KINETICS OF A MONOMOLECULAR REACTION BETWEEN *n* COMPONENTS

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The reaction kinetics has been investigated of a general monomolecular reaction between *n* components, where reactions between some components are reversible and between others irreversible. The reacting components may be divided into groups so that all the components inside one group may change reversibly into each other, while reactions between components of different groups are irreversible. The reaction kinetics for each reversible group may be found similarly to the case where all the reactions are reversible; solutions for the individual reversible groups may be used to obtain solution for the whole system. A solution was also found to a difficult case in which matrices have multiple eigenvalues for irreversible consecutive reactions, namely, for a general case of degeneracy. Formulas are given for the calculation of derivatives of concentrations of the individual components with respect to parameters. The equations thus derived were applied to the reaction kinetics of a polymeranalogous reaction (*e.g.*, hydrolysis of polyacrylonitrile).

In the preceding paper[1] we investigated the reaction kinetics of a reversible monomolecular reaction between *n* components. In this paper, a solution is found for a general case where some reactions are reversible and some others are irreversible. In this case the components may be divided into groups so that components of the same group may reversibly change into each other, while reactions between components of different groups are irreversible. In order to solve the reaction kinetics, the kinetics of each reversible group is solved separately by employing a procedure analogous to the solution of a reversible system in ref.[1]; solutions for the individual groups are then used to obtain a solution for the whole system. In this step, a loss of accuracy occurs, if different reversible groups possess very close eigenvalues λ_k. For the case of the equal eigenvalues in the different reversible groups the solution fails. This difficulty is rather easily removed by dividing the matrices **R** and **S** into a regular part, which does not contain differences between very close eigenvalues in the denominator, and a singular part, which has non-zero off-diagonal elements only between very close eigenvalues. Results of the solution to the reaction kinetics are applied to a polymeranalogous reaction[2-6] (*e.g.*, hydrolysis of polyacrylonitrile), where they allow us to find a general solution to the kinetics without introducing any statistical assumptions. In this case all the reactions are irreversible,

so that each of the reversible groups contains a single component only and the solution to the kinetics of the reversible groups is not requested.

Since the mathematical part of this paper is very closely related to ref.[1], the numbering of equations started in ref.[1] is continued in this paper. In other words, equations in this paper are numbered starting from number (*30*), while references in the text to Eqs (*1*)–(*29*) mean automatically references to Eqs (*1*)–(*29*) in ref.[1]. Also all the mathematical symbols introduced in ref.[1] keep their meaning in this paper.

Derivation of the Time Dependence of Concentrations of the Individual Components and Their Derivatives with Respect to Parameters for a Monomolecular Reaction Between n *Components, where Some Reactions Are Irreversible*

If in the reaction scheme of a monomolecular reaction between n components some reactions are reversible and some are irreversible, it follows from the second law of thermodynamics (*i.e.* from the validity of Eq. (*7*) – as has been pointed out in the introduction, the reference regards Eq. (*7*) of ref.[1]) that the reacting components may be divided into groups, so that

1) the reaction between two components belonging to the same group proceeds either in both directions or in neither of them, and each component may change into any other in the same group either directly or through one or several intermediates;

2) between two components which belong to different groups the reaction proceeds either in one direction or does not proceed at all; more generally, if component A can change into component B (either directly or through intermediates), component B cannot change into component A (either directly or through intermediates), if A and B belong to different groups.

It follows from property (*2*) that the groups may be arranged so that the component of any group may change into components in the following groups only and not into those in the preceding ones. If matrix $\mathbf{K}$ (ref.[1]) is divided into blocks with respect to groups, then in such an arrangement the off-diagonal block matrices lying below the main diagonal are zero. Hence, the diagonalization of matrix $\mathbf{K}$ is separated into the diagonalization of blocks, each of which corresponds to one reversible group.

If neither of the components of a group changes into the components of the other groups, the respective block $\mathbf{K}_{kk}$ of matrix $\mathbf{K}$ is quite identical with the reversible scheme and the solution is the same[1]. In the opposite case we need to define c_i^b values in this block, which here have not the meaning of equilibrium concentrations, but are needed for the definition of the matrix $\mathbf{\Gamma}$ and for further calculation. For this purpose, we put the rate constants of all the reactions to components of other groups equal to zero and define c_i^b for the reversible scheme thus obtained. The reintroduction

of neglected rate constants affects only the diagonal elements of the block $\mathbf{K}_{kk}$ of the matrix $\mathbf{K}$ corresponding to the group in question, so that the matrix $\mathbf{A}_{kk} = \mathbf{\Gamma K}_{kk}\,\mathbf{\Gamma}^{-1}$ remains symmetrical also after this reintroduction. The solution of this block is analogous to that of the reversible scheme, but $\lambda_n = 0$, $r_{in} = 1$, and $s_{ni} = c_i^b$ does not hold. If the smallest (in the absolute value) eigenvalue λ_n is not too close to the second smallest λ_{n-1}, the group attains after some time a quasistationary state, in which the concentration of the i-th component is proportional to s_{ni} and concentrations of all the components decrease as $e^{\lambda_n t}$ with time. Of course, the s_{ni} values are generally different from the c_i^b values introduced above.

This solution yields for each reversible group matrices $\mathbf{R}_{kk}$ and $\mathbf{S}_{kk}$ and a diagonal matrix $\mathbf{\Lambda}_k$. Now, it is our task to obtain matrices $\mathbf{R}$, $\mathbf{S}$, and $\mathbf{T}$ for the whole system from these data. Similarly to the matrix $\mathbf{K}$, also in these matrices the off-diagonal block-matrices below the main diagonal are zero, *i.e.* $\mathbf{R}_{km} = 0$, $\mathbf{S}_{km} = 0$, $\mathbf{T}_{km} = 0$ for $k > m$. The diagonal blocks of matrices $\mathbf{R}$ and $\mathbf{S}$ are matrices $\mathbf{R}_{kk}$ and $\mathbf{S}_{kk}$ found in the solution of the individual groups. In order to determine off-diagonal blocks, we introduce the auxiliary block-diagonal matrix $\mathbf{R}_0$, the diagonal blocks of which are equal to $\mathbf{R}_{kk}$ and the off-diagonal ones are zero, and matrix $\mathbf{S}_0$ with diagonal blocks equal to $\mathbf{S}_{kk}$ and off-diagonal ones equal to zero. We also introduce matrices $\mathbf{P} = \mathbf{S}_0\mathbf{R}$, $\mathbf{Q} = \mathbf{S}\mathbf{R}_0$, and $\mathbf{F} = \mathbf{S}_0\mathbf{K}\mathbf{R}_0$. For their blocks it holds that $\mathbf{P}_{kk} = \mathbf{Q}_{kk} = \mathbf{E}$, $\mathbf{F}_{kk} = \mathbf{\Lambda}_k$, $\mathbf{P}_{km} = \mathbf{S}_{kk}\mathbf{R}_{km}$, $\mathbf{Q}_{km} = \mathbf{S}_{km}\mathbf{R}_{mm}$, $\mathbf{F}_{km} = \mathbf{S}_{kk}\mathbf{K}_{km}\mathbf{R}_{mm}$. For $k > m$ all the block-matrices $\mathbf{X}_{km}$ are zero. The matrix $\mathbf{F}$ is triangular, which makes possible an easy calculation of the blocks of matrices $\mathbf{R}$ and $\mathbf{S}$. The equation $\mathbf{KR} = \mathbf{R}\,\mathbf{\Lambda}$ is multiplied by $\mathbf{S}_0$ from the left and rewritten as $\mathbf{S}_0\mathbf{K}\mathbf{R}_0 \,.\, \mathbf{S}_0\mathbf{R} = \mathbf{S}_0\mathbf{R} \,.\, \mathbf{\Lambda}$, or $\mathbf{FP} = \mathbf{P}\,\mathbf{\Lambda}$. The last equation is rewritten with respect to blocks and components, with the first and last terms separated in the block multiplication:

$$\lambda_i^{(k)}(\mathbf{P}_{km})_{ij} + \Big(\sum_{s=k+1}^{m-1} \mathbf{F}_{ks}\mathbf{P}_{sm}\Big)_{ij} + (\mathbf{F}_{km})_{ij} = (\mathbf{P}_{km})_{ij}\,\lambda_j^{(m)}\,,$$

where $\lambda_i^{(k)}$ is the i-th eigenvalue of the k-th block $\mathbf{K}_{kk}$ of the matrix $\mathbf{K}$, and the notation $(\mathbf{X}_{km})_{ij}$ denotes the element (i, j) of the block $\mathbf{X}_{km}$ of the matrix $\mathbf{X}$. Hence,

$$(\mathbf{P}_{km})_{ij} = \Big((\mathbf{F}_{km})_{ij} + \Big(\sum_{s=k+1}^{m-1} \mathbf{F}_{ks}\mathbf{P}_{sm}\Big)_{ij}\Big)\Big/\big(\lambda_j^{(m)} - \lambda_i^{(k)}\big)\,. \qquad (30)$$

For $k = m - 1$, the sum in this equation is empty, and the matrix $\mathbf{P}_{m-1,m}$ may be calculated directly. Thus, Eq. (*30*) is a recurrent formula for the calculation of matrices $\mathbf{P}_{km}$ with fixed m and decreasing k.

