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Theory of Complex Unimolecular Reactions

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A general approach to the study of complex reacting systems, including first-order reactions, is considered. The method consists in the identification of the disposition of the characteristic vectors of the kinetic matrix for a linear system and their eigenvalues. Linear reaction pathways in the composition space correspond to non-equilibrium characteristic vectors. For an experimental determination of the kinetic constants in a complex system, it is sufficient to find all the linear reaction pathways.
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I. INTRODUCTION

The theory of complex reactions deals with the general characteristics of their occurrence, i.e. the structural features of complex systems. Suppose that a system of non-linear differential equations describing the kinetics of a process has been specified:

$$\frac{da_i}{dt} = f_i(a_1 \dots a_n); \quad i = 1, \dots n, \tag{1}$$

where a_i are the reactant concentrations and t is the time. The theory of steady-state reactions is concerned with problems of deriving kinetic equations from the steady-state condition:

$$f_i(a_1 \dots a_n) = 0. \tag{2}$$

These problems were described in detail by Temkin, Kiperman, and Horiuti[1-5] and are not considered in the present review. Only a few general results have been obtained for the non-linear system (1). They are mainly restricted to the development of methods for the integration of the equations in specific instances and the consideration of methods for the determination of kinetic constants from experimental data—by analysing the number and stability of steady states. However, all these results are fairly specific.

Complex systems of unimolecular reactions have been investigated most fully. It is now already possible to describe in fair detail the structure of linear systems. A general method for the determination of the rate constants for individual pathways can be proposed on the basis of a theoretical analysis of experimental data. The new approach to the determination of first-order rate constants is based on finding "linear pathways" in the reaction, which will be discussed in detail below.

The present review considers mainly the general results of the theory of linear systems with a subsequent brief discussion of second-order reactions.

II. THEORY OF FIRST-ORDER REACTIONS

1. FUNDAMENTAL CONCEPTS AND NOTATION

We shall denote the ith substance in the system by A_i and its concentration by a_i. k_{ij} is defined as the rate constant for the conversion of the ith substance into the jth substance, i.e. we shall write $A_i \xrightarrow{k_{ij}} A_j$. We introduce a linear composition space, the dimensions of which are the same as the number of reactants. The elements of this space consist of vectors, whose coordinates are the same as the concentrations of the components at the outlet from the reactor: $a = \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix}$. The general system of first-order reactions can then be described by the following equation in the matrix form:

$$\frac{da}{dt} = Ka \quad , \tag{3}$$

where K is the kinetic matrix. The form of this matrix depends on the specific reaction mechanism.

We shall attempt to answer two main questions concerning the general theory of first-order systems.

1. We shall elucidate the nature of the approach of the system to equilibrium, the possibility of decaying and non-decaying oscillations.

2. We shall attempt to devise a general method for the determination of rate constants from experimental data by studying the structure of the system.

The formulation of the first problem does not require special comment. We shall note only that the stability of the system is inferred from the sign of the real root of the characteristic equation

$$|K - \lambda E| = 0, \tag{4}$$

where E is the unit matrix. If all the roots are real and negative, the system is stable and oscillations are impossible. If the roots are complex with a negative real component, decaying oscillations are possible.

The problem of the determination of kinetic constants will be considered in somewhat greater detail. The determination of constants for a system of complex reactions is known to involve considerable difficulties[6,7]. The constants for system (1) can be determined from the initial rates of formation of each substance. However, this entails significant errors in the determination of contact times and also errors in chemical analysis for low degrees of conversion[6]. It is possible to obtain a general solution to Eqns. (3), [8] but this hardly facilitates the determination of kinetic constants from experimental data. The point is that each kinetic curve can be described by an expression of the type

$$a_i = \sum_{i=1}^{n} c_i e^{\lambda_i t},$$

where c_i are constant and λ_i are the roots of the characteristic equation. It is therefore possible to obtain only c_i and λ_i from the experimental data. This is also not a simple problem, which has to be solved by non-linear programming methods[9]. A new method has been proposed recently for the determination of these quantities, which is apparently useful in the simplest cases[10]. The method is based on the fact that the function

$$\varphi = \sum_{i=1}^{n} a_i t e^{\lambda_i t}$$

has n maxima at the points $t_i = -1/\lambda_i$. It is therefore possible to find λ_i by plotting φ against t. However, it is difficult to expect the method to be applicable when $n > 3$ or 4. We shall assume that we have nevertheless succeeded in determining c_i and λ_i. The relation between the λ_i and the kinetic constants is so complex that an accurate determination of the latter is still a problem. A number of studies have been made on the analysis of the errors arising in the determination of the contact time and temperature[6,11-15]. Owing to the inaccuracy of the temperature measurements, the errors in the calculation of the rate constants are higher for larger activation energies. When the relative rate constants are determined, the error associated with the inaccurate determination of the constants diminishes, since the rate constant ratios depend less on temperature than the absolute values of the constants.

The approach to the problem of the calculation of the constants, based on the study of the structure of a system of unimolecular reactions, is of considerable interest[16]. Using this approach, it is possible to suggest a method for the determination of the relative rate constants without measuring contact times.

2. REVERSIBLE REACTIONS

We shall begin the consideration of systems of unimolecular reactions with first-order reversible reactions. The structure of such systems is simpler than the structure of systems including irreversible stages, despite the fact that a larger number of constants is required for the description of reversible reactions. The causes of this at first sight paradoxical fact will be clarified by further exposition.

In order to permit a simple geometrical interpretation of the results, we shall restrict the treatment initially to a three-component system. The following kinetic equations can be formulated:

$$\begin{aligned} \frac{da_1}{dt} &= -(k_{21}+k_{31})a_1 + k_{12}a_2 + k_{13}a_3, \\ \frac{da_2}{dt} &= k_{21}a_1 - (k_{12}+k_{32})a_2 + k_{23}a_3, \\ \frac{da_3}{dt} &= k_{31}a_1 + k_{32}a_2 - (k_{13}+k_{23})a_3. \end{aligned} \tag{5}$$

In this case the matrix K can be written thus:

$$K = \begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & k_{13} \\ k_{21} & -(k_{12}+k_{32}) & k_{23} \\ k_{31} & k_{32} & -(k_{13}+k_{23}) \end{pmatrix}. \tag{6}$$

The column matrix $a = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$ can be imagined as a vector in a three-dimensional composition space. During the reaction, the vector a migrates in the space. The matrix

$$\frac{da}{dt} = \begin{pmatrix} \frac{da_1}{dt} \\ \frac{da_2}{dt} \\ \frac{da_3}{dt} \end{pmatrix}$$

specifies the rate of this migration. The trajectory of the end of the vector a will be called the reaction pathway.

For an n-component system, the form of the matrix K remains the same, i.e. the non-diagonal elements consist of the rate constants for the corresponding transitions. The diagonal elements consist of sums of the elements of each column with the sign reversed. The constants k_{ii} are disregarded, since they have no physical significance.

We impose two restrictions:

$$\sum_{i=1}^{n} a_i = 1; \tag{7}$$

$$a_i \geqslant 0. \tag{8}$$

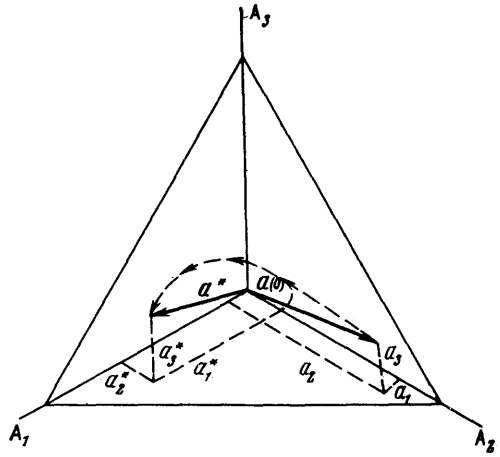


Figure 1. The composition space and the reaction triangle for a three-component system. The dashed curve represents a typical reaction pathway.

The first expresses the law of conservation of mass in the system and the second expresses the impossibility of the appearance of negative amounts of the substance.

Definition 1. The vector $a(a_1 \ldots a_n)$ is said to be positively defined if $a_i > 0$ ($i = 1, \ldots, n$); on the other hand, if $a_i \geqslant 0$ ($i = 1, \ldots, n$), then the vector a is said to be non-negatively defined. The geometrical implication of these conditions is that the end of the vector a is bounded by a plane passing through the points (1, 0, 0), (0, 1, 0), and (0, 0, 1). Furthermore, all the reaction pathways lie in the positive octant of the coordinate system (Fig. 1). During the reaction, the end of the vector $a(t)$ moves along the reaction plane in the direction towards the equilibrium point a^*. In the general case, these reactions pathways are curved.

A. Characteristic Directions

The directions in the composition space for which the condition

$$K\bar{a} = \lambda\bar{a} \tag{9}$$

is valid are called characteristic. Here a is the characteristic vector corresponding to the eigenvalue λ. It will be shown below that a linear reaction pathway corresponds to each characteristic direction.

It is known from linear algebra[17] that there can exist not more than n independent eigenvectors for an arbitrary matrix K. In terms of the coordinate system comprising eigenvectors, the matrix assumes the simplest form. If n independent eigenvectors exist (complete system), the matrix is reduced to a diagonal form. The introduction of an equivalent system of substances, each of which reacts independently of the others in the mixture, corresponds to the reduction of the kinetic matrix to the diagonal form. Evidently the calculation of constants for such a system does not present difficulties. If the eigenvectors and eigenvalues are known, it is possible to devise a transformation relating the characteristic coordinate system to the initial system. In this case, one can calculate the entire initial rate constant matrix. If the λ_i are known, then, as stated above, it is also possible to deduce the stability of the system. The study of linear reaction pathways is therefore of considerable interest for the understanding of the structure of complex systems.

The existence of a complete system of real eigenvectors for symmetrical matrices has been demonstrated in linear algebra. In the majority of instances, kinetic matrices are not symmetrical. It is therefore impossible to reach any conclusions concerning the number of eigenvectors of kinetic matrices directly on the basis of conditions (7) and (8). For reversible reactions, the kinetic matrix can be reduced to a symmetrical form. This is done using the principle of "detailed balance".

B. The Principle of Detailed Balance

This principle is important in the theory of linear systems. It states that, for each stage at equilibrium, we have

$$k_{ji}a_i^* = k_{ij}a_j^*, \tag{10}$$

and that $\kappa_{ij} > 0$ implies that $\kappa_{ji} > 0$.

We may note that the principle of detailed balance cannot always be obtained from the steady-state condition. For example, for the three-component system of reversible reactions considered above, one cannot obtain Eqn. (10) from the equality

$$Ka^* = 0 \tag{11}$$

without additional conditions. For $n = 2$, Eqn. (10) always follows from Eqn. (11), but for $n = 3$ this is the case only provided that the Wegsheider conditions are fulfilled[18]:

$$k_{12}k_{23}k_{31} = k_{21}k_{32}k_{13}. \tag{12}$$

For $n > 3$, analogous conditions have been obtained by other investigators[19,20]. The general conditions for which the principle of detailed balance follows from steady-state equations have been obtained by Lee[21]. For reversible reactions in closed systems, the validity of Eqn. (10) can be proved from thermodynamic considerations. However, it has been noted in the literature that, in relation to kinetics, the thermodynamic derivation of the principle of detailed balance is not always rigorous, since it is difficult to take into account multistage reaction mechanisms and deviations from ideality[22]. In the present section, we shall assume that condition (10) is valid.

C. Axiomatic Definition of a System of Unimolecular Reversible Reactions

We shall now formulate an exact definition of a system of reversible reactions and shall discuss certain mathematical results obtained from this definition.

Definition 2. A system described by the equations

$$\frac{d\boldsymbol{a}}{dt}=K\boldsymbol{a}, \quad \boldsymbol{a}(0)=\boldsymbol{a}_0, \tag{13}$$

where $\boldsymbol{a}$ is an n-dimensional composition vector and K an $n\times n$ matrix, is called a system of unimolecular reversible reactions. Furthermore, the following conditions are fulfilled:

$$\begin{gathered} a_i\geqslant 0,\\ \sum_{i=1}^{n} a_i=\text{const},\\ k_{ij}a_j^*=k_{ji}a_i^*, \end{gathered} \tag{14}$$

where a_j^* and a_i^* are equilibrium concentrations.

Theorem 1. For a system of unimolecular reversible reactions, there is a unique equilibrium point.

Theorem 2. For a system of reversible unimolecular reactions, there are n independent characteristic composition vectors, whose eigenvalues are not positive.

The proof of theorem 2 is based significantly on the principle of detailed balance [condition (14)]. The idea of the proof is as follows. Knowing the equilibrium composition, it is possible to set up the diagonal matrices

$$D^{-1/2}=\begin{pmatrix} \frac{1}{\sqrt{a_1^*}} & & \\ & \ddots & \\ & & \frac{1}{\sqrt{a_n^*}} \end{pmatrix}; \quad D^{1/2}=\begin{pmatrix} \sqrt{a_1^*} & & \\ & \ddots & \\ & & \sqrt{a_n^*} \end{pmatrix}. \tag{15}$$

These matrices are evidently non-degenerate. We now consider the trans-formation of the vector composition space in accordance with the formula $\alpha = D^{-1/2}a$. Here we again obtain a system of reversible unimolecular reactions:

$$\frac{d\boldsymbol{\alpha}}{dt}=\hat{K}\boldsymbol{\alpha}, \tag{16}$$

where $\hat{K}=D^{-1/2}KD^{1/2}$. By virtue of conditions (14), the matrix $\hat{K}$ is symmetrical, as a result of which it has n independent eigenvectors. Theorem 2 is now confirmed by the similarity of matrices K and $\hat{K}$.

The non-positive nature of the eigenvalues leads to a corollary.

Corollary 1. In a system of unimolecular reversible reactions, oscillations are impossible.

The characteristic vectors of a symmetrical matrix are linked by orthogonality relations. Since these relations will be used below to find the characteristic vectors, we may also note another corollary.

Corollary 2. The characteristic vectors $X_j(x_{j1}, \ldots, x_{jn})$ of the matrix K are linked by relations of the type

$$(X_i, D^{-1}\cdot X_i)=0, \tag{17}$$

where the brackets indicate a scalar product and the matrix D^{-1} is defined thus:

$$D^{-1}=\begin{pmatrix} \frac{1}{a_1^*} & & \\ & \ddots & \\ & & \frac{1}{a_n^*} \end{pmatrix}. \tag{18}$$

D. Solution for a First-Order Reaction System in Terms of the Concentrations of the Characteristic Substances

We saw above that there exist n characteristic composition vectors in the composition space for a system of reversible unimolecular reactions. Suppose that the unit characteristic vector in the initial coordinate system is designated by X_i. We select the unit vectors X_i as the new coordinate system. We shall refer to the system as the characteristic system or the system of equivalent substances B. Any composition vector can be written in the form

$$\alpha=\sum_{i=0}^{n-1} b_i(t)\,X_i. \tag{19}$$

When α is substituted in the initial equation (3), we obtain

$$\frac{d\boldsymbol{\alpha}}{dt}=\sum_{i=0}^{n-1}\frac{db_i}{dt}X_i=K\boldsymbol{\alpha}=\sum_{i=0}^{n-1} b_i(t)\cdot\lambda_i X_i,$$

whence

$$\frac{db_i}{dt}=\lambda_i b_i, \quad \lambda_i\leqslant 0. \tag{20}$$

The solution of Eqn. (20) presents no difficulties:

$$b_i(t)=b_i^0 e^{\lambda_i t}; \quad i=0, \ldots n-1. \tag{21}$$

If $\lambda_i < 0$, then $b_i(t)\to 0$ when $t\to\infty$. Substitution of $b_i(t)$ defined by Eqn. (21) in Eqn. (19) yields

$$\alpha=\sum_{i=0}^{n-1} b_i^0 e^{\lambda_i t}X_i. \tag{22}$$

Since material balance must hold, then at least one eigenvalue should be zero. We shall denote it by λ_0. Then

$$\alpha=b_0^0X_0+\sum_{i=1}^{n-1} b_i^0 e^{\lambda_i t}X_i. \tag{23}$$

Since the sum of the concentrations of the components at any instant is unity, we obtain

$$\sum_{j=1}^{n}\alpha_j=b_0^0\sum_{j=1}^{n}x_{0j}+\sum_{i=1}^{n-1}b_i^0 e^{\lambda_i t}\cdot\sum_{j=1}^{n}x_{ij}\equiv 1. \tag{24}$$

It follows from Eqn. (24) that $\sum_{j=1}^{n} x_{ij}=0$ and that the following relation holds when the length X_0 is suitably chosen

$$\sum_{j=1}^{n} x_{0j}=1. \tag{25}$$

Evidently there exists only one positively defined characteristic composition vector X_0 in the system. All other characteristic vectors contain negative elements,

since otherwise the equality $\sum_{j=1}^{n} x_{ij}=0$ would have been impossible. Geometrically this condition implies that the characteristic vectors are perpendicular to the vector $I\{1, 1, 1\}$. For a three-dimensional system, the vectors $X_i(i \neq 0)$ are parallel to the plane of the reaction triangle. Since the vectors X_i contain negative coordinates, linear reaction pathways directed along these vectors cannot be observed experimentally. A significant feature of reversible reactions is that at equilibrium the system contains all the substances for which the equilibrium characteristic vector X_0 does not have zero coordinates. One can therefore always find a linear combination of X_0 and X_i such that the resultant vector is non-negatively defined.

