AN INVESTIGATION OF THE KINETICS OF A REVERSIBLE MONOMOLECULAR REACTION BETWEEN *n* COMPONENTS

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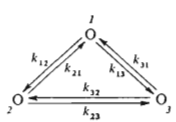
Received July 25th, 1975

It has been shown that the solution of kinetic equations can be transformed into diagonalization of a symmetrical matrix, in contrast with the solution known so far and requiring diagonalization of a nonsymmetrical matrix. Simple formulas are given for the calculation of derivatives of the concentrations of individual components with respect to the parameters. All formulas are presented in a compact matrix form; their uniformity for a large number of cases recognized in the existing literature greatly facilitates writing computer programs for calculations of reaction kinetics.

In our studies of the reaction kinetics of conversion of the rotational isomers of 2-chlorobutane and 4-chloroheptane we met with the reaction scheme



(*I*)

The scheme can be generalized for *n* components in the form

$$C_i \underset{k_{ji}}{\overset{k_{ij}}{\rightleftharpoons}} C_j \,. \tag{2}$$

In order to solve this scheme (cf^{1-3} and the references therein), we introduce

$$k_{ii} = -\sum_{j \neq i} k_{ij} \,;$$

then

$$\frac{dc_i}{dt} = \sum_{j=1}^{n} k_{ji} c_j \tag{3}$$

or briefly

$$\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}t} = \tilde{K}\mathbf{C}\,, \tag{4}$$

where $\mathbf{C}$ is the column vector of concentrations of the individual components at a time t, $\tilde{C} \equiv (c_1, c_2, \ldots, c_n)$, and $\tilde{K}$ is a matrix transposed to the matrix $\mathbf{K} \equiv k_{ij}$. The solution of the system of differential equations (3) may be written as

$$c_i = \sum_{k=1}^{n} s_{ki} e^{\lambda_k t} \sum_{j=1}^{n} r_{jk} c_j^0\,, \tag{5}$$

where c_i^0 is the concentration of the i-th component at the time 0, λ_k is the k-th eigenvalue of the matrix $\mathbf{K}$, $(r_{1k}, r_{2k}, \ldots, r_{nk})$ is its k-th right eigenvector, $(s_{k1}, s_{k2}, \ldots, s_{kn})$ is its k-th left eigenvector; the eigenvectors are normalized so that $\sum_{i=1}^{n} s_{ki} r_{ik} = 1$. The respective matrix notation is

$$\mathbf{C} = \tilde{S} \exp(\Lambda t)\, \tilde{R} \mathbf{C}^0\,, \tag{6}$$

where $\mathbf{S}$, $\exp(\Lambda t)$, $\mathbf{R}$ are matrices with the elements s_{ki}, $\exp(\lambda_k t)\,\delta_{kk'}$, r_{jk} respectively and $\mathbf{C}^0$ is the column vector of the initial concentrations of individual components in the reaction mixture. Eqs (5) and (6) may fail if the matrix $\mathbf{K}$ possesses degenerate eigenvalues because in this case the matrices $\mathbf{R}$ and $\mathbf{S}$ need not be defined. It will be seen below, however, that for a reversible reaction scheme the matrices $\mathbf{R}$ and $\mathbf{S}$ are defined always.

The above solution, known from the literature, calls for diagonalization of the nonsymmetrical matrix $\mathbf{K}$. It will be demonstrated in the further part of the paper, that owing to the second law of thermodynamics the diagonalization of the nonsymmetrical matrix $\mathbf{K}$ can be transformed into that of the symmetrical matrix. For the latter procedure, very fast and numerically very stable algorithms can be used, such as the Givens or Jacobi method[4].

Application of the Second Law of Thermodynamics to the Reaction Scheme

In a reversible reaction of two components i, j it holds for the equilibrium concentrations c_i^b, c_j^b:

$$c_i^b / c_j^b = k_{ji} / k_{ij}\,.$$

It follows from the second law of thermodynamics, that c_i^b / c_j^b remains unchanged,

even if side reactions to further components are permitted. From the identity $(c_i^b/c_j^b) : (c_i^b/c_k^b) = c_k^b/c_j^b$ one obtains

$$(k_{ji}/k_{ij})/(k_{ki}/k_{ik}) = k_{jk}/k_{kj} ,$$

or

$$k_{ik}k_{kj}k_{ji} = k_{ij}k_{jk}k_{ki} . \qquad (7)$$

Eq. (7) holds for each triad of the components i, j, k.

Some rate constants in the reaction scheme may be zero. We assume, however, that in the reaction scheme each component may be changed into any other, if not directly, then at least indirectly through one or several intermediates. Under such assumption, each component has a nonzero equilibrium concentration c_i^b; we assume that $\sum_{i=1}^{n} c_i^0 = 1$, and thus $\sum_{i=1}^{n} c_i^b = 1$. The constants k_{ij}, k_{ji} are then either both nonzero or both zero for any pair of the components i, j, *i.e.* each reaction proceeds either in both directions or in none.