Similarly, from the equation $\mathbf{QF} = \mathbf{\Lambda Q}$ we derive

$$(\mathbf{Q}_{km})_{ij} = \Big((\mathbf{F}_{km})_{ij} + \Big(\sum_{s=k+1}^{m-1} \mathbf{Q}_{ks}\mathbf{F}_{sm}\Big)_{ij}\Big)\Big/\big(\lambda_i^{(k)} - \lambda_j^{(m)}\big)\,. \qquad (31)$$

Eq. (*31*) is a recurrent formula for the calculation of matrices $\mathbf{Q}_{km}$ with fixed k and increasing m. A simpler way for obtaining the matrix $\mathbf{Q}$ consists in the inversion of matrix $\mathbf{P}$ according to

$$(\mathbf{Q}_{km})_{ij} = -\left(\sum_{s=k}^{m-1} \mathbf{Q}_{ks}\mathbf{P}_{sm}\right)_{ij}, \quad k < m, \quad \mathbf{Q}_{kk} = \mathbf{E}, \tag{32}$$

which is a recurrent formula with fixed k and increasing m, or on the contrary, we may calculate the matrix $\mathbf{Q}$ using Eq. (*31*) and the matrix $\mathbf{P}$ using the equation

$$(\mathbf{P}_{km})_{ij} = -\left(\sum_{s=k+1}^{m} \mathbf{Q}_{ks}\mathbf{P}_{sm}\right)_{ij}, \quad k < m, \quad \mathbf{P}_{mm} = \mathbf{E}, \tag{33}$$

which is a recurrent formula with fixed m and decreasing k.

One can see from Eqs (*30*), (*31*) that the matrices $\mathbf{P}$, $\mathbf{Q}$ exist, if one cannot find two equal eigenvalues corresponding to two different reversible groups. If, however, in the reaction scheme components of one of these groups (that with the lower index) cannot change into those of the other group, either directly or through intermediates, the numerators in Eqs (*30*), (*31*) are zero, and hence the matrices $\mathbf{P}_{km}$, $\mathbf{Q}_{km}$ are zero. If such a situation arises for all the pairs of equal eigenvalues in different blocks, the matrices $\mathbf{P}$, $\mathbf{Q}$ exist in this case also. If, on the other hand, at least one of the numerators in Eqs (*30*) or (*31*) is nonzero for at least one pair of equal eigenvalues, each of which belongs to another reversible group, the matrices $\mathbf{P}$ and $\mathbf{Q}$ do not exist. For very close eigenvalues (*i.e.* if the numerator is very large compared to the denominator), the procedure described below becomes numerically unstable.

If the matrices $\mathbf{P}$, $\mathbf{Q}$ do exist, the matrices $\mathbf{R}$ and $\mathbf{S}$, $\mathbf{R} = \mathbf{R}_0\mathbf{P}$ and $\mathbf{S} = \mathbf{Q}\mathbf{S}_0$ can be calculated from them. The latter may be employed without change in Eqs (*11*), (*19*), (*20*), and (*22*); using Eqs (*12*), (*18*), and (*13*), it is then possible to calculate concentrations of the individual components and their derivatives with respect to the parameters.

Among reversible groups there is at least one the components of which cannot change into components of other groups. Such a group has just one zero eigenvalue; all the eigenvalues of the other groups are negative. If such a group is just one, there is a single zero eigenvalue in the whole system, and the respective eigenvectors have the form $r_{in} = 1$ for all the components i in all the groups, and $s_{ni} = c_i^b$, where c_i^b is the equilibrium concentration of the i-th component, which is of course zero for the components of the other groups. If, however, there are several such groups, each such group has one corresponding zero eigenvalue. This degeneracy does not prevent the definition of the matrices $\mathbf{R}$, $\mathbf{S}$, because the components of one of such groups cannot change into components of other such groups. r_{ip} then indicates which relative part of the i-th component passes after completion of the reaction

into the group which contains the respective eigenvalue $\lambda_p = 0$; it holds $\sum_p r_{ip} = 1$, with summation running over those p for which $\lambda_p = 0$. The equation $s_{pi} = c_i^b$ holds for components i from that reversible group which contains the eigenvalue $\lambda_p = 0$, while for components of the other groups $s_{pi} = 0$. Here, c_i^b has the meaning of an equilibrium concentration of the i-th component in the isolated group containing the eigen-value $\lambda_p = 0$ only. Universal equilibrium concentrations of the whole system do not exist, because the final state depends on the initial state of the system.

To calculate derivatives of concentrations with respect to the rate constants, one must first define an independent system of parameters. The rate constants may be divided into two groups, namely, reversible constants characterizing reactions inside each reversible group and irreversible constants characterizing transitions between different reversible groups. The irreversible constants are independent and derivatives with respect to them may be calculated using Eq. (*26*). If, however, there is more than one zero eigenvalue in the whole system, the summation with respect to q must run also over indices corresponding to zero eigenvalues, because $r_{mq} - r_{lq} = 0$ for $\lambda_q = 0$ is not generally valid in this case. Independent reversible parameters inside each reversible group may be introduced using Eq. (*24*). Derivatives with respect to these parameters may be calculated using Eqs (*27*), (*28'*); for the summation with respect to q, the same is valid as for Eq. (*26*), while in Eq. (*28'*) in the summation with respect to m only those indices m are considered which belong to the same reversible group as component l. If also the irreversible constants were replaced by the parameters w_{ij} according to Eq. (*24*), w_{ji} being zero for $j > i$, the derivatives of concentrations with respect to $\ln R_l$ would be calculated according to Eq. (*28*), and for irreversible w_{lm}, derivatives with respect to $\ln w_{lm}$ would be identical with derivatives with respect to $\ln k_{lm}$. Let it be noticed that the values $\partial t_{ij}/\partial k_{lm}$, $\partial t_{ij}/\partial w_{lm}$, and $\partial t_{ij}/\partial R_l$ are nonzero only if the components of the reversible group containing the component i may change (either directly or through intermediates) into components of the group containing the component l (including the case where both i and l are in the same group), and at the same time, components of the group containing the component l may change into components of the group containing the component j (again including the case where l and j are in the same group).

Let us consider now the case where the system contains at least one pair of very close eigenvalues corresponding to different reversible groups. In this case, the matrices $\mathbf{P}$, $\mathbf{Q}$ are rewritten as $\mathbf{P} = \mathbf{P}^r\mathbf{P}^s$ and $\mathbf{Q} = \mathbf{Q}^s\mathbf{Q}^r$; for the sake of simplicity, we further omit the distribution of indices into reversible groups, which for the triangular matrices $\mathbf{P}$, $\mathbf{P}^r$, $\mathbf{P}^s$, $\mathbf{Q}$, $\mathbf{Q}^r$, and $\mathbf{Q}^s$ only indicates that off-diagonal elements corresponding to two indices from the same group are zero, and denote the element (i, j) of the matrix $\mathbf{P}^s$ by a simplified symbol P^s_{ij} instead of $(\mathbf{P}^s)_{ij}$ and similarly for the matrices $\mathbf{Q}^s$, $\mathbf{P}^r$, $\mathbf{Q}^r$, $\mathbf{P}$, $\mathbf{Q}$, and $\mathbf{F}$. The matrices $\mathbf{P}^s$, $\mathbf{Q}^s$ are chosen according to Eqs (*30*) and (*31*), with F_{ij} replaced by A_{ij}; the elements A_{ij} are suitably chosen below, being

nonzero only if λ_i and λ_j are very close (and belong to different reversible groups):

$$P^s_{ij} = \sum_{s=i+1}^{j} A_{is} P^s_{sj} / (\lambda_j - \lambda_i) , \tag{34}$$

$$Q^s_{ij} = \sum_{s=i}^{j-1} Q^s_{is} A_{sj} / (\lambda_i - \lambda_j) , \tag{35}$$

further, $P^s_{ii} = Q^s_{ii} = 1$. Hence, $(\mathbf{Q}^s)^{-1} = \mathbf{P}^s$, and thus also $(\mathbf{Q}^r)^{-1} = \mathbf{P}^r$, because $\mathbf{Q}^{-1} = \mathbf{P}$. It also holds that $Q^r_{ii} = P^r_{ii} = 1$, and for the other elements of the matrix $\mathbf{P}^r$ we derive

$$P^r_{si} = \sum_{r=s}^{i} P_{sr} Q^s_{ri} = \Big(\sum_{r=s+1}^{i} (\lambda_r - \lambda_s) P_{sr} Q^s_{ri} - \sum_{r=s}^{i-1} (\lambda_r - \lambda_i) P_{sr} Q^s_{ri} \Big) / (\lambda_i - \lambda_s) .$$

In the first summation we substitute for P_{sr} using Eq. (*30*), while in the second one the substitution for Q^s_{ri} is carried out using Eq. (*35*), and the order of summation indices is interchanged:

$$P^r_{si} = \Big(\sum_{r=s+1}^{i} \sum_{m=s+1}^{r} F_{sm} P_{mr} Q^s_{ri} - \sum_{r=s}^{i-1} \sum_{j=r}^{i-1} P_{sr} Q^s_{rj} A_{ji} \Big) / (\lambda_i - \lambda_s) =$$

$$= \Big(\sum_{m=s+1}^{i} \sum_{r=m}^{i} F_{sm} P_{mr} Q^s_{ri} - \sum_{j=s}^{i-1} \sum_{r=s}^{j} P_{sr} Q^s_{rj} A_{ji} \Big) / (\lambda_i - \lambda_s) .$$

Now, the substitution for

$$\sum_{r=m}^{i} P_{mr} Q^s_{ri} = P^r_{mi} \quad \text{and} \quad \sum_{r=s}^{j} P_{sr} Q^s_{rj} = P^r_{sj}$$

yields the final expression

$$P^r_{si} = \Big(\sum_{m=s+1}^{i} F_{sm} P^r_{mi} - \sum_{j=s}^{i-1} P^r_{sj} A_{ji} \Big) / (\lambda_i - \lambda_s) . \tag{36}$$