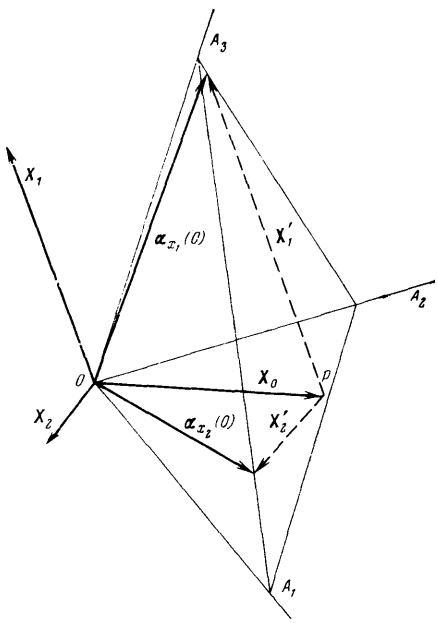


Figure 2. Disposition of the characteristic vectors for a three-component system. The dashed lines represent the characteristic vectors transferred to the equilibrium point P.

We now turn to the geometrical interpretation for a three-component system. Since the vectors X_1 and X_2 are parallel to the plane of the reaction triangle and during the reaction move to the equilibrium point P (Fig. 2) located in the plane of the reaction triangle, one may assert that the vectors X_1 and X_2 lie in this plane. We have not so far refined the lengths of the vectors X_1 and X_2 which are the unit vectors in the system B. We shall choose them in such a way that their ends are located on the sides of the reaction triangle. The vector sums

$$\alpha_{x_1}(0)=X_0+X_1 \quad \text{and} \quad \alpha_{x_2}(0)=X_0+X_2 \tag{26}$$

then correspond to real compositions.

Definition 3. The characteristic vectors $X_i(i \neq 0)$ satisfy Eqn. (26), where X_0 is a positively defined vector and $\alpha_{X_i}(0)$ a non-negatively defined vector, will be called quasipositive. At least one element of each vector $\alpha_{X_i}(0)$ is zero owing to the above choice of the length of the vectors X_i, which restricts $\alpha_{X_i}(0)$ to the area bounded by the reaction triangle.

Eqns. (26) are equivalent to Eqns. (22) for $n = 3$, $b_0^0 = b_1^0 = 1$, $b_2^0 = 0$ or $b_0^0 = b_2^0 = 1$, $b_1^0 = 0$. Using Eqns. (22) and (26), we obtain equations for the migration of $\alpha_{X_1}(t)$ and $\alpha_{X_2}(t)$ towards equilibrium:

$$\alpha_{x_1}(t)=X_0+e^{\lambda_1 t}X_1, \tag{27}$$

$$\alpha_{x_2}(t)=X_0+e^{\lambda_2 t}X_2. \tag{28}$$

Eqns. (27) and (28) define linear reaction pathways in the composition space. They show that

$$X_i=\alpha_{x_i}(0)-X_0. \tag{29}$$

Thus, in order to determine the characteristic vectors, it is necessary to know the points of intersection of the linear reaction pathways with the sides of the reaction triangle and the equilibrium composition vector. The problem of the determination of the eigenvectors has been reduced to finding the linear reaction pathways. The eigenvectors are fully defined within the composition space and their determination does not require the knowledge of the reaction time.

E. Method for the Determination of Rate Constants from Experimental Data

The following method has been proposed for the experimental determination of linear pathways. We select any convenient initial composition and determine the corresponding reaction pathway. Fairly close to equilibrium, the reaction pathway is determined by the characteristic vector with the lowest eigenvalue. Linear extrapolation of the section of the pathway near equilibrium yields a new initial composition. This process is repeated until the reaction pathway becomes linear. Having eliminated the time t from Eqns. (21), we obtain

$$\ln b_i=\text{const}+\left(\frac{\lambda_i}{\lambda_j}\right)\ln b_j. \tag{30}$$

By determining the compositions along two linear sections, it is possible to find b_i and b_j and then λ_i/λ_j from the slope of the linear plot of $\ln b_i$ against $\ln b_j$. The matrix X can be set up using the coordinates of the characteristic vectors and the eigenvalues can be used to obtain the diagonal matrix Λ.

These data are sufficient to determine the relative rate constants from the relation

$$K=X\Lambda X^{-1} \quad . \tag{31}$$

The inverse of a matrix X^{-1} can be calculated as follows[16]. One evaluates initially the diagonal matrix L from the formula

$$L=X^{T}D^{-1}X, \tag{32}$$

where X^T is the transpose of a matrix. After this, the inverse of a matrix can be calculated from the equation

$$X^{-1}=L^{-1}X^{T}D^{-1}. \tag{33}$$

The graphical method, which is convenient for a three-component system, is virtually inapplicable to a system with a larger number of components. In this case, the

reaction pathway can be conveniently specified in a parametric form having selected as the parameter the concentration a_j of one of the components (which varies monotonically with time). For an n-component system, there are $n - 1$ equations of the type

$$a_{x_l}(t) = X_0 + e^{\lambda_l t} X_l, \tag{34}$$

corresponding to linear reaction pathways. We shall consider the linear pathway corresponding to the lth characteristic vector and shall formulate equations which follow from Eqn. (34):

$$\begin{aligned} a_1 &= x_{10} + e^{\lambda_l t} x_{1l}, \\ a_2 &= x_{20} + e^{\lambda_l t} x_{2l}, \\ &\cdots\cdots\cdots\cdots \\ a_n &= x_{n0} + e^{\lambda_l t} x_{nl}. \end{aligned} \tag{35}$$

If t is eliminated with the aid of the jth equation from the remaining equations, we obtain $n - 1$ equations of the type

$$a_m = \left(a_m^* - \frac{x_{ml}}{x_{jl}} a_j^*\right) + \frac{x_{ml}}{x_{jl}} a_j. \tag{36}$$

Thus the linear pathway in the $(n-1)$-dimensional space is converted into $n - 1$ straight lines in two-dimensional spaces. The method of approximations described above for $n = 3$ can be applied also to the general case with two-dimensional representations of the reaction pathways.

For n-component systems, one must bear in mind that, after the linear pathway corresponding to the characteristic vector X_j has been found, the new initial composition used to find the vector X_{j+1} cannot be selected arbitrarily. The point is that, for certain initial compositions, the method of approximations can lead to the same linear reaction pathway. To prevent this, the initial composition is chosen in such a way that the vector $[X_0 - a(0)]$ in the system B is orthogonal with respect to X_j. The procedure will be elucidated in detail in relation to the example described below.

F. Pseudounimolecular Systems of Heterogeneous Catalytic Reactions

We considered above unimolecular reactions only. However, there exists an important class of non-linear systems for which the above results are valid. Consider a pseudounimolecular system of reactions, which will be referred to as the reaction system, where the rate of change of the amounts of various substances is expressed as first order by the law of mass action, each term of the equation being multiplied by the same function of composition and time. For example, heterogeneous first-order reactions occurring on the homogeneous catalyst surface are pseudounimolecular. For the simplest mechanism of reversible reactions A $\rightleftharpoons$ B, one can write

$$\frac{dc_A}{dt} = -(k_1 c_A - k_2 c_B)\,\varphi(c_A, c_B), \tag{37}$$

$$\frac{dc_B}{dt} = (k_1 c_A - k_2 c_B)\,\varphi(c_A, c_B), \tag{38}$$

where

$$\varphi(c_A, c_B) = \frac{1}{1 + c_A b_A + c_B b_B}. \tag{39}$$

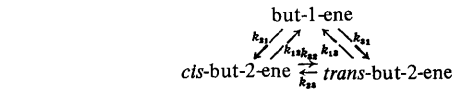
It was shown above that the matrix of the relative rate constants can be determined using only the information about the compositions and disregarding the reaction time. It is therefore possible to reduce pseudounimolecular reactions to the case analysed above by introducing a new time scale. For this purpose, we shall assume that $\varphi[c_A(t), c_B(t)]$ is a function of time and shall replace the independent variable:

$$d\tau = \varphi(t)\,dt, \tag{40}$$

which yields a system of unimolecular reactions.

G. Examples of the Determination of the Rate Constants for Reversible Unimolecular Reactions

Example 1. We shall consider initially a three-component system. The isomerisation of butenes on alumina has been investigated by Haag and Pines[23]. If it is assumed that the catalyst surface is homogeneous, the system may be regarded as pseudounimolecular. The method described above has been used[16] to calculate the rate constants. The designation of the rate constants is indicated in the scheme below:



(I)

Fig. 3 illustrates the reaction pathway obtained when pure *cis*-but-2-ene is introduced into the reactor. The dashed line represents the tangent to the curved reaction pathway drawn near the equilibrium point. The intersection of the tangent with the side of the triangle yields a new initial composition:

$$a(0) = \begin{pmatrix} 0.24 \\ 0.76 \\ 0 \end{pmatrix}.$$

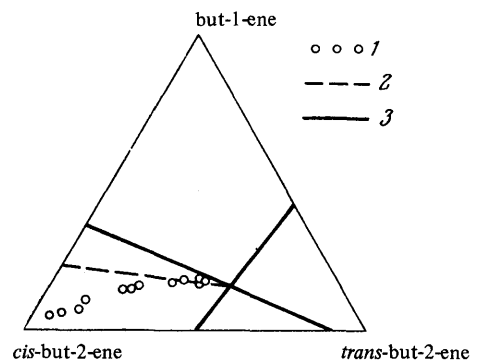


Figure 3. The study of the isomerisation of butenes in the presence of Al_2O_3: 1) reaction pathway obtained following the introduction of pure *cis*-but-2-ene into the reactor; 2) tangent to the reaction pathway; 3) linear pathways.

The sequence of components in the column matrix is

$$\begin{pmatrix} \text{but-1-ene} \\ \textit{cis}\text{-but-2-ene} \\ \textit{trans}\text{-but-2-ene} \end{pmatrix}.$$

Next, experiments were performed with the new initial composition. Table 1 presents the last twelve points forming an approximately linear section in the vicinity of equilibrium. A straight line passing through these points and the equilibrium point was fitted by the method of least squares:

$$\alpha^* = X_0 = \begin{pmatrix} 0.1436 \\ 0.3213 \\ 0.5351 \end{pmatrix} .$$

Table 1. Series of compositions for the second approximation in the isomerisation of butenes.

But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene	But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene
0.1622	0.3604	0.4775	0.1537	0.3471	0.4992
0.1776	0.3769	0.4455	0.1571	0.3464	0.4965
0.1664	0.3595	0.4741	0.1542	0.3431	0.5027
0.1654	0.3622	0.4724	0.1521	0.3451	0.5028
0.1690	0.3671	0.4639	0.2525	0.3408	0.5067
0.1603	0.3441	0.4955	0.1532	0.3416	0.5052

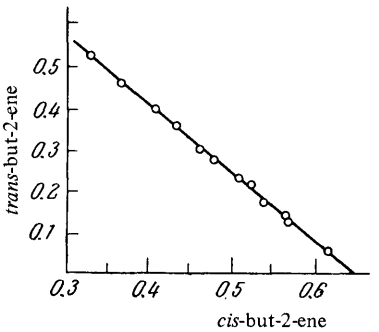


Figure 4. The linear reaction pathway in the isomerisation of butenes.

Its extrapolation to the side of the triangle yielded a new initial composition:

$$\alpha'(0) = \begin{pmatrix} 0.3286 \\ 0.6714 \\ 0.0000 \end{pmatrix} .$$

Fig. 4 presents the composition points for the reaction pathway corresponding to the last initial composition in the fourth approximation. This composition,

$$\alpha(0) = \begin{pmatrix} 0.3492 \\ 0.6508 \\ 0.0000 \end{pmatrix}$$

was used to determine the vector X_1. Using $\alpha(0)$ and X_0, we obtain

$$X_1 = \alpha(0) - X_0 = \begin{pmatrix} 0.2056 \\ 0.3295 \\ -0.5351 \end{pmatrix} .$$

Calculation of the third characteristic vector. The vector X_2 may be calculated without additional measurements using the orthogonality relations (17). In our case the matrices $D^{1/2}$ and $D^{-1/2}$ are

$$D^{1/2} = \begin{pmatrix} 0.3789 & 0 & 0 \\ 0 & 0.5668 & 0 \\ 0 & 0 & 0.7315 \end{pmatrix},$$

$$D^{-1/2} = \begin{pmatrix} 2.6389 & 0 & 0 \\ 0 & 1.7642 & 0 \\ 0 & 0 & 1.3670 \end{pmatrix} .$$

We calculate the vectors

$$\bar{X}_0 = D^{-1/2} X_0 = \begin{pmatrix} 0.3789 \\ 0.5668 \\ 0.7315 \end{pmatrix}$$

$$\bar{X}_1 = D^{-1/2} X_1 = \begin{pmatrix} 0.5426 \\ 0.5812 \\ -0.7315 \end{pmatrix} .$$

$\bar{X}_1$ is adjusted to unit length:

$$l_1 = (\bar{X}_1, \bar{X}_1) = 1.1673 .$$

The round brackets indicate a scalar product.

$$\bar{X}_1 / \sqrt{l_1} = \begin{pmatrix} 0.5022 \\ 0.5380 \\ -0.6771 \end{pmatrix} .$$

The vector X_2 is orthogonal with respect to $\bar{X}_0$ and $\bar{X}_1$. We take initially the vector $\bar{\gamma}_1$, orthogonal with respect to X_0; this can be readily done, for example, by interchanging the first two elements of X_0, reversing the sign of one of them, and setting the third equal to zero:

$$\bar{\gamma}_1 = \begin{pmatrix} -0.5668 \\ 0.3789 \\ 0.0000 \end{pmatrix} .$$

We shall now seek $\bar{\gamma}_2$ in the form of a linear combination of $\bar{X}_1$ and $\bar{\gamma}_1$:

$$\bar{\gamma}_2 = \bar{X}_1 + \lambda \bar{\gamma}_1 .$$

From the condition that $\bar{X}_2$ and $\bar{\gamma}_1$ are perpendicular, it is easy to find that

$$\lambda = -\frac{1}{(\bar{\gamma}, \bar{X}_1)};$$

$$\bar{\gamma}_2 = \bar{X}_1 - \frac{\bar{\gamma}}{(\bar{\gamma}_1, \bar{X}_1)} = \begin{pmatrix} -0.5262 \\ 0.4224 \\ -0.0547 \end{pmatrix} .$$

We now retransform $\bar{\gamma}$ so that it applies to a non-orthogonal system:

$$\gamma_2 = D^{1/2} \bar{\gamma}_2 = \begin{pmatrix} -0.1994 \\ 0.2394 \\ -0.0400 \end{pmatrix} .$$

The vectors γ_2 and X_2 are parallel. The length of X_2 is chosen so that the first coordinate of the vector $X_2 + X_0 = \alpha_{X_2}(0)$ is zero:

$$X_2 = \begin{pmatrix} -0.1436 \\ 0.1724 \\ -0.0288 \end{pmatrix} .$$

We now find

$$\alpha_{x_2} = X_2 + X_0 = \begin{pmatrix} 0.0000 \\ 0.4937 \\ 0.5063 \end{pmatrix} .$$

On combining the vectors X_0, X_1, and X_2, we obtain the matrix

$$X=\begin{pmatrix}0.1436 & 0.2056 & -0.1436\\ 0.3219 & 0.3295 & 0.1724\\ 0.5351 & -0.5351 & -0.0288\end{pmatrix}.$$

Calculation of the inverse of a matrix. The matrix D^{-1} will be determined from the equilibrium amounts:

$$D^{-1}=\begin{pmatrix}6.9638 & 0 & 0\\ 0 & 3.1123 & 0\\ 0 & 0 & 1.8688\end{pmatrix}.$$

We calculate the matrix

$$L=X^{T}D^{-1}X=\begin{pmatrix}1.000 & 0 & 0\\ 0 & 0.8566 & 0\\ 0 & 0 & 4.2077\end{pmatrix}.$$

The inverse of the matrix is found from the equation

$$X^{-1}=L^{-1}X^{T}D^{-1}=\begin{pmatrix}1.000 & 1.000 & 1.000\\ 1.2265 & 0.8784 & -0.8560\\ -4.2077 & 2.2579 & -0.2269\end{pmatrix}.$$

Experimental determination of the ratios of the characteristic roots and calculation of the matrix of the relative rate constants. We now transform the reaction pathway for pure *cis*-but-2-ene so that it applies to the system B by means of the formula $\beta = X^{-1}\alpha$. The results of the recalculation are presented in Table 2.

