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Reversible Reactions Regarded as a Series of Irreversible Processes. Solution of a Stereochemical Problem

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Reversible reactions

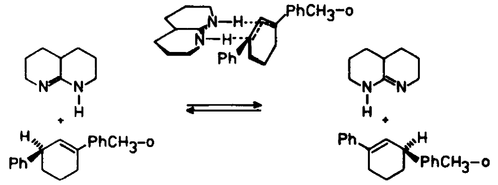
$$(A)\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}(B)$$

are regarded as a series of irreversible processes, *i.e.*

$$(A)_{B0} \xrightarrow{k_1} (B)_{A1} \xrightarrow{k_{-1}} (A)_{B1} \xrightarrow{k_1} (B)_{A2} \cdots \xrightarrow{k_{-1}} (A)_{Bi-1} \xrightarrow{k_1} (B)_{Ai} \xrightarrow{k_{-1}} (A)_{Bi} \xrightarrow{k_1} (B)_{Ai+1} \xrightarrow{k_{-1}} etc.$$

$(A)_{B0}$-molecules ((A)-molecules that have been (B) zero times) are, of course, irreversibly transformed into $(B)_{A1}$-molecules ((B)-molecules that have only been (A) once) and these, in turn, into $(A)_{B1}$. $(A)_{Bi}$ and $(B)_{Ai}$ denote those (A)- and (B)-molecules that have been (B) or (A) i times, respectively. This transformation has a formal resemblance with non-branched radioactive decay but the rate constants alternate between k_1 and k_{-1}. Solutions of the linear differential equations describing the time dependence of the $(A)_{Bi}$- and $(B)_{Ai}$-molecules and features of these solutions are reported for the general case $K=k_1/k_{-1}\neq 1$ as well as for the special case $K=1$. The results are used for accurate determination of the stereospecificity of reversible first- and pseudo first-order reactions. By comparing only the specific rotation of partially resolved (A) with that of recovered (A) after some reaction, the stereospecificity of the reaction may be estimated using the results above since a fraction of the recovered (A)-molecules have been (B) one or more times. Thus the method demands only partially resolved (A) and no knowledge of the absolute stereochemistry of either (A) or (B).

The stereochemistry of the reaction shown in Scheme 1 has been investigated[1] as part of our reaction mechanistic studies of potentially bifunctionally catalyzed 1,3-proton transfer reactions.[2]



Scheme 1.

We wished to find out to what extent the rearrangement takes place in the way shown in Scheme 1, *i.e.*, enantiospecifically and suprafacially. Such investigations usually involve considerable work.[3] Sometimes completely optically resolved starting material and product, as well as knowledge of their relative configurations, are needed. Since the catalyzed rearrangement in Scheme 1 is a reversible reaction, the thought of a labour-saving possibility occurred to us. Let us consider the generalized reversible reaction (1) and assume that, at the start of the reaction, pure but only partially resolved compound (A) is present.

$$(A)\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}(B) \qquad (1)$$

The reaction transforms (A)-molecules into (B)-molecules and these are converted back to (A)

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because of the reversibility. Therefore, as the reactions proceeds, the fraction of the (A)-molecules that have reacted to (B)-molecules will increase. If the degree of stereospecificity of the reaction is <100 %, the optical purity of (A) will decrease with time. This indicates the possibility of determining the stereospecificity using *only* the specific rotation of compound (A) at the reaction start and at time t, *i.e.*, knowledge of the optical purity of compound (B) would be unnecessary. A closer inspection of this possibility shows, however, that of the (A)-molecules there are those that have been (B)-molecules not only once but twice, three times, *etc.* This led us to the formulation of reaction (1) as a series of irreversible processes as shown by eqn. (2). $(A)_{B0}$-molecules ((A)-molecules that have been

$$(A)_{B0} \xrightarrow{k_1} (B)_{A1} \xrightarrow{k_{-1}} (A)_{B1} \xrightarrow{k_1} (B)_{A2} \ldots\ldots \xrightarrow{k_{-1}}$$

$$(A)_{Bi-1} \xrightarrow{k_1} (B)_{Ai} \xrightarrow{k_{-1}} (A)_{Bi} \xrightarrow{k_1} (B)_{Ai+1} \longrightarrow$$

$$\textit{etc.} \qquad (2)$$

(B) zero times) are of course irreversibly transformed into $(B)_{A1}$-molecules ((B)-molecules that have been (A) only once) and these in turn into $(A)_{B1}$. $(A)_{Bi}$ and $(B)_{Ai}$ denote those (A)- and (B)-molecules that have been (B) or (A) i times, respectively. $(A)_{Bi}$- and $(B)_{Ai}$-molecules can, of course, never become $(A)_{Bi-1}$- or $(B)_{Ai-1}$-molecules again. This transformation of reaction (1) bears a formal resemblance to non-branched radioactive decay (3).