If the values of A_{ji} are given, it is possible, by employing Eq. (*36*), to calculate the off-diagonal elements of the matrix $\mathbf{P}^r$ so that we start with $i = 2$ and increase the index i one by one; for each fixed i, we start with $s = i - 1$, and decrease the index s one by one. The A_{sj} values are chosen simultaneously with the calculation of the P^r_{si} values using Eq. (*36*). If λ_i is sufficiently different from λ_s, we choose

$$P^r_{si} = \Big(\sum_{m=s+1}^{i} F_{sm} P^r_{mi} - \sum_{j=s+1}^{i-1} P^r_{sj} A_{ji} \Big) / (\lambda_i - \lambda_s) , \quad A_{si} = 0 . \tag{37}$$

This choice may also be employed in the case where λ_i and λ_s are very close, but also

$$\sum_{m=s+1}^{i} F_{sm} P^r_{mi} - \sum_{j=s+1}^{i-1} P^r_{sj} A_{ji}$$

is so small, that after dividing we obtain a value for P^r_{si} which is not too high to cause a loss of accuracy in the calculation. In the opposite case we choose

$$P^r_{si} = 0\,, \quad A_{si} = \sum_{m=s+1}^{i} F_{sm} P^r_{mi} - \sum_{j=s+1}^{i-1} P^r_{sj} A_{ji}\,. \tag{38}$$

Let it be pointed out that the choice by Eq. (*38*) is not unambiguous: to satisfy Eq. (*36*), we may choose P^r_{si} arbitrarily with the only restriction that it should not be too high, and calculate A_{si} from Eq. (*36*). The choice according to Eq. (*38*) has been made because it is the simplest way. Using Eqs (*37*), (*38*) and the relation $P^r_{ii} = 1$, we can obtain the matrix $\mathbf{P}^r$ and hence by its inversion according to Eq. (*32*) the matrix $\mathbf{Q}^r$. Let it be pointed out that from $A_{si} \neq 0$ it does not follow that $Q^r_{si} = 0$.

Similarly to Eq. (*36*), we may derive

$$Q^r_{is} = \Big(\sum_{m=i}^{s-1} Q^r_{im} F_{ms} - \sum_{j=i+1}^{s} A_{ij} Q^r_{js}\Big)/(\lambda_i - \lambda_s)\,. \tag{39}$$

The relation (*39*) is not suited for the calculation of the Q^r_{is} values, if the A_{is} and P^r_{is} values have already been calculated from (*37*) or (*38*), because due to the loss of accuracy the matrices $\mathbf{P}^r$ and $\mathbf{Q}^r$ thus calculated do not satisfy the relation $\mathbf{P}^r\mathbf{Q}^r = \mathbf{E}$ with sufficient accuracy. On the other hand, however, the matrix $\mathbf{Q}^r$ and the A_{is} values may be calculated from the equations

$$Q^r_{is} = \Big(\sum_{m=i}^{s-1} Q^r_{im} F_{ms} - \sum_{j=i+1}^{s-1} A_{ij} Q^r_{js}\Big)/(\lambda_i - \lambda_s)\,, \quad A_{is} = 0 \tag{40}$$

which are used if λ_i is sufficiently different from λ_s, or if at close λ_i and λ_s the value Q^r_{is} is not too high to cause a loss of accuracy; or from the equations

$$Q^r_{is} = 0\,, \quad A_{is} = \sum_{m=i}^{s-1} Q^r_{im} F_{ms} - \sum_{j=i+1}^{s-1} A_{ij} Q^r_{js}\,, \tag{41}$$

which are used in the opposite case. The matrix $\mathbf{P}^r$ is then obtained from the matrix $\mathbf{Q}^r$ thus obtained by the inversion according to Eq. (*33*). However, the $\mathbf{P}^r$, $\mathbf{Q}^r$ matrices and A_{is} values obtained by employing this procedure are different from those ob-

tained by Eqs (*37*), (*38*), (*32*), which is a consequence of the ambiguity of choice in Eq. (*38*). On the other hand, both sets give the same matrices **T** and **RUS**.

In order to calculate the time dependence of concentrations, let us now calculate the matrix **T**. We have

$$\mathbf{T} = \mathbf{R}e^{\wedge t}\mathbf{S} = \mathbf{R}_0\mathbf{P}e^{\wedge t}\mathbf{Q}\mathbf{S}_0 = \mathbf{R}_0\mathbf{P}^r\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s\mathbf{Q}^r\mathbf{S}_0 = \mathbf{R}^r\left(\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s\right)\mathbf{S}^r ,$$

where we have put $\mathbf{R}^r = \mathbf{R}_0\mathbf{P}^r$, $\mathbf{S}^r = \mathbf{Q}^r\mathbf{S}_0$. The matrix $\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s$ remains to be found. For this purpose, let us first distribute the eigenvalues into groups so that λ_i and λ_j fall into the same group, if $A_{ij} \neq 0$ or if $A_{ji} \neq 0$, or if there is such a sequence of indices starting with i and ending with j that for its each two adjacent indices r, s, either $A_{rs} \neq 0$ or $A_{sr} \neq 0$ is valid. A_{ij} may differ from zero only if λ_i and λ_j are close, *i.e.* $|\lambda_i - \lambda_j| < \varepsilon$ where ε is the limit below which the eigenvalues λ_i, λ_j are regarded as degenerate. If the group contains n eigenvalues, then for each two of them it holds that $|\lambda_i - \lambda_j| < (n-1)\varepsilon$. Thus, all the eigenvalues in the same group are very close. The element (i, j) of the matrices $\mathbf{P}^s$, $\mathbf{Q}^s$, $\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s$ may be nonzero, only if λ_i and λ_j fall into the same group. Hence, these matrices decompose into blocks, each of which corresponds to one group of degenerate eigenvalues. In particular, in the row and column corresponding to a nondegenerate eigenvalue, only the diagonal element is nonzero. For the elements P^s_{ij}, Q^s_{ij} of matrices $\mathbf{P}^s$, $\mathbf{Q}^s$, expressions (*34*), (*35*) are valid, in which it is sufficient to consider only those values of j and s which are in the same degenerate group as the index i, because otherwise we have either $A_{ij} = 0$, or $A_{is} = 0$; the same holds for the elements of matrices $\mathbf{P}^s$ and $\mathbf{Q}^s$. From (*34*), (*35*) we derive

$$P^s_{ij} = \sum_{r_1, r_2, \ldots, r_u} \frac{A_{ir_1}A_{r_1r_2}\ldots A_{r_{u-1}r_u}A_{r_uj}}{(\lambda_j - \lambda_i)(\lambda_j - \lambda_{r_1})(\lambda_j - \lambda_{r_2})\ldots(\lambda_j - \lambda_{r_u})}, \qquad (42)$$

$$Q^s_{ij} = \sum_{r_1, r_2, \ldots, r_u} \frac{A_{ir_1}A_{r_1r_2}\ldots A_{r_{u-1}r_u}A_{r_uj}}{(\lambda_i - \lambda_{r_1})(\lambda_i - \lambda_{r_2})\ldots(\lambda_i - \lambda_{r_u})(\lambda_i - \lambda_j)}. \qquad (43)$$

In Eqs (*42*), (*43*) the summation is carried out over all the choices of $r_1, r_2, \ldots, r_u$, for which $i < r_1 < r_2 < \ldots < r_u < j$, including $u = 0$, when the numerator is A_{ij}. Of course, the values of $r_1, r_2, \ldots, r_u$ are chosen only from that degenerate group which contains i and j, because otherwise the numerator is zero. If between the indices i and j there are n further indices of the same degenerate group, the sums in the equations have 2^n terms, because each of these n indices may be either chosen or not chosen for the sequence $r_1, r_2, \ldots, r_u$.

By using Eqs (*42*), (*43*), we obtain for $\left(\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s\right)_{ij}$, $i < j$

$$\left(\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s\right)_{ij} = \sum_{r_1, r_2, \ldots, r_u} A_{ir_1}A_{r_1r_2}\ldots A_{r_uj}\,\mathrm{F}^{u+1}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_j), \qquad (44)$$

where the summation is carried out as in Eqs. (*42*), (*43*), and

$$F^{m-1}(x_1, x_2, \ldots, x_m) = \sum_{i=1}^{m} \left[e^{x_i t} / \prod_{\substack{j=1 \\ j \neq i}}^{m} (x_i - x_j) \right] . \qquad (45)$$

In particular, if between the indices i, j there is no other index of the same degenerate group, we have

$$(\mathbf{P}^s e^{\wedge t} \mathbf{Q}^s)_{ij} = A_{ij} \frac{e^{\lambda_i t} - e^{\lambda_j t}}{\lambda_i - \lambda_j} ;$$

if, however, there is a single index r of the same degenerate group, it holds that

$$(\mathbf{P}^s e^{\wedge t} \mathbf{Q}^s)_{ij} = A_{ij} \frac{e^{\lambda_i t} - e^{\lambda_j t}}{\lambda_i - \lambda_j} + A_{ir} A_{rj} \left(\frac{e^{\lambda_i t}}{(\lambda_i - \lambda_r)(\lambda_i - \lambda_j)} + \right.$$
$$\left. + \frac{e^{\lambda_r t}}{(\lambda_r - \lambda_i)(\lambda_r - \lambda_j)} + \frac{e^{\lambda_j t}}{(\lambda_j - \lambda_i)(\lambda_j - \lambda_r)} \right),$$

and if there are two indices $r < s$ of the same degenerate group, it holds

$$(\mathbf{P}^s e^{\wedge t} \mathbf{Q}^s)_{ij} = A_{ij} \frac{e^{\lambda_i t} - e^{\lambda_j t}}{\lambda_i - \lambda_j} + A_{ir} A_{rj} F^2(\lambda_i, \lambda_r, \lambda_j) +$$
$$+ A_{is} A_{sj} F^2(\lambda_i, \lambda_s, \lambda_j) + A_{ir} A_{rs} A_{sj} \left(\frac{e^{\lambda_i t}}{(\lambda_i - \lambda_r)(\lambda_i - \lambda_s)(\lambda_i - \lambda_j)} + \right.$$
$$+ \frac{e^{\lambda_r t}}{(\lambda_r - \lambda_i)(\lambda_r - \lambda_s)(\lambda_r - \lambda_j)} + \frac{e^{\lambda_s t}}{(\lambda_s - \lambda_i)(\lambda_s - \lambda_r)(\lambda_s - \lambda_j)} +$$
$$\left. + \frac{e^{\lambda_j t}}{(\lambda_j - \lambda_i)(\lambda_j - \lambda_r)(\lambda_j - \lambda_s)} \right).$$

For $i = j$, $(\mathbf{P}^s e^{\wedge t} \mathbf{Q}^s)_{ii} = e^{\lambda_i t}$.