Let us now introduce a diagonal matrix $\mathbf{\Gamma}$ with the elements $\delta_{ij}\sqrt{c_i^b}$. The matrix $\mathbf{A} = \mathbf{\Gamma K \Gamma}^{-1}$ has the elements $a_{ij} = k_{ij}\sqrt{(c_i^b/c_j^b)}$. If $k_{ij} \neq 0$, $c_i^b/c_j^b = k_{ji}/k_{ij}$, so that

$$a_{ij} = \sqrt{(k_{ij}k_{ji})} ; \qquad (8)$$

if $k_{ij} = 0$, it also holds that $a_{ij} = 0$, so that Eq. (8) is also valid in this case. We see, consequently, that the matrix $\mathbf{A}$ is symmetrical. Its eigenvalues are identical with the eigenvalues of the matrix $\mathbf{K}$. If the eigenvector of the matrix $\mathbf{A}$ corresponding to the eigenvalue λ_k is designated by $(v_{1k}, v_{2k}, \ldots, v_{nk})$, we obtain

$$\mathbf{R} = \mathbf{\Gamma}^{-1}\mathbf{V} , \quad \mathbf{S} = \tilde{V}\mathbf{\Gamma} , \qquad (9)$$

where $\mathbf{V}$ is the matrix v_{ik}, and thus

$$r_{ik} = v_{ik}/\sqrt{c_i^b} , \quad s_{ki} = v_{ik}\sqrt{c_i^b} \qquad (10)$$

whence $s_{ki} = r_{ik}c_i^b$. This is a relationship between the right and left eigenvectors of the matrix $\mathbf{K}$. Diagonalization of the symmetrical matrix $\mathbf{A}$ gives the eigenvalues λ_k of the matrix $\mathbf{K}$ and the matrix of the eigenvectors $\mathbf{V}$. Hence, by using Eqs (9) and (10), one obtains the matrices $\mathbf{R}$ and $\mathbf{S}$ of the eigenvectors of the matrix $\mathbf{K}$. The number of linearly independent eigenvectors corresponding to each degenerate eigenvalue of the matrix $\mathbf{A}$, and thus also of $\mathbf{K}$, is equal to the degeneracy of the eigenvalue. However, these eigenvectors of the matrix $\mathbf{A}$ must be orthogonalized. This is done automatically in the case of the Jacobi method, while the Givens method

requires an additional orthogonalization of the eigenvectors, which is necessary also in the case of very close eigenvalues. Thus, the matrices **R** and **S** exist and Eqs (5) and (6) hold of course under the above assumption that all components have a nonzero equilibrium concentration. An opposite case, *i.e.* a case arising if some reactions are irreversible, will be dealt with in a forthcoming paper.

The matrices **A** and **K** have their eigenvalue $\lambda_n = 0$; the respective eigenvectors have the form $v_{in} = \sqrt{c_i^b}$, $r_{in} = 1$, $s_{nl} = c_i^b$. Hence it can be seen that in Eq. (5) the term of the sum for $k = n$ equals c_i^b.

Calculation of the Derivatives of Concentrations of the Individual Components with Respect to the Parameters

To adjust the parameters of kinetic equations, *e.g.* activation energies and frequency factors in the Arrhenius or Eyring equation, one must calculate the derivatives of concentrations with respect to these parameters. If a kinetic equation is integrated at varying temperature so that the time interval is divided into sufficiently small parts within which a constant temperature is assumed, the resulting concentrations from the preceding part are the initial concentrations of the subsequent part, so that generally it should be assumed that the initial concentrations are also functions of the parameters. If one puts

$$\mathbf{T} = \mathbf{R}e^{\Lambda t}\mathbf{S}\,, \tag{11}$$

it holds

$$\mathbf{C} = \mathbf{T}\mathbf{C}^0 \tag{12}$$

and differentiation of Eq. (12) with respect to the parameter p gives

$$\frac{\partial \mathbf{C}}{\partial p} = \frac{\partial \mathbf{T}}{\partial p}\mathbf{C}^0 + \mathbf{T}\frac{\partial \mathbf{C}^0}{\partial p}\,. \tag{13}$$

Calculation of the matrix $\partial \mathbf{T}/\partial p$ requires the matrices $\partial \mathbf{S}/\partial p$, $\partial \Lambda/\partial p$ and $\partial \mathbf{R}/\partial p$. This is dealt with by the perturbation theory[5]; here, the results of this theory are derived in a simple way.

