1, 2, \ldots, m)$$

If the chemical reaction equation (12) is written so that the $B_j$ are linearly independent (i.e. are in the basis of the space to which the reactants $A_j$ belong), then, by interchanging the summation signs, we obtain

$$\sum_{j=1}^{n} \sum_{i=1}^{N} (\alpha_{ki}\beta_{ij}) B_j = 0 \tag{15}$$

and

$$\sum_{i=1}^{N} \alpha_{ki}\beta_{ij} = 0.$$
$$(j = 1, \ldots, n; \quad k = 1, \ldots, m)$$

Having designated the row vector of the elements $\alpha_{ki}$ by $\vec{\alpha}_k$, we obtain

$$\vec{\alpha}_k \beta = 0. \tag{16}$$

Thus for each $k$th reaction there is a system of $n$ linear homogeneous equations. The coefficient $\alpha_{ki}\beta_{ij}$ must satisfy the valence rules and the laws of conservation of mass and charge.

The system of linear homogeneous equations (16) has been actually employed to find the stoichiometric coefficients $\alpha_{ki}$ in chemical reactions. The numbers $\alpha_{ki}\beta_{ij}$ constitute a matrix $\vec{\alpha}\vec{\beta}$ (rectangular in the general case) with dimensions $n \times N$ (the number of basis elements is smaller than the number of substances in the reacting mixture). Since the rank of this matrix is $n$, the system of Eqns. (16) is consistent but undetermined. A method for the solution of such systems of equations has been described, for example by Golovina[5].

It may appear strange that the set of reactions occurring in the given system is not unique but has been defined only to within the number of independent reactions. However, for many thermodynamic problems it is unimportant, since the mechanism of equilibration in the system does not affect the thermodynamic functions.

On the other hand, in the study of reaction kinetics, such an approach is unsuitable: if no account has been taken of the mechanism of equilibration, then the rate of equilibration also remains undetermined.

Nevertheless it is found that, with certain assumptions, it is possible to investigate also the problem of reaction rates if one considers stoichiometric equations which reflect the process kinetics. Such equations will be henceforth called molecular-stoichiometric. For molecular-stoichiometric equations, it is possible to define a power function of the reactant concentrations—the reaction rate. However, these equations lose the property of molecularity on being multiplied by a scalar and then added together. An interesting procedure in operations involving such equations consists in their comparison with a system of stoichiometric equations. The problems arising in this connection are considered in Section IV.

The fact that for stoichiometric and molecular-stoichiometric equations it is possible to define certain useful functions, is the reason why linear stoichiometry is of real interest for the chemist.

## III. THERMODYNAMIC APPLICATIONS

It is known from thermodynamics that for any chemical reaction it is possible to determine the changes in certain functions of state (thermodynamic functions), such as the internal energy $U$, the enthalpy $H$, the Helmholtz free energy $F$, and the Gibbs free energy $G$. Since $U$, $H$, $F$, and $G$ are functions of state, then for any chemical reaction under specified external conditions, for example the standard conditions ($T$ = 298°K and $p$ = 1 atm), one can write

$$\Delta P_k^0 = \sum_{i=1}^{n} \alpha_{ij} \Delta P_i^0, \tag{17}$$

where $\Delta P_k^0$ is the change in any thermodynamic function ($U$, $H$, $F$, and $G$) in the chemical reaction of the number of

moles of reactants corresponding to the stoichiometric reaction equation and the $\Delta P_i^0$ are the changes in $U$, $H$, $F$, and $G$ for the formation of the individual reactants from the elements.

When the thermodynamic functions are introduced in this way, they are not always susceptible to experimental determination. Therefore one frequently employed the method of the algebraic summation of the chemical reaction equations and the corresponding thermodynamic functions. This procedure was employed for the first time by Hess to determine the enthalpies of formation of substances.

As shown in Section II, the set of reactions $R_k$ involving a set of substances $\{A_i\}$ ($i = 1, 2, \ldots, N$) can be regarded as the vector $\vec{\alpha_k}$ in a linear vector space. Since the change in thermodynamic functions is associated with the chemical reaction, each vector $\vec{\alpha_k}$ in the space is associated with a certain number—the change in the thermodynamic function. Thus for a linear combination of vectors (reactions), these numbers obey Eqn. (17), i.e. they form linear functions in the vector space (in the space of chemical reactions) [5].