In our case all the x_i values in Eq. (*45*) are very close, because the λ_i in question belong to the same degenerate group. For this reason, the function $F^{m-1}(x_1, x_2, \ldots, x_m)$ cannot be calculated using Eq. (*45*) because of the loss of accuracy. The function can be calculated so that the function $e^{x_i t}$ is expanded in a Taylor series in a suitably chosen point x_0 (common for all the x_i). x_0 is selected inside the interval which comprises the x_i values (we may choose *e.g.* one of the x_i values or their

arithmetic mean). The result of the expansion in a series and of further rearrangements is that

$$F^{m-1}(x_1, x_2, \ldots, x_m) = e^{x_0 t} \sum_{s=0}^{\infty} \frac{t^{s+m-1}}{(s+m-1)!} X_s , \qquad (46)$$

where $X_0 = 1$,

$$X_s = \sum_{\substack{s_1, s_2, \ldots \\ \sum i s_i = s}} \prod_{i=1} \left(M_i^{s_i} / (s_i!\, i^{s_i}) \right) ; \qquad (47)$$

the product is formed over all the i for which $s_i > 0$, and the summation is performed over all the choices $s_1, s_2, s_3, \ldots$; s_i non-negative integers, which fulfil the condition

$$\sum_{i=1} i s_i = s , \quad \text{and} \quad M_i = \sum_{j=1}^{m} (x_j - x_0)^i .$$

The explicit expressions for X_i for $i = 1$ to 7 are

$$X_1 = M_1 ,$$

$$X_2 = \tfrac{1}{2} M_1^2 + \tfrac{1}{2} M_2 ,$$

$$X_3 = \tfrac{1}{6} M_1^3 + \tfrac{1}{2} M_1 M_2 + \tfrac{1}{3} M_3 ,$$

$$X_4 = \tfrac{1}{24} M_1^4 + \tfrac{1}{4} M_1^2 M_2 + \tfrac{1}{8} M_2^2 + \tfrac{1}{3} M_1 M_3 + \tfrac{1}{4} M_4 ,$$

$$X_5 = \tfrac{1}{120} M_1^5 + \tfrac{1}{12} M_1^3 M_2 + \tfrac{1}{8} M_1 M_2^2 + \tfrac{1}{6} M_1^2 M_3 + \tfrac{1}{6} M_2 M_3 + \tfrac{1}{4} M_1 M_4 + \tfrac{1}{5} M_5 ,$$

$$X_6 = \tfrac{1}{720} M_1^6 + \tfrac{1}{48} M_1^4 M_2 + \tfrac{1}{16} M_1^2 M_2^2 + \tfrac{1}{48} M_2^3 + \tfrac{1}{18} M_1^3 M_3 + \tfrac{1}{6} M_1 M_2 M_3 + \tfrac{1}{18} M_3^2 + \tfrac{1}{8} M_1^2 M_4 + \tfrac{1}{8} M_2 M_4 + \tfrac{1}{5} M_1 M_5 + \tfrac{1}{6} M_6 ,$$

$$X_7 = \tfrac{1}{5040} M_1^7 + \tfrac{1}{240} M_1^5 M_2 + \tfrac{1}{48} M_1^3 M_2^2 + \tfrac{1}{48} M_1 M_2^3 + \tfrac{1}{72} M_1^4 M_3 + \tfrac{1}{12} M_1^2 M_2 M_3 + \tfrac{1}{24} M_2^2 M_3 + \tfrac{1}{8} M_1 M_3^2 + \tfrac{1}{24} M_1^3 M_4 + \tfrac{1}{8} M_1 M_2 M_4 + \tfrac{1}{12} M_3 M_4 + \tfrac{1}{10} M_1^2 M_5 + \tfrac{1}{10} M_2 M_5 + \tfrac{1}{6} M_1 M_6 + \tfrac{1}{7} M_7 .$$

X_s may also be calculated using the following expression, recurrent with respect to the number of arguments m

$$X_s(x_1) = (x_1 - x_0)^s , \quad X_s(x_1, x_2, \ldots, x_m) = \sum_{k=0}^{s} (x_m - x_0)^k X_{s-k}(x_1, x_2, \ldots, x_{m-1}) . \qquad (47')$$

Here we have explicitly shown to which x_j quantities the respective X_s is related. A proof of the validity of Eqs (46), (47), and (47') is given in the Appendix.

Using Eqs (*44*), (*46*), and (*47*) or (*47'*), it is now possible to obtain the matrix $\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s$. The calculation is most suitably carried out by selecting one of the λ_p values of the respective degenerate group for x_0. In such a case, the X_s values do not depend on the fact if the index p has been or has not been chosen for the sequence in the summation in Eq. (*44*), and number of sets of X_s values needed for the calculation is reduced to one half. If the arithmetic mean from x_j values were chosen for x_0, the expressions for X_s would be considerably simplified with respect to $M_1 = 0$, but x_0 would depend on the choice of the sequence, and the $(x_j - x_0)^l$ values would have to be calculated again for each choice. Eqs (*44*), (*46*) and (*47*) or (*47'*) may also be used if some pairs or groups of λ_p values are exactly equal, even though they have been derived only for the λ_p values pairwise different. The validity of the equations for this case follows from the continuity of the solution of a differential equation as a function of a parameter. In this case, λ_p with the highest (exact) degeneracy is chosen for x_0. Let it be pointed out that the function *e.g.* $F^2(\lambda_i, \lambda_i, \lambda_j)$ cannot be replaced by the function $F^1(\lambda_i, \lambda_j)$. The series in Eq. (*46*) converges very rapidly, because all the x_i values are very close to x_0, so that the X_s quantities decrease very rapidly with increasing s; two or three members of this series are usually sufficient for the calculation of the series. If all the arguments of the function F^{m-1} are exactly equal (*i.e.* if $x_1 = x_2 = \ldots = x_m$), it holds that $F^{m-1}(\lambda, \lambda, \ldots, \lambda) = e^{\lambda t} t^{m-1}/(m-1)!$. From the matrix $\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s$ and matrices $\mathbf{R}^r$, $\mathbf{S}^r$, the matrix $\mathbf{T}$ is calculated from

$$\mathbf{T} = \mathbf{R}^r(\mathbf{P}^s e^{\wedge t}\mathbf{Q}^s)\,\mathbf{S}^r\,; \tag{48}$$

using this matrix, time dependence of concentrations is calculated from Eq. (*12*).

In order to calculate the derivatives of concentrations with respect to a parameter, we introduce the matrix $\mathbf{U}^r = \mathbf{P}^s\mathbf{U}\mathbf{Q}^s$, and rewrite Eq. (*18*) to

$$\frac{\partial \mathbf{T}}{\partial p} = \mathbf{R}^r\mathbf{P}^s\mathbf{U}\mathbf{Q}^s\mathbf{S}^r\,,$$

or

$$\frac{\partial \mathbf{T}}{\partial p} = \mathbf{R}^r\mathbf{U}^r\mathbf{S}^r\,. \tag{49}$$

It also holds that

$$u_{mn} = \left(\mathbf{Q}^s\mathbf{Q}^r\mathbf{S}_0\,\frac{\partial \mathbf{K}}{\partial p}\,\mathbf{R}_0\mathbf{P}^r\mathbf{P}^s\right)_{mn} F^1(\lambda_m, \lambda_n)\,, \tag{50}$$

because according to Eq. (*45*), $F^1(\lambda_m, \lambda_n) = (e^{\lambda_m t} - e^{\lambda_n t})/(\lambda_m - \lambda_n)$ for $\lambda_m \neq \lambda_n$ and according to Eq. (*46*), $F^1(\lambda_m, \lambda_m) = te^{\lambda_m t}$, if we choose $x_0 = \lambda_m$. The matrix

$\mathbf{S}_0(\partial\mathbf{K}/\partial p)\,\mathbf{R}_0$ is not triangular, but only block-triangular with respect to blocks of the reversible groups. For this reason also the matrices $\mathbf{Q}^r\mathbf{S}_0(\partial\mathbf{K}/\partial p)\,\mathbf{R}_0\mathbf{P}^r$, $\mathbf{U}$, and $\mathbf{U}^r$ are only block-triangular, but not triangular. Eq. (*50*) is then rewritten to

$$u_{mn} = \left(\mathbf{Q}^s\left(\mathbf{S}^r\frac{\partial\mathbf{K}}{\partial p}\,\mathbf{R}^r\right)\mathbf{P}^s\right)_{mn} \mathrm{F}^1(\lambda_m, \lambda_n)$$

whence

$$(\mathbf{U}^r)_{ij} = \sum_{m,k,l,n} P^s_{im}Q^s_{mk}\left(\mathbf{S}^r\frac{\partial\mathbf{K}}{\partial p}\,\mathbf{R}^r\right)_{kl} P^s_{ln}Q^s_{nj}\,\mathrm{F}^1(\lambda_m, \lambda_n).$$