Table 2. Isomerisation of butene.

t	$\alpha(t)$	$\beta(t)$	t	$\alpha(t)$	$\beta(t)$
t_0	0.0000	1.0000	t_3	0.1411	1.000
	1.0000	0.8784		0.6487	0.5629
	0.0000	2.2579		0.2102	0.8233
t_1	0.0543	1.0000	t_4	0.1620	1.0000
	0.8897	0.8001		0.5230	0.3883
	0.0560	1.7677		0.3150	0.4279
t_2	0.0854	1.000			
	0.8177	0.7400			
	0.0969	1.4650			

Fig. 5 illustrates the variation of $\ln b_1$ with $\ln b_2$. Evidently Eqn. (30) yields a straight line whose slope can be used to find the ratio of the characteristic roots λ_1/λ_2. Having determined $\lambda_1/\lambda_2 = 0.4769$ from the graph, we obtain the matrix:

$$\Lambda'=\begin{pmatrix}0.0000 & 0.0000 & 0.0000\\ 0.0000 & -0.4769 & 0.0000\\ 0.0000 & 0.0000 & -1.0000\end{pmatrix}.$$

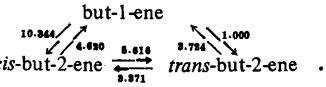
The matrix K^1 is calculated from the formula

$$K^1=X\Lambda'X^{-1}=\begin{pmatrix}-0.72 & 0.2381 & 0.0515\\ 0.5327 & -0.5273 & 0.1736\\ 0.1918 & 0.2982 & -0.2251\end{pmatrix}.$$

The matrix of the relative rate constants K can now be readily evaluated after dividing all the elements by 0.0515:

$$K=\begin{pmatrix}-14.068 & 4.623 & 1.000\\ 10.344 & -10.239 & 3.371\\ 3.724 & 5.616 & -4.371\end{pmatrix}.$$

Thus the relative rate constants are



(II)

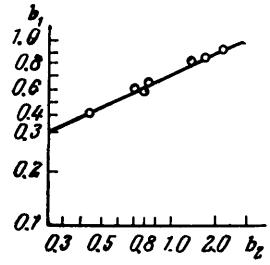


Figure 5. Variation of $\ln b_1$ with $\ln b_2$ for pure *cis*-but-2-ene as the initial species. The slope of the straight line is 0.4769.

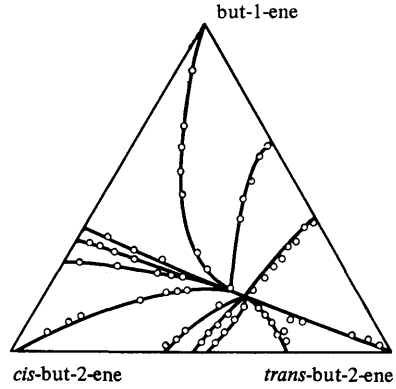
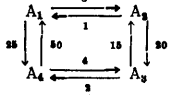


Figure 6. Comparison of the calculated reaction pathways (continuous lines) with the experimental compositions (circles) for the isomerisation of butenes.

Fig. 6 illustrates the comparison of the calculated and experimental reaction pathways.

Example 2. We shall now examine a hypothetical four-component system to which the following scheme corresponds:



(III)

Subsequently "experimental" data were obtained[16] by calculation from the exact characteristic vectors and roots based on scheme (III). Errors obeying the normal distribution for the standard deviation $\sigma = 1\%$ were added to the exact compositions.

The pure substance A was used as the initial composition. Nine "experimental compositions" along the reaction pathway were used to plot a_m against a_j in Fig. 7. The equilibrium values are located on the vertical dashed line on the left-hand side. The Figure also shows the linear approximations for each curve near equilibrium. The tangents have been produced to the a_1 axis. A vertical line is drawn from the point of intersection with the a_1 axis (corresponding to the substance A_2) nearest to the origin of coordinates. The ordinates of the intercepts of the tangents with this straight line form the matrix

$$\begin{pmatrix} 0.3274 \\ 0.0000 \\ 0.0397 \\ 0.6329 \end{pmatrix}.$$

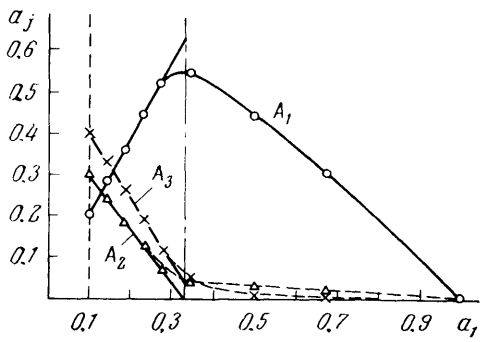


Figure 7. Method for the determination of the new initial composition in the search for a linear reaction pathway in a four-component system.

The sum of the elements of this matrix is 0.008 owing to random errors. In order to obtain a new composition, we therefore divide the matrix elements by 1.008:

$$\alpha_{x_1'}(0) = \begin{pmatrix} 0.3248 \\ 0.0000 \\ 0.0394 \\ 0.6279 \end{pmatrix}.$$

The above procedure was then repeated until a sufficiently close agreement was obtained between successive values found on extrapolation. This yielded the matrix

$$\alpha_{x_1}(0) = \begin{pmatrix} 0.3214 \\ 0.0000 \\ 0.0382 \\ 0.6404 \end{pmatrix}.$$

The equilibrium vector is

$$\alpha^* = X_0 = \begin{pmatrix} 0.1000 \\ 0.2000 \\ 0.4000 \\ 0.2000 \end{pmatrix}.$$

We now calculate

$$X_1 = \alpha_{x_1}(0) - X_0 = \begin{pmatrix} 0.2214 \\ -0.3000 \\ -0.3618 \\ 0.4404 \end{pmatrix}.$$

In order to select a new composition, we use the following procedure. We calculate the vectors $\bar{X}_0$ and $\bar{X}_1$ in the coordinate system B:

$$\bar{X}_0 = D^{-1/2} X_0 = \begin{pmatrix} 0.316228 \\ 0.547723 \\ 0.632456 \\ 0.447214 \end{pmatrix}.$$

After similar calculations and normalisation, we obtain

$$\bar{X}_1 = \begin{pmatrix} 0.484615 \\ -0.379123 \\ -0.395966 \\ 0.681634 \end{pmatrix}.$$

We now contruct a vector orthogonal with respect to X_1 and X_0 and use it to calculate the initial composition. We set up the vector

$$\bar{\gamma}_1 = \begin{pmatrix} 0.0000 \\ -0.622456 \\ 0.547723 \\ 0.000000 \end{pmatrix}.$$

Evidently γ_1 is orthogonal with respect to $\bar{X}_1$. We calculate

$$\bar{\gamma}_2 = \bar{\gamma}_1 - (\bar{X}_1, \bar{\gamma}_1) = \begin{pmatrix} -0.011097 \\ -0.623774 \\ 0.556790 \\ -0.015609 \end{pmatrix}.$$

After the transformation of γ_2 so that it applies to a non-orthogonal coordinate system and a change in length, we obtain

$$X_{2'} = \begin{pmatrix} -0.003081 \\ -0.30000 \\ 0.309211 \\ -0.006130 \end{pmatrix},$$

$$\alpha(0) = X_{2'} + X_0 = \begin{pmatrix} 0.0969 \\ 0.0000 \\ 0.7092 \\ 0.1939 \end{pmatrix}.$$

After repeating the successive approximations, starting from this composition, we obtain the vector

$$X_2 = \begin{pmatrix} -0.011748 \\ -0.300000 \\ 0.309178 \\ 0.002571 \end{pmatrix}.$$

The vector X_3 may be calculated from the orthogonality relations. Further calculations differed in insignificant details only from the case of a three-dimensional system examined above.

The isomerisation reactions of xylenes have been investigated[24] by a similar method. The experimental linear reaction pathways have been used[25] to test the calculated rate constants.

H. The Structure of Systems of First-Order Reversible Reactions

We shall now summarise the discussion of systems of unimolecular reversible reactions. The structure of these systems is fully described by the theorems formulated above. We found that there are n characteristic vectors with non-positive eigenvalues for reversible reactions in an n-dimensional composition space. Any solution of Eqns. (3) (or the reaction pathway) is a linear combination of characteristic vectors with time-dependent coefficients. One of the characteristic vectors, with a zero eigenvalue, is a positively defined equilibrium vector. The remaining characteristic vectors contain negative elements. However, a linear combination of each non-equilibrium characteristic vector with the equilibrium vector yields a non-negatively defined vector. Therefore all non-equilibrium characteristic vectors are quasi-positive. A linear reaction pathway located in the positive octant of the vector space corresponds to any quasipositive vector. All these linear pathways can be observed experimentally. The determination of $n-1$ linear reaction pathways makes it possible to calculate the matrix of relative rate constants without measuring the reaction time. The system of reversible unimolecular reactions approaches the unique equilibrium point monotonically, oscillations in the system being impossible. Curved reaction pathways approaching the equilibrium point via a spiral curve are therefore also impossible.

3. FIRST-ORDER SYSTEMS INVOLVING REVERSIBLE AND IRREVERSIBLE REACTIONS

A. The Form of the Kinetic Matrix

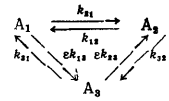
The structure of systems containing irreversible steps is significantly more complex than the structure of reversible reactions examined above. This is associated primarily with the fact that the principle of detailed balancing does not hold for systems involving irreversible steps. On the basis of this principle, we showed above that there is a complete system of characteristic vectors for reversible reactions in an n-dimensional composition space and also that the positive octant of the vector space contains $n-1$ linear reaction pathways. The study of these pathways actually made it possible to devise a method for the determination of the rate constants. A system of reversible reactions approaches the unique equilibrium point regardless of the chosen initial composition. When irreversible steps are present in the system, there may be an infinite number of equilibrium points, there may not be a complete system of characteristic vectors, and the linear reaction pathways may originate from the positive octant of the vector space. The study of irreversible reactions therefore requires a new approach, which will now be discussed.

We shall consider irreversible steps as the limiting cases of reversible stages, involving large changes in free energy or a large decrease in the corresponding rate constants[26]. For example, the simple scheme



(IV)

can be regarded as the limiting case of the scheme



(V)

when $\epsilon \to 0$. We shall show what information can be derived from the principle of detailed balancing in such a limiting transition. The Wegsheider condition for scheme (V) yields $k_{12}k_{23}k_{31} = k_{32}k_{21}k_{13}$. The rate constant matrix for scheme (V)

$$\begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & \varepsilon k_{13} \\ k_{21} & -(k_{12}+k_{32}) & \varepsilon k_{23} \\ k_{31} & k_{32} & -\varepsilon(k_{13}+k_{23}) \end{pmatrix}$$

becomes the kinetic matrix for system (IV) when $\epsilon \to 0$:

$$\begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & 0 \\ k_{21} & -(k_{12}+k_{32}) & 0 \\ k_{31} & k_{32} & 0 \end{pmatrix} \qquad (41)$$

The equilibrium concentrations for scheme (V) are calculated from the principle of detailed balancing:

$$\begin{aligned} a_1^* &= \varepsilon\,(k_{13}/k_{31})\,a_3^*, \\ a_2^* &= \varepsilon\,(k_{23}/k_{32})\,a_3^*, \\ a_3^* &= a_3^*. \end{aligned} \qquad (42)$$

The equilibrium composition matrix D changes in the following way when $\epsilon \to 0$:

$$\begin{pmatrix} a_1^* & 0 & 0 \\ 0 & a_2^* & 0 \\ 0 & 0 & a_3^* \end{pmatrix} \to \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The matrix D for scheme (IV) is degenerate, so that $D^{-1/2}$ does not exist and reduction to the symmetrical form which we used above is no longer possible. However, it follows from the principle of detailed balance that the ratio of the equilibrium concentrations is independent of ϵ:

$$\frac{a_1^*}{a_2^*} = \frac{k_{13}k_{23}}{k_{21}k_{32}} = \frac{k_{12}}{k_{21}}. \qquad (43)$$

It follows from Eqn. (43) that

$$\frac{a_1^*}{a_1^*+a_2^*} = \frac{k_{12}}{k_{12}+k_{21}}; \quad \frac{a_2^*}{a_1^*+a_2^*} = \frac{k_{21}}{k_{12}+k_{21}}.$$

We now construct the matrix

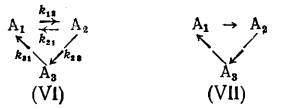
$$D = \begin{pmatrix} \frac{k_{12}}{k_{12}+k_{21}} & 0 & 0 \\ 0 & \frac{k_{21}}{k_{12}+k_{21}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (44)$$

and calculate

$$D^{-1/2}KD^{1/2} = \begin{pmatrix} \begin{bmatrix} -(k_{21}+k_{31}) & (k_{12}k_{21})^{1/2} \\ (k_{12}k_{21})^{1/2} & -(k_{12}+k_{23}) \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ k_{13} \quad k_{32} & 0 \end{pmatrix}. \qquad (45)$$

Evidently the submatrix enclosed in brackets is symmetrical. Thus, using the limiting form of the principle of detailed balancing, it is possible to reduce to a symmetrical form the submatrices corresponding to subsystems with reversible reactions. We shall use this fact below for the description of complex systems involving irreversible steps. However, one should note here that we shall be forced to restrict somewhat the range of subsystems considered. We shall postpone until the next

section the study of systems involving cycles of irreversible reactions. For example, schemes of the type

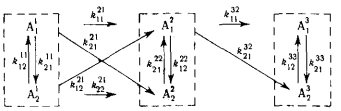


(VI) (VII)

are not analysed, because they cannot be regarded as limiting cases of the corresponding schemes for reversible reactions, since the Wegsheider condition is infringed in the limiting transition, i.e. the principle of detailed balance ceases to hold. In fact, we shall attempt to represent scheme (VI) as the limiting case of scheme (V) when the constants k_{32} and k_{13} tend to zero. Both these constants enter into the right-hand side of Eqn. (12), so that the condition defined by this equation breaks down when k_{32} and k_{13} decrease.

Below we shall formulate rigorously the class of systems to be considered. To extend the treatment from an example to the general case, we shall introduce certain concepts and symbols.