As stated in Section II, for each system of substances $\{A_i\}$ there is a minimum set $\bar{R}_k$ of reactions describing the chemical processes in the system. If for each reaction $\bar{R}_k$ forming part of the fundamental set the $\Delta P_k^0$ are known, then for any $l$th linear combination of fundamental reactions,

$$R_l = \sum_{k=1}^{m} \lambda_{lk} \bar{R}_k \left( \bar{R}_k = \sum_{i=1}^{N} \bar{\alpha}_{ki} A_i \right), \qquad (18)$$

it is also possible to find $\Delta P_l^0$ using the properties of the linear functions in the vector space [5]:

$$f(x + y) = f(x) + f(y), \qquad (19)$$

$$f(\lambda x) = \lambda f(x). \qquad (20)$$

Then, if one wants to determine the change in an unknown thermodynamic function $\Delta P_l^0$ for a reaction $Rl$, one must choose a system of fundamental equations for chemical reactions with known $\Delta P_k^0$. This system must be such that the reaction $Rl$ is a linear combination of the $\bar{R}_k$ i.e. Eqn. (18) holds.

In practice, for example in thermochemistry, the so called thermochemical cycles are set up for this purpose. There are several methods for the determination of the coefficients $\lambda_{lk}$, one of which has been described by Luzanov [33].

Substitution of Eqn. (12) in Eqn. (18) yields

$$\sum_{i=1}^{N} \alpha_{li} A_i = \sum_{k=1}^{m} \lambda_{lk} \sum_{i=1}^{N} \bar{\alpha}_{ki} A_i. \qquad (21)$$

By changing the order of the summation and by setting the coefficients of the independent $A_i$ equal to one another, we obtain a system of linear equations in the unknowns $\lambda_{lk}$:

$$\alpha_{li} = \sum_{k=1}^{m} \lambda_{lk} \bar{\alpha}_{ki} \quad (i = 1, \ldots, N) \qquad (22)$$

or

$$\begin{Vmatrix} \alpha_{l1} \\ \vdots \\ \alpha_{lN} \end{Vmatrix} = \bar{\alpha}^T \begin{Vmatrix} \lambda_{l1} \\ \vdots \\ \lambda_{lm} \end{Vmatrix}.$$

The number of components $A_i$ entering into the reaction is always greater than or equal to the number of fundamental reactions. Therefore the $\bar{\alpha}$ matrix of the coefficients $\{\bar{\alpha}_{ki}\}$ will have the dimensions $m \times N (N \times m)$ for each reaction with the index $l$. However, the system obtained is consistent since $N - m$ equations are linearly dependent. Having chosen $m$ independent equations and having solved the resulting system, we obtain $\lambda_{lk}$.

After the determination of $\lambda_{lk}$, the changes in thermodynamic functions in the $l$th reaction can be found in accordance with the properties of the linear functions (19) and (20) in terms of

$$\Delta P_l = \sum_{k=1}^{m} \lambda_{lk} \bar{P}_k, \qquad (23)$$

where $\Delta \bar{P}_k$ are the changes in thermodynamic functions for the fundametal chemical reaction equations.

Consider the following simple example from a collection of problems [34]. From a specified system of fundamental reactions for which the enthalpies of formation $\Delta H^0$ are known,

| | $\Delta H^0$, kcal mole$^{-1}$ |
|---|---|
| ZnS(solid) - Zn(solid) - S (orthorhom.) = 0 | $\Delta H_I^0 = -44.0$ |
| $2ZnO + 2SO_2 - 2ZnS - 3O_2 = 0$ | $\Delta H_{II}^0 = -221.88$ |
| $2SO_3 - O_2 - 3SO_2 = 0$ | $\Delta H_{III}^0 = -46.88$ |
| $ZnSO_4 - ZnO - SO_3 = 0$ | $\Delta H_{IV}^0 = -55.1$ |

