Rhonhof. Wir fügten eine dreidimensionale Interpolationsroutine nach dem Verfahren von Dawson [10] bei.

LSQ2 und LSQ2AN. Diese Programme dienen zur Strukturfaktorenberechnung und "least squares"-Verfeinerung und besitzen die Möglichkeit zur Rechnung mit den Basisparametern einer starren Atomgruppe, die nach einem "full matrix"-Verfahren verfeinert werden. Die Programmgrundform stammt von Scheringer.[11] Das schnellere Programm LSQ2 gestattet nur die Benutzung von isotropen Temperaturfaktoren und erfordert für jede Raumgruppe ein spezielles Unterprogramm. LSQ2AN ist allgemein geschrieben und ermöglicht die Benutzung anisotroper Temperaturfaktoren. Dispersionskorrektur und Gewichtsanalysen werden durchgeführt.

ORFFE. Dieses Programm basiert auf dem bekannten Programm von Busing, Martin und Levy [12] und dient zur weiteren Auswertung von Lageparametern und thermischen Parametern und von deren Fehlergrenzen. In Anlehnung an ein Programm von C.-I. Brändén, Uppsala, fügten wir eine "least squares"-Ebenen-Routine ein.

Listen der einzelnen Programme können von uns angefordert werden.

1. Dahl, T., Gram, F., Groth, P., Klewe, B. und Römming, C. *Acta Chem. Scand.* **24** (1970) 2232.
2. Dräger, M. *Dissertation*, Mainz 1970.
3. Lindqvist, O. und Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
4. Hesse, R. *Acta Cryst.* **1** (1948) 200.
5. Lipson, H. *Acta Cryst.* **2** (1949) 43.
6. Busing, W. R. und Levy, H. A. *Acta Cryst.* **10** (1957) 180.
7. Wehe, D. J., Busing, W. R. und Levy, H. A. *IUCr World List of Crystallographic Computer Programs*, 1962, Nr. 362.
8. Rogers, D. *Computing Methods in Crystallography*, Pergamon, Oxford 1965, S. 117.
9. Schultze-Rhonhof, E. *IUCr World List of Crystallographic Computer Programs*, 1966, Nr. 5063.
10. Dawson, B. *Acta Cryst.* **14** (1961) 999.
11. Scheringer, C. *Acta Cryst.* **16** (1963) 546.
12. Busing, W. R., Martin, K. O. und Levy, H. A. *ORNL-TM-306*.

Eingegangen am 12. Dezember 1970.

Integrated Solutions for a Generalized System of First-order Reactions

WILLIAM H. SACHS

Department of Organic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Integrated solutions to rate equations are those generally used in some form to extract information from a series of measurements in terms of a kinetic model. Obtaining this information is by no means a trivial problem, since it has in practice been difficult to develop reliable statistical and numerical procedures which are capable of analyzing the complex equations that often arise. For first-order systems where the uncertainty in the measurement of the dependent variable exceeds one part promille, it has not been possible to proceed beyond an equation containing three coefficients and two exponential terms.[1]

$$y_i = c_1 \exp(\lambda_1 t_i) + c_2 \exp(\lambda_2 t_i) + c_3 \qquad (1)$$

Thus integrated algebraic solutions to rate equations for complex kinetic systems would appear to be of little else than academic interest. The concentrations of the components of a system, however, are rarely measured directly. Instead, some quantity is observed that is generally a linear transformation of these concentrations,[2] and the expressions for the time dependence of the concentrations in the kinetic system may reduce to much simpler equations involving a set of observables (*e.g.* NMR studies of H – D exchange at CH_n under irreversible conditions [3]). The opposite may of course also occur. Thus if one desires to know whether a given kinetic model and experimental method of measurement will produce one or more equations which are feasible to treat numerically, explicitly integrated solutions to the rate equations of the model are desirable. Explicit expressions are also useful if one wishes to simulate the time dependence of the system for a hypothetical set of parameters.

Matrix methods have been found useful for integrating the differential equations for first-order kinetic systems,[2,4] however, the algebraic effort required with this process may be enormous for fairly com-

plex systems: assuming of course that analytical solution is possible. A considerable improvement has been achieved by using Laplace transforms within a matrix formalism,[5] but the paper quoted considered only a sequence of first-order reactions. Integrated expressions have also been derived for a large number of first-order kinematic systems using a Laplace-Carson transform, however, no explicit solution was developed for the general case, owing in part to having overlooked the advantages of matrix notation.[6]

The purpose of this work has been to develop a general method for rapidly and conveniently integrating the rate equations for systems of first-order reactions. Application of Laplace transforms permits the introduction of the initial conditions from the outset and eliminates the need to solve explicitly for the eigenvectors central to the classical matrix formulation. An explicit algebraic formula for the integrated solutions to a general first-order system is derived and expressed in matrix notation. No table of inverse transformations is required.