Differentiation of the equations $\mathbf{SR} = \mathbf{E}$ and $\Lambda = \mathbf{SKR}$ with respect to p gives

$$\frac{\partial \mathbf{S}}{\partial p}\mathbf{R} + \mathbf{S}\frac{\partial \mathbf{R}}{\partial p} = 0 \tag{14}$$

and

$$\frac{\partial \Lambda}{\partial p} = \frac{\partial \mathbf{S}}{\partial p}\mathbf{KR} + \mathbf{SK}\frac{\partial \mathbf{R}}{\partial p} + \mathbf{S}\frac{\partial \mathbf{K}}{\partial p}\mathbf{R}\,.$$

We substitute $\mathbf{K} = \mathbf{R}\Lambda\mathbf{S}$ into the above equation and put $(\partial\mathbf{S}/\partial p)\,\mathbf{R} = \mathbf{M}$; hence, $\mathbf{S}\,\partial\mathbf{R}/\partial p = -\mathbf{M}$, according to Eq. (*14*):

$$\frac{\partial\Lambda}{\partial p} = \frac{\partial\mathbf{S}}{\partial p}\mathbf{R}\Lambda + \Lambda\mathbf{S}\frac{\partial\mathbf{R}}{\partial p} + \mathbf{S}\frac{\partial\mathbf{K}}{\partial p}\mathbf{R}\,,$$

or

$$\frac{\partial\Lambda}{\partial p} = \mathbf{M}\Lambda - \Lambda\mathbf{M} + \mathbf{S}\frac{\partial\mathbf{K}}{\partial p}\mathbf{R}\,. \tag{15}$$

By comparing both sides of Eq. (*15*), we obtain (since the matrices Λ and $\partial\Lambda/\partial p$ are diagonal)

$$\frac{\partial\lambda_i}{\partial p} = \left(\mathbf{S}\frac{\partial\mathbf{K}}{\partial p}\mathbf{R}\right)_{ii} \tag{16}$$

and

$$m_{ij} = \left(\mathbf{S}\frac{\partial\mathbf{K}}{\partial p}\mathbf{R}\right)_{ij} /(\lambda_i - \lambda_j)\,, \quad i \neq j\,. \tag{17}$$

The diagonal elements of the matrix $\mathbf{M}$ are not determined as a consequence of the fact that the right eigenvector may be multiplied by a constant, if at the same time the corresponding left vector is divided by the same constant. It will be seen below that these diagonal elements are not needed in the calculations of the matrix $\partial\mathbf{T}/\partial p$.

Now let us differentiate Eq. (*11*) with respect to p and substitute $\partial\mathbf{S}/\partial p = \mathbf{MS}$, $\partial\mathbf{R}/\partial p = -\mathbf{RM}$:

$$\frac{\partial\mathbf{T}}{\partial p} = \frac{\partial\mathbf{R}}{\partial p}e^{\Lambda t}\mathbf{S} + \mathbf{R}e^{\Lambda t}\frac{\partial\mathbf{S}}{\partial p} + \mathbf{R}\frac{\partial\Lambda}{\partial p}te^{\Lambda t}\mathbf{S} = \mathbf{R}\left(e^{\Lambda t}\mathbf{M} - \mathbf{M}e^{\Lambda t} + \frac{\partial\Lambda}{\partial p}te^{\Lambda t}\right)\mathbf{S}\,,$$

or

$$\frac{\partial\mathbf{T}}{\partial p} = \mathbf{RUS}\,, \tag{18}$$

where $\boldsymbol{U} = \exp(\Lambda t)\,\mathbf{M} - \mathbf{M}\exp(\Lambda t) + (\partial\Lambda/\partial p)\,t\exp(\Lambda t)$ is a matrix whose elements u_{ij} are given by

$$u_{ij} = m_{ij}(e^{\lambda_i t} - e^{\lambda_j t})\,, \quad i \neq j\,,$$

$$u_{ii} = \left(\mathbf{S}\frac{\partial\mathbf{K}}{\partial p}\mathbf{R}\right)_{ii} te^{\lambda_i t}\,. \tag{19}$$

After substituting for m_{ij} we obtain

$$u_{ij} = \left(\mathbf{S}\frac{\partial \mathbf{K}}{\partial p}\mathbf{R}\right)_{ij}\frac{e^{\lambda_i t} - e^{\lambda_j t}}{\lambda_i - \lambda_j}. \qquad (20)$$