Let us now introduce a four-index quantity D_{iklj} by using the relation

$$D_{iklj} = \sum_{m=1}^{k}\sum_{n=1}^{j} P^s_{im}Q^s_{mk}P^s_{ln}Q^s_{nj}\,\mathrm{F}^1(\lambda_m, \lambda_n), \qquad (51)$$

which particularly for $i = k$ and $l = j$ becomes $D_{iijj} = \mathrm{F}^1(\lambda_i, \lambda_j)$. Hence we obtain

$$(\mathbf{U}^r)_{ij} = \sum_{k,l}\left(\mathbf{S}^r\frac{\partial\mathbf{K}}{\partial p}\,\mathbf{R}^r\right)_{kl} D_{iklj}\,. \qquad (52)$$

In Eqs (*51*), (*52*) $i \leqq k$; i, m and k belong to the same degenerate group; k and l belong either to the same reversible group, or components of the group containing k may change directly or through intermediates into components of the group containing l (otherwise $(\mathbf{S}^r(\partial\mathbf{K}/\partial p)\,\mathbf{R}^r)_{kl} = 0$ would hold); $l \leqq j$; l, n and j again belong to the same degenerate group (which may be different from the group containing i, m and k). For nondegenerate indices i and j, Eq. (*52*) has the same form as Eqs (*19*), (*20*) and (*22*):

$$(\mathbf{U}^r)_{ij} = \left(\mathbf{S}^r\frac{\partial\mathbf{K}}{\partial p}\,\mathbf{R}^r\right)_{ij}\mathrm{F}^1(\lambda_i, \lambda_j)\,.$$

For the other cases the formulas for D_{iklj} have been derived in the Appendix. For a case where λ_i and λ_j belong to the same degenerate group or are very close to each other (λ_i and λ_j may not belong to the same degenerate group, even if they are very close, if $A_{ij} = 0$ or $A_{ji} = 0$), we have for $i \neq k$

$$D_{ikjj} = \sum_{r_1,r_2,\ldots,r_u} A_{ir_1}A_{r_1r_2}\ldots A_{r_{u-1}r_u}A_{r_uk}\,\mathrm{F}^{u+2}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k, \lambda_j), \qquad (53)$$

where the summation is carried out as in Eq. (*42*); for $l \neq j$,

$$D_{iij} = \sum_{s_1, s_2, \ldots, s_v} A_{is_1} A_{s_1 s_2} \ldots A_{s_{v-1} s_v} A_{s_v j} \, F^{v+2}(\lambda_i, \lambda_i, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) , \qquad (54)$$

where the summation is carried out similarly to Eq. (*42*); and finally, for $i \neq k$, $l \neq j$

$$D_{ikj} = \sum_{\substack{r_1, r_2, \ldots, r_u \\ s_1, s_2, \ldots, s_v}} A_{ir_1} A_{r_1 r_2} \ldots A_{r_{u-1} r_u} A_{r_u k} \times A_{is_1} A_{s_1 s_2} \ldots A_{s_{v-1} s_v} A_{s_v j} \times$$
$$\times F^{u+v+3}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k, \lambda_l, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) , \qquad (55)$$

where the summation is carried out over all the choices $r_1, r_2, \ldots, r_u, s_1, s_2, \ldots, s_v$, for which it holds $i < r_1 < r_2 < \ldots < r_u < k$ and $l < s_1 < s_2 < \ldots < s_v < j$, including $u = 0$, where the first factor is A_{ik}, and/or $v = 0$, where the second factor is A_{lj}.

The functions F^{u+2}, F^{v+2} and F^{u+v+3} which appear in these relations are calculated using Eq. (*46*). If λ_i and λ_j are not close enough, Eqs (*53*), (*54*) and (*55*) also hold, but are not suited for the calculation of D_{iklj}, because the series in Eq. (*46*) converges slowly. For this case we introduce first

$$G_{ii}(x) = \frac{1}{x - \lambda_i} , \quad G_{ik}(x) = \sum_{s=i}^{k-1} G_{is}(x) \, A_{sk} / (x - \lambda_k)$$

and after that

$$G_{ii}^{m-1}(x_1, x_2, \ldots, x_m) = - G_{ii}^{m-2}(x_1, x_2, \ldots, x_{m-1}) / (x_m - \lambda_i) ,$$
$$G_{ik}^{m-1}(x_1, x_2, \ldots, x_m) =$$
$$= \Big(\sum_{s=i}^{k-1} G_{is}^{m-1}(x_1, x_2, \ldots, x_m) \, A_{sk} - G_{ik}^{m-2}(x_1, x_2, \ldots, x_{m-1}) \Big) / (x_m - \lambda_k) ,$$

$G_{ik}^0(x_1) \equiv G_{ik}(x_1)$. By using these quantities, the D_{iklj} values are expressed as

$$D_{ikjj} = \sum_{r_1, r_2, \ldots, r_u} A_{ir_1} A_{r_1 r_2} \ldots A_{r_{u-1} r_u} A_{r_u k} \Big[e^{\lambda_i t} G_{jj}^{u+1}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k) +$$
$$+ \sum_{m=1}^{u} F^m(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_m}) \, G_{jj}^{u+1-m}(\lambda_{r_m}, \lambda_{r_{m+1}}, \ldots, \lambda_{r_u}, \lambda_k) +$$
$$+ F^{u+1}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k) \, G_{jj}(\lambda_k) \Big] + e^{\lambda_j t} G_{ik}(\lambda_j) \qquad (56)$$

for $i \neq k$; the external summation is carried out as the summation in Eq. (*42*);

$$D_{111j} = e^{\lambda_1 t} G_{1j}(\lambda_1) +$$
$$+ \sum_{s_1, s_2, \ldots, s_v} A_{1s_1} A_{s_1 s_2} \ldots A_{s_{v-1} s_v} A_{s_v j} \left[e^{\lambda_1 t} G_{11}^{v+1}(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) + \right.$$
$$+ \sum_{n=1}^{v} F^n(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_n}) \, G_{11}^{v+1-n}(\lambda_{s_n}, \lambda_{s_{n+1}}, \ldots, \lambda_{s_v}, \lambda_j) +$$
$$\left. + F^{v+1}(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) \, G_{11}(\lambda_j) \right] \qquad (57)$$

for $l \neq j$; the external summation is carried out similarly to Eq. (*42*); and eventually,

$$D_{1kij} = \sum_{r_1, r_2, \ldots, r_u} A_{ir_1} A_{r_1 r_2} \ldots A_{r_{u-1} r_u} A_{r_u k} \left[e^{\lambda_1 t} G_{ij}^{u+1}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k) + \right.$$
$$+ \sum_{m=1}^{u} F^m(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_m}) \, G_{1j}^{u+1-m}(\lambda_{r_m}, \lambda_{r_{m+1}}, \ldots, \lambda_{r_u}, \lambda_k) +$$
$$+ F^{u+1}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k) \, G_{1j}(\lambda_k) \left. \right] +$$
$$+ \sum_{s_1, s_2, \ldots, s_v} A_{1s_1} A_{s_1 s_2} \ldots A_{s_{v-1} s_v} A_{s_v j} \left[e^{\lambda_1 t} G_{ik}^{v+1}(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) + \right.$$
$$+ \sum_{n=1}^{v} F^n(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_n}) \, G_{ik}^{v+1-n}(\lambda_{s_n}, \lambda_{s_{n+1}}, \ldots, \lambda_{s_v}, \lambda_j) +$$
$$\left. + F^{v+1}(\lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) \, G_{ik}(\lambda_j) \right] \qquad (58)$$

for $i \neq k$ and $l \neq j$, the first external summation being carried out as in Eq. (*42*) and the second external summation being carried out similarly. In Eqs (*56*), (*57*), (*58*) there appear the functions $\mathbf{F}^p$ of arguments of the same degenerate group only, so that they may be calculated using Eq. (*46*), where the series converges quickly.

After calculating the D_{1kij} values using Eqs (*53*), (*54*), and (*55*), or (*56*), (*57*), and (*58*), the matrix $\mathbf{U}^r$ is calculated by means of Eq. (*52*); the matrix $\partial \mathbf{T}/\partial p$ is calculated by means of Eq. (*49*), and eventually the vector $\partial \boldsymbol{C}/\partial p$ is obtained from Eq. (*13*).

Application to a Polymeranalogous Reaction

The equations derived above are applied to the reaction of a chain of reactive groups, in which the rate constants depend on the number of adjacent groups (none, one, or two) already reacted. If we denote the unreacted group by X and the reacted one by Y, we have

$$\ldots XXX \ldots \xrightarrow{k_1} \ldots XYX \ldots, \quad \ldots XXY \ldots \xrightarrow{k_2} \ldots XYY \ldots,$$
$$\ldots YXY \ldots \xrightarrow{k_3} \ldots YYY \ldots .$$

Such a reaction is called polymeranalogous, because it resembles the polymerization

reaction, k_1, k_2, and k_3 corresponding to the rate constants of initiation, propagation, and termination by recombination, respectively.

In order to investigate the reaction kinetics of the polymeranalogous reaction, it is quite sufficient to examine the time dependence of concentrations of the sequences YX_nY. Keller[2] obtained a solution to kinetic equations by assuming that the probability of XX being followed by X is independent of what precedes XX. Arends[3] found a solution by assuming the same, but employing a somewhat different procedure. Keller[4] used an equivalent assumption, namely, that the concentrations of YX_nY decrease for $n \geqq 2$ in a geometric series with n, and arrived at the same results. Alfrey and coworkers[5] used a different assumption and obtained a solution to the equations numerically. McQuarrie and coworkers[6] obtained simpler differential equations by expressing kinetics in concentrations of the sequences X_n.