Matrix formulation. For any system obeying first-order kinetics it is possible to abbreviate the rate equations in matrix form.[2,4] Thus one may write

$$\dot{\mathbf{A}} = \mathbf{KA} \qquad (2)$$

where $\dot{\mathbf{A}}$ is an $(m \times 1)$ column vector formed from the first-derivatives of the concentrations A_i as functions of time, $\mathbf{K}$ is the $(m \times m)$ matrix formed by the rate constants that determine the extent, degree of branching, reversibility, *etc.*, of the system, and $\mathbf{A}$ is an $(m \times 1)$ column vector of the concentrations A_i of the components of the system.

Laplace transforms [7] are now applied to both sides of eqn. (2)

$$\alpha(\dot{\mathbf{A}}) = \alpha(\mathbf{KA})$$

where the operation is understood to occur for each element of $\dot{\mathbf{A}}$ and $\mathbf{KA}$, and

$$\alpha(A_i) \equiv \mathrm{L}(p)_i = \int_0^\infty \mathrm{d}t \exp(-pt)\, A_i \qquad i = 1,m \quad (3)$$

$$\alpha(\dot{A}_i) = p\mathrm{L}(p)_i - A^0{}_i$$

$A^0{}_i$ and $\mathrm{L}(p)_i$ are the initial concentration and Laplace transform of component i, respectively. p is a complex variable. Making use of the linear property of the transformation and abbreviating (3) in matrix form gives

$$p\mathbf{L}(p) - \mathbf{A}^0 = \mathbf{KL}(p)$$

where $\mathbf{A}^0$ and $\mathbf{L}(p)$ are $(m \times 1)$ column vectors. Solving for $\mathbf{L}(p)$, one obtains [5]

$$\mathbf{L}(p) = (\mathbf{P} - \mathbf{K})^{-1}\mathbf{A}^0 \qquad (4)$$

$\mathbf{P}$ is the diagonal matrix $p\mathbf{I}$. ($\mathbf{I}$ is the unit matrix). An explicit expression for the ith element of $\mathbf{L}(p)$ may be obtained from determinants as

$$L(p)_i = \sum_{\varrho=1}^{m} \left(\frac{(-1)^{\varrho+i} \mathrm{M}_{\varrho i} A^0{}_\varrho}{|\mathbf{P} - \mathbf{K}|} \right) \qquad i = 1,m \qquad (5)$$

where $\mathrm{M}_{\varrho i}$ is the minor formed from $|\mathbf{P} - \mathbf{K}|$ by omitting the ϱth row and the ith column.

The inverse Laplace transforms are found from Bromwich's integral formula and the residue theorem.[7]

$$\alpha^{-1}(\mathrm{L}(p)_i) = A_i = (2\pi\sqrt{-1})^{-1} \int_C \mathrm{d}p \exp(pt) \{(\mathbf{P} - \mathbf{K})^{-1}\mathbf{A}^0\}_i \qquad (6)$$

where the contour C is chosen to the right of all singularities in $\{(\mathbf{P} - \mathbf{K})^{-1}\mathbf{A}^0\}_i$. In practice, the integral in (6) is evaluated as a closed integral over a contour C′. The residue theorem, the validity of whose application is guaranteed by the fact that $\mathrm{L}(p)_i$ in (5) will always be the ratio of two polynomials R/S in p, where R is always of degree less than S, gives for the closed integral

$$A_i = \text{sum of residues of } \exp(pt) \{(\mathbf{P} - \mathbf{K})^{-1}\mathbf{A}^0\}_i \qquad (7)$$

evaluated at the poles $p = \lambda_k$, $k = 1,m$. For nondegenerate values of λ_k,

$$\text{residue} = \lim_{p \to \lambda_k} \{\exp(pt) (p - \lambda_k) \{(\mathrm{P} - \mathrm{K})^{-1}\mathrm{A}^0\}_i\} \qquad (8)$$

Combining eqns. (5,7,8) one arrives at an explicit algebraic formula for the time dependence of A_i

$$A_i = \sum_{k=1}^{m} \lim_{p \to \lambda_k} \left\{ \exp(pt)\, (p - \lambda_k) \sum_{\varrho=1}^{m} \left[\frac{(-1)^{\varrho+i} \mathrm{M}_{\varrho i} A^0{}_\varrho}{|\mathbf{P} - \mathbf{K}|} \right] \right\} \quad i = 1,m \qquad (9)$$

which requires only the evaluation of the roots λ_k of the polynomial $|\mathbf{P} - \mathbf{K}|$ (equiv-

alent to the eigenvalues of **K**) and the inverse of $(\mathbf{P}-\mathbf{K})$ shown above in determinantal form. The factor $(p-\lambda_k)$ cancels an identical term in $|\mathbf{P}-\mathbf{K}|$ when this polynomial is in the factorized form necessary to obtain the roots λ_k. By defining the operator **Q**