The irreversible stages in the general system can be isolated by subdividing the system into reversible subsystems linked by irreversible stages. We shall combine substances linked by reversible reactions into subsystems and shall consider the reactions between these subsystems, assuming them to be identical with fictitious simple substances. We shall consider the following scheme:



(VIII)

This system can be divided into subsystems:

$$M^1 \leftrightarrow \begin{matrix} A_1^1 \\ \updownarrow \\ A_2^1 \end{matrix}; \quad M^2 \leftrightarrow \begin{matrix} A_1^2 \\ \updownarrow \\ A_2^2 \end{matrix}; \quad M^3 \leftrightarrow \begin{matrix} A_1^3 \\ \updownarrow \\ A_2^3 \end{matrix} . \qquad (IX)$$

The entire system can then be represented thus: $M^1 \rightarrow M^2 \rightarrow M^3$. In designating the substances, the superscript refers to the number of the subsystem and the subscript to the number of the substance in the subsystem. The kinetic matrix assumes the following form:

$$K = \begin{Vmatrix} \begin{bmatrix} -(k_{21}^{11}+k_{11}^{21}+k_{21}^{21}) & k_{12}^{11} \\ k_{21}^{11} & -(k_{12}^{11}+k_{12}^{21}+k_{22}^{21}) \end{bmatrix} \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \\ \begin{bmatrix} k_{11}^{21} & k_{12}^{21} \\ k_{21}^{21} & k_{22}^{21} \end{bmatrix} \begin{bmatrix} -(k_{11}^{22}+k_{11}^{32}+k_{21}^{32}) & k_{12}^{22} \\ k_{21}^{22} & -k_{12}^{22} \end{bmatrix} \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} k_{11}^{32} & 0 \\ k_{21}^{32} & 0 \end{bmatrix} \begin{bmatrix} -k_{21}^{33} & k_{12}^{33} \\ k_{21}^{33}-k_{12}^{33} \end{bmatrix} \end{Vmatrix}.$$

In designating the rate constants, the superscripts again refer to the numbers of the subsystems and the subscripts to the numbers of the substances. The first subscript refers to the reaction product and the second to the starting material. Thus the rate constant for the reaction $A_5^1 \rightarrow A_4^3$ is designated by k_{45}^{31}.

If the submatrices enclosed in square brackets are designated by K^{ij}, we find that

$$K = \begin{pmatrix} K^{11} & 0 & 0 \\ K^{21} & K^{22} & 0 \\ 0 & K^{32} & K^{33} \end{pmatrix}. \qquad (46)$$

Evidently the kinetic matrix in the example considered is triangular.

We shall now deal with the general case. We shall put $M^\alpha \rightarrow M^\beta$ only when there is a series of consecutive reactions leading from subsystem M^α to subsystem M^β. For example $M^\alpha \rightarrow M^\beta$ if the following sequence of reactions occurs:

$$M^\alpha \rightarrow M^{\alpha+1} \rightarrow M^\beta \quad . \qquad (X)$$

We shall consider systems in which there are only three possibilities: (1) $M^\alpha \rightarrow M^\beta$; (2) $M^\beta \rightarrow M^\alpha$; (3) there is no interaction between M^α and M^β. Conditions 1 and 2 cannot be fulfilled simultaneously. It is readily seen that cycles are thus excluded from consideration. Conditions 1–3 determine the form of the kinetic matrix. We shall assign to the subsystems superscripts such that $\beta > \alpha M^\alpha \not\rightarrow M^\beta$, i.e. all the rate constants for the conversion of A_i^β into A_i^α are zero. After the introduction of such numbering of the subsystems, it is possible to formulate the kinetic matrix as follows:

$$K = \begin{pmatrix} K^{11} & \cdots & \cdots \\ K^{21} & K^{22} & \cdots \\ \cdots & \cdots & \cdots \\ K^{\nu 1} & \cdots & K^{\nu\nu} \end{pmatrix}, \qquad (47)$$

where the submatrices $K^{\beta\alpha}$ are the matrices of the rate constants for the irreversible reactions leading from M^α to M^β.

The diagonal submatrices $K^{\alpha\alpha}$ can be written as follows:

$$K^{\alpha\alpha} = K^{m\alpha} + \Sigma^{\cdot\alpha}, \qquad (48)$$

where $\Sigma^{\cdot\alpha}$ is the diagonal matrix corresponding to the irreversible reactions leading from M^α. The diagonal elements of $\Sigma^{\cdot\alpha}$ are equal to the sum of the elements of the corresponding column with the sign reversed. Systems with a kinetic matrix of type (47) are considered below.

B. The Eigenvalues

We shall set up for each diagonal submatrix a matrix of equilibrium ratios D^α, as was done in the example analysed above. We define for the entire system a non-degenerate diagonal matrix $D^{1/2}$:

$$D^{1/2} = \begin{pmatrix} (D^1)^{1/2} & & \\ & (D^2)^{1/2} & \\ & & \ddots \\ & & (D^\nu)^{1/2} \end{pmatrix}, \qquad (49)$$

where $(D^i)^{1/2}$ is the matrix of the equilibrium ratios for the irreversible subsystem M^i. The element with the number jj in the matrix $(D^i)^{1/2}$ is

$$[(a_j^i)^*]^{1/2} / \left[\sum_i (a_i)^*\right]^{1/2}.$$

It can be shown that the diagonal submatrices $B^{\alpha\alpha}$ of the matrix $B = D^{-1/2} K D^{1/2}$ are symmetrical. Hence follows theorem 3: The diagonal submatrices $K^{\alpha\alpha}$ of the triangular kinetic matrix K for a system involving reversible and irreversible stages possess a complete system of characteristic vectors.

It has also been shown[26] that the matrix of the characteristic vectors for the kinetic matrix K is triangular:

$$X = \begin{pmatrix} X^{11} & 0 & \cdots & 0 \\ X^{21} & X^{22} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ X^{\nu 1} & \cdots & \cdots & X^{\nu\nu} \end{pmatrix}, \qquad (50)$$

where $X^{\alpha\beta}$ is the matrix of the characteristic vectors of the submatrix $K^{\alpha\beta}$. There are m relations of the type

$$K^{\alpha\alpha} X^{\alpha\alpha} = X^{\alpha\alpha} \Lambda^\alpha, \qquad (51)$$

where m is the total number of reversible subsystems and Λ^{α} the matrix of the eigenvalues of the submatrix $K^{\alpha\alpha}$.

We therefore have theorem 4: all the eigenvalues of the kinetic matrix K are fully defined by the submatrices $K^{\alpha\alpha}$.

Corollary 1. All the eigenvalues of the matrix K are non-positive.

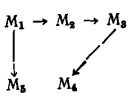
Corollary 2. Oscillations are impossible in a system involving reversible and irreversible first-order reactions with a triangular matrix K.

We found that each diagonal submatrix $K^{\alpha\alpha}$ has a complete system of characteristic vectors. However, from this it does not yet follow that the entire matrix K is a complete system of characteristic vectors. This is true only when the eigenvalues of the submatrices $K^{\alpha\alpha}$ and $K^{\beta\beta}$ are not the same. When the eigenvalues are the same, cases are possible where the kinetic matrix cannot be reduced to the diagonal form. Nevertheless, in practice the matrix K should usually have a complete system of eigenvectors. We shall prove the validity of this case and shall discuss it below.

C. Disposition of the Characteristic Vectors

We recall that a linear reaction pathway in the composition space corresponds to each characteristic vector. We are interested only in the linear pathways located in the positive octant of the space. For a system of reversible reactions, the non-equilibrium vectors were found to be quasipositive and the corresponding linear reaction pathways could be observed experimentally. We shall attempt to elucidate the disposition of the characteristic vectors in a system involving reversible and irreversible stages.

Definition 4. The subsystem M^{ν} is called finite if there are no irreversible reactions leading from this subsystem to others. A system may contain several finite subsystems. For example the subsystems M_5 and M_4 in the scheme



(XI)

are finite.

In each of s finite closed subsystems, there is an equilibrium positively defined characteristic vector $X_e^{\nu\nu}$. Thus the entire system contains s characteristic vectors of the type

$$X_e^{\nu} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ X_e^{\nu\nu} \end{pmatrix}, \qquad (52)$$

where X_e^{ν} is a column vector of the matrix X. All the linear combinations of these vectors are the equilibrium points of the system involving irreversible stages and all the equilibrium points are linear combinations of the equilibrium vectors. Thus the system contains s independent positive vectors in the positive octant.

A linear combination of equilibrium and non-equilibrium characteristic vectors in the systems considered does not necessarily give rise to a positively defined vector, since the equilibrium point is located in the composition subspace. In fact a criterion for the existence of quasipositive vectors, arising from the open subsystem $M^{\alpha} \rightarrow$, readily follows from the equation for a system with a unique equilibrium point:

$$\alpha_{x_i} = X_i^{\alpha} + X_e^{\nu} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ X_i^{\alpha\alpha} \\ X_i^{\alpha+1,\alpha} \\ \vdots \\ X_i^{\nu\alpha} \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ X_e^{\nu\nu} \end{pmatrix}. \qquad (53)$$

Theorem 5. For the characteristic vector X_i^{α}, where $\alpha < \nu$, to be quasipositive, it is necessary and sufficient that all the subvectors $X_i^{\beta\alpha}$ should contain only non-negative elements.

Theorem 6 [26]: The matrix $X^{\alpha\alpha}$ for the open subsystem $M^{\alpha} \rightarrow$ contains one and only one subvector $X_i^{\alpha\alpha}$, all the elements of which are non-negative. The existence of the positively defined vector follows from Wei's theorem[27], namely theorm 7: one of the following statements is valid for a system of first-order reactions including any number of components: either the equilibrium composition is non-zero or there is at least one linear pathway in the positive octant of the space.

Hence follows the conclusion that, which the system contains u open subsystems of type $M^{\alpha} \rightarrow$, there are at most u quasipositive vectors arising from these subsystems.

We shall consider yet another special case of subsystems such that there are no reactions leading from them to other open subsystems and there are only reactions leading to a finite subsystem. Subsystems of this kind are called adjacent to the finite system. Since the characteristic vector X_i^{α} for such a subsystem does not contain the subvectors $X_i^{\beta\alpha}$, where β is an open subsystem, it follows that there is always one quasipositive vector for each subsystem adjoining the finite system. If the system contains v adjacent subsystems, one can assert that there are v quasipositive vectors.

We shall also consider a pair of transitional subsystems of the type

$$\begin{matrix} M^{\alpha} & \rightarrow & M^{\beta} \\ \downarrow & & \downarrow \end{matrix}. \qquad (XII)$$

It is of interest to obtain a criterion of the absence of negative elements from the subvectors $X_r^{\beta\alpha}$.

This criterion is given by theorem 8: for transitional subsystems (XII), the subvector $X_r^{\beta\alpha}$, where M^{β} is an intermediate subsystem (not adjacent to the finite system) will not contain negative elements when $|\lambda_r^{\alpha}| < |\lambda_r^{\beta}|$ and will contain non-positive elements when $|\lambda_r^{\alpha}| > |\lambda_r^{\beta}|$.

We can now summarise the findings obtained from the consideration of the structure of systems involving irreversible stages. A complex system with reversible and irreversible stages can be conveniently represented by reversible subsystems linked by irreversible stages. It is possible to isolate two principal differences from systems involving reversible reactions only. The first is that the matrix K cannot always be reduced to a

diagonal form. However, in practice such instances should not arise frequently. It is therefore more important that not all the characteristic vectors are quasipositive and the corresponding linear pathways cannot be observed experimentally. The following statements may be made about the disposition of the eigenvectors:

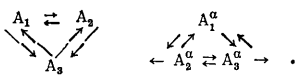
1. There exists a positively defined equilibrium characteristic vector for each finite subsystem.
2. All non-equilibrium characteristic vectors, arising from a finite subsystem, are quasipositive. The corresponding linear pathways can be observed experimentally.
3. The number q of quasipositive vectors arising from intermediate subsystems is between u (the number of all intermediate subsystems) and v (the number of subsystems adjoining the finite system).

Thus the characteristic vectors for systems involving irreversible stages are frequently not located in the positive quadrant of the composition space and it is impossible to obtain the positive vector from a linear combination of equilibrium and non-equilibrium characteristic vectors. A "projection" method has therefore been proposed[28] whereby artificial linear reaction pathways may be obtained.

D. Artificial Linear Reaction Pathways. Projection Method

The essential feature of the method in the simplest case reduces to the consideration, instead of the open subsystem $M^{\alpha}\rightarrow$, of a closed subsystem $\hat{M}^{\alpha}$, which is obtained by adding to the subsystem the mass loss as a result of irreversible reactions away from the subsystem. Geometrically this implies the projection of the reaction pathways on the $(1, 1, \ldots, 1)$ hyperplane.

Projection of the principal subvectors $X^{\alpha\alpha}$. We shall compare initially a reversible closed system M with a subsystem $M^{\alpha}\rightarrow$ in relation to three-component systems:



(XIII) (XIV)

In each of these systems, there is a positively defined characteristic vector. In the first case, this is an equilibrium vector X_e and in the second a vector $X_r^{\alpha\alpha}$. The equilibrium vector X_e contains the entire mass of the system M and the sum of all the elements of non-equilibrium characteristic vectors is zero. In other words, all the characteristic vectors X_i with $i \neq e$ are perpendicular to the unit vector I $(1, \ldots, 1)$ and they are therefore located in the $(1, 1, \ldots, 1)$ hyperplane. On the other hand, the $X_r^{\alpha\alpha}$ does not contain the mass of the entire system and the vectors $X_r^{\alpha\alpha}$ and I may not in fact be perpendicular. The disposition of the characteristic vectors is illustrated in Figs. 8 and 9. When the initial vector $a_x(0)$ of a closed system M is located in the plane of the equilibrium vector and one of the non-equilibrium characteristic vectors, the movement of the system towards equilibrium is given by the equation

$$a_x(t) = X_e + b_i(t)\,X_i. \qquad (54)$$

Thus a natural linear reaction pathway in the $(1, 1, \ldots, 1)$ hyperplane arises for each characteristic vector X_i. All the curved reaction pathways are also located in the $(1, 1, \ldots, 1)$ hyperplane. For the system $M^{\alpha}\rightarrow$, the reaction pathways can no longer be located in the plane perpendicular to the vector I, since the equilibrium point which the system approaches coincides with the origin of coordinates. If the initial vector is located in the plane of the vector $X_r^{\alpha\alpha}$ and one of the other characteristic vectors $X_i^{\alpha\alpha}$, then the movement towards equilibrium can be described by the equation

$$a_x(t) = b_r^{\alpha} X_r^{\alpha\alpha} + b_i^{\alpha}(t)\,X_i^{\alpha\alpha}. \qquad (55)$$

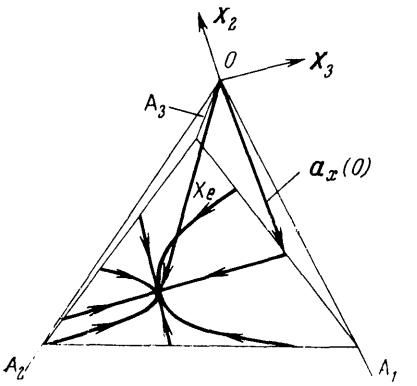


Figure 8. Reaction pathways and characteristic vectors for the system (XIII).

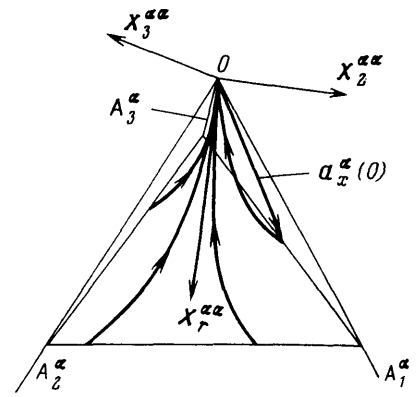


Figure 9. Reaction pathways and characteristic vectors for the system (XIV).