When using the procedure described in this paper, we must obtain the matrix **T** as a function of time. The time dependence of the element T_{km} gives us the time dependence of concentration of the sequence YX_mY, if only the sequences YX_kY were present at the beginning of reaction (*i.e.*, *e.g.*, a polymer regularly reacted at each $k + 1$-th group). As we disregard the concentration of reacted groups Y, it does not hold that $\sum c_i = 1$. All the reactions are irreversible, so that each reversible group contains a single component, the matrices $\mathbf{R}_0$, $\mathbf{S}_0$ are unit matrices, the matrices **F**, **K** are identical, the same are the matrices **P**, **R** and the matrices **Q**, **S**. Eqs (*30*), (*31*) may be rewritten as

$$R_{km} = (K_{km} + \sum_{s=k+1}^{m-1} K_{ks} R_{sm}) / (K_{mm} - K_{kk}) \qquad (59)$$

and

$$S_{km} = (K_{km} + \sum_{s=k+1}^{m-1} S_{ks} K_{sm}) / (K_{kk} - K_{mm}) \,. \qquad (60)$$

The sequences YX_nY as components of the reaction scheme must be arranged with decreasing n. The matrix **K** then is

$$\begin{array}{c|cccccc} & \ldots & 6 & 5 & 4 & 3 & 2 \quad 1 \\ \ldots & \multicolumn{6}{c}{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots} \\ 6 & \ldots & -2k_2 - 4k_1 & 2k_2 & 2k_1 & 2k_1 & 2k_1 \quad 2k_1 \\ 5 & \ldots & 0 & -2k_2 - 3k_1 & 2k_2 & 2k_1 & 2k_1 \quad 2k_1 \\ 4 & \ldots & 0 & 0 & -2k_2 - 2k_1 & 2k_2 & 2k_1 \quad 2k_1 \\ 3 & \ldots & 0 & 0 & 0 & -2k_2 - k_1 & 2k_2 \quad 2k_1 \\ 2 & \ldots & 0 & 0 & 0 & 0 & -2k_2 \quad 2k_2 \\ 1 & \ldots & 0 & 0 & 0 & 0 & 0 \quad -k_3 \end{array}$$

i.e. $K_{11} = -k_3$, $K_{kk} = -(k-2)\,k_1 - 2k_2$ for $k \geqq 2$, $K_{k+1,k} = 2k_2$, $K_{mk} = 2k_1$ for $m \geqq k+2$, $K_{mk} = 0$ for $m < k$. From Eqs (*59*) and (*60*), we obtain

$$R_{n+r,r} = \left(2k_1 + 2k_1 \sum_{i=1}^{n-1} R_{i+r,r} + 2(k_2 - k_1)\, R_{n-1+r,r}\right)/(nk_1) \quad \text{for} \quad r \geqq 2\,,$$

and

$$S_{n+r,r} = -\left(2k_1 + 2k_1 \sum_{i=1}^{n-1} S_{n+r,i+r} + 2(k_2 - k_1)\, S_{n+r,r+1}\right)/(nk_1)$$

$$\text{for } r \geqq 2\,.$$

Hence it can be seen that for $r \geqq 2$, $R_{n+r,r}$ and $S_{n+r,r}$ depend only on n; if they are denoted respectively by R_n and S_n, and if we also put $2k_2/k_1 - 2 = x$, we obtain

$$R_n = \left(xR_{n-1} + 2\sum_{i=0}^{n-1} R_i\right)/n \quad \text{and} \quad S_n = -\left(xS_{n-1} + 2\sum_{i=0}^{n-1} S_i\right)/n\,.$$

It can be seen from these recurrent equations that R_n and S_n are polynomials of the n-th degree in the variable x; it is then easy to derive that

$$\left(\mathrm{d}^k R_n/\mathrm{d}x^k\right)_{x=0} = n + 1 - k\,, \quad \left(\mathrm{d}^n S_n/\mathrm{d}x^n\right)_{x=0} = (-1)^n\,,$$

$$\left(\mathrm{d}^{n-1} S_n/\mathrm{d}x^{n-1}\right)_{x=0} = 2(-1)^n\,, \quad \left(\mathrm{d}^{n-2} S_n/\mathrm{d}x^{n-2}\right)_{x=0} = (-1)^n\,,$$

$\left(\mathrm{d}^k S_n/\mathrm{d}x^k\right)_{x=0} = 0$ for $k < n-2$. Hence,

$$R_{n+r,r} = \sum_{k=0}^{n} (n+1-k)\frac{x^k}{k!}\,, \quad r \geqq 2\,, \tag{61}$$

and

$$S_{n+r,r} = (-1)^n \left(\frac{x^n}{n!} + 2\,\frac{x^{n-1}}{(n-1)!} + \frac{x^{n-2}}{(n-2)!}\right), \quad r \geqq 2\,. \tag{62}$$

According to Eq. (*11*),

$$T_{n+r,r} = \sum_{m=0}^{n} R_{n+r,m+r} \exp\left(-(x+m+r)\,k_1 t\right) S_{m+r,r} =$$

$$= \exp\left(-(x+r)\,k_1 t\right) \sum_{m=0}^{n} \sum_{k=0}^{n-m} \left((n-m+1-k)\,x^k/k!\right)(-1)^m \left(x^m/m! + \right.$$

$$\left. + 2x^{m-1}/(m-1)! + x^{m-2}/(m-2)!\right) \exp\left(-mk_1 t\right).$$

In the double sum we first perform summation at constant $k + m$; the internal sum is expressed by means of the binomial theorem, and in the external sum the summation index $k + m$ is again denoted by k. Hence,

$$T_{n+r,r} = (\sum_{k=0}^{n}(n + 1 - k)(x(1 - \exp(-k_1 t)))^k/k! -$$

$$-2\exp(-k_1 t)\sum_{k=0}^{n-1}(n - k)(x(1 - \exp(-k_1 t)))^k/k! +$$

$$+ \exp(-2k_1 t)\sum_{k=0}^{n-2}(n - 1 - k)(x(1 - \exp(-k_1 t)))^k/k!)\exp(-(x + r)k_1 t).$$

Further rearrangement gives the final relation

$$T_{n+r,r} = ((n + 1)s_n - (2ne^{-k_1 t} + u)s_{n-1} + ((n - 1)e^{-2k_1 t} + 2ue^{-k_1 t})s_{n-2} -$$

$$- ue^{-2k_1 t}s_{n-3})e^{-(x+r)k_1 t}, \quad r \geqq 2, \tag{63}$$

where $u = x(1 - \exp(-k_1 t))$ and $s_m = \sum_{k=0}^{m} u^k/k!$. All the relations derived so far, including Eqs (*61*), (*62*), (*63*), hold also for $r = 1$, if $k_1 + k_3 = 2k_2$.

$T_{n+r,r}$ given by Eq. (*63*) gives the time dependence of concentration of the sequence YX_rY, if at the time $t = 0$ only the sequence $YX_{n+r}Y$ was present in unit concentration. If we want to recalculate the concentration to the unit concentration of X, we must calculate $T_{n+r,r}/(n + r)$. For n going to infinity, this expression goes to the limit $(1 - \exp(-k_1 t))^2 \exp(u - (x + r)k_1 t)$, because the s_m values which appear in Eq. (*63*) go to the limit e^u. The limit agrees with Eq. (*14*) of ref.[4] (after correcting the incorrect sign before $nk_0 t$). By comparing the limit with Eq. (*63*), one can see that the limit is attained, if both r and u may be neglected with respect to n. This is a condition allowing us to neglect the effect of chain termination. If this condition is not satisfied, but n is sufficiently large compared to u, the s_m values in Eq. (*63*) may be replaced by e^u. In this case we have

$$T_{nr}/n \doteq e^{u-(x+r)k_1 t}(1 - e^{-k_1 t})(n + 1 - r - u - (n - 1 - r - u)e^{-k_1 t})/n,$$

$$r \geqq 2. \tag{64}$$

Eq. (*64*) allows us to estimate the error caused by neglecting the effect of chain termination in the chain of reacting groups.

For $k_1 + k_3 \neq 2k_2$, let us put $(k_1 + k_3 - 2k_2)/k_1 = y$. For $m = 1$, only the denominator changes in Eq. (*60*), so that

$$S_{n+1,1} = (-1)^n(x^n/n! + 2x^{n-1}/(n-1)! + x^{n-2}/(n-2)!)\, n/(n-y) =$$
$$= (-x)^{n-2}\left((x+n)^2 - n\right)/((n-1)!\,(n-y))\,.$$

For $R_{n+1,1}$, we obtain from Eq. (*33*)

$$R_{n+1,1} = -\sum_{s=1}^{n}\Big(\sum_{k=0}^{n-s}(n+1-s-k)\,x^k/k!\Big)(-x)^{s-2}\left((x+s)^2 - s\right)/((s-1)!\,(s-y))$$

and further from Eq. (*11*)

$$T_{n+1,1} = -\sum_{s=1}^{n}(-x)^{s-2}\,\frac{(x+s)^2 - s}{(s-1)!}\,\frac{e^{-(x+y+1)k_1 t} - e^{-(x+s+1)k_1 t}}{s-y}\sum_{k=0}^{n-s}\frac{x^k}{k!}\times$$
$$\times\,(n+1-s-k)\,. \qquad (65)$$

If y is close or equal to a positive integer m, a loss of accuracy occurs in the m-th term of the sum in Eq. (*65*). This loss of accuracy is removed similarly to Eq. (*20*).