$$(C) \xrightarrow{k_2} (D) \xrightarrow{k_3} (E) \xrightarrow{k_4} (F) \xrightarrow{k_5} \ldots\ldots \qquad (3)$$

The solutions of the differential equations describing the time-dependence of the concentrations in (3) have been reported by Rutherford, Chadwick and Ellis.[4] The rate constants in a radioactive decay chain are usually all different. However, for a transformed reversible reaction (2), the rate constants are either all equal ($K=k_1/k_{-1}=1$) or alternate between k_1 and k_{-1} ($K=k_1/k_{-1}\neq 1$). The special case $K=1$ has been treated by us previously in a short communication,[5] and in this paper both these special cases will be treated in detail. The results will be used for accurate determination of the stereospecificity of reversible first- or pseudo first-order reactions.

This view of reversible reactions as a series of irreversible processes also applied to the reversible transport of molecules between stationary and mobile phases in chromatography and led to an improved theory of chromatography.[6] It has also been used in the study of degenerate carbocation rearrangements.[7]

Note. Two of the three reviewers of this paper expressed their opinion that the present authors in their treatment have regarded identical molecules as distinguishable particles. To avoid further confusion we wish to make the following statement: it is only claimed that the reversibility of the reaction $(A)\rightleftarrows(B)$ implies that there are (A)- and (B)-molecules that have been (B) and (A) respectively once, twice, ... i times etc. By using the formulation of the reversible reaction as a series of irreversible processes and common rate equations, analytical expressions are obtained for *e.g.* the numbers of (A)-molecules that have been (B) once, twice... i times *etc.* It is of course not possible to point out a specific molecule and claim that just this molecule has been (B) i times.

RESULTS AND DISCUSSION

Using the above classification of (A)- and (B)-molecules with respect to the number of times they have reacted to compounds (B) or (A), respectively, the optical rotation of (A) at time t can be expressed as:

$$\alpha_{At}=l\cdot[\alpha_{At}]\cdot\sum_{i=0}^{\infty}[(A)_{Bi}] \qquad (4)$$

In (4), $[\alpha_{At}]$ is the specific rotation of (A) at time t, l is the length of the polarimetric cell and $[(A)_{Bi}]$ is the concentration of (A)-molecules which have been (B) i times. In eqn. (4),

$$\sum_{i=0}^{\infty}[(A)_{Bi}]$$

is, of course, equal to the total concentration of (A).

However, for reactions that are partially stereospecific, eqn. (4) is a convenient starting point for a derivation of an expression for α_{At}. Let us assume that the partial stereospecificity is only due to the reaction $(A)\rightarrow(B)$ and $(B)\rightarrow(A)$ and denote these stereospecificities by x and y, respectively. In addition, we assume that no racemizations of either (A) or (B) take place independently of the just mentioned reactions.

The specific rotation of the $(A)_{B1}$-molecules must therefore be $[\alpha_{A0}] \cdot x \cdot y$, and that of the $(A)_{Bi}$ becomes $[\alpha_{A0}] \cdot x^i \cdot y^i$.

Thus, under these conditions α_{At} is described by

$$\alpha_{At}=l \cdot [\alpha_{A0}] \cdot \sum_{i=0}^{\infty} [(A)_{Bi}] x^i y^i \qquad (5)$$

For simplicity, we therefore denote $x^i y^i = z^i$. The specific rotation $[\alpha_{At}]$ of (A) at time t, which can be measured after isolation of (A), divided by $[\alpha_{A0}]$ can be written:

$$\frac{[\alpha_{At}]}{[\alpha_{A0}]} = \frac{\sum_{i=0}^{\infty} [(A)_{Bi}] z^i}{\sum_{i=0}^{\infty} [(A)_{Bi}]} = \sum_{i=0}^{\infty} a_i z^i \qquad (6)$$

where $a_i = [(A)_{Bi}] / \sum_{i=0}^{\infty} [(A)_{Bi}]$.