Since the vectors $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$ are non-zero, we obtain a curved reaction pathway. The only linear reaction pathway located in the positive octant of the vector space therefore coincides with the direction of the vector $X_r^{\alpha\alpha}$. Furthermore, Eqn. (55) shows that any composition vector located in the plane of $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$ for $t = 0$ remains in this plane subsequently. Thus the reaction pathway for the system $M^{\alpha}\rightarrow$ consists in the general case of a spatial curve. If this curve is projected onto the

(1, 1, ..., 1) hyperplane, it is possible to obtain an artificial linear reaction pathway. Fig. 10 illustrates a projection parallel to the vector $X_r^{\alpha\alpha}$, which yields an artificial linear reaction pathway.

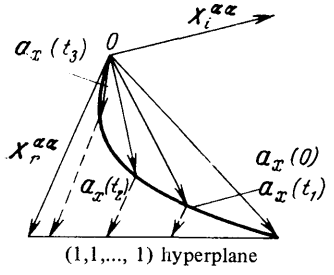
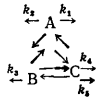


Figure 10. Projection of curved reaction pathways on the (1, 1, ..., 1) hyperplane.

We shall consider initially the specific case of the subsystems $M^{\alpha}\rightarrow$, where the sum of the rate constants for the irreversible reactions involving the ith substance of the subsystem is independent of the number i. Thus, for the subsystem



(XV)

this implies that $k_1 + k_2 = k_3 = k_4 + k_5 = c = \text{const}$. When the length of the characteristic vectors is chosen suitably, the following expression can be formulated for the reaction pathway in the subsystems considered:

$$a^{\alpha}(t) = e^{-ct} X_r^{\alpha\alpha} + \sum_{i=2}^{n^{\alpha}} b_i(t)\, X_i^{\alpha\alpha}, \qquad (56)$$

where n^{α} is the dimension of the subsystem $M^{\alpha}\rightarrow$. The entire mass of the system is concentrated at $X_r^{\alpha\alpha}$ and the remaining characteristic vectors are perpendicular to the unit vector $I = (1, 1, ..., 1)$. The loss of mass from the system owing to irreversible reactions is $X_r^{\alpha\alpha} - e^{-ct} X_r^{\alpha\alpha}$. Projection parallel to the direction of the vector $X_r^{\alpha\alpha}$ is equivalent to an artificial compensation for the mass lost as a result of the irreversible reactions. The artificial composition vector $\hat{a}^{\alpha}(t)$, arising on projection, is defined by the equation

$$\hat{a}^{\alpha}(t) = X_r^{\alpha\alpha} + \sum_{i=2}^{n^{\alpha}} b_i(t)\, X_i^{\alpha\alpha}. \qquad (57)$$

We obtained an equation for a closed system of reversible reactions with an artificial equilibrium point $X_r^{\alpha\alpha}$.

We shall now consider the general case of subsystems $M^{\alpha}\rightarrow$. In the general case, it is no longer possible to assume that all the vectors $X_i^{\alpha\alpha}$ are orthogonal with respect to the unit vector I (1, 1, ..., 1). The following equation holds for the reaction pathway:

$$a^{\alpha}(t) = b_r^{\alpha}(t)\, X_r^{\alpha\alpha} + \sum_k b_k^{\alpha}(t)\, X_k^{\alpha\alpha} + \sum_j b_j^{\alpha}(t)\, X_j^{\alpha\alpha}, \qquad (58)$$

where the vectors $X_k^{\alpha\alpha}$ are orthogonal with respect to the unit vector I, a condition which does not hold for the $X_j^{\alpha\alpha}$. The number of vectors $X_k^{\alpha\alpha}$ and $X_j^{\alpha\alpha}$ is unimportant and the only significant factor is that the total number of characteristic vectors $X_i^{\alpha\alpha}$ (for $i \neq r$) is equal to $n^{\alpha} - 1$. The length of the characteristic vectors orthogonal with respect to I will be chosen so that the vectors are located in the (1, 1, ..., 1) hyperplane.

We showed above that, when $M^{\alpha}\rightarrow$ is projected, it is converted into a closed subsystem $\hat{M}^{\alpha}$ with an equilibrium point $X_r^{\alpha\alpha}$. Since $X_r^{\alpha\alpha}$ contains the entire mass in the transformed subsystem $\hat{M}^{\alpha}$, the remaining characteristic vectors must be orthogonal to the unit vector I. Eqn. (58) can therefore be transformed in such a way that all the vectors other than $X_r^{\alpha\alpha}$ are orthogonal to the unit vector. Since the vectors $X_r^{\alpha\alpha}$ and $X_j^{\alpha\alpha}$ are located in the (1, 1, ..., 1) hyperplane, the vector $X_r^{\alpha\alpha} - X_r^{\alpha\alpha}$ must be located in a plane parallel to this hyperplane. The required transformation can therefore be obtained by adding $\Sigma b_i(t) X_r^{\alpha\alpha}$ to the first term of Eqn. (58) and by substracting it from the last term:

$$a^{\alpha}(t) = \left\{ b_r(t) + \sum_j b_j(t) \right\} X_r^{\alpha\alpha} + \sum_k b_k^{\alpha}(t)\, X_k^{\alpha\alpha} + \sum_j b_j^{\alpha}(t)\, (X_j^{\alpha\alpha} - X_r^{\alpha\alpha}). \qquad (59)$$

We shall now consider an artificial system $\hat{M}^{\alpha}\rightarrow$ obtained by projecting the vector $a^{\alpha}(t)$ onto the (1, 1, ..., 1) hyperplane parallel to $X_r^{\alpha\alpha}$. The weight loss from the system is

$$\left[b_r^{\alpha}(0) + \sum_j b_j^{\alpha}(0) \right] X_r^{\alpha\alpha} - \left[b_r^{\alpha}(t) + \sum_j b_j^{\alpha}(t) \right] X_r^{\alpha\alpha}. \qquad (60)$$

In order to obtain the artificial system, we add this amount to $a^{\alpha}(t)$ defined by the Eqn. (59):

$$\hat{a}^{\alpha}(t) = X_r^{\alpha\alpha} + \sum_k b_k^{\alpha}(t)\, X_k^{\alpha\alpha} + \sum_j b_j^{\alpha}(t)\, (X_j^{\alpha\alpha} - X_r^{\alpha\alpha}). \qquad (61)$$

The last equation is valid for an artificial closed system of reversible first-order reactions with a matrix $\hat{K}_{\alpha\alpha}$. The eigenvector matrix for $\hat{K}_{\alpha\alpha}$ is

$$\hat{X}^{\alpha\alpha} = (X_r^{\alpha\alpha}, \ldots\ldots X_k^{\alpha\alpha} \ldots\ldots (X_j^{\alpha\alpha} - X_r^{\alpha\alpha})). \qquad (62)$$

Projection in non-diagonal subsystems. In the previous section we considered the principal systems whose kinetic matrices are located on the diagonal of the matrix for the entire system. We shall now consider non-diagonal transitional subsystems.

We shall analyse initially two special cases: the system

$$M^{\alpha} \rightarrow M^{\nu}, \qquad (XVI)$$

where M^{ν} is a finite subsystem and

$$\begin{matrix} M^{\alpha} & \rightarrow & M^{\beta} \\ \downarrow & & \downarrow \end{matrix} \quad \text{when} \quad K^{\beta\alpha} \neq 0 . \qquad (XVII)$$

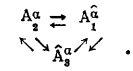
The system (XVI) is closed and all the characteristic vectors, except the equilibrium vector X_e^{ν}, are perpendicular to the vector I. The equilibrium vector X_e^{ν} is of the form $X_e^{\nu} = \begin{pmatrix} 0 \\ X_e^{\nu\nu} \end{pmatrix}$. The only quasipositive characteristic vector will be designated by X_e^{α}. The possibility

of obtaining artificial reaction pathways by projection will be examined in relation to the system



(XVIII)

Fig. 11 illustrates the (1, 1, 1, 1) hyperplane for the system (XVIII). The natural linear reaction pathway X_2^{α} is not located in the positive octant of the vector space. The curved reaction pathway, beginning in the $(X_r^{\alpha}, X_i^{\alpha})$ plane, remains in this plane until the attainment of the equilibrium point X_e^{α}. By projecting the curved pathway onto the subspace (1, 1, 0, 1), one can therefore obtain an artificial linear pathway in a finite segment of the positive octant. Such projection converts the system (XVIII) into the artificial system



(XIX)

The artificial equilibrium point N for the system (XIX) coincides with the point of intersection of the line of the vector X_r^{α} with subspace (1, 1, 0, 1).

Returning now to the general case, the equation for the system $M^{\alpha} \rightarrow M^{\nu}$ will be written in the form

$$a(t) = X_e^{\nu} + b_r^{\alpha}(t)\, X_r^{\alpha} + \sum_{i=2}^{n^{\nu}} b_i^{0}(t)\, X_i^{\nu} + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)\, X_i^{\alpha}. \tag{63}$$

We transform Eqn. (63) into the equation for a system of reversible reactions from which the component A_j^{ν} has been excluded. The final result is

$$\hat{a}(t) = \{X_e^{\nu} + CX_r^{\alpha}\} + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)\{X_i^{\alpha} - \varphi_i^{\alpha} X_r^{\alpha}\} + \sum_{i=2}^{n^{\nu}} b_i^{\nu}(t)\{X_i^{\nu} - \varphi_i^{\nu} X_r^{\alpha}\}, \tag{64}$$

where the scalars φ_i^k ($k = \alpha$ or ν) have been chosen so that $(X_{ik} - \varphi_i^k X_{jr}) = 0$; the constant C is chosen so that

$$\hat{a}_j^{\nu} = X_{je}^{\nu\nu} + CX_{jr}^{\nu\alpha} = 0. \tag{65}$$

The initial composition for the artificial linear pathway is determined from the equation

$$\hat{a}(0) = \{X_e^{\nu} + CX_r^{\alpha}\} + b_i^{k}(0)\{X_i^{k} - \varphi_i^{k} X_r^{\alpha}\}, \tag{66}$$

where $k = \alpha$ or ν.

It must be emphasised that a natural linear reaction pathway is a simple linear combination of the equilibrium vector and one non-equilibrium characteristic vector. On the other hand, an artificial linear pathway is a linear combination of several characteristic vectors,

We shall now consider the open system (XVII). We shall ignore all stages after $M^{\alpha} \rightarrow$ and $M^{\beta} \rightarrow$ and shall take into account only the subspace corresponding to $M^{\alpha} \rightarrow$ and $M^{\beta} \rightarrow$. The subvectors

$$X_i^{u} = \begin{pmatrix} X_i^{\alpha\alpha} \\ X_i^{\beta\alpha} \end{pmatrix}, \quad X_i^{\beta} = \begin{pmatrix} 0 \\ X_i^{\beta\beta} \end{pmatrix} \tag{67}$$

are the characteristic vectors of the subsystem (XVII).

We shall consider two cases of interest. It was shown previously that, when $\lambda_r^{\alpha} < \lambda_r^{\beta}$, then X_r^{u} should be a non-negative vector. It is possible to show that X_r^{u} consists of positive elements only. For the scheme (XVII), one can write the following equation:

$$a^{u}(t) = b_r^{\alpha}(t) + b_r^{\beta}(t)\, X_r^{\beta} + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)\, X_i^{u} + \sum_{i=2}^{n^{\beta}} b_i^{\beta}(t)\, X_i^{\beta}. \tag{68}$$

We shall assume, to make the treatment concrete, that none of the characteristic vectors is perpendicular to the vector I. Furthermore, the length of the characteristic vectors is chosen so that they are located in the (1,1,...,1) hyperplane.

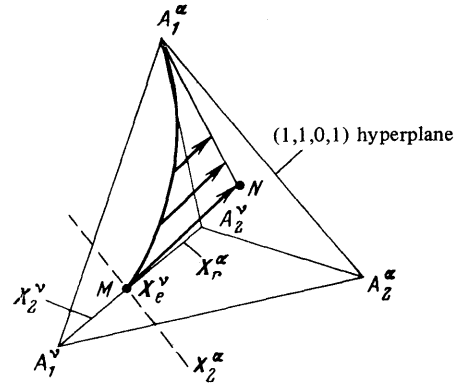


Figure 11. Parallel projection for the system (XVIII); M—equilibrium point; N—artificial equilibrium point.

Eqn. (68) can then be rewritten in the form

$$a^{u}(t) = (b_r^{\alpha}(t) + b_r^{\beta}(t)) + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t) + \sum_{i=2}^{n^{\beta}} b_i^{\beta}(t)\, X_r^{u} + \\ + b_r^{\beta}(t)\{X_r^{\beta} - X_i^{u}\} + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)(X_i^{u} - X_r^{u}) + \sum_{i=2}^{n^{\beta}} b_i^{\beta}(t)(X_i^{\beta} - X_r^{u}). \tag{69}$$

In Eqn. (69) the vectors $X_j^{R} - X_r^{u}$ ($j = i$ or r, $R = u$ or β) are perpendicular to the vector I. The entire loss of mass takes place along X_r^{u}. Parallel projection results in compensation for the loss of mass from the system:

$$\hat{a}^{u}(t) = X^{u} + b_r^{\beta}(t)\{X_r^{\beta} - X_i^{u}\} + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)\{X_i^{u} - X_r^{u}\} + \sum_{i=2}^{n^{\beta}} b_i^{\beta}(t)(X_i^{\beta} - X_r^{u}). \tag{70}$$

Eqn. (70) is the equation for a closed system of reversible reactions with an artificial equilibrium point X_r^{u}. The initial compositions for artificial linear reaction pathways are

$$\hat{a}_x(0) = X_r^{u} + b_i^{\alpha}(0)(X_i^{u} - X_r^{u}),\ i \neq r; \\ \hat{a}_x(0) = X_r^{u} + b_i^{\beta}(0)(X_i^{\beta} - X_r^{u}). \tag{71}$$

We shall now consider the case where $\lambda_r^{\alpha} > \lambda_r^{\beta}$. The subvector $X_r^{\beta\alpha}$ must contain negative elements and X_r^{u} is not located in the positive octant. In this case, the vector X_r^{u} can be used to transform the open system (XVII) into a closed system. By carrying out transformations similar to those described above, we obtain

$$\hat{a}^{u}(t) = X_r^{\beta} + b_r^{\alpha}(t)\{X_r^{u} - X_r^{\beta}\} + \\ + \sum_{i=2}^{n^{\alpha}} b_i^{\alpha}(t)\{X_i^{u} - X_r^{\beta}\} + \sum_{i=2}^{n^{\beta}} b_i^{\beta}(t)\{X_i^{\beta} - X_r^{\beta}\}. \tag{72}$$

The initial composition for a linear reaction pathway is determined from

$$\hat{a}_x(0) = X_r^\beta + b_r^\alpha(0)\{X_r^u - X_r^\beta\}. \quad (73)$$

Since $X_r^\beta = \begin{pmatrix} 0 \\ X_i^{\beta\beta} \end{pmatrix}$ and X_i^u contains negative elements for $i \neq r$, a linear pathway located in the positive octant is obtained only when the vector X_r^β is used. Next, suppose that $i \neq r$. Eqn. (72) can be regarded as one describing an artificial closed system $\hat{M}^\alpha \rightarrow \hat{M}^\beta$. Using a method similar to that described above, this system can be transformed into a system of reversible reactions with the exclusion of one component. The final result is

$$\hat{\hat{a}}^u(t) = X_r^\beta + C(X_r^u - X_r^\beta) + \sum_{i=1}^{n^\alpha} b_i^\alpha(t)\{X_i^u - X_r^\beta - \varphi_i^u(X_r^u - X_r^\beta)\} + \sum_{i=1}^{n^\beta} b_i^\beta(t)\{X_i^\beta - X_r^\beta - \varphi_i^\beta(X_r^u - X_r^\beta)\}. \quad (74)$$

The initial composition for a linear pathway is given by the formula

$$\hat{\hat{a}}_x(0) = X_r^\beta + C(X_r^u - X_r^\beta) + b_r^\alpha(0)\{X_i^u - X_r^\beta - \varphi_i^u(X_r^u - X_r^\beta)\}. \quad (75)$$

We shall now show how these results can be used to determine the rate constants.