Appendix

Eqs (*46*), (*47*), (*47'*) and (*53*)–(*58*) are suitably derived by employing the apparatus of divided differences. The usual notation $f[x_1, x_2, \ldots, x_m]$ for the $m-1$-th divided difference of the function $f(x)$ is not suited for this purpose, however, because in this notation the form of the function $f(x)$ and, if f is a function of several variables, the variable with respect to which the divided difference is formed cannot be expressed explicitly. For this reason, we introduce for the $m-1$-th divided difference the expression $\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\, f(x)$. Eq. (*4*) on p. 247, ref.[7], becomes

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\, f(x) = \sum_{i=1}^{m}\Big(f(x_i)\Big/\prod_{\substack{j=1\\ j\neq i}}^{m}(x_i - x_j)\Big)\,, \quad m \geqq 1\,. \qquad (66)$$

Especially for $f(x) = e^{xt}$, we have

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\, e^{xt} = F^{m-1}(x_1, x_2, \ldots, x_m)\,.$$

For the divided differences, it holds that

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\, f(x) =$$
$$= \Delta^{m-s}\{y = x_s, x_{s+1}, \ldots, x_m\}\left(\Delta^{s-1}\{x = x_1, x_2, \ldots, x_{s-1}, y\}\, f(x)\right) \qquad (67)$$

$$\Delta^{u+v-1}\{x = x_1, x_2, \ldots, x_u, y_1, y_2, \ldots, y_v\}\, f(x) =$$

$$= \Delta^{u-1}\{x = x_1, x_2, \ldots, x_u\}\,(f(x)/\prod_{i=1}^{v}(x - y_i)) +$$

$$+ \Delta^{v-1}\{y = y_1, y_2, \ldots, y_v\}\,(f(y)/\prod_{i=1}^{u}(y - x_i)) \qquad (68)$$

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\,(f(x)\,g(x)) = \sum_{s=1}^{m}(\Delta^{s-1}\{x = x_1, x_2, \ldots, x_s\}\, f(x)) \times$$

$$\times\, \Delta^{m-s}\{x = x_s, x_{s+1}, \ldots, x_m\}\, g(x) \qquad (69)$$

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\, f(x) =$$

$$= \sum_{r=m-1}^{\infty} f^{(r)}(x_0)\, \Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\,(x - x_0)^r/r! \qquad (70)$$

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\,(x - x_0)^s = \sum_{\substack{r_1, r_2, \ldots, r_m \\ r_1 + r_2 + \ldots + r_m = s+1-m}} \prod_{i=1}^{m}(x_i - x_0)^{r_i}\,,$$

$$s \geqq 0 \qquad (71)$$

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\,(x - x_0)^s = \sum_{\substack{s_1, s_2, \ldots \\ \sum i s_i = s+1-m}} \prod_{i=1} M_i^{s_i}/(s_i!\, i^{s_i})\,, \quad s \geqq 0\,, \qquad (72)$$

where $M_i = \sum_{j=1}^{m}(x_j - x_0)^i$. Eq. (*70*) holds, if the function $f(x)$ may be expanded at the point $x = x_0$ in the Taylor series which converges to the function $f(x)$ in all the points $x = x_1, x_2, \ldots, x_m$. In Eq. (*71*), the summation is carried out over all the non-negative integers $r_1, r_2, \ldots, r_m$, which fulfil the condition $\sum_{i=1}^{m} r_i = s + 1 - m$. In Eq. (*72*), the product is formed over all the i for which $s_i > 0$, and the summation is performed over all the non-negative integers $s_1, s_2, \ldots$, which meet the condition $\sum_{i=1} i s_i = s + 1 - m$. For $s < m - 1$, the sums on the right-hand sides of Eqs (*71*), (*72*) are empty, so that the right-hand sides are zero. For $s = m - 1$, there is only one addend of unit value in the sums, so that the right-hand sides are unity. The right-hand side of Eq. (*71*) may also be calculated by employing the subsequent relation, recurrent with respect to m:

$$\Delta^0\{x = x_1\}\,(x - x_0)^s = (x_1 - x_0)^s,$$

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}\,(x - x_0)^s = \sum_{k=0}^{s+1-m}(x_m - x_0)^k \times$$

$$\times\, \Delta^{m-2}\{x = x_1, x_2, \ldots, x_{m-1}\}\,(x - x_0)^{s-1-k}\,, \quad s \geqq 0\,. \qquad (73)$$

Eq. (67) for $s = m - 1$ follows from Eq. (6) on p. 248 of ref.[7]. By an $m - s$-fold application of the equality for $s = m - 1$ to the left-hand side of Eq. (67), we obtain a chain of $m - s$ operators Δ^1 and the operator Δ^{s-1}, and by a reverse application of the equality to the chain of operators Δ^1 starting from the right, we obtain the right-hand side of Eq. (67). Eq. (68) follows from the direct substitution of the definition relation (66) into its right-hand side. For $m = 2$, Eq. (69) is obtained by direct substitution from the definition (66). For $m > 2$, Eq. (69) is proved by complete induction; the induction transition is performed by first using Eq. (67) for $s = m - 1$ and then using the validity of the relation to be proved for $m = 2$ in the last term of the sum with respect to s. If in definition (66) the function $f(x_i)$ is expanded in the Taylor series at the point x_0, we obtain the right-hand side of Eq. (70), the summation with respect to r being carried out starting with zero instead with $m - 1$. We shall prove later that terms of the sum for $r = 0, 1, \ldots, m - 2$ are zero, which proves the correctness of Eq. (70). From Corollary on p. 250 in ref.[7], $\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}(x - x_0)^s = 0$ for $s < m - 1$ and $\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}(x - x_0)^s = 1$ for $s = m - 1$. Hence follows the correctness of Eqs (71), (72) for $s < m$ and the fact that terms of the sum on the right-hand side of Eq. (70) are zero for $r = 0, 1, \ldots, m - 2$. The sum on the right-hand side of Eq. (73) is empty for $s < m - 1$, while for $s = m - 1$ the only term in the sum is unity. Hence it follows that Eq. (73) is correct for $s < m$. For $s \geq m$ we apply Eq. (69) with $f(x) = (x - x_0)^{s-1}$, $g(x) = x - x_0$ to the left-hand side of Eq. (73), whence

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}(x - x_0)^s = \Delta^{m-2}\{x = x_1, x_2, \ldots, x_{m-1}\}(x - x_0)^{s-1} + (x_m - x_0)\,\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}(x - x_0)^{s-1}.$$

Eq. (69) is repeatedly applied to the operator Δ^{m-1} in the last term of this equation until the term containing the operator Δ^{m-1} becomes zero. In this way we obtain the right-hand side of Eq. (73), and Eq. (73) is proved. For $m = 1$, Eq. (71) is the identity $(x_1 - x_0)^s = (x_1 - x_0)^s$; for $m > 1$, it follows from Eq. (73) by complete induction with respect to m.

In order to prove the equality between the right-hand sides of Eqs (71) and (72), let us first expand the product $\prod_{i=1} M_i^{s_i}$ with the condition $\sum_{i=1} i s_i = s + 1 - m$. This product is the product of s_1 factors M_1, of s_2 factors M_2, of s_3 factors M_3, *etc.* To each of the s_1 factors M_1, we assign one of the numbers $1, 2, \ldots, s + 1 - m$, to each of the s_2 factors M_2 we assign two of these numbers, to each of the s_3 factors M_3 we assign three of these numbers, *etc.*, all the numbers assigned being chosen to be pairwise different. With respect to the equation $\sum_{i=1} i s_i = s + 1 - m$, all the numbers $1, 2, \ldots, s + 1 - m$ are just exhausted in this way. The expanded product is obtained so that of each of the $s_1 + s_2 + s_3 + \ldots$ factors, one of the $(x_1 - x_0)^1$, $(x_2 - x_0)^1, \ldots, (x_m - x_0)^1$ values is chosen, the chosen values are multiplied by each

other and the products are summed up for all the possible choices (the number of which is $m^{s_1+s_2+s_3+\cdots}$). Now for each choice we define the assignment of numbers $1, 2, \ldots, s + 1 - m$ to the numbers $1, 2, \ldots, m$, so that those of numbers $1, 2, \ldots$ $\ldots, s + 1 - m$ which are assigned to a certain factor M_i (their number being i) are assigned to the number j (j being one of the numbers $1, 2, \ldots, m$), if $(x_j - x_0)^1$ was chosen from this factor M_i. Two different choices yield different assignments, because in the case of a change in the choice even in a single factor, the numbers assigned to this factor are assigned to another of the numbers $1, 2, \ldots, m$. Let in this assignment, r_1 of the numbers $1, 2, \ldots, s + 1 - m$ be assigned to the number 1, r_2 of them be assigned to the number 2, r_3 of them be assigned to the number 3, and so on. Obviously, we then have $\sum_{j=1}^{m} r_j = s + 1 - m$. In the choice corresponding to such an assignment, we obtain after multiplication of the values chosen the value $\prod_{j=1}^{m} (x_j - x_0)^{r_j}$.

Let us now examine all possible assignment in which $r_1, r_2, \ldots r_m$ of the numbers $1, 2, \ldots, s + 1 - m$ are assigned to the numbers $1, 2, \ldots, m$, respectively, the assignments differing only in the order of the r_j numbers assigned to the same j being regarded as identical. If we now permute the numbers $1, 2, \ldots, s + 1 - m$, each assignment either does not change or changes into another assignment with the same $r_1, r_2, \ldots, r_m$. Thus, each permutation of numbers $1, 2, \ldots, s + 1 - m$ defines a permutation of all the assignments considered here, and by a suitably chosen permutation any assignment may be changed into any other. Consequently, permutations of assignments form a permutational transitive representation of the permutation group of $s + 1 - m$ elements S_{s+1-m}. The matrices of this permutational representation cause only permutations of components of the vectors which they apply to; owing to transitiveness, each component of a vector may be transformed into any other component of this vector. Hence, a vector is invariant with respect to all the matrices of this representation then and only then if all of its components are identical. This means that this representation contains the identical representation just once.

Let us further introduce a permutation P of numbers $1, 2, \ldots, s + 1 - m$, the cycles of which are formed so that into each cycle we put all the numbers assigned to the same factor M_i. We thus obtain the permutation P as a product of s_2 transpositions, of s_3 cycles of the length 3, of s_4 cycles of the length 4, *etc.*; s_1 numbers assigned to factors M_1 remain invariant in the permutation P. Let it now be asked which assignments of the numbers $1, 2, \ldots, s + 1 - m$ to the numbers $1, 2, \ldots, m$ are obtained from the choices in expanding the product $\prod_{i=1} M_i^{s_i}$. The answer is that these are the assignments where for all the factors all the numbers assigned to the same factor M_i (i in number) are assigned to the same of numbers $1, 2, \ldots, m$. This is fulfilled, however, only if the assignment does not change with the permutation P.