This reasoning holds if all eigenvalues of the matrix **K** are nondegenerate. For degenerated eigenvalues the off-diagonal elements m_{ij} corresponding to the degenerated eigenvalues $\lambda_i = \lambda_j$ are undefined (this follows from Eq. (*15*)) as a consequence of the fact that the degenerated eigenvectors may be replaced by their linear combination. To fulfil Eq. (*15*), it must be assumed that the respective off-diagonal elements of the matrix $(\partial\mathbf{\Lambda}/\partial p)_{ij}$ are nonzero,

$$\left(\frac{\partial \mathbf{\Lambda}}{\partial p}\right)_{ij} = \left(\mathbf{S}\frac{\partial \mathbf{K}}{\partial p}\mathbf{R}\right)_{ij} \qquad (21)$$

for the diagonalization of the matrix $\partial\mathbf{\Lambda}/\partial p$ it is then necessary to transform degenerated coordinates, as is known from the perturbation theory[5]. By using Eq. (*21*), one obtains for the respective element u_{ij}

$$u_{ij} = \left(\mathbf{S}\frac{\partial \mathbf{K}}{\partial p}\mathbf{R}\right)_{ij} te^{\lambda_i t}, \quad \lambda_i = \lambda_j. \qquad (22)$$

Eqs (*20*) and (*22*) show that u_{ij} is a continuous function of the variables λ_i, λ_j in the surroundings of $\lambda_i = \lambda_j$. However, if $|\lambda_i t - \lambda_j t| \ll 1$, loss of accuracy takes place in Eq. (*20*) due to round-off errors. In this case the fraction in Eq. (*20*) must be rearranged to

$$\frac{e^{\lambda_i t} - e^{\lambda_j t}}{\lambda_i - \lambda_j} = \frac{1 - e^{(\lambda_j - \lambda_i)t}}{-(\lambda_j - \lambda_i)t} te^{\lambda_i t} \qquad (23)$$

while the fraction on the right-hand side of Eq. (*23*) must be calculated by the Taylor series expansion of the exponential function in the form

$$1 + \frac{1}{2}x + \frac{1}{6}x^2 + \frac{1}{24}x^3 + \frac{1}{120}x^4 + \ldots,$$

where $x = (\lambda_j - \lambda_i)t$. Such a rearrangement in Eq. (*20*) and postorthogonalization of the eigenvectors corresponding to the degenerated and very close eigenvalues (need not be carried out if the Jacobi method is used) guarantees complete numerical stability of the solution of kinetic equations and of the derived formulas for the deri-

vatives of concentrations of the individual components with respect to the parameters.

Differentiation of Concentrations with Respect to the Rate Constants

Eq. (7) shows that the rate constants are not all of them independent. Independent parameters are best introduced by means of the equation

$$k_{ij} = w_{ij}/R_i\,, \quad i \neq j\,, \tag{24}$$

with the conditions $w_{ij} = w_{ji}$ and $R_i = 1$ (or $R_n = 1$). Hence, the total number of independent parameters in the system is $n(n-1)/2 + n - 1 = (n+2)(n-1)/2$. From $(\partial \mathbf{K}/\partial k_{lm})_{ij} = \delta_{il}(\delta_{jm} - \delta_{jl})$ we obtain

$$\left(\mathbf{S}\frac{\partial \mathbf{K}}{\partial k_{lm}}\mathbf{R}\right)_{pq} = s_{pl}(r_{mq} - r_{lq})\,. \tag{25}$$

For further considerations, let us introduce lnk_{lm} as the parameter (in other words, we shall calculate $k_{lm}\,\partial c_i/\partial k_{lm}$) and denote $\alpha_{pq} = (\exp(\lambda_p t) - \exp(\lambda_q t))/(\lambda_p - \lambda_q)$ for $\lambda_p \neq \lambda_q$ and $\alpha_{pq} = t\exp(\lambda_p t)$ for $\lambda_p = \lambda_q$. Hence,

$$k_{lm}\frac{\partial t_{ij}}{\partial k_{lm}} = k_{lm}\sum_{p,q} r_{ip}s_{pl}\alpha_{pq}(r_{mq} - r_{lq})\,s_{qj}$$

and thus

$$k_{lm}\left(\frac{\partial \bar{\mathbf{T}}}{\partial k_{lm}}\mathbf{C}^0\right)_J = k_{lm}\sum_{p,q} s_{pl}\alpha_{pq}(r_{mq} - r_{lq})\,s_{qj}\sum_i r_{ip}c_i^0\,.$$

To calculate the right-hand side of this equation, let us first calculate $g_p = \sum_i r_{ip}c_i^0$ and after that, $\beta_{ql} = \sum_p s_{pl}\alpha_{pq}g_p$. Hence,

$$k_{lm}\left(\frac{\partial \bar{\mathbf{T}}}{\partial k_{lm}}\mathbf{C}^0\right)_j = k_{lm}\sum_{q=1}^{n-1}(r_{mq} - r_{lq})\,\beta_{ql}s_{qj}\,. \tag{26}$$