one is required to find the enthalpy $\Delta H_V^0$ of the reaction

$$ZnSO_4 - Zn - S(orthorhom.) - 2O_2 = 0 \qquad \Delta H_V^0 = ?$$

We formulate the $\bar{\alpha}$ matrix for this system of chemical equations:

| Zn | S | $O_2$ | $SO_2$ | $SO_3$ | ZnO | ZnS | $ZnSO_4$ |
|---|---|---|---|---|---|---|---|
| −1 | −1 | 0 | 0 | 0 | 0 | 1 | 0 |
| 0 | 0 | −3 | 2 | 0 | 2 | −2 | 0 |
| 0 | 0 | −1 | −3 | 2 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | −1 | −1 | 0 | 1 |

,

whereupon we have according to Eqn. (22)

$$\begin{Vmatrix} -1 \\ -1 \\ -2 \\ 0 \\ 0 \\ 0 \\ 0 \end{Vmatrix} = \begin{Vmatrix} -1 & -1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & -3 & 2 & 0 & 2 & -2 & 0 \\ 0 & 0 & -1 & -3 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & -1 & 0 & 1 \end{Vmatrix}^T \begin{Vmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \lambda_4 \end{Vmatrix}. \qquad (24)$$

Having chosen from Eqns. (24) obtained any four which are linearly independent, we find $\lambda_1 = 1$, $\lambda_2 = 2$, $\lambda_3 = 1/2$, and $\lambda_4 = 1$ and we obtain for $H_V^0$

$$\Delta H_V^0 = \Delta H_I^0 + {}^1/_2 \Delta H_{II}^0 + {}^1/_2 \Delta H_{III}^0 + \Delta H_{IV}^0 =$$
$$= -(1 \times 44.0) - ({}^1/_2 \times 221.88) - ({}^1/_2 \times 46.88) - (1 \times 55.1) =$$
$$= -223.48 \text{ kcal mole}^{-1}.$$

The method of finding the thermodynamic functions for reactions from the known thermodynamic functions for fundamental reactions is suitable also for the determination of the equilibrium constants.

If the equilibrium constants for the fundamental reactions $K_{Rk}$ are known, then since

$$\lg K_R = -\Delta F_R^0/RT, \text{ and } \lg K_{\bar{R}_k} = -\Delta F_{\bar{R}_k}^0/RT,$$

the condition

$$\Delta F_R^0 = \sum_k \lambda_k \Delta F_{\bar{R}_k}$$

leads to

$$\lg K_R = \sum_k \lambda_k \lg K_{\bar{R}_k}.$$

An example of the calculation of the equilibrium constant for the oxidation of arsenic sulphides by nitric acid from the known equilibrium constants for five fundamental reactions is quoted by Luzanov[33].

The efficiency of the method for the calculation of thermodynamic functions described above is illustrated particularly clearly in problems which give rise to large systems of equations, the solution of which requires the employment of a computer. For example, for a certain class of compounds one can consider simultaneously not one thermochemical cycle, but a set of such cycles involving a chosen set of fundamental reactions and one can find all possible linear combinations of the cycles corresponding to the formation of various compounds of the given class. A problem of this kind for boron compounds was formulated and solved by Guest and Pedley[35].

As stated above, the molecular formula of any substance can be written thus:

$$A_i = \sum_{j=1}^{n} \beta_{ij} B_j, \qquad (25)$$

where $B_j$ are structural fragments (atoms, bonds, and groups of atoms) and $\beta_{ij}$ are their numbers in the molecule. Formally, the formation of a molecule of type $A_i$ from the structural elements can be regarded as a reaction in which the stoichiometric coefficients are $\beta_{ij}$. One can show that these "reactions" are vectors in a linear space[27].