Thus eqn. (6) shows that if $[\alpha_{At}]/[\alpha_{A0}]$ is measured and the coefficients a_i can be estimated, then the stereospecificity z may be simulated. Obviously, we neither need to start with completely resolved (A) nor have any knowledge of the optical purity of (B) at any time if the assumptions above are fulfilled.

We will show below that the coefficients a_i may be evaluated, using the transformation shown in the introduction of reversible reactions into a series of irreversible processes.

The special case when the reversible reaction has an equilibrium constant $K=1$ is particularly simple. Such reactions include racemizations, when (A) and (B) are enantiomers, or symmetric reactions (degenerate reactions) where (A) and (B) are identical. For symmetric reactions, eqn. (2) transforms into eqn. (7) in which all the rate constants are equal and where $(A)_i$ represents those (A)-molecules that have reacted i times to give (A) again

$$(A)_0 \xrightarrow{k} (A)_1 \xrightarrow{k} (A)_2 \ldots\ldots \xrightarrow{k} (A)_i \ldots\ldots \xrightarrow{k}$$
$$(A)_{2i} \xrightarrow{k} (A)_{2i+1} \xrightarrow{k} etc. \qquad (7)$$

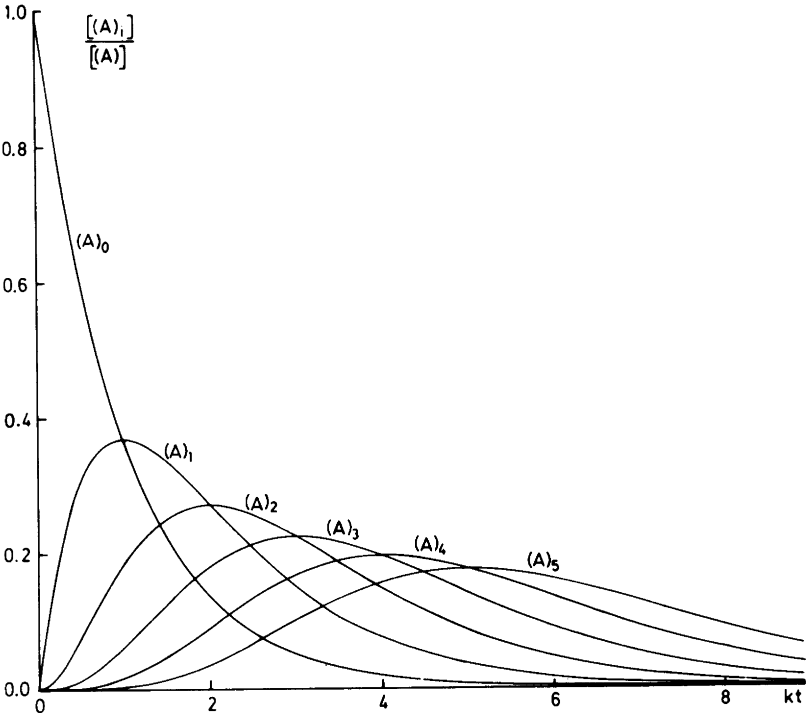

Fig. 1. Shows the dependence of $[(A)_i]/[(A)]$ for i=0−5 on kt. The curves make up a universal representation of all reversible first- or pseudo first-order reactions with $K=1$ and all degenerate or symmetric reactions.