For $w_{lm}\left(\frac{\partial \bar{\mathbf{T}}}{\partial w_{lm}}\mathbf{C}^0\right)_j$ we obtain, eventually,

$$w_{lm}\left(\frac{\partial \bar{\mathbf{T}}}{\partial w_{lm}}\mathbf{C}^0\right)_j = \sum_{q=1}^{n-1}(r_{mq} - r_{lq})\,(k_{lm}\beta_{ql} - k_{ml}\beta_{qm})\,s_{qj}\,, \tag{27}$$

and further,

$$R_l\left(\frac{\partial \tilde{T}}{\partial R_l}\,\mathbf{C}^0\right)_j = -\sum_{q=1}^{n-1}\beta_{ql}s_{qj}\sum_m (r_{mq} - r_{lq})\,k_{lm}\,. \qquad (28')$$

The last sum with respect to m is $(\mathbf{KR})_{lq} = (\mathbf{R\Lambda})_{lq} = \lambda_q r_{lq}$. This gives the resulting relation

$$R_l\left(\frac{\partial \tilde{T}}{\partial R_l}\,\mathbf{C}^0\right)_j = -\sum_{q=1}^{n-1}\lambda_q r_{lq}\beta_{ql}s_{qj}\,. \qquad (28)$$

Eqs (27) and (28) make possible a simple calculation of the derivatives of the concentrations of individual components of the reaction mixture with respect to independent parameters, lnw_{lm} and lnR_l.

The Case of Three Components

In this case it is possible to derive expressions for λ_k, s_{ki} and r_{ik} in a closed form without diagonalization of the matrix **A**. For simplicity's sake, let us write $x = k_{21} - k_{31}$, $y = k_{32} - k_{12}$, $z = k_{13} - k_{23}$. Then,

$$\lambda_1 = -(k_{12} + k_{21} + k_{13} + k_{31} + k_{23} + k_{32} + \sqrt{D})/2\,,$$
$$\lambda_2 = -(k_{12} + k_{21} + k_{13} + k_{31} + k_{23} + k_{32} - \sqrt{D})/2\,,$$

where $D = (x - y)^2 - 2(x + y)\,z + z^2$. (The expression D remains unchanged after permutation of the x, y, z). In the expression for λ_2, loss of accuracy occurs if λ_1, λ_2 differ by several orders of magnitude, *e.g.* if $\lambda_1 \sim 10^8$, $\lambda_2 \sim 1$. This happens, *e.g.*, if one of the reversible reactions is faster by several orders of magnitude than the remaining two, *e.g.* $k_{12} \sim k_{21} \sim 10^8$, $k_{13} \sim k_{31} \sim k_{23} \sim k_{32} \sim 1$. In this case, one must employ the formula

$$\lambda_2 = (k_{12}(k_{31} + k_{23} + k_{32}) + k_{21}(k_{13} + k_{31} + k_{32}) + k_{13}(k_{23} + k_{32}) + k_{31}k_{23})/\lambda_1\,,$$

which follows from a relation for the product of the roots of a quadratic equation. It also holds that

$$s_{3i} = c_i^b = R_i/(R_1 + R_2 + R_3)\,,$$
$$s'_{11} = 2x\,,\quad s'_{12} = -x - y + z - \sqrt{D}\,,\quad s'_{13} = -x + y - z + \sqrt{D}\,,$$
$$s'_{21} = 2x\,,\quad s'_{22} = -x - y + z + \sqrt{D}\,,\quad s'_{23} = -x + y - z - \sqrt{D}$$

(prime in the above equations means that the eigenvectors are not normalized according to the equation $s_{ki} = r_{ik}c_i^b$). For very small x, loss of accuracy occurs in these formulas; for $x = 0$, one of the vectors thus obtained is zero. In this case formulas must be used which are obtained by interchanging the subscripts 1 and 2, or 1 and 3:

$$s'_{11} = -x - y + z + \sqrt{D}\,, \quad s'_{12} = 2y\,, \quad s'_{13} = x - y - z - \sqrt{D}\,,$$

or

$$s'_{11} = -x + y - z - \sqrt{D}\,, \quad s'_{12} = x - y - z + \sqrt{D}\,, \quad s'_{13} = 2z\,.$$