Next, if we associate each "reaction" of this kind with a number, for example the enthalpy of formation, evaporation, and fusion or the specific volume, i.e. any extensive property $P(A_i)$ of the substance $A_i$, and postulate that these numbers obey the conditions

$$P(A_i + A_j) = P(A_i) + P(A_j), \qquad (26)$$

$$P(\gamma A_i) = \gamma P(A_i), \qquad (27)$$

where $A_i$ and $A_j$ are arbitrary substances and $\gamma$ is an arbitrary real number, then $P$ is a linear function in the given linear space. If the fundamental reaction in this space consists of the $\{B_j\}$, the linear function $P$ can be represented by the linear formula

$$P(A_i) = \sum_{j=1}^{n} \beta_{ij} P_j, \qquad (28)$$

where $\beta_{ij}$ are the coordinates of the vector $A_i$ in the space and $P_j$ are coefficients independent of $\beta_{ij}$.

Then, if we have a series of substances $\{A_1, A_2, \ldots, A_N\}$ for which an experimental property $P$ is known, it is possible to formulate the following equations:

$$P(A_i) = \sum_{j=1}^{n} \beta_{ij} P_j \quad (i = 1, \ldots, N). \qquad (29)$$

These equations are inconsistent, since for real systems Eqns. (26) and (27) hold only approximately and in addition the quantities $P(A_i)$ are themselves not entirely accurate having been determined with an experimental error.

Since the rank of the "stoichiometric" matrix is in this case $n$, only $n$ of the numbers $P(A_i)$ are linearly independent. The remaining $N - n$ quantities $P(A_i)$ are linear combinations of the chosen $n$ independent $P(A_i)$. For simplicity we shall assume that the first $n$ equations of set (29) are independent. Then any $P(A_S)$ is

$$P(A_s) = \sum_{i=1}^{n} \lambda_i \bar{P}(A_i),$$

where $\lambda_i$ may be determined by solving equations of type (22). The above equation permits the determination of the unknown quantities $P(A_S)$ having chosen an appropriate system of fundamental equations with experimental $\bar{P}(A_i)$.

However, this method for the calculation of unknown physicochemical properties of substances suffers from two significant disadvantages, namely (1) the experimental errors in the quantities $\bar{P}(A_i)$ in the fundamental equations enter wholely into the required quantity $P(A_S)$; (2) this method permits the calculations of $P(A_S)$ from the given set of fundamental equations for a comparatively narrow range of compounds.

Therefore another procedure, in which the coefficients $P_j$ in Eqn. (28) are evaluated by least squares from experimental points for a large number of compounds, is used much more frequently. Then in principle it is possible to calculate from Eqn. (28), using known values of $P_j$, a given property $P$ for any compound of the given class. Methods involving this procedure have been called additive. For example, those of Souders et al.[36] and Franklin[37], Laidler[38], Bernstein[39], Allen[40], Benson and Buss[41], Tatevskii[42], and others may be included among them. The methods differ only in the way the basis (structural elements $B_j$) is chosen and hence have different numbers of terms in Eqn. (28). A detailed analysis of various additive methods for the calculation of the physicochemical properties of compounds and a comparison of the accuracy of the corresponding computational formulae have been carried out[43-45].

Questions relating to the mathematical formulation of the problem and the analysis of the reliability and accuracy of the results obtained by additive methods have been considered[46,47].

## IV. KINETICS OF STEADY-STATE REACTIONS

A complex chemical process can be represented by a set of molecular chemical equations (the reaction mechanism) if in addition to the reactants and products one considers also "intermediates".[48,49] It is interesting that, in order to account for chemical changes in a system, it is sufficient to postulate the existence of intermediates in very small amounts. Here the situation is approximately the same as in the boundary layer theory where one introduces the hypothesis of a high property flux gradient in a very thin layer next to the wall.

Together with stoichiometry, molecular equations describe also the kinetics, i.e. they obey the law of mass action on the basis of which it is possible to determine the rate $r_S$ for any molecular equation $s$ included in the mechanism of the complex reaction. For ideal systems $r_S$ is expressed as follows[8]:

$$r_s = k_s \prod_{i=1}^{N} [A_i]^{\theta_{is}} - k'_s \prod_{i=1}^{N} [A_i]^{\gamma_{is}}, \qquad (30)$$

where $\theta_{iS} = |\alpha_{iS}|$ for the reactants and $\theta_{iS} = 0$ for the products, $\gamma_{iS} = |\alpha_{iS}|$ for the products and $\gamma_{iS} = 0$ for the reactants, $[A_i]$ are the concentrations of the products and reactants (these can be both bulk-phase and surface concentrations), and $k_S$ and $k'_S$ are the concentration-independent rate constants for the forward and reverse reactions.