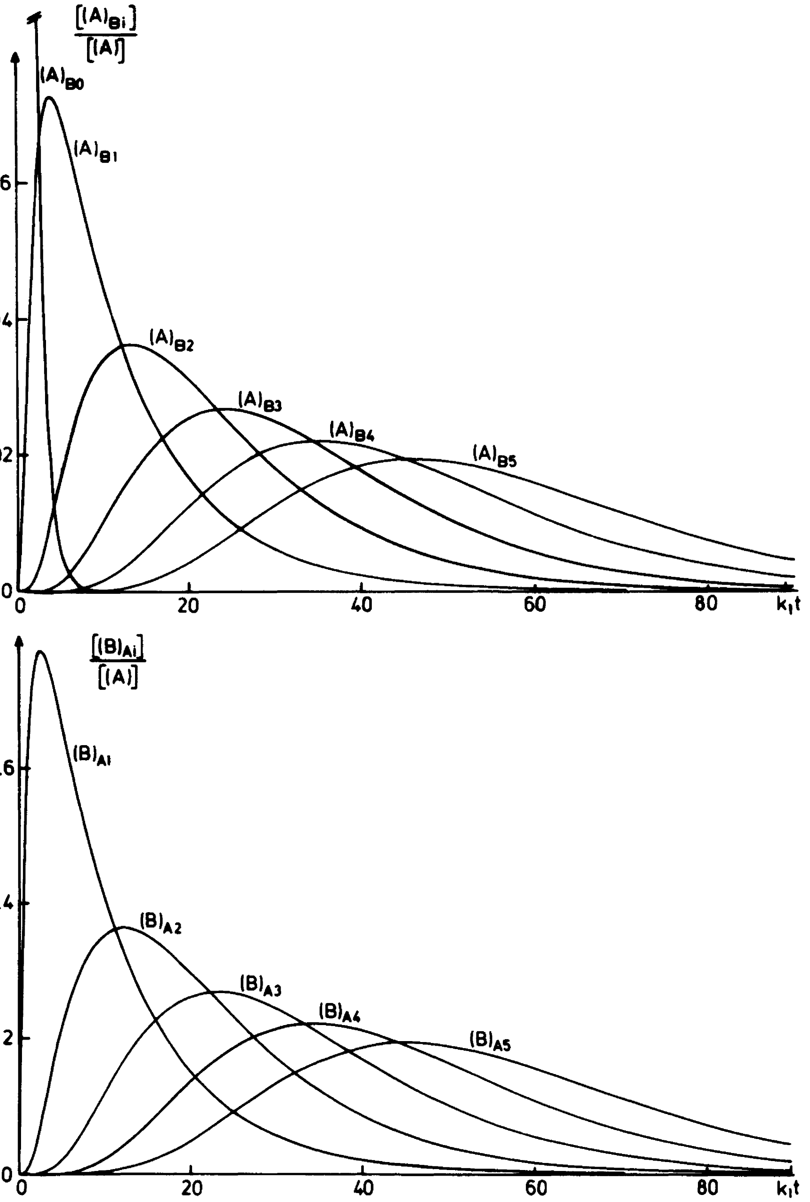

Fig. 2. Shows the dependence of $[(A)_{Bi}]/[(A)]$ and $[(B)_{Ai}]/[(A)]$ on k_1t for reversible first-order or pseudo first-order reactions having $K=k_1/k_{-1}=10$. The curves make up a universal representation of all such reactions with $K=10$ in the sense that the curve sets are independent of the absolute values of k_1 and k_{-1}.

($(A)_{2i+1}$ and $(A)_{2i}$ in eqn. (7) correspond to $(B)_{Ai+1}$ and to $(A)_{Bi}$, respectively, in eqn. (2)). The solutions to the rate equations are particularly simple for this special case (*cf.* eqn. (8)) and have

$$[(A)_i]=[(A)](k^it^i/i!)\,e^{-kt} \tag{8}$$

previously been reported by us[5] and some of them are graphically displayed in Fig. 1.

The solution of the general case when $K\neq1$ will be outlined below. The time-dependence of $[(\mathrm{A})_{\mathrm{B}i}]$ and $[(\mathrm{B})_{\mathrm{A}i}]$ can be obtained by solving the following rate eqns. (9)–(11):

$$\frac{d[(\mathrm{A})_{\mathrm{B}0}]}{dt} = -k_1[(\mathrm{A})_{\mathrm{B}0}]; \quad (i=0) \tag{9}$$

$$\frac{d[(\mathrm{B})_{\mathrm{A}i}]}{dt} = k_1[(\mathrm{A})_{\mathrm{B}i-1}] - k_{-1}[(\mathrm{B})_{\mathrm{A}i}]; \quad (i\neq 0) \tag{10}$$

$$\frac{d[(\mathrm{A})_{\mathrm{B}i}]}{dt} = k_{-1}[(\mathrm{B})_{\mathrm{A}i}] - k_1[(\mathrm{A})_{\mathrm{B}i}]; \quad (i\neq 0) \tag{11}$$