Expressions for s'_{2l} are obtained from those for s'_{1l} by changing the sign before the term $\sqrt{D}$. x, y, z satisfy the equation

$$x/R_1 + y/R_2 + z/R_3 = 0\,. \tag{29}$$

If in the calculation of each of the values of x, y, z several significant orders of magnitude are lost in the subtraction, the validity of Eq. (*29*) may be violated. In this case, x, y, z must be changed so as to preserve the validity of Eq. (*29*); otherwise, the validity of $\mathbf{SR} = \mathbf{E}$ would be violated. Such change in x, y, z lies within the limits of round-off errors. If $x = y = z = 0$, the eigenvectors s'_{1i}, s'_{2i} may be calculated using any arbitrary triad of x, y, z satisfying Eq. (*29*). Such cases arise if λ_1, λ_2 are very close or identical, and the above rearrangement is equivalent to the postorthogonalization of the eigenvectors at almost degenerated or degenerated eigenvalues. Finally, one obtains for r'_{ik}

$$r'_{ik} = \frac{s'_{ki}}{c_i^b N_k}\,,$$

where $N_k = s'^2_{k1}/c_1^b + s'^2_{k2}/c_2^b + s'^2_{k3}/c_3^b$. Unnormalized eigenvectors s'_{ki} and r'_{ik} thus obtained may be employed instead of the vectors s_{ki}, r_{ik} in Eqs (*5*), (*18*), (*19*), (*20*), (*27*) and (*28*). Normalized eigenvectors are obtained from the equations $s_{ki} = s'_{ki}N_k^{-1/2}$, $r_{ik} = s_{ki}/c_i^b$. They must be used, *e.g.*, in Eq. (*27'*).

Exclusion of a Superfluous Coordinate

With respect to $\sum_{i=1}^{n} c_i = 1$ (and thus, $\sum_{i=1}^{n} c_i^0 = 1$), one of the coordinates, *e.g.* c_n, may be excluded from the above equations, according to $c_n = 1 - \sum_{i=1}^{n-1} c_i$. At the same time, in sums with respect to the eigenvalues of the matrix $\mathbf{K}$ it is advantageous to separate the term corresponding to $\lambda_n = 0$. We define

$$t'_{ij} = \sum_{p=1}^{n-1} s_{pj}e^{\lambda_p t}(r_{ip} - r_{np}) = t_{ij} - t_{nj}\,.$$

Then,

$$\left(\bar{T}\frac{\partial \mathbf{C}^0}{\partial p}\right)_j = \sum_{i=1}^{n-1} t'_{ij}\frac{\partial c_i^0}{\partial p}, \quad (\bar{T}\mathbf{C}^0)_j = c_j^b + \sum_{i=1}^{n-1} t'_{ij}(c_i^0 - c_i^b).$$

For g_p and β_{ql} we obtain

$$g_p = r_{np} + \sum_{l=1}^{n-1}(r_{ip} - r_{np})\, c_i^0 = \sum_{i=1}^{n-1}(r_{ip} - r_{np})(c_i^b - c_i^0) + \delta_{np},$$

$$\beta_{ql} = c_l^b\alpha_{qn} + \sum_{p=1}^{n-1} s_{pl}\alpha_{pq}g_p,$$

where α_{pq} have the same meaning as before, $\alpha_{qn} = (\exp(\lambda_q t) - 1)/\lambda_q$. These quantities may then be used without change in Eqs (*26*), (*27*), (*28*). The equations thus rearranged do not contain the concentration of the n-th component and its derivatives with respect to the parameters, so that this component need not be calculated in course of integration of the kinetic equation.

The Case where the Eigenvalues of the Matrix **K** *Differ by Many Orders of Magnitude*

In this case the procedure just described does not provide sufficient accuracy. The error involved in the eigenvalues λ_i obtained by the diagonalization of the matrix **K** is given by the product of the largest eigenvalue and the relative accuracy of the calculation. Consequently, with the required accuracy of results 10^{-6} and the accuracy of calculation 10^{-14} (practically attainable in REAL 8 variables with IBM computers), our expressions are quite sufficient for a range of the eigenvalues up to 10^8. The procedure which allows us to calculate the eigenvalues at any range of orders of magnitude is presented below.

The secular equation of our problem $|\mathbf{K} - \lambda\mathbf{E}| = 0$ becomes

$$|\mathbf{W} - \lambda\mathbf{D}| = 0,$$

where $\mathbf{W} \equiv w_{ij}$ is a symmetrical and $\mathbf{D} \equiv R_i\delta_{ij}$ is a diagonal matrix from w_{ij} and R_i introduced by Eq. (*24*). The matrix of the eigenvectors of this secular problem is identical (but for the normalization) with the matrix **R**. In this form the secular equation is identical with the secular equation of vibrations of a set of n mass points having masses R_i and forces w_{ij} between the *i*-th and *j*-th point. A way for removing the numerical instability of the problem consists in introducing the Jacobian coordinates of the system of mass points, starting from the pair of points having the highest vibrational frequency.