Suppose that the proposed reaction mechanism consists of $S$ stages:

$$\sum_{i=1}^{N} \alpha_{is} A_i = 0 \qquad (31)$$

$$s = 1, 2, \ldots, S,$$

in which $N$ reactants participate, including $Q$ intermediates and $P = N - Q$ reactants and products.

By considering the rate $r_i$ of the disappearance or evolution of the $i$th substance,

$$r_i = \sum_{s=1}^{S} \alpha_{is} r_s \quad (i = 1, \ldots, N), \tag{32}$$

we can obtain a system of equations describing the local rate of the chemical reaction in terms of the known rates $r_s$ of the individual stages. However, this equation includes also the concentrations of the intermediates, which are not usually measured. The above difficulty can be obviated by adducing the classical hypothesis of the steady-state concentrations of the intermediates, according to which they should obey the following conditions:

$$\begin{gathered} r_q = \sum_{s=1}^{S} \alpha_{qs} r_s = 0, \\ q = P+1, P+2, \ldots, Q. \end{gathered} \tag{33}$$

Here $\alpha_{qs}$ are the stoichiometric coefficients of the intermediates $q$ in the $s$th stage of the mechanism. Eqns. (33) makes it possible in many cases to express explicitly the concentrations of the intermediates in terms of those of the products and reagents and hence solve the problem. A critical analysis of the steady-state hypothesis has been carried out [50].

Horiuti [14] and also Horiuti and Nakamura [15] showed that there is another method of expressing the steady-state conditions which is more convenient for complex mechanisms than that specified by Eqns. (33). These workers suggested that one should consider linear combinations of stages involved in the mechanism of the complex reaction. The stoichiometric equations resulting from these linear combinations can be called routes. The stoichiometric coefficients of route $m$ are of the form

$$\alpha_{im} = \sum_s \alpha_{is} \nu_{sm}, \tag{34}$$

where $\nu_{sm}$ are the so called stoichiometric numbers, i.e. multipliers for stage $s$, which are introduced before adding to subtracting from other stages.

Formally, we can write, as for the set of stages, an equation of type (32) for a set of routes:

$$r_i = \sum_m \alpha_{im} r_m, \tag{35}$$

where $r_m$ is the rate for route $m$ but the form of $r_m$ is still unknown. By setting equal Eqns. (32) and (35) and taking into account Eqn. (34), we obtain,

$$\sum_s \alpha_{is} r_s = \sum_m \left( \sum_s \alpha_{is} \nu_{sm} \right) r_m.$$

By altering the order of summation, we find

$$\sum_s \alpha_{is} r_s = \sum_s \alpha_{is} \sum_m \nu_{sm} r_m.$$

Assuming that the coefficients of $\alpha_{is}$ are equal, we obtain finally

$$r_s = \sum_m \nu_{sm} r_m \tag{36}$$

Eqn. (36) describes the relation between the unknown rates for different routes and the known rates for different stages. It only remains to decide on the method of choosing the stoichiometric numbers $\nu_{sm}$. According to Horiuti's hypothesis [14,15], the stoichiometric numbers are chosen by solving the homogeneous system of equations

$$\sum_s \alpha_{qs} \nu_{sm} = 0 \quad (q = P+1, P+2, \ldots, Q). \tag{37}$$

It is possible to show that Eqn. (37) is a consequence of the hypothesis that the concentrations of the intermediate correspond to a steady-state. Indeed Eqn. (33) can be put in the form

$$\sum_s \alpha_{qs} r_s = \sum_s \alpha_{qs} \sum_m \nu_{sm} r_m$$

and, by changing the order of summation, we find

$$\sum_m r_m \sum_s \alpha_{qs} \nu_{sm} = 0.$$

This leads to Eqn. (37). Eqn. (37) should in fact be regarded as an expression of Horiuti's steady-state condition but in the literature [17,18] this term is given to Eqn. (36).