The solution of eqn. (9) is straightforward, and eqn. (12) is obtained where $[(\mathrm{A})]$ represents the initial concentration of (A).

$$[(\mathrm{A})_{\mathrm{B}0}] = [(\mathrm{A})]\cdot e^{-k_1 t} \tag{12}$$

Equations (10) and (11), on the other hand, are linear differential equations of the first order[8] and have as solutions eqns. (13) and (14), respectively

$$[(\mathrm{B})_{\mathrm{A}i}] = e^{-k_{-1}t}\left(\int^{t} e^{k_{-1}t} k_1[(\mathrm{A})_{\mathrm{B}i-1}]\,dt + D_1\right) \tag{13}$$

$$[(\mathrm{A})_{\mathrm{B}i}] = e^{-k_1 t}\left(\int^{t} e^{k_1 t} k_{-1}[(\mathrm{B})_{\mathrm{A}i}]\,dt + D_2\right) \tag{14}$$

where D_1 and D_2 are constants which are obtained using the conditions $[(\mathrm{B})_{\mathrm{A}i}]=0$ and $[(\mathrm{A})_{\mathrm{B}i}]=0$ at $t=0$ and $i\neq 0$.

Thus we use the solution of $[(\mathrm{A})_{\mathrm{B}0}]$ to solve for $[(\mathrm{B})_{\mathrm{A}1}]$, which in turn is used in the solution for $[(\mathrm{A})_{\mathrm{B}1}]$, and so on. Through studies of the systematics of a number of solutions of $[(\mathrm{B})_{\mathrm{A}i}]$ and $[(\mathrm{A})_{\mathrm{B}i}]$ we have arrived at the following recursion formulas:

$$[(\mathrm{A})_{\mathrm{B}i}] = [(\mathrm{A})]\frac{k_1{}^{i} k_{-1}^{i}}{(k_{-1}-k_1)^{2i}} \sum_{j=0}^{i} (k_{-1}-k_1)^{j} \frac{t^{j}}{j!}\left(a_{ij}e^{-k_1 t} + b_{ij}e^{-k_{-1}t}\right) \tag{15}$$

$$[(\mathrm{B})_{\mathrm{A}i}] = [(\mathrm{A})]\frac{k_1^{i} k_{-1}^{i-1}}{(k_{-1}-k_1)^{2i-1}} \sum_{j=0}^{i-1} (k_{-1}-k_1)^{j} \frac{t^{j}}{j!}\left(c_{ij}e^{-k_1 t} + d_{ij}e^{-k_{-1}t}\right) \tag{16}$$

The coefficients a_{ij}, b_{ij}, c_{ij} and d_{ij} are all obtained using the coefficients in the expressions for $(\mathrm{A})_{\mathrm{B}i-1}$ and $(\mathrm{B})_{\mathrm{A}i-1}$, respectively, as shown below in Appendix 1.

Some of the solutions for symmetric (degenerate) reactions or nondegenerate reactions having $K=1$ (eqn. (8)) are displayed in Fig. 1, which shows $[(\mathrm{A})_i]/[(\mathrm{A})]$ plotted vs. kt. For nondegenerate reactions ($\mathrm{A}\rightleftarrows\mathrm{B}$, $\mathrm{A}\not\equiv\mathrm{B}$) having $K=1$, $(\mathrm{A})_{2i+1}$ and $(\mathrm{A})_{2i}$ have to be identified as $(\mathrm{B})_{\mathrm{A}i+1}$ and $(\mathrm{A})_{\mathrm{B}i}$, respectively. In Fig. 2 some of the solutions (eqns. (15) and (16)) for reversible reactions having $K=10$ are shown. $[(\mathrm{A})_{\mathrm{B}i}]/[(\mathrm{A})]$ and $[(\mathrm{B})_{\mathrm{A}i}]/[(\mathrm{A})]$ have been plotted vs. $k_1 t$ ($K=k_1/k_{-1}$), respectively.

In both figures the curves describing the behaviour of $(\mathrm{A})_0$ and $(\mathrm{A})_{\mathrm{B}0}$ decline. All the other curves first grow to maxima before they decline. Furthermore, the maxima decrease in size with kt and $k_1 t$ as the curves become broader.