To carry out the above transformation, one should first determine the highest value of $k_{ij} + k_{ji}$, *i.e.* $w_{ij}(1/R_i + 1/R_j)$. (It is also sufficient to find the maximum value of k_{ij}, *i.e.* w_{ij}/R_i, but in this case the search should proceed over arranged pairs (i, j)). Now, the matrices **W** and **D** are subjected to the transformation **Q** between the coordinates i and j in the form $\mathbf{W}' = \tilde{\mathbf{Q}}\mathbf{W}\mathbf{Q}$ and $\mathbf{D}' = \tilde{\mathbf{Q}}\mathbf{D}\mathbf{Q}$, where $q_{ii} = R_j/(R_iR_j(R_i + R_j))^{1/2}$, $q_{ji} = -R_i/(R_iR_j(R_i + R_j))^{1/2}$, $q_{ij} = q_{jj} = 1$ while the other diagonal elements of the matrix **Q** are unity and the other off-diagonal ones are zero. Without loss of generality, one may assume that $i = 1$, $j = 2$, and introduce $\varrho_1 = R_2/(R_1R_2(R_1 + R_2))^{1/2}$, $\varrho_2 = R_1/(R_1R_2(R_1 + R_2))^{1/2}$. By using the relationship $w_{ii} = -\sum_{j \neq i} w_{ij}$, we obtain for the transformed quantities

$$w'_{11} = -(\varrho_1 + \varrho_2)^2 w_{12} - \varrho_1^2 \sum_{i=3}^{n} w_{1i} - \varrho_2^2 \sum_{i=3}^{n} w_{2i},$$

$$w'_{22} = -\sum_{i=3}^{n} w'_{2i},$$

$$w'_{12} = -\sum_{i=3}^{n} w'_{1i},$$

$$w'_{1i} = \varrho_1 w_{1i} - \varrho_2 w_{2i}. \quad i = 3, 4, \ldots, n,$$

$$w'_{2i} = w_{1i} + w_{2i}, \quad i = 3, 4, \ldots, n,$$

$$R'_1 = 1,$$

$$R'_2 = R_1 + R_2;$$

it holds that $w'_{ji} = w'_{ij}$; the other elements of the matrices **W** and **D** remain unchanged after the transformation.

If before the transformation $\sum_{j=1}^{n} w_{ij} = 0$, after the transformation it holds that $\sum_{j=2}^{n} w'_{ij} = 0$. To facilitate the description, the transformed coordinate 1 will be called „internal", while the transformed coordinate 2 and all untransformed coordinates will be referred to as „external".

In order to introduce the Jacobian coordinates throughout the system, the transformation just described must be repeated $(n - 1)$ times. In the k-th step we look for the maximum of $w_{ij}(1/R_i + 1/R_j)$ only between (different) subscripts i and j, both of which correspond to the external coordinates. After the subscripts i and j have been moved into the first and second positions transformation is carried out

using the same formulas as in the first step. Only in the case that some value of w_{1i} or w_{2i} is given from the preceding steps in the form $-\sum_j w_{ji}$, where j passes through the indices of all external coordinates with the exception of the one considered in this case, formulas

$$w'_{1i} = -(\varrho_1 + \varrho_2)\, w_{2i} - \varrho_1 \sum_j w_{ji} ,$$

or

$$w'_{1i} = (\varrho_1 + \varrho_2)\, w_{1i} + \varrho_2 \sum_j w_{ji} ,$$

and

$$w'_{2i} = -\sum_j w_{ji} ,$$

are used, in which the summation with respect to j passes in all cases over all indices j corresponding to the external coordinates, with the exception of the indices 1 and 2. Such a case may arise only if i is an index corresponding to an internal coordinate; in this case, the element w_{ji} is given by the above sum for just one index j (j corresponds to an external coordinate). Such an analytical subtraction of the w_{12}, or of the w_{1i} or w_{2i} values from the sum guarantees numerical stability of the calculation at any range of orders of magnitude of the λ_i values.

After the k-th step there are k internal coordinates, while the other $(n - k)$ coordinates are external. For all indices i, whether they correspond to the internal or external coordinates, the summation rule $\sum_j w_{ij} = 0$ is valid, where the summation index j passes only values corresponding to the external coordinates. After $n - 1$ steps a single external coordinate remains, but owing to the summation rule the row and column in the matrix **W** corresponding to this coordinate contain only zeros.

After completion of the transformation it is easy to see that the order of magnitude of each off-diagonal element of the transformed matrix is equal to or smaller than that of the smaller of the two respective diagonal elements. In further analysis analogy with vibrations of mass points is used, for which it is known that the Jacobian coordinates obtained by the above procedure are a good approximation to the normal coordinates, so that the diagonal elements of the transformed matrix are of the same order of magnitude as eigenvalues of the matrix **K**. Only for a chain of n resonating oscillators there is a more considerable decrease in the value of the eigenvalue compared with the original diagonal element, in a ratio $1 : n^2$. It may be expected, therefore, that the eigenvalues of the matrix **K** do not differ by more than two orders of magnitude from the diagonal elements of the transformed matrix.