E. Definition of the Rate Constants

Rate Constants for Reversible Reactions. All the constants for reversible reactions are located in the diagonal submatrices $K^{\alpha\alpha}$. It was shown above that

$$K^{\alpha\alpha} = X^{\alpha\alpha}\Lambda^\alpha(X^{\alpha\alpha})^{-1}. \quad (76)$$

If the principal subvectors $X_i^{\alpha\alpha}$ have been found, it is possible to determine the eigenvalues λ^α. Then, knowing $X_i^{\alpha\alpha}$ and the matrix Λ^α, it is possible to calculate the rate constant matrix from Eqn. (76).

The principal subvectors $X_i^{\alpha\alpha}$ are the characteristic vectors of the system $M^\alpha \rightarrow$. Since such a scheme involves a zero equilibrium composition, there exists only one natural linear reaction pathway located in the positive octant of the vector space and coinciding with the directions of the vector $X_r^{\alpha\alpha}$. However, if the composition vector $a_x^\alpha(t)$ is located initially in the plane of the vectors $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$, the movement of the system towards equilibrium is described by the equation

$$a_x^\alpha(t) = b_r^\alpha(t)\,X_r^{\alpha\alpha} + b_i^\alpha(t)\,X_i^{\alpha\alpha}. \quad (77)$$

When this curved pathway is projected onto the $(1, 1, \ldots, 1)$ hyperplane, it is possible to obtain an artificial linear reaction pathway. Using a projection parallel to the vector $X_r^{\alpha\alpha}$, we obtain the equation for the artificial composition vector $\hat{a}(t)$:

$$\hat{a}^\alpha(t) = a^\alpha(t) + \delta_i(t)\,X_{ri}^{\alpha\alpha}. \quad (78)$$

The scalar $\delta(t)$ is chosen so that

$$\delta(t) = 1 - \sum_{i=1;i}^{n^\alpha} a_i^\alpha(t). \quad (79)$$

The transformation of the subsystem A^α leads to a subsystem $\hat{M}^\alpha$ in which there are $n^\alpha - 1$ artificial linear reaction pathways for each vector $X_i^{\alpha\alpha}$ with $i \neq r$. These artificial linear pathways can be found by the procedure used to find the natural linear pathways in a system of reversible reactions. Thus the following steps are necessary for the determination of the rate constants in the subsystem $M^\alpha \rightarrow$:

1. One must find the natural linear reaction pathway and the unique quasipositive characteristic vector $X_r^{\alpha\alpha}$. This can be done as described above when reversible reactions were considered.
2. The experimental reaction pathways are recalculated in terms of Eqns. (78) and (79), which gives rise to the artificial subsystems $\hat{M}^\alpha$.
3. The linear reaction pathways and the vectors $\alpha_{xi}(0)$ must be found for the artificial subsystem $\hat{M}^\alpha$. This is again done by the procedure described above.
4. The vectors $X_i^{\alpha\alpha}$ with $i \neq r$ must be determined. Since the vectors $\hat{a}_x^\alpha(0)$, $X_i^{\alpha\alpha}$, and $X_r^{\alpha\alpha}$ are coplanar, it is sufficient to determine the constant γ in the equation

$$X_i^{\alpha\alpha} = \hat{a}_x^\alpha(0) + \gamma X_r^{\alpha\alpha}. \quad (80)$$

Using the orthogonality relations, we obtain

$$\gamma = -\frac{[(X_r^{\alpha\alpha})^T (D^\alpha)^{-1} a_x^\alpha(0)]}{[(X_r^{\alpha\alpha})^T (D^\alpha)^{-1} (X_r^{\alpha\alpha})]}, \quad (81)$$

where the superscript T implies the transpose of a matrix; the matrix $(D^\alpha)^{-1}$ is of the form

$$(D^\alpha)^{-1} = \begin{pmatrix} 1/a_1^* & & & \\ & \ddots & & \\ & & \ddots & \\ & & & 1/a_n^* \end{pmatrix}, \quad (82)$$

where a_i^* are the equilibrium concentrations in the absence of irreversible stages.

5. The eigenvalues must be determined.

For the subvector $X_r^{\alpha\alpha}$, located in positive octant of the space A^α, we can observe directly the rate of movement towards zero characteristic composition:

$$\hat{a}_x^\alpha(t) = b_r^\alpha(t)\,X_r^{\alpha\alpha} = b_r^\alpha(0)\cdot e^{\lambda_r^\alpha t} X_r^{\alpha\alpha}. \quad (83)$$

Consequently

$$\ln \frac{b_r^\alpha(t)}{b_r^\alpha(0)} = \lambda_r^\alpha t. \quad (84)$$

λ_r^α can therefore be found from the plot of $\ln[b_r^\alpha(t)/b_r^\alpha(0)]$ against t. However, this method cannot be applied to the subvectors $X_i^{\alpha\alpha}$ $(i \neq r)$, since they are not located in the positive octant of the vector space. On the other hand, we can determine the ratio $\lambda_i^\alpha/\lambda_r^\alpha$ from any curved pathway located in the plane of the vectors X_r and X_i.

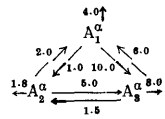
The corresponding equation is

$$\frac{b_i^\alpha(t)}{b_r^\alpha(t)} = \left[\frac{b_r^\alpha(t)}{b_r^\alpha(0)}\right]^{\lambda_i^\alpha/\lambda_r^\alpha}. \quad (85)$$

Having plotted $\ln[b_i^\alpha(t)/b_i^\alpha(0)]$ against $\ln[b_r^\alpha(t)/b_r^\alpha(0)]$ we should obtain a straight line with a slope equal to $\lambda_i^\alpha/\lambda_r^\alpha$. Furthermore, Eqn. (85) provides a method for the determination of the relative rate constants from experimental composition data without the need to know λ_r^α and the contact time. However, if we determine only the relative characteristic numbers λ_i^α for each subsystem $M^\alpha \rightarrow$, then

all the elements $K^{\alpha\alpha}$ will be referred to one of the constants within each subsystem of the reversible reactions. In order to obtain the final result, it is therefore necessary to reduce all the submatrices $K^{\alpha\alpha}$ to a single basis. The foregoing will be made clear by an example.

Example 3. Suppose that the following reaction scheme is specified:



(XX)

The rate constant matrix then assumes the following form:

$$K=\begin{pmatrix}-15.0 & 1.0 & 6.0\\ 1.0 & -8.8 & 1.5\\ 10.0 & 5.0 & -15.5\end{pmatrix}. \qquad (86)$$

Table 3 presents several points along the reaction pathway, which corresponds to the initial composition

$$a^\alpha(0)=\begin{pmatrix}1\\0\\0\end{pmatrix}. \qquad (87)$$

Table 3. Parallel projections for the system (XX).

t	$a^\alpha(t)$	$\sum_{i=1}^{n} a^\alpha(t)$	$\delta(t)$	$\delta(t)\,X_r^{\alpha\alpha}$	$\hat{a}^\alpha(t)$
0	$\begin{pmatrix}1\\0\\0\end{pmatrix}$	1.0	0	$\begin{pmatrix}0\\0\\0\end{pmatrix}$	$\begin{pmatrix}1\\0\\0\end{pmatrix}$
0.02	$\begin{pmatrix}0.7500\\0.0182\\0.1489\end{pmatrix}$	0.9171	0.0829	$\begin{pmatrix}0.0260\\0.0215\\0.0354\end{pmatrix}$	$\begin{pmatrix}0.7760\\0.0397\\0.1843\end{pmatrix}$
0.20	$\begin{pmatrix}0.1336\\0.0557\\0.1605\end{pmatrix}$	0.3498	0.6502	$\begin{pmatrix}0.2032\\0.1692\\0.2778\end{pmatrix}$	$\begin{pmatrix}0.3368\\0.2249\\0.4383\end{pmatrix}$

It also illustrates the course of the calculation for a parallel projection of the reaction pathway. The positively defined vector

$$X_r^{\alpha\alpha}=\begin{pmatrix}0.3126\\0.2602\\0.4272\end{pmatrix}, \qquad (88)$$

to which corresponds a natural linear reaction pathway, is assumed to be known in these calculations. Fig. 12 illustrates artificial linear pathways for the system (XX). In our example, the matrix $(D^\alpha)^{-1}$ is

$$(D^\alpha)^{-1}=\begin{pmatrix}1/0.3158 & 0 & 0\\ 0 & 1/0.1579 & 0\\ 0 & 0 & 1/0.5263\end{pmatrix}. \qquad (89)$$

We now determine the vector $X_2^{\alpha\alpha}$ from the initial composition for the linear section

$$\hat{a}_x^\alpha(0)=\begin{pmatrix}0.4510\\0\\0.549\end{pmatrix}. \qquad (90)$$

We obtain from Eqn. (81)

$$\gamma=-\frac{0.8920}{1.0850}=-0.8221. \qquad (91)$$

Eqn. (80) yields

$$X_2^{\alpha\alpha}=\begin{pmatrix}0.4510\\0\\0.5490\end{pmatrix}-0.8221\begin{pmatrix}0.3126\\0.2602\\0.4272\end{pmatrix}=\begin{pmatrix}0.1940\\-0.2139\\0.1978\end{pmatrix}. \qquad (92)$$

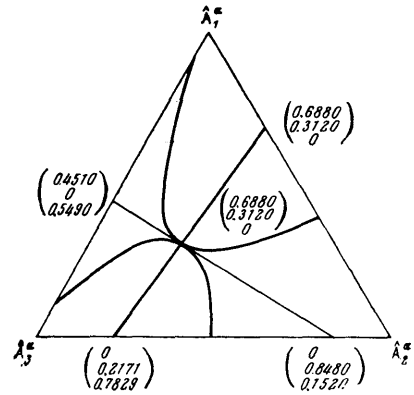


Figure 12. Artificial linear pathways for the system (XX).

The rate constant for irreversible reactions. In order to employ the above method for the determination of the individual constants for all irreversible reactions, it is necessary to determine the characteristic vectors for the systems containing both the main subvectors and the subvectors of the transitional systems. We shall consider initially two special cases: the system $M^\alpha \rightarrow M^\nu$ (where M^ν is a finite subsystem) and the open system

$$\begin{array}{ccc} M^\alpha & \rightarrow & M^\beta \\ \downarrow & & \downarrow \\ \text{when } K \neq 0 & & \end{array} \qquad (XXI)$$

The system $M^\alpha \rightarrow M^\nu$ is closed and the equilibrium characteristic vector is

$$X_e^\nu=\begin{pmatrix}0\\X_e^{\nu\nu}\end{pmatrix}. \qquad (93)$$

The system contains a unique natural linear reaction pathway corresponding to the vector X_r^α. We shall show below how to obtain artificial linear pathways corresponding to the vectors X_i^α $(i \neq r)$ by parallel projection. These linear pathways lie in a subspace of the composition space. We saw above that parallel projection gives rise to an artificial system $\hat{M}$ with the equilibrium vector $X_e^\alpha + CX_r^\alpha$.

The algorithm for the calculation of the rate constants for the system $M^\alpha \rightarrow M^\nu$ reduces to the following steps:

1. We find the natural linear reaction pathway and the positively defined vector X_r^α. The equilibrium vector X_e^ν is assumed to be known.

2. We consider the subsystem $M^{\alpha}\rightarrow$ and determine the subvectors $X_i^{\alpha\alpha}$ and the rate constants for the reversible reactions (see subsection D above).

3. We carry out a projection parallel to the vector X_r^{α} in accordance with the formula

$$\hat{a}(t) = a(t) + \delta(t) X_r^{\alpha}, \tag{94}$$

where $\delta(t)$ is chosen so that the ith coordinate of the vector $\hat{a}(t)$ should be zero, i.e. $\hat{a}_i(t) = 0$.

4. We find the equilibrium point in the artificial system $X_e^{\nu} + CX_r^{\alpha}$. The constant C is chosen on the basis of the condition that the ith coordinate of the equilibrium vector is equal to zero.

5. We find the artificial linear pathways and the vectors $\hat{a}_i(0)$.

6. We determine the vectors X_i^{α}, which requires the determination of the constants γ_1 and γ_2 in the equation

$$\begin{pmatrix} X_i^{\alpha\alpha} \\ X_i^{\nu\alpha} \end{pmatrix} = \gamma_1 \begin{pmatrix} X_r^{\alpha\alpha} \\ X_r^{\nu\alpha} \end{pmatrix} + \gamma_2 \left\{ \begin{pmatrix} a_x^{\alpha}(0) \\ a_x^{\nu}(0) \end{pmatrix} - \begin{pmatrix} 0 \\ X_e^{\nu\nu} \end{pmatrix} - C \begin{pmatrix} X_r^{\alpha\alpha} \\ X_r^{\nu\alpha} \end{pmatrix} \right\}. \tag{95}$$

The constants γ_1 and γ_2 are determined from the vector equation

$$X_i^{\alpha\alpha} = \gamma_1 X_r^{\alpha\alpha} + \gamma_2 \{a_x^{\alpha}(0) - CX_r^{\alpha\alpha}\} \tag{96}$$

using the known subvectors $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$.

7. The eigenvalues λ_i^{α} are determined in the study of the subsystem $M^{\alpha}\rightarrow$. The values of λ_i^{ν} are found when the subsystem M^{ν} is examined, as described in the discussion of reversible reactions.

Consider now the open system

$$\begin{array}{ccc} M^{\alpha} & \rightarrow & M^{\beta} \\ \downarrow & & \downarrow \end{array} \tag{XXII}$$

It was shown above that, when $|\lambda_r^{\alpha}| < |\lambda_r^{\beta}|$, the vector $X_r = \begin{matrix} 0 \\ X_r^{\beta\beta} \end{matrix}$ contains only positive elements. Depending on the relative eigenvalues, we should therefore project the reaction pathways parallel to X_r^{u} or X_r^{β}. Since natural linear pathways in the positive octant of the vector space correspond to positively defined vectors, the linear pathways should be found first and λ_r^{β} and λ_r^{α} should be determined. Assuming that this step has already been carried out, we shall consider two cases.

I. Let

$$|\lambda_r^{\alpha}| < |\lambda_r^{\beta}|. \tag{97}$$

(1) We set up an artificial subsystem by a projection parallel to X_r^{u} in accordance with the equation

$$\hat{a}^{u}(t) = a^{u}(t) + \delta(t) X_r^{u}, \tag{98}$$

where the scalar $\delta(t)$ is chosen so that the sum of the elements $a(t)$ is unity.

(2) We determine the linear pathways in the artificial subsystems $a_{x_i}(0)$.

(3) We determine the vectors

$$X_i^{u} = \gamma_1 \hat{a}_x(0) + \gamma_2 X_r^{u}. \tag{99}$$

The constants γ_1 and γ_2 are determined from the known subvector $X_i^{\alpha\alpha}$, which is found beforehand by studying the subsystem $M^{\alpha}\rightarrow$.

II. Let

$$|\lambda_r^{\alpha}| > |\lambda_r^{\beta}|.$$

(1) Projection parallel to the vector X_r^{β} leads to the equation

$$\hat{a}^{u}(t) = a^{u}(t) + \delta_1(t) X_r^{\beta}, \tag{100}$$

where $\delta_1(t)$ is chosen in such a way that the sum of the coordinates $\hat{a}_i^{u}(t)$ is unity. Such projection leads to an artificial closed system of the type $\hat{M}^{\alpha} \rightarrow \hat{M}^{\beta}$, in which there is a unique linear reaction pathway in the positive octant of the vector space and a unique characteristic vector X_r^{u} without negative elements.

(2) We find the linear reaction pathway and the vector $\hat{a}_x^{u}(0)$.