The representation in Fig. 1 is universal for reactions having $K=1$. For reactions with $K\neq 1$, Fig. 2 represents only the reactions for which $k_1/k_{-1}=K=10$, *i.e.*, the curves do not depend on k_1 and k_{-1} as long as $k_1/k_{-1}=10$.

If K is increased, the $(\mathrm{A})_{\mathrm{B}i}$-curves in Fig. 2, with the exception of $(\mathrm{A})_{\mathrm{B}0}$, will become broader and have lower maxima. The $(\mathrm{B})_{\mathrm{A}i}$-curves will also become broader but their maxima increase in size.

The areas under the curves may be calculated by integration of the recursion formulas, eqns (8), (15) and (16), as shown in Appendix 2. In Fig. 1 the area under each of the curves is equal to 1. In Fig. 2 the area under each of the $[(\mathrm{A})_{\mathrm{B}i}]/[(\mathrm{A})]$-curves is also equal to 1 but the area under each of the $[(\mathrm{B})_{\mathrm{A}i}]/[(\mathrm{A})]$ ones is equal to K.

The maxima of the curves in Fig. 1 may be shown by differentiation of eqn. (8) to appear at regular time intervals, *i.e.*, $t_{\max}=i/k$. Furthermore, the $(\mathrm{A})_{i-1}$-curve intersects the $(\mathrm{A})_i$-curve at the maximum of the $(\mathrm{A})_i$-curve.

For the general case ($K\neq 1$) described by eqns (15) and (16) and Fig. 2, there are also regularities. If all these curves are put on the same scale it can be shown that the point of intersection of an $(\mathrm{A})_{\mathrm{B}i}$-curve and the $(\mathrm{B})_{\mathrm{A}i}$-curve appears at the maximum of the $(\mathrm{A})_{\mathrm{B}i}$-curve. It may also be proved that the intersection of the $K\cdot[(\mathrm{A})_{\mathrm{B}i-1}]/[(\mathrm{A})]$-curve and the $[(\mathrm{B})_{\mathrm{A}i}]/[(\mathrm{A})]$-curve is at the maximum of the $[(\mathrm{B})_{\mathrm{A}i}]/[(\mathrm{A})]$-curve.

APPENDIX 1

The coefficients a_{ij}, b_{ij}, c_{ij} and d_{ij} in eqns. (15) and (16) were evaluated in the following way. Combination of eqns. (16) and (14) yields eqn. (17) if i≠0.

$$[(A)_{Bi}]=e^{-k_1t}\Big(\int^{t} e^{k_1t}k_{-1}P_i\sum_{j=0}^{i-1}(k_{-1}-k_1)^j\frac{t^j}{j!}\cdot \\ \cdot(c_{ij}e^{-k_1t}+d_{ij}e^{-k_{-1}t})dt+D_2\Big) \qquad (17)$$

where $P_i=\dfrac{k_1^ik_{-1}^{i-1}}{(k_{-1}-k_1)^{2i-1}}[(A)]$

Integration of the first part of the sum and partial integration of the second one (after multiplication with e^{k_1t}) gives eqn. (18)

$$[(A)_{Bi}]=e^{-k_1t}\Big(k_{-1}P_i\Big(\sum_{j=0}^{i-1}(k_{-1}-k_1)^j\frac{t^{j+1}}{(j+1)!}c_{ij}+ \\ +\sum_{j=0}^{i-1}-d_{ij}\sum_{n=0}^{j}(k_{-1}-k_1)^{j-1-n}\frac{t^{j-n}}{(j-n)!}e^{-(k_{-1}-k_1)t}\Big)+D_2\Big) \qquad (18)$$

which may also be written as eqn. (19)

$$[(A)_{Bi}]=\frac{k_{-1}\cdot P_i}{k_{-1}-k_1}\Big(\sum_{j=0}^{i-1}(k_{-1}-k_1)^{j+1}\frac{t^{j+1}}{(j+1)!}c_{ij}e^{-k_1t}+ \\ +\sum_{j=0}^{i-1}-d_{ij}\sum_{n=0}^{j}(k_{-1}-k_1)^{j-n}\frac{t^{j-n}}{(j-n)!}e^{-k_{-1}t}\Big)+D_2e^{-k_1t} \qquad (19)$$