In the case of the Givens method the above estimate of the eigenvalue error cannot be improved. Therefore, this method is not applicable in our case. In the case of the

Jacobi method one can see that in the Jacobian transformation of a pair of coordinates in which the diagonal elements differ by their orders of magnitude, the Jacobian rotation is only a small one, because the off-diagonal element is small compared to the difference between the diagonal elements. This means, that throughout the diagonalization it also holds that the order of magnitude of each off-diagonal element is equal to or smaller than that of the smaller of the two respective diagonal elements, because in the transformations the large off-diagonal elements cannot contribute considerably to the small off-diagonal elements owing to the small angle of rotation. The Jacobi method can then be programmed so that in the transformation one obtains correction of each element (*i.e.* $w'_{ij} - w_{ij}$) with full accuracy. Then the accuracy of each eigenvalue is given by the maximum reached by the respective diagonal element of the matrix during the diagonalization, multiplied by the relative accuracy of calculation. For instance, the eigenvalue of 10^3 at an accuracy of 10^{-14} and if the respective diagonal element has reached the maximum of 10^5 is calculated with an error of 10^{-9}, *i.e.* with a relative accuracy of 10^{-12}. In the diagonalization it must be kept in mind that in the transformation by the method of differences the indices after transformation should be arranged so that the smaller diagonal element before the transformation corresponds to the smaller element after the transformation, and *vice versa*; otherwise, the accuracy would be lost and the method would lose its sense.

Hence, it may be expected that the maximum assumed by the diagonal element during the diagonalization does not exceed the respective eigenvalue by more than two orders of magnitude. Since, however, no exact mathematical proof of such statement was given, it should be recommended that the maxima of the diagonal elements during the diagonalization ought to be followed, and any violation of this statement ought to be indicated.

Thus, the procedure just described allows us to obtain eigenvalues λ_i with an almost complete relative accuracy. It can be easily seen that the eigenvectors of the transformed matrix **W** are obtained by means of this procedure with the same accuracy as the eigenvalues. To say it more exactly, a small element of an eigenvector (corresponding to a small eigenvalue), which corresponds to a coordinate with a large diagonal element and which is equal to or less than (by order of magnitude) the ratio of the eigenvalue and the diagonal element taken for consideration have been calculated with an error equal to the ratio of the maximum reached by the diagonal element corresponding to the eigenvalue in the diagonalization to the value of the diagonal element of the respective coordinate, multiplied by the relative accuracy of calculation. (*E.g.*, in the eigenvector corresponding to the eigenvalue 10^3, if the maximum of the respective diagonal element at diagonalization was 10^5, the element of this vector corresponding to the coordinate with the diagonal element 10^9 at the accuracy 10^{-14} is calculated with the maximum error of 10^{-18}, the value of this element being 10^{-6} at most).

Finally, in the back transformation of the eigenvectors (in which the matrix **R** is obtained) one should bear in mind that the values $r_{mq} - r_{lq}$ should be obtained with sufficient accuracy. If λ_q is very small with respect to k_{lm}, then $r_{mq} - r_{lq}$ is very small compared to r_{lq}, and in the calculation of the latter some significant digits are lost by subtraction. Consequently, $r_{mq} - r_{lq}$ cannot be calculated by mere subtraction but it should be calculated directly from the eigenvector of the transformed matrix **W**. Here, only those transformed coordinates become operative which contain the difference $c_m - c_l$. The diagonal elements corresponding to these coordinates are equal at least to k_{lm} (by order of magnitude), so that all components of the eigenvector corresponding to these coordinates are very small and have been calculated with sufficient accuracy. The s_{ki} values can be calculated from $s_{ki} = r_{ik}c_i^b$.

The values of λ_q, s_{qj} and $r_{mq} - r_{lq}$ thus obtained can be used in Eqs (*5*), (*26*) and (*28*). However, in Eq. (*27*) significant digits may be lost by subtraction $k_{lm}\beta_{ql} - k_{ml}\beta_{qm}$; it must therefore be rewritten in the form

$$w_{lm}\left(\frac{\partial \bar{T}}{\partial w_{lm}}\,\boldsymbol{C}^0\right)_j = c_l^b k_{lm} \sum_{q=1}^{n-1} (r_{mq} - r_{lq})\, s_{qj} \sum_{p=1}^{n-1} (r_{lp} - r_{mp})\, \alpha_{pq} g_p\,, \qquad (27')$$

of course, $r_{lp} - r_{mp}$ is not calculated by subtraction, but similarly to $r_{mq} - r_{lq}$ directly from the eigenvector of the transformed matrix **W**. By employing this procedure, one obtains the concentrations of individual components and their derivatives with respect to R_l and w_{lm} with sufficient accuracy even if the range of the eigenvalues λ_p comprises many orders of magnitude.

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Translated by L. Kopecká.