(3) We determine the vector X_2 from the equation

$$X_2^{u} = \begin{pmatrix} \hat{a}_x^{\alpha}(0) \\ \hat{a}_x^{\beta}(0) \end{pmatrix} + \gamma \begin{pmatrix} 0 \\ X_r^{\beta\beta} \end{pmatrix}. \tag{101}$$

The coefficient γ is determined by studying the curved pathway in the hyperplane of the vectors X_r^{u} and X_r^{β}. The reaction pathway in this hyperplane is given by the equation

$$a(t) = b_r^{\alpha}(t) X_r^{u} + b_r^{\beta}(t) X_r^{\beta}. \tag{102}$$

Using Eqn. (101), it can be shown that

$$b_r^{\alpha}(t) = e^{\lambda_r^{\alpha} t}; \; b_r^{\beta}(t) = -\gamma e^{\lambda_r^{\beta} t}. \tag{103}$$

It follows from Eqns. (102) and (103) that

$$F_1 = \left(\sum a_i^{\beta}(t) - e^{\lambda_r^{\alpha} t} \sum a_{x_i}^{\beta}(0)\right) = \gamma F_2 = \gamma (e^{\lambda_r^{\alpha} t} - e^{\lambda_2^{\beta} t}). \tag{104}$$

Since λ_r^{α} and λ_r^{β} may be assumed to have been determined from the study of the subsystems $M^{\alpha}\rightarrow$, the constant γ a can be found from the slope of the linear plot of F_1 against F_2.

(4) In order to determine the characteristic vectors X_i^{u}, where $i \neq r$, it is necessary to carry out a second projection using the vector $X_r^{u} - X_r^{\beta}$ in accordance with the formula

$$\hat{\hat{a}}^{u}(t) = \hat{a}^{u}(t) + \delta_2(t)(X_r^{u} - X_r^{\beta}), \tag{105}$$

where $\delta_2(t)$ is chosen so that one of the coordinates of the vector $\hat{\hat{a}}^{u}(t)$ is zero and the others are positive.

(5) We find the characteristic vectors X_i^{u}. For this purpose, it is necessary to determine the three constants in the equation

$$X_2^{u} = \gamma_1 \begin{pmatrix} \hat{\hat{a}}_x^{\alpha}(0) \\ \hat{\hat{a}}_x^{\beta}(0) \end{pmatrix} + \gamma_2 \begin{pmatrix} X_r^{\alpha\alpha} \\ X_r^{\beta\alpha} \end{pmatrix} + \gamma_3 \begin{pmatrix} 0 \\ X_r^{\beta\beta} \end{pmatrix}. \tag{106}$$

Since the subvector $X_2^{\alpha\alpha}$ may be regarded as known, a system of equations for the determination of γ_1 and γ_2 follows from the first row of Eqn. (106):

$$X_2^{\alpha\alpha} = \gamma_1 \hat{\hat{a}}^{\alpha}(0) + \gamma_2 X_r^{\alpha\alpha}. \tag{107}$$

The curved pathway in the subspace stretched over the three vectors X_i^{u}, X_r^{u}, and X_r^{β} may be used to determine γ_3:

$$a(t) = b_i^{\alpha}(t) X_i^{u} + b_r^{\alpha}(t) X_r^{u} + b_r^{\beta}(t) X_r^{\beta}; \tag{108}$$

and it can be shown that in our case

$$b_i^{\alpha}(t) = \frac{1}{\gamma_1} e^{-\lambda_1^{\alpha} t},$$

$$b_r^{\alpha}(t) = -\frac{\gamma_2}{\gamma_1} e^{-\lambda_r^{\alpha} t},$$

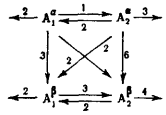
$$b_r^{\beta}(t) = -\frac{\gamma_3}{\gamma_1} e^{\lambda_r^{\beta} t}.$$

The constant γ_3 can be found from the slope of the linear plot of F_3 against F_4, where

$$F_3=\gamma_1\Big[\sum_i a_i^\beta(t)-e^{\lambda_i^\alpha t}\sum_i \hat{a}_x^\beta(0)\Big]-\gamma_2[e^{\lambda_i^\alpha t}-e^{\lambda_r^\alpha t}]X_r^{\beta\alpha};$$
$$F_4=[e^{\lambda_i^\alpha t}-e^{\lambda_r^\beta t}]\cdot\sum X_{ri}^{\beta\beta}. \qquad (109)$$

The procedure for the calculation of the constants can be made clear by the following artificial example[29].

Example 4. Consider the scheme



(XXIII)

The rate constant matrix is

$$K=\begin{pmatrix}-8 & 2 & 0 & 0\\ 1 & -13 & 0 & 0\\ 3 & 2 & -5 & 2\\ 2 & 6 & 3 & -6\end{pmatrix}, \qquad (110)$$

$\lambda_r^\alpha=-7.6277$ and $\lambda_r^\beta=-3.0$.

and the characteristic vector matrix assumes the following form:

$$X=\begin{pmatrix}-2.7446 & 8.7445 & 0 & 0\\ -0.5109 & -3.4891 & 0 & 0\\ 1.1861 & -1.6861 & 0.5 & -2\\ 3.0694 & 17.4307 & 0.5 & 3\end{pmatrix}. \qquad (111)$$

Fig. 13 illustrates the reaction pathways for the initial composition

$$\begin{pmatrix}0.5341\\ 0.0994\\ 0.3665\\ 0\end{pmatrix}.$$

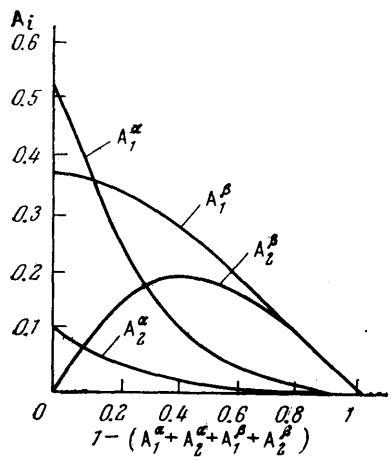


Figure 13. Reaction pathway for the system (XXIII).

Table 4 presents the calculations for a projection parallel to the vector

$$X_r^\beta=\begin{pmatrix}0\\ X_r^{\beta\beta}\end{pmatrix}=\begin{pmatrix}0\\ 0\\ 0.5\\ 0.5\end{pmatrix}. \qquad (112)$$

The artificial linear reaction pathway for the initial composition

$$\begin{pmatrix}0.5341\\ 0.0994\\ 0.3665\\ 0\end{pmatrix}$$

is illustrated in Fig. 14.

Table 4.

t	$a^u(t)$	$\sum_i a_i^u(t)$	$\delta_1(t)$	$\delta_1(t)X_r^\beta$	$\hat{a}^u(t)$
0	$\begin{pmatrix}0.5341\\0.0944\\0.3665\\0\end{pmatrix}$	1.0	0	$\begin{pmatrix}0\\0\\0\\0\end{pmatrix}$	$\begin{pmatrix}0.5341\\0.0944\\0.3665\\0\end{pmatrix}$
0.05	$\begin{pmatrix}0.3644\\0.0653\\0.3561\\0.3552\end{pmatrix}$	0.8910	0.1090	$\begin{pmatrix}0\\0\\0.0545\\0.0545\end{pmatrix}$	$\begin{pmatrix}0.3644\\0.0553\\0.4106\\0.1597\end{pmatrix}$
0.10	$\begin{pmatrix}0.2488\\0.0450\\0.3342\\0.1626\end{pmatrix}$	0.7906	0.2094	$\begin{pmatrix}0\\0\\0.1047\\0.1047\end{pmatrix}$	$\begin{pmatrix}0.2488\\0.0450\\0.4389\\0.2673\end{pmatrix}$
0.15	$\begin{pmatrix}0.1698\\0.0309\\0.3066\\0.1893\end{pmatrix}$	0.6966	0 0.3034	$\begin{pmatrix}0\\0\\0.1517\\0.1517\end{pmatrix}$	$\begin{pmatrix}0.1698\\0.0309\\0.4583\\0.3410\end{pmatrix}$
0.35	$\begin{pmatrix}0.0369\\0.0068\\0\ 1923\\0.1668\end{pmatrix}$	0.4028	0.5972	$\begin{pmatrix}0\\0\\0.2986\\0.2986\end{pmatrix}$	$\begin{pmatrix}0.0369\\0.0068\\0.4909\\0.4654\end{pmatrix}$

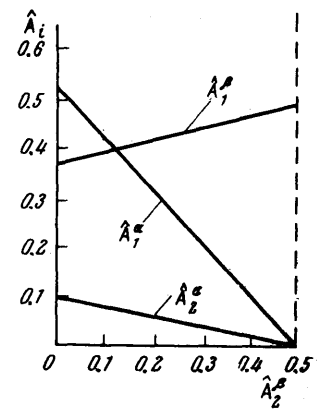


Figure 14. Artificial linear reaction pathway for the system (XXIII).

The functions F_1 and F_2 are calculated from Eqn. (104). A linear plot of F_1 against F_2 is obtained, whose slope yields $\gamma = -1.189$. We now calculate X_r^u from Eqn. (99):

$$X_r^u=\begin{pmatrix}0.5341\\0.0994\\0.3665\\0\end{pmatrix}-1.189\begin{pmatrix}0\\0\\0.5\\0.5\end{pmatrix}=\begin{pmatrix}0.5341\\0.0994\\-0.2280\\-0.5945\end{pmatrix}. \qquad (113$$

The vector X_r^u differs only by its length and sign from the first column of the matrix X [Eqn. (111)].

In order to determine X_2, we make use of a further projection, but this time the projection is parallel to the vector $X_r^u - X_r^\beta$. The course of the calculations is illustrated in Table 5.

Table 5.

t	$a^u(t)$	$\delta_1(t)$	$\hat{a}^u(t)$	$\delta_2(t)$	$\hat{\hat{a}}^u(t)$
0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$	0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$	0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$
0.06	$\begin{pmatrix}0.0321\\0.2301\\0.4199\\0.1737\end{pmatrix}$	0.1442	$\begin{pmatrix}0.0321\\0.2301\\0.4920\\0.2458\end{pmatrix}$	−0.0957	$\begin{pmatrix}0.2947\\0.2790\\0.4263\\0\end{pmatrix}$
0.20	$\begin{pmatrix}0.0259\\0.0393\\0.2832\\0.2310\end{pmatrix}$	0.4206	$\begin{pmatrix}0.0259\\0.0393\\0.4935\\0.4413\end{pmatrix}$	−0.1718	$\begin{pmatrix}0.4973\\0.1270\\0.3757\\0\end{pmatrix}$

The reaction pathway for the initial composition

$$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$$

is illustrated in Fig. 15. Fig. 16 presents an artificial linear pathway. We shall now determine the constant of the equation

$$X_i^u = \begin{pmatrix}X_i^{\alpha\alpha}\\X_i^{\beta\alpha}\end{pmatrix} = \gamma_1\begin{pmatrix}\hat{a}_x^\alpha(0)\\\hat{a}_x^\beta(0)\end{pmatrix} + \gamma_2\begin{pmatrix}X_r^{\alpha\alpha}\\X_r^{\beta\alpha}\end{pmatrix} + \gamma_3\begin{pmatrix}0\\X_r^{\beta\beta}\end{pmatrix}. \qquad (114)$$

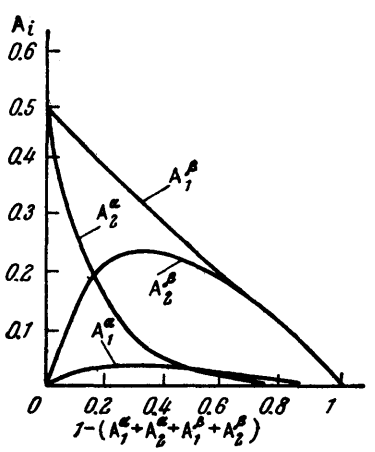


Figure 15. Reaction pathway for the system (XXIII).

Using the known subvectors $X_r^{\alpha\alpha}$ and $X_2^{\alpha\alpha}$, we obtain the following system of equations:

$$X_2^{\alpha\alpha} = \gamma_1\hat{\hat{a}}_x^\alpha(0) + \gamma_2 X_r^{\alpha\alpha} = \begin{pmatrix}-0.5931\\1.5931\end{pmatrix} + \gamma_1\begin{pmatrix}0\\0.5\end{pmatrix} + \gamma_2\begin{pmatrix}-2.7446\\-0.5109\end{pmatrix}. \qquad (115)$$

It follows from Eqn. (115) that $\gamma_1 = 3.4069$ and $\gamma_2 = 0.2161$. γ_3 is determined from the plot of F_3 against F_4. F_3 and F_4 are calculated from Eqns. (109) and $\gamma_3 = -3.691$ is found. We now determine

$$X_2^u = 3.4069\begin{pmatrix}0\\0.5000\\-0.5000\\0\end{pmatrix} + 0.21\begin{pmatrix}-2.7446\\0.5109\\1.1861\\3.0694\end{pmatrix} - 3.691\begin{pmatrix}0\\0\\0.5\\0.5\end{pmatrix} = \begin{pmatrix}-0.5931\\1.5931\\0.1142\\-1.1824\end{pmatrix}.$$

It is readily seen that X_2^u is identical with the second column of the matrix X apart from the length and sign.

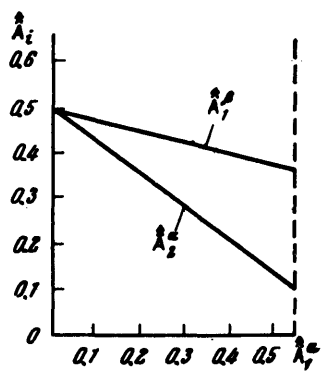


Figure 16. Artificial linear reaction pathway for the system (XXIII); initial composition.

$$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$$

4. THE GENERAL CHARACTERISTICS OF FIRST-ORDER REACTIONS

We examined above systems of reversible first-order reactions and systems involving certain irreversible stages. In both cases we employed the principle of detailed balance or its corollaries, which can be found by considering irreversible stages as the limiting cases of reversible reactions obtained on decreasing the rates of the corresponding transitions. However, there exist systems of pseudofirst order, to which the principle of detailed balance is in general inapplicable. We shall consider initially certain examples of such systems[30].

Example 5.

$$\begin{array}{l}A_1 + B_1 \rightleftarrows A_2 + B_2\ ;\\ A_2 + B_2 \rightleftarrows A_3 + B_3\ ;\\ A_3 + B_3 \rightleftarrows A_1 + B_3\ .\end{array} \qquad (XXIV)$$

If the reactions are carried out in a closed system, the usual thermodynamic conditions are valid. On the other hand, when the system contains an excess of substances

B, the reactions can be described by the equivalent pseudofirst order scheme:

$$A_1 \rightleftarrows A_2;\ A_2 \rightleftarrows A_3;\ A_3 \rightleftarrows A_4 \qquad \text{(XXV)}$$

One can then speak only of steady-state conditions. The Wegsheider conditions[18] may therefore not in fact hold for the matrix.

Example 6. Consider copolymerisation reactions, which can be described sometimes by first-order systems. We denote by $P_i(\nu)$ a polymer of type i with a chain length ν and by M_j a monomer of type j. The reaction mechanism can be formulated thus:

$$P_i(\nu) + M_j \rightarrow P_j(\nu + 1). \qquad (116)$$

The second-order reaction constant will be designated by κ_{ij}. If the monomer concentration does not change, the process can be described by a system of unimolecular reactions with constants which depend on the monomer concentration. The diagonal elements of the kinetic matrix K then possess physical significance. The principle of detailed balance does not hold in such a system. Polymerisation kinetics have been examined in a number of studies[31-33].

Example 7. Suppose that the process takes place on a discretely inhomogeneous catalyst surface with two types of centres. A system of reactions with the kinetic matrices K_1 and K_2 takes place at each type of centres. Then the overall transformation can also be described by a first-order equation with the matrix $\lambda K_1 + (1 - \lambda)K_2$, where λ is the fraction of centres of the first type on the catalyst surface. It can be easily shown that, even if the principle of detailed balance holds for each set of centres, it may not hold for the system as a whole. In the specific instance where the matrices K_1 and K_2 have identical equilibrium vectors, the principle of detailed balance holds for the entire system. This can be readily understood, since in the latter case a thermodynamic equilibrium is established in the steady-state and the thermodynamic conditions are the same for both types of centres. On the other hand, when one is dealing with a system of pseudofirst order, there is no thermodynamic equilibrium and the steady-state conditions may be different for each type of centre. This factor is extremely important for the kinetics of complex reactions on polyfunctional catalysts[34-37].