Since $[(A)_{Bi}]=0$ for $t=0$ and i≠0, the use of the definition

$Q_i=\dfrac{k_{-1}P_i}{k_{-1}-k_1}$ yields eqn. (20)

$$[(A)_{Bi}]=Q_i\Big(\sum_{j=1}^{i}(k_{-1}-k_1)^j\frac{t^j}{j!}c_{i,j-1}e^{-k_1t}+ \\ +\sum_{j=0}^{i-1}-d_{ij}\sum_{n=0}^{j}(k_{-1}-k_1)^{j-n}\frac{t^{j-n}}{(j-n)!}e^{-k_{-1}t}+\sum_{j=0}^{i-1}d_{ij}e^{-k_1t}\Big) \qquad (20)$$

Comparison of eqn. (20) with eqn. (15) gives directly that

$a_{i0}=\sum_{j=0}^{i-1}d_{ij}$ and that $a_{ij}=c_{i,j-1}$ for j≠0.

The double sum in eqn. (20) may be rearranged into

$$\sum_{j=0}^{i-1}\sum_{k=j}^{i-1}(-d_{ik})(k_{-1}-k_1)^j\frac{t^j}{j!}$$

and comparison with eqn. (15) yields that $b_{ij}=\sum_{k=j}^{i-1}-d_{ik}$ if $b_{ij}=0$ for i=j and that $b_{i0}=-a_{i0}$. That $b_{ij}=0$ for i=j is conluded from the results of calculations of a number of $[(A)_{Bi}]$.

Similarly, combination of eqns. (15) and (13) and comparison with eqn. (16) yields relations for c_{ij}, c_{i0}, d_{i0} and d_{ij}. The results are summarized by eqns. (21)–(29).

$$a_{i0}=-b_{i0}=\sum_{j=0}^{i-1}d_{ij}=\sum_{j=0}^{i-1}((-1)^{j+1}a_{i-1,j}+b_{i-1,j}) \qquad (21)$$

$$a_{ij}=c_{i,j-1}=\sum_{k=j-1}^{i-1}(-1)^{k-(j-1)}a_{i-1,k}\ \text{for j}\neq 0 \qquad (22)$$

$$b_{ij}=-\sum_{k=j}^{i-1}d_{ik}=\sum_{k=j-1}^{i-1}-b_{i-1,k}\ \text{for j}\neq 0 \qquad (23)$$

$$c_{i0}=-d_{i0}=\sum_{j=0}^{i-1}(-1)^ja_{i-1,j} \qquad (24)$$

and for i>1

$$c_{i0}=-d_{i0}=\sum_{j=0}^{i-2}(d_{i-1,j}+(-1)^{j+1}c_{i-1,j}) \qquad (25)$$

$$c_{ij}=\sum_{k=j}^{i-1}(-1)^{k-j}a_{i-1,k}\ \text{for j}\neq 0$$

and for i>1 and j≠0 (26)

$$c_{ij}=\sum_{k=j-1}^{i-2}(-1)^{k-(j-1)}c_{i-1,k} \qquad (27)$$

$$d_{ij}=b_{i-1,j-1}\ \text{for j}\neq 0 \qquad (28)$$

and for i>1 and j≠0

$$d_{ij}=-\sum_{k=j-1}^{i-2}d_{i-1,k} \qquad (29)$$

Using $a_{00}=1$, all coefficients a_{ij}, b_{ij}, c_{ij} and d_{ij} may be calculated, *e.g.*, $a_{ii}=1$,$b_{i,i-1}=(-1)^{i+1}$, $c_{i,i-1}=1$ and $d_{i,i-1}=(-1)^i$.

APPENDIX 2

The areas under the curves in Figs. 1 and 2 may be calculated by integration of the recursion formulas, eqs (8), (15) and (16), from kt or k_1t equal to zero to infinity.

Integration of eqn. (8) yields

$$\int_0^\infty [(\mathrm{A})_\mathrm{i}]\mathrm{d}(kt) = k\int_0^\infty [(\mathrm{A})]\frac{k^\mathrm{i}t^\mathrm{i}}{\mathrm{i}!}\,\mathrm{e}^{-kt}\mathrm{d}t =$$

$$= \left[-k[(\mathrm{A})]\sum_{n=0}^{\mathrm{i}}\frac{k^{\mathrm{i}-(\mathrm{n}+1)}t^{\mathrm{i}-\mathrm{n}}}{(\mathrm{i}-\mathrm{n})!}\,\mathrm{e}^{-kt}\right]_{t=0}^{\infty} = k[(\mathrm{A})]k^{-1} =$$

$$[(\mathrm{A})]$$

i.e., the area under each of the curves in Fig. 1 is equal to 1.