$$\mathbf{Q}=\begin{Bmatrix} \lim\limits_{p\to\lambda_1} & 0 & \cdot & \cdot \\ 0 & \lim\limits_{p\to\lambda_2} & 0 & \\ 0 & 0 & \cdot & \\ \cdot & \cdot & & \lim\limits_{p\to\lambda_m} \end{Bmatrix}$$

eqn. (9) may be written in matrix notation as

$$\mathbf{A}=\{\mathbf{Q}(\mathbf{P}-\Lambda)\mathbf{1}_c\{(\mathbf{P}-\mathbf{K})^{-1}\mathbf{A}^0\}\dagger\}\dagger\mathbf{E} \qquad (10)$$

where Λ is a diagonal matrix formed from the roots λ_k, **E** the column vector,

$$\mathbf{E}=\begin{Bmatrix} \exp(\lambda_1 t) \\ \exp(\lambda_2 t) \\ \cdot \\ \cdot \\ \exp(\lambda_m t) \end{Bmatrix}$$

and $\mathbf{1}_c$ a column vector of 1's. The symbol "†" indicates the transpose of a matrix.

A more general solution for A_i which takes into account possible degeneracy of the roots λ_i is given by [7]

$$A_i=\sum_{k=1}^{m-(\tilde{r}-\tilde{s})} \lim_{p\to\lambda_k}\left[\frac{1}{(n-1)!}\frac{\mathrm{d}^{n-1}}{\mathrm{d}p^{n-1}}\left[\exp(pt)\ (p-\lambda_k)^n\ \{(\mathbf{P}-\mathbf{K})^{-1}\mathbf{A}^0\}_i\right]\right] \quad i=1,m \qquad (11)$$

where n is the degeneracy of the λ_kth root, $\tilde{s}$ the number of distinguishable sets of degenerate roots, and $\tilde{r}$ the sum of all n greater than or equal to two.

In practical applications, considerable effort is saved by noting that often only one component A^0_i is nonzero: only one column of $(\mathbf{P}-\mathbf{K})^{-1}$ need therefore be evaluated, and the summation sign in (5) is superfluous.

Bergson has derived the time dependence of **A** from matrix algebra as

$$\mathbf{A}=\tilde{\mathbf{C}}(\tilde{\mathbf{C}}^{-1}\mathbf{A}^0)_d\mathbf{E} \qquad (12)$$

where the subscript d indicates that the quantity in parentheses is a diagonal matrix.[2] $\tilde{\mathbf{C}}$ and the λ_k of **E** have been determined from an associated eigenvalue problem

$$\mathbf{K}\mathbf{C}=\mathbf{C}\Lambda$$

where $\tilde{\mathbf{C}}$ has been evaluated from **C** in such a way that its diagonal elements are unity. Generally, $\tilde{\mathbf{C}}$ requires the solution of m $(m\times m)$ linearly dependent systems of simultaneous equations, or equivalently, m $\{(m-1)\times(m-1)\}$ linearly independent systems of equations. The correspondence between (10) and (12), however, gives

$$\tilde{\tilde{\mathbf{C}}}(\tilde{\mathbf{C}}^{-1}\mathbf{A}^0)_d=\{\mathbf{Q}(\mathbf{P}-\Lambda)\mathbf{1}_c\{(\mathbf{P}-\mathbf{K})^{-1}\mathbf{A}^0\}\dagger\}\dagger \qquad (13)$$

If for some reason the algebraic form of $\tilde{\tilde{\mathbf{C}}}$ is required, then the complete eigenvalue problem must be solved in due fashion.

Linear transformations of the concentrations **A** in terms of a set of observables[2] may be included in the formulation of eqn. (10)

Acknowledgements. The author is indebted to Professor Göran Bergson for an introduction to the use of matrix methods in reaction kinetics in a series of lectures in the autumn of 1969.

It is also a pleasure to acknowledge financial support from the *Swedish Natural Science Research Council.*

1. Ohlsson, L., Wold, S. and Bergson, G. *Arkiv Kemi* **29** (1968) 351; Wold, S. *Private communication.*
2. Bergson, G. *To be published*; *cf.* also Bergson, G. and Ohlsson, L. *Acta Chem. Scand.* **23** (1969) 2175.
3. Rappe, C. *Acta Chem. Scand.* **20** (1966) 2236.
4. Wei, J. and Prater, C. D. *Advan. Catalysis* **13** (1962) 203.
5. Ninham, B., Nossal, R. and Zwanzig, R. *J. Chem. Phys.* **51** (1969) 5028.
6. Rodiguin, N. M. and Rodiguina, E. N. *Consecutive Chemical Reactions*, Van Nostrand, Princeton, N.J. 1964.
7. Spiegel, M. R. *Theory and Problems of Laplace Transforms*, McGraw, New York 1965.

Received February 3, 1971.