Hence, of all possible assignments considered in the preceding paragraph (*i.e.* of those which assign r_1 of the numbers $1, 2, \ldots, s + 1 - m$ to the number 1, r_2 of them to the number $2, \ldots, r_m$ of them to the number m) we obtain, after expanding the product $\prod_{i=1} M_i^{s_i}$, those which are invariant with the permutation P, each of them once. The number of these assignments equals to the character of the permutation P in the representation introduced in the preceding paragraph, because in the matrix of permutational representation there is unity in the diagonal, if the element corresponding to this row remains unchanged in the permutation under consideration, and there is zero in the diagonal, if the element changes into some other element. If this character is denoted by $\chi_{s_1,s_2,\ldots}^{r_1,r_2,\ldots r_m}$, we obtain

$$\prod_{i=1} M_i^{s_i} = \sum_{\substack{r_1,r_2,\ldots,r_m \\ r_1+r_2+\ldots+r_m=s+1-m}} \chi_{s_1,s_2,\ldots}^{r_1,r_2,\ldots r_m} \prod_{j=1}^{m} (x_j - x_0)^{r_j} ,$$

where the summation runs over all the non-negative integers $r_1, r_2, \ldots, r_m$, which meet the condition $r_1 + r_2 + \ldots + r_m = s + 1 - m$. If we multiply each character by the number of permutations in the corresponding class of equivalent permutations, sum up over all the classes, and divide by the number of elements of the group S_{s+1-m} (*i.e.* $(s + 1 - m)!$), we find out how many times the identical representation is contained in the representation under consideration, which in our case is unity. A class of equivalent permutations contains all the permutations having the same lengths of cycles, *i.e.* it is characterized by the numbers $s_1, s_2, \ldots$, and contains $(s + 1 - m)! / \prod_{i=1} (s_i!\, i^{s_i})$ permutations. Hence,

$$\frac{1}{(s+1-m)!} \sum_{\substack{s_1,s_2,\ldots \\ \sum i s_i = s+1-m}} \chi_{s_1,s_2,\ldots}^{r_1,r_2,\ldots,r_m} (s + 1 - m)! \Big/ \prod_{i=1} (s_i!\, i^{s_i}) = 1 ,$$

where the summation runs over all the non-negative integers $s_1, s_2, \ldots$, which meet the condition $\sum_{i=1} i s_i = s + 1 - m$, and also

$$\sum_{\substack{s_1,s_2,\ldots \\ \sum i s_i = s+1-m}} \prod_{i=1} M_i^{s_i} / (s_i!\, i^{s_i}) =$$

$$= \sum_{\substack{s_1,s_2,\ldots \\ \sum i s_i = s+1-m}} \frac{1}{\prod_{i=1} (s_i!\, i^{s_i})} \sum_{\substack{r_1,r_2,\ldots,r_m \\ r_1+r_2+\ldots+r_m=s+1-m}} \chi_{s_1,s_2,\ldots}^{r_1,r_2,\ldots,r_m} \sum_{j=1}^{m} (x_j - x_0)^{r_j} =$$

$$= \sum_{\substack{r_1,r_2,\ldots,r_m \\ r_1+r_2+\ldots+r_m=s+1-m}} \prod_{j=1}^{m} (x_j - x_0)^{r_j} \sum_{\substack{s_1,s_2,\ldots \\ \sum i s_i = s+1-m}} \chi_{s_1,s_2,\ldots}^{r_1,r_2,\ldots,r_m} \Big/ \prod_{i=1} (s_i!\, i^{s_i}) =$$

$$= \sum_{\substack{r_1, r_2, \ldots, r_m \\ r_1 + r_2 + \ldots + r_m = s + 1 - m}} \prod_{j=1}^{m} (x_j - x_0)^{r_j} .$$

This proves the equality of the right-hand sides of Eqs (*71*), (*72*).

Since for $f(x) = e^{xt}$, there is $f^{(r)}(x_0) = t^r \exp(x_0 t)$, Eq. (*46*) follows from Eq. (*70*), if X_s is given by $X_s = \Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\}(x - x_0)^{s+m-1}$, and further, the correctness of Eqs (*47*) and (*47'*) follows from Eqs (*72*) and (*73*). If we put $f(x) = e^{xt}$, $s = 2$, $m = u + 3$ in Eq. (*67*), we obtain

$$\Delta^{u+1}\{x = \lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k\}\, F^1(x, \lambda_j) =$$
$$= F^{u+2}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k, \lambda_j) ,$$

and consequently, Eq. (*53*) is correct. Similarly,

$$\Delta^{v+1}\{x = \lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j\}\, F^1(\lambda_i, x) =$$
$$= F^{v+2}(\lambda_i, \lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j)$$

and consequently, Eq. (*54*) is correct. The respective expression in Eq. (*55*) may be written as

$$\Delta^{v+1}\{y = \lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j\}\,(\Delta^{u+1}\{x = \lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k\}\, F^1(x, y)) .$$

By twofold application of Eq. (*61*), we obtain for it the value

$$F^{u+v+3}(\lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k, \lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j) ,$$

which proves the correctness of Eq. (*55*). The definitions of $G_{ii}(x)$ and $G_{ik}(x)$ introduced in Eqs (*56*)–(*58*) give

$$G_{ik}(x) = \sum_{r_1, r_2, \ldots, r_u} \frac{A_{ir_1} A_{r_1 r_2} \ldots A_{r_{u-1} r_u} A_{r_u k}}{(x - \lambda_i)(x - \lambda_{r_1})(x - \lambda_{r_2}) \ldots (x - \lambda_{r_u})(x - \lambda_k)} ,$$

the summation being carried out as in Eq. (*42*). Now, if we put $u + 2$ instead of u and $v + 2$ instead of v in Eq. (*68*) and apply it to the right-hand side of Eq. (*55*), we may put the indicated sum with respect to $s_1, s_2, \ldots, s_v$ after the operator Δ^{u+1} in the first term, and the indicated sum with respect to $r_1, r_2, \ldots, r_u$ after the operator Δ^{v+1} in the second term. This yields

$$D_{ik1j} = \sum_{r_1, r_2, \ldots, r_u} A_{ir_1} A_{r_1 r_2} \ldots A_{r_{u-1} r_u} A_{r_u k} \, \Delta^{u+1}\{x = \lambda_i, \lambda_{r_1}, \lambda_{r_2}, \ldots, \lambda_{r_u}, \lambda_k\} \, (e^{xt} G_{1j}(x)) +$$

$$+ \sum_{s_1, s_2, \ldots, s_v} A_{1s_1} A_{s_1 s_2} \ldots A_{s_{v-1} s_v} A_{s_v j} \, \Delta^{v+1}\{x = \lambda_1, \lambda_{s_1}, \lambda_{s_2}, \ldots, \lambda_{s_v}, \lambda_j\} \, (e^{xt} G_{ik}(x)) \,. \quad (74)$$

Further, it holds that

$$\Delta^1\{x = x_1, x_2\} \, G_{ii}(x) = -G_{ii}(x_1)/(x_2 - \lambda_i)$$

and

$$\Delta^1\{x = x_1, x_2\} \, G_{ik}(x) = \Big(\sum_{s=1}^{k-1} \Delta^1\{x = x_1, x_2\} \, G_{is}(x) \, A_{sk} - G_{ik}(x_1)\Big)/(x_2 - \lambda_k) \,,$$

so that for $m = 2$ we have the same recurrent relation for

$$\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\} \, G_{ik}(x) \quad \text{as for} \quad G_{ik}^{m-1}(x_1, x_2, \ldots, x_m) \,,$$

including the case $i = k$. That this recurrent relation holds also for $m > 2$ can be proved by complete induction; the induction transition is performed by the application of the operator $\Delta^1\{x_1 = a, b\}$ to both sides of the recurrent relation and subsequent re-labelling of the set of arguments $(a, b, x_2, x_3, \ldots, x_m)$ to $(x_1, x_2, \ldots, x_{m+1})$. Hence, $\Delta^{m-1}\{x = x_1, x_2, \ldots, x_m\} \, G_{ik}(x) = G_{ik}^{m-1}(x_1, x_2, \ldots, x_m)$, including the case $i = k$. Bearing in mind this equality, we obtain Eq. (*58*) by applying Eq. (*69*) to Eq. (*74*). If Eq. (*68*) with $v = 1$ is applied to Eq. (*53*), the indicated summation with respect to $r_1, r_2, \ldots, r_u$ is carried out in the second term, and Eq. (*69*) is applied in the first term, Eq. (*56*) is obtained. Similarly, by applying Eq. (*68*) with $u = 1$ to Eq. (*54*), carrying out the indicated summation with respect to $s_1, s_2, \ldots, s_v$ in the first term and applying Eq. (*69*) in the second term, we obtain Eq. (*57*).

REFERENCES

1. Jakeš J.: This Journal *44*, 1146 (1979).
2. Keller J. B.: J. Chem. Phys. *37*, 2584 (1962).
3. Arends C. B.: J. Chem. Phys. *38*, 322 (1963).
4. Keller J. B.: J. Chem. Phys. *38*, 325 (1963).
5. Alfrey T., jr, Lloyd W. G.: J. Chem. Phys. *38*, 318 (1963).
6. McQuarrie D. A., McTague J. P., Reiss H.: Biopolymers *3*, 657 (1965).
7. Isaacson E., Keller H. B.: *Analysis of Numerical Methods*. Wiley, New York, London, Sydney 1966.

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