Integration of eqn. (15) may be performed in the following way

$$\int_0^\infty [(\mathrm{A})_{\mathrm{Bi}}]\mathrm{d}(k_1t) = k_1\int_0^\infty \frac{k_1^\mathrm{i}k_{-1}^\mathrm{i}}{(k_{-1}-k_1)^{2\mathrm{i}}}[(\mathrm{A})]\sum_{\mathrm{j}=0}^{\mathrm{i}}(k_{-1}-k_1)^\mathrm{j}\frac{t^\mathrm{j}}{\mathrm{j}!}\cdot$$

$$\cdot(a_{\mathrm{ij}}\mathrm{e}^{-k_1t}+b_{\mathrm{ij}}\mathrm{e}^{-k_{-1}t})\mathrm{d}t = k_1\Bigg[\frac{k_1^\mathrm{i}k_{-1}^\mathrm{i}}{(k_{-1}-k_1)^{2\mathrm{i}}}[(\mathrm{A})]\sum_{\mathrm{j}=0}^{\mathrm{i}}$$

$$\left(-\sum_{\mathrm{n}=0}^{\mathrm{i}}(k_{-1}-k_1)^\mathrm{j}\cdot\frac{t^{\mathrm{j}-\mathrm{n}}}{(\mathrm{j}-\mathrm{n})!}\left(\mathrm{a}_{\mathrm{ij}}\frac{\mathrm{e}^{-k_1t}}{k_1^{\mathrm{n}+1}}+b_{\mathrm{ij}}\frac{\mathrm{e}^{-k_{-1}t}}{k_{-1}^{\mathrm{n}+1}}\right)\right)\Bigg]_{t=0}^{\infty} =$$

$$= k_1[(\mathrm{A})]\frac{k_1^\mathrm{i}k_{-1}^\mathrm{i}}{(k_{-1}-k_1)^{2\mathrm{i}}}\sum_{\mathrm{j}=0}^{\mathrm{i}}\left(\frac{a_{\mathrm{ij}}}{k_1^{\mathrm{j}+1}}+\frac{b_{\mathrm{ij}}}{k_{-1}^{\mathrm{j}+1}}\right)(k_{-1}-k_1)^\mathrm{j}$$

Similarly, integration of eqn. (16) yields

$$\int_0^\infty [(\mathrm{B})_{\mathrm{Ai}}]\mathrm{d}(k_1t) =$$

$$k_1[(\mathrm{A})]\frac{k_1^\mathrm{i}k_{-1}^{\mathrm{i}-1}}{(k_{-1}-k_1)^{2\mathrm{i}-1}}\sum_{\mathrm{j}=0}^{\mathrm{i}-1}\left(\frac{c_{\mathrm{ij}}}{k_1^{\mathrm{j}+1}}+\frac{d_{\mathrm{ij}}}{k_{-1}^{\mathrm{j}+1}}\right)(k_{-1}-k_1)^\mathrm{j}$$

These results may be used to prove that

$$\int_0^\infty [(\mathrm{A})_{\mathrm{Bi}}]\mathrm{d}(k_1t) = \int_0^\infty [(\mathrm{A})_{\mathrm{Bi}-1}]\mathrm{d}(k_1t) \text{ and that}$$

$$\int_0^\infty [(\mathrm{B})_{\mathrm{Ai}}]\mathrm{d}(k_1t) = \int_0^\infty [(\mathrm{B})_{\mathrm{Ai}-1}]\mathrm{d}(k_1t)$$

Calculation of $\int_0^\infty [(\mathrm{A})_{\mathrm{B1}}]\mathrm{d}(k_1t)$ and $\int_0^\infty [(\mathrm{B})_{\mathrm{A1}}]\cdot$ $\cdot\mathrm{d}(k_1t)$ then yields the result that the areas under the $(\mathrm{A})_{\mathrm{Bi}}$- and $(\mathrm{B})_{\mathrm{Ai}}$-curves in Fig. 2 are 1 and K, respectively.

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