Eqns. (37) comprise $Q$ equations in $S$ unknowns $\nu_s$ and $Q < S$. The number $M$ of the linearly independent solutions of these equations is equal to the number of routes and is given by the condition $M = S - Q$. Since $Q < S$, some of the $\nu_s$ are free variables and must be fixed in order to obtain a solution to Eqn. (37).

Thus each set of molecular equations (mechanisms) can be associated with a set of stoichiometric equations (routes) and Eqns. (36) with the $\nu_{sm}$ determined from Eqn. (37) can be used to find $r_m$ and the concentrations of the intermediates.

We shall consider as an example a complex reaction (pyrolysis of ethane) the suggested multiphase mechanism of which is of the following form [51]

$$C_2H_6 = 2CH_3^{\cdot}, \tag{I}$$

$$CH_3^{\cdot} + C_2H_6 = CH_4 + C_2H_5^{\cdot}, \tag{II}$$

$$C_2H_5^{\cdot} = C_2H_4 + H^{\cdot}, \tag{III}$$

$$H^{\cdot} + C_2H_6 = H_2 + C_2H_5^{\cdot}, \tag{IV}$$

$$2C_2H_5^{\cdot} = C_2H_4 + C_2H_6, \tag{V}$$

where $C_2H_6$, $CH_4$, $C_2H_4$, and $H_2$ are the reactants and reaction products ($i = 1, 2, 3, 4$) and $CH_3^{\cdot}$, $H^{\cdot}$, and $C_2H_5^{\cdot}$ are intermediates ($q = 5, 6, 7$).

Eqns. (37) for mechanism (I)–(V) can be formulated as follows:

$$\begin{gathered} \nu_{1m}(2) + \nu_{2m}(-1) + \nu_{3m}(0) + \nu_{4m}(0) + \nu_{5m}(0) = 0 \quad E_1, \\ \nu_{1m}(0) + \nu_{2m}(0) + \nu_{3m}(1) + \nu_{4m}(-1) + \nu_{5m}(0) = 0 \quad E_2, \\ \nu_{1m}(0) + \nu_{2m}(1) + \nu_{3m}(-1) + \nu_{4m}(1) + \nu_{5m}(-2) = 0 \quad E_3, \end{gathered}$$

This system is reduced to a canomical form by the method of leading operations [52]. The essential feature of the method involves the replacement of the initial equations $E_1$, $E_2$, and $E_3$ by an equivalent system where a variable has a coefficient of unity in one equation and zero in all the others.

In our case the canomical system comprises the equations

$$\begin{gathered} \nu_{1m}(1) + \ldots + \nu_{4m}(0) + \nu_{5m}(-1) = 0 \quad (E_1 + E_2 + E_3)/2, \\ \nu_{2m}(1) + \ldots + \nu_{4m}(0) + \nu_{5m}(-2) = 0 \quad (E_3 + E_2), \\ \nu_{3m}(1) + \nu_{4m}(-1) + \nu_{5m}(0) = 0 \quad E_2, \end{gathered}$$

and we can obtain the complete set of solutions $\nu_{sm}$ ($m = 1, 2$) of equations $E_1$, $E_2$, and $E_3$ by assigning any values to the independent variables $\nu_{4m}$ and $\nu_{5m}$. We shall now consider the permissible solutions generated by trial and error:

$$\begin{gathered} m = 1: \quad \nu_{41} = 0; \quad \nu_{51} = 1 \\ m = 2: \quad \nu_{42} = 1; \quad \nu_{52} = 0. \end{gathered}$$

The route $\nu_{s1}$ is of the form

$$\nu_{s1}^T = (\nu_{11}, \nu_{21}, \nu_{31}, \nu_{41}, \nu_{51}) = 1, 2, 0, 0, 1).$$

Similarly

$$\nu_{52}^T = (\nu_{12}, \nu_{22}, \nu_{32}, \nu_{42}, \nu_{52}) = (0, 0, 1, 1, 0).$$