Example 8. Consider the class of first-order reactions which have been called[30] "bound". This class includes systems containing cycles of irreversible reactions which we previously excluded from consideration. We introduce the following definitions. We call a substance A_i the descendant of A_j if a sequence of reactions $A_j \rightarrow A_k \rightarrow \ldots A_i$ with strictly positive constants exists. The system of unimolecular reactions is called bound if each substance is the descendant of another. For example, the system $A_1 \rightleftharpoons A_2 \rightarrow A_3$ is a bound system of an L-system. The system $A_1 \rightleftharpoons A_2$, $A_3 \rightleftharpoons A_4$ is not bound. A system of reversible reactions is an L-system if it cannot be subdivided into subsystems between which there is no interaction. The following two schemes do not belong to the L-class:

$$A_1 \rightleftarrows A_2 \rightarrow A_3 \rightleftarrows A_4; \qquad \text{(XXVI)}$$

$$A_1 \rightarrow A_2 \rightarrow A_3;\ A_4 \rightleftarrows A_5. \qquad \text{(XXVII)}$$

If the system can be subdivided into ν subsystems, each of which is an L-system, it belongs to the class L_ν. The following results have been obtained for L-systems.

1. All L-systems have a unique positively defined equilibrium vector.

2. A positively defined equilibrium vector exists when and only when the system of unimolecular reactions belong to the class L_ν. The multiplicity of the zeroth eigenvalue of the kinetic matrix is ν.

3. All the eigenvalues of the kinetic matrix (other than the zeroth eigenvalue) have negative real components and are located on a complex plane in a circle $|z + r| \leq r$, where r is the maximum modulus of the diagonal elements of the matrix K.[30] This assertion can be proved by the Perron theorem familiar in matrix theory[38].

Thus, in contrast to the systems of reversible reactions discussed above, decaying oscillations are possible in L-systems containing cycles. The introduction of non-linear stages into these systems leads to non-decaying auto-oscillations[39-41].

5. Group Kinetics

An enormous number of substances are sometimes involved simultaneously in complex systems, which precludes not only kinetic calculations on individual reactions but also even a simple chemical analysis of such mixtures. It is therefore necessary to subdivide substances into definite classes and to investigate the interactions between individual classes. For example, in the cracking of petroleum, hydrocarbons are subdivided into olefins, paraffins, naphthenes, and aromatic compounds. However, it is by no means always clear to what extent this distorts the kinetic relations and in what cases the subdivision of the reactants into groups is legitimate. An attempt has been made[42,43] to answer these questions in relation to systems of unimolecular reactions. We shall assume that conditions (14), formulated in the definition of a system of reversible reactions, have been fulfilled. We introduce a linear transformation of an n-dimensional vector composition space into an $\hat{n}$-dimensional space where $\hat{n} < n$. Such a transformation is achieved with the aid of a rectangular $\hat{n} \times n$ matrix M with the rank $\hat{n}$:

$$\hat{a} = Ma. \qquad (117)$$

In the simplest case this transformation can be represented as projection. Three substances can be divided into two classes (Fig. 17):

$$\hat{a}_1 = a_1 + a_2,\quad \hat{a}_2 = a_3. \qquad (118)$$

In this case, the transformation matrix M is

$$M = \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (119)$$

In this transformation the same vector $\hat{a}$ corresponds to vectors a' and a'' (see Fig. 17). We now introduce certain definitions.

Definition 5. Vectors a and a' will be called equivalent if the equality

$$Ma = Ma' \qquad (120)$$

holds. In an abbreviated form, Eqn. (120) can be written in the form

$$a \simeq a'.$$

Definition 6. The system of unimolecular reactions $da/dt = Ka$ is called exactly divisible into classes if, after transforming the composition space with the matrix $M: \hat{a} = Ma$, the kinetics can be described by the equation

$$\frac{d\hat{a}}{dt} = \hat{K}\hat{a}, \tag{121}$$

where $\hat{K}$ is a matrix.

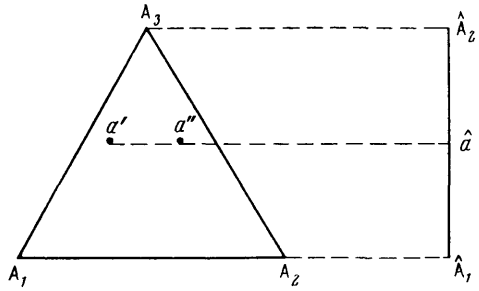


Figure 17. Transformation of the three-dimensional space specified by the matrix

$$\begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

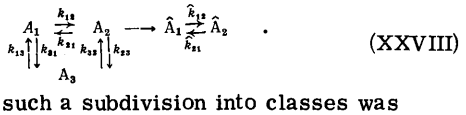
If the initial kinetic matrix has the dimensions $n \times n$, then the matrix $\hat{K}$ has the dimensions $m \times n$, where $m < n$. We shall now formulate the necessary and sufficient conditions under which the system is exactly divisible into classes.

Theorem 9. For the system to be exactly divisible into classes, the following conditions is necessary and sufficient:

$$MK = \hat{K}M, \tag{122}$$

where M is an $n \times m$ matrix. We shall make clear the significance of this condition in terms of examples. Consider a three-component system of reversible reciprocal reactions A_1, A_2, and A_3. We shall combine A_1 and A_2 in one class, while the second class will consist of A_3. This yields a two-component system:

Example 9.



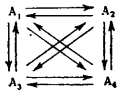
(XXVIII)

The matrix M for such a subdivision into classes was quoted above [matrix (119)]. The conditions (120) are

$$k_{31} = k_{32} = k_{13} + k_{23} = \hat{k}_{21} = \hat{k}_{12}. \tag{123}$$

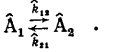
We shall consider yet another example.

Example 10.



(XXIX)

We combine A_1 and A_2 in the first class and A_3 and A_4 in the second class. The equivalent scheme is the same as in the previous case:



The conditions (120) then become

$$\begin{aligned} k_{31} + k_{41} = k_{32} + k_{42} = \hat{k}_{21}\ ; \\ k_{13} + k_{23} = k_{14} + k_{24} = \hat{k}_{12}. \end{aligned} \tag{124}$$

Thus the conditions (120) impose sufficiently rigid limitations on the rate constants.

It has been shown[37] that the composition $\hat{a}(t)$ for systems divisible into classes can be calculated both from kinetic $a(t)$ curves and from the matrix K, i.e.

$$\hat{a}(t) = Me^{-Kt}a(0) = e^{-\hat{K}t}Ma(0). \tag{125}$$

This relation yields yet another definition of systems exactly divisible into classes.

Definition 7. A system of unimolecular reactions is called exactly divisible into classes if equivalence is maintained for the reaction pathways for each pair of M-equivalent vectors $a(0)$ and $a'(0)$. In other words, it follows from $a(0) \sim a'(0)$ that $a(t) \sim a'(t)$.

A consequence of this definition is that we should obtain a single reaction pathway $\hat{a}(t)$ in the transformed three-component system in experiments with the initial compositions (1, 0, 0) and (0, 1, 0) when the substances A_1 and A_2 are combined in one class. Different reaction pathways are of course obtained in the initial composition space. This can be used for experimental tests of the possibility of the subdivision of the system into classes. Suppose that the first three components in a system of five components are combined in one class and the fourth and fifth components are combined in the second class. The experiment is carried out for the initial composition (1, 0, 0, 0, 0). We determine the kinetic relations

$$\begin{aligned} \hat{a}_1(t) = a_1(t) + a_2(t) + a_3(t), \\ \hat{a}_2(t) = a_4(t) + a_5(t). \end{aligned} \tag{126}$$

We then repeat the experiment with the initial compositions (0, 1, 0, 0, 0) and (0, 0, 1, 0, 0). If we obtain similar relations $a_1(t)$ in all three experiments, the combination of substances A_1, A_2, and A_3 in a single class is legitimate. After this, it is possible to carry out experiments with the compositions (0, 0, 0, 1, 0) and (0, 0, 0, 0, 1). If the relations $\hat{a}_2(t)$ are the same in these experiments, the substances A_4 and A_5 can be combined in a single class.

We shall now consider how the characteristic vectors vary when the dimensions of the vector space are diminished on subdivision into classes.

Theorem 10. If $\boldsymbol{X}_i$ is the eigenvector of the rate constant matrix for a system which is exactly divisible into classes, corresponding to the eigenvalue λ_i, then the vector $M\boldsymbol{X}_i$ is zero or is the eigenvector of the matrix $\hat{K}$ with the same eigenvalue λ_i.

Thus, when the matrix K has n eigenvectors, the matrix $\hat{K}$ has $\hat{n}$ eigenvectors for the same values of λ_i and the equality $M\boldsymbol{X}_i = 0$ hold for $n - \hat{n}$ vectors. Thus, by studying the reaction pathways in the space A_n, it is possible to determine $\hat{n}$ eigenvectors $\boldsymbol{X}_i = M\boldsymbol{X}_i$ for the exact values of λ_i. The remaining eigenvectors of the initial system cannot be determined.

The subdivision of complex systems into classes taking into account diffusion has also been examined[42]. An

approach has been described[43], in terms of the above definitions, to the study of unimolecular systems which cannot be exactly subdivided into classes. However, this can be done only approximately. Expressions are given whereby it is possible to estimate the errors arising in the approximate subdivision of complex systems into classes containing several substances.

In the present section, we have considered only those investigations in which an attempt has been made to approach group kinetics from the standpoint of the general theory of unimolecular reactions. Naturally, other approaches to the problem are also possible. For example, reactants can be represented by mixtures with continuous compositions[44-46]. The extensive literature on this problem cannot be discussed here.

III. AN OUTLINE OF THE STRUCTURE OF NON-LINEAR SYSTEMS

1. Canonical Forms

It is possible to find simple canonical forms for linear systems which are convenient for the solution of equations and the analysis of the structure. For non-linear systems of complex reaction, the situation is much more involved. Consider a non-linear system of complex reactions[27]:

$$\frac{dx_i}{dt} = f^i(x^1, \ldots x^n); i = 1, \ldots n. \quad (127)$$

In the general case, there exists a non-linear transformation leading to the system (127) in the canonical form:

$$\begin{aligned} &\frac{dy^1}{dt} = g(y^1, \ldots y^n), \\ &\frac{dy^i}{dt} = 0;\ i = 2, \ldots n. \end{aligned} \quad (128)$$

However, there is no general method for deducing these transformations. We shall consider a system of chemical kinetic equations obtained in accordance with the Law of Mass Action. For reactions whose order is not greater than the third, one can write

$$\frac{dx^i}{dt} = \sum_j a_j^i x^j + \sum_{k,j} b_{jk} x^j x^k + \sum_{j,k,p} c_{jkp} x^j x^k x^p. \quad (129)$$

The first term of Eqn. (129) corresponds to first-order reactions and the second term describes second-order reactions. It can be shown[47,48] that equations of type (129) with up to sth order terms can be reduced to homogeneous sth order equations. Henceforth we shall consider only homogeneous systems having specified

$$\frac{dX}{dt} = P_n(X), \quad (130)$$

where $P_n(X)$ is the polynomial form of the vector X.[49] For a polylinear operator, there exist canonical forms which can be solved.

1. $P_n(X)$ is a semilinear operator:

$$\begin{aligned} P_n(X+Y) &= P_n(X) + P_n(Y), \\ P_n(\alpha X) &= f(\alpha) P_n(X). \end{aligned} \quad (131)$$

This form arises, for example, for the scheme

$$\begin{aligned} &2A \rightarrow B\ , \\ &3C \rightarrow D\ . \end{aligned}$$

2. The triangular scheme:

$$2A \rightarrow 2B \rightarrow 2C\ .$$

3. The scheme

$$\begin{aligned} &A_1 + A_2 \xrightarrow{k_1} A_3\ , \\ &A_1 + A_3 \xrightarrow{k_2} A_4 \end{aligned} \quad (XXX)$$

and the more complex scheme

$$\begin{aligned} &A_1 + A_2 \rightarrow A_3\ , \\ &A_3 + A_2 \rightarrow A_4\ , \\ &A_5 + A_2 \rightarrow A_6\ , \\ &A_6 + A_2 \rightarrow A_7 \end{aligned} \quad (XXXI)$$

have also been considered[50,51]. Unfortunately other canonical forms do not permit a solution of the initial system. The problem of the canonical forms of second-order equations has still been little studied.

2. Linear Reaction Pathways

For a linear system, a linear reaction pathway is specified by the formula

$$X(t) = X_e + \alpha(t) Y, \quad (132)$$

where X_e is the equilibrium vector. We shall consider a second-order homogeneous system:

$$\frac{dX_i}{dt} = B(X, X). \quad (133)$$

The possibility of the existence of linear reaction pathways will now be elucidated. Having substituted Eqn. (132) in Eqn. (133), we obtain

$$Y\frac{d\alpha}{dt} = B(X_e, X_e) + 2\alpha B(X_e, Y) + \alpha^2 B(Y, Y). \quad (134)$$

The first term is zero, since at equilibrium $dX_e/dt = 0$. For Eqn. (134) to hold, it is necessary and sufficient that the following conditions should be fulfilled:

$$B(X_e, Y) = \beta Y, \quad (135)$$

$$B(Y, Y) = \lambda Y. \quad (136)$$

These conditions are rarely fulfilled, but they are valid in some cases, for example for the scheme $2A \rightleftharpoons 2B \rightleftharpoons 2C$. For closed systems, linear pathways are rare. However, for systems with irreversible stages involving open subsystems, this is not the case.

Consider the system

$$2A \rightarrow C;\ 2B \rightarrow E;\ A + B \rightarrow D.$$

It contains the open subsystem (A, B). When $t \rightarrow \infty$, we have $c_A \rightarrow 0$ and $c_B \rightarrow 0$. In the general case of a system with irreversible stages, the equilibrium vector is $X_e(0, 0, 0, \ldots, x_e^{n+1}, x_e^n)$. When an m-dimensional space is considered, the equilibrium point coincides with the origin of coordinates. For such subsystems, linear pathways are possible, since $B(X_e, Y) = 0$ and it is only necessary that $B(Y, Y) = \lambda Y$; for a homogeneous sth order system, condition (136) assumes the following form:

$$P_s(\alpha X) = \alpha^s P_s(X). \quad (137)$$

The following Wei theorem is valid:

Theorem 11. For chemical reactions involving any number of components, and of any homogeneous order, the equilibrium point either does not coincide with the origin of coordinates or there is at least one pathway in the positive octant of the vector space.

We shall now discuss the problem of the number of possible linear pathways. The number of such pathways is equal to the number of the roots of the equation

$$P_s(\alpha X) = \alpha^s \lambda X. \qquad (138)$$

We found above that for linear systems there can be not more than n independent eigenvectors or that an infinite number of eigenvectors corresponds to a single eigenvalue.

In the non-linear case, reliable results have been obtained mainly for a two-component system. Table 6 presents the maximum number of linear pathways as a function of the number of components and the order of the reaction.

Table 6. Number of possible linear reaction pathways.

No. of components	Reaction order				
	1	2	3	4	5
2	2	3	4	5	6
3	3	(8)	—	—	—

It is seen from these results that analysis of linear reaction pathways in non-linear systems cannot yield far-reaching results similar to those obtained for unimolecular reactions. At the same time, some of the theorems quoted above are useful also in the consideration of non-linear systems. In particular, they are useful in the analysis of stability, since Lyapunov theorems reduce the problem to the analysis of the stability of the linearised system. Thus the impossibility of non-decaying oscillations in the vicinity of thermodynamic equilibrium follows from theorem 2. A detailed proof of this assertion can be found in Zhabotinskii's book[39]. Interesting communications on the qualitative theory of chemical kinetic equations have been published very recently[52-56]. However, their discussion is outside the scope of the present review.

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