According to Eqn. (34), the stoichiometric equations for the routes are

$$2C_2H_6 = 2CH_4 + C_2H_4,$$
$$C_2H_6 = C_2H_4 + H_2.$$

We shall now find the rates for these routes on the assumption that the reactions occurring in accordance with Eqns. (I), (II), and (V) are irreversible and reactions (III) and (IV) are reversible. Equations of type (36) assume the following form in this case:

$$k_1[C_2H_6] = r_1(1) + r_2(0), \quad \text{(IA)}$$
$$k_3[CH_3^{\cdot}][C_2H_6] = r_1(2) + r_2(0), \quad \text{(IIA)}$$
$$k_5[C_2H_5^{\cdot}] - k_5[C_2H_4][H^{\cdot}] = r_1(0) + r_2(1), \quad \text{(IIIA)}$$
$$k_7[H^{\cdot}][C_2H_6] - k_8[C_2H_5^{\cdot}][H_2] = r_1(0) + r_2(1), \quad \text{(IVA)}$$
$$k_9[C_2H_5^{\cdot}]^2 = r_1(1) + r_2(0). \quad \text{(VA)}$$

We find from Eqns. (IA) and (IIA)

$$[CH_3^{\cdot}] = 2k_1/k_3.$$

Eqns. (IA) and (VA) yield

$$[C_2H_5^{\cdot}] = \sqrt{\frac{k_1}{k_9}[C_2H_6]},$$

and from Eqns. (IIIA) and (IV) we obtain

$$[H^{\cdot}] = \frac{\sqrt{\frac{k_1}{k_9}[C_2H_6]}(k_5 + k_8[H^{\cdot}])}{k_7[C_2H_6] + k_8[C_2H_4]}.$$

Then, according to Eqns. (IA) and (IIA),

$$r_1 = k_1[C_2H_6],$$
$$r_2 = k_7[C_2H_6][C_2H_5^{\cdot}]\left(\frac{k_5 + k_8[H_2]}{k_7[C_2H_6] + k_8[C_2H_4]} - k_8[H_2]\right).$$

Knowing $r_1$ and $r_2$, it is easy to find the rate of consumption of ethane in the pyrolysis process from Eqn. (32):

$$r_{C_2H_6} = 2r_1 + r_2.$$

If the concentrations of the intermediates are related in some way, as sometimes happens when reactions on the surface are considered, then the above relations must be employed in addition to Eqns. (36). The results obtained, expressed by Eqn. (35), may be compared with experimental data and the adequacy of the mechanism may be tested. For reactions with several routes, a convenient method of comparing theory with experiment involves a comparison of the calculated and experimental selectivities [53, 54].

One should also note the possibility of the occurrence of reactions with several independent mechanisms. A distinctive feature of such reactions is that the number of routes involved is greater than the number of independent reactions which can occur in the given reactant system [18].

In many cases, when the intermediates are excluded, it is convenient to employ the equations proposed by Temkin [55, 56], which are related to Eqns. (36), rather than Eqns. (36) themselves. Finally, it is possible in principle to carry out numerically all the calculations based on Eqns. (36), [57] but in this case we do not have kinetic equations of type (35) in an explicit form.

Apart from facilitating the derivation of kinetic equations on the hypothesis of steady-state concentrations of intermediates, the introduction of routes provides to some extent a basis for the classification of complex reactions. Whereas previously a distinction was drawn between complex consecutive or parallel reactions, when the routes are employed, the difference between them is insignificant and such reactions are simply processes with several routes. An interesting class of complex reactions comprises processes with a single route. These include, for example, the synthesis of ammonia and methanol, the reaction of hydrogen and bromine, etc. A reaction with a single route permits a more detailed theoretical study than reactions with several routes [16, 17]. In particular, the rate of a single-route reaction can be expressed, along the route, as the difference between the rates in the forward ($r'_m$) and reverse ($r''_m$) directions and for reversible routes it is possible to find the relation between the equilibrium constant $r'_m/r''_m$ for the route and the rate constants $k_s$ and $k'_s$ for the stages by introducing the so called average stoichiometric number [58, 59], which can be determined experimentally [59-61].

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