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Determining the values at equilibrium and constant rates in inter-conversion processes

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ABSTRACT

A mathematical method of determining the values at equilibrium and the constant rates in inter-conversion process of conformational labile molecules is proposed. No measuring method is used. In most of the cases, at equilibrium, the concentrations of the main species are equal. Thus, we have equilibrium of concentrations too. The symmetry plays a central role.

KEYWORDS

Equilibrium;
Eigenvectors;
Symmetry;
Constant rates;
Area of complex domains.

INTRODUCTION AND PRELIMINARIES

Inter-conversion processes of configurationally labile molecules isolated from all external influences, are similar to the reversible first-order reactions:

$$\mathbf{S} \xrightarrow{k_1} \mathbf{R}$$
$$\mathbf{S} \xleftarrow{k_2} \mathbf{R}$$
$$\frac{d[S]}{dt} = k_2[R] - k_1[S],$$
$$\frac{d[R]}{dt} = -k_2[R] + k_1[S], \quad (1)$$
$$t_0 = 0, [S]_0 = 1, [R]_0 = 0,$$
$$\lim_{t\to\infty} \frac{d[S]}{dt}(t) = \lim_{t\to\infty} \frac{d[R]}{dt}(t) = 0 \Rightarrow k_2[R]_e = k_1[S]_e$$

The molecules in states $[S]$, $[R]$ are going to rearrange such that those from one state to become mirror image of those of the other state.

Determining the constant rates k_1, k_2 is an important and quite difficult task.

This problem, as well as similar problems for consecutive and parallel reactions have been studied by many authors[1-3,5,7]. In[3], an exponentially stripping method and least square approach are used to obtain constant rates from analytical and simulating data. The references on this subject are far from being complete. The present review is an improved version of[5].

By addition of equations, one obtains $[S] + [R] = C$, where $C > 0$ is constant. By the initial conditions, this constant can be equal to one. At least one of the rate constants appearing below is positive. Derivation in the second equation yields:

$$\frac{d^2[R]}{dt^2} = -(k_2+k_1)\frac{d[R]}{dt} \Rightarrow \log\left|\frac{d[R]}{dt} \Big/ \left(\frac{d[R]}{dt}\right)_0\right| = -(k_2+k_1)t,$$
$$\frac{d[R]}{dt} = \left(\frac{d[R]}{dt}\right)_0 \cdot \exp[-(k_2+k_1)t] = k_1 \cdot \exp[-(k_2+k_1)t], \quad (2)$$
$$[R](t) = \frac{k_1}{k_2+k_1}[1-\exp[-(k_2+k_1)t]],$$
$$[S](t) = \frac{k_2}{k_2+k_1} + \frac{k_1}{k_2+k_1}\exp[-(k_2+k_1)t]$$

Review

The problem is to find the rate constants k_1, k_2. In the present paper, we determine the rate constants of (1), and consider a particular case, when the inter-conversion occurs through an achiral intermediate, in two first order equilibriums:

$$S \xrightarrow{k_{-1}} A \xrightarrow{k_1} R$$
$$S \xleftarrow[k_1]{} A \xleftarrow[k_{-1}]{} R,$$
$$\frac{d[S]}{dt} = k_1[A] - k_{-1}[S];$$
$$\frac{d[R]}{dt} = k_1[A] - k_{-1}[R]; \qquad (3)$$
$$\frac{d[A]}{dt} = k_{-1}([S]+[R]) - 2k_1[A],$$
$$[A]+[B]+[C] = 1$$
$$k_1[A]_e = k_{-1}[S]_e = k_{-1}[R]_e \Rightarrow [S]_e = [R]_e$$

Here solving Cauchy problems related to the system is the "easy" problem, while determining the rate constants is the difficult one[1,4]. The following two initial data on pure states are considered:

$[A]_0 = 1$; $[S]_0 = 1$.

By using elements of real and complex analysis[3,2], both constant rates are determined in Theorem 2.1 from below.

ON THE VALUES AT EQUILIBRIUM AND CONSTANT RATES

Theorem 2.1

(i) The general problem described by (1) leads to the following values at equilibrium, respectively of the time-moment $t_{1/2}$:

$$k_1 = k_2 := k, \quad [S]_e = [R]_e = 1/2,$$
$$[S](t) = (1/2)(1 + e^{--2kt}), [R](t) = (1/2)(1 - e^{-2kt}), t \ge 0 \qquad (4)$$
$$t^* = t_{1/2} = \ln 2/2k, \ t_{E,\max|(0,\infty)} = 1/(2k)$$

Here $E(t)$ is the kinetic energy at t, and $t_{E,\max|0,\infty}$ is its strictly positive maximum point.

(ii) The optimal solution is:

$$k = 1/2, [S](t) = (1/2)(1 + e^{-t}),$$
$$[R](t) = (1/2)(1 - e^{-t}), t \ge 0, t_{1/2} = \ln 2, \ t_{E,\max|(0,\infty)} = 1 \qquad (5)$$

Proof

(i) From (1), (2) we infer that:

$$\varphi(t) = \frac{[R](t)}{[R]_e} = 1 - \exp(-(k_1/[R]_e)t), \ \varphi(0) = 0, \varphi(\infty -) = 1,$$
$$\psi(t) = 1 - \varphi(t) = \exp(-(k_1/[R]_e t) \Rightarrow \psi(0) = 1, \psi(\infty -) = 0.$$

The function φ increases, while ψ is decreasing in $[0, \infty)$. Their graphs have as unique common point $M\left(t^*, \frac{1}{2}\right)$. Thus we must have:

$$\frac{1}{2} = 1 - \exp\left(-\frac{k_1}{[R]_e} t^*\right) \Rightarrow t^* = \frac{[R]_e \ln 2}{k_1}$$

To find the values of the rate constants in terms of equilibrium-values, we observe that one of the eigenvalues of the matrix *A* of the linear differential system (1) is zero, and the other one is

$\lambda_2 = -(k_1 + k_2)$,

the associated eigenvector being $\vec{v} = (1/\sqrt{2}, -1/\sqrt{2})$. **It follows that the range of the linear operator defined by *A* is the one dimensional subspace generated by $\vec{v}$. Decomposing any vector from R^2 as Fourier sum related to the basis formed by the eigenvectors of *A*, one obtains:**

$$A\begin{pmatrix}[S]\\ [R]\end{pmatrix} = -(k_1+k_2)\langle([S],[R]),(1/\sqrt{2},-1/\sqrt{2})\rangle \cdot (1/\sqrt{2},-1/\sqrt{2}) =$$
$$\frac{d}{dt}\begin{pmatrix}[S]\\ [R]\end{pmatrix} = k_1 \exp(-(k_1+k_2)t)\begin{pmatrix}-1\\ 1\end{pmatrix} = \frac{k_1+k_2}{2}([S]-[R])(-1,1) \qquad (6)$$
$$\Rightarrow \frac{[S]-[R]}{2} = \frac{k_1}{k_1+k_2} e^{-(k_1+k_2)t} = \frac{1}{2}([S_0]-[R_0])e^{-(k_1+k_2)t} = \frac{1}{2} e^{-(k_1+k_2)t}$$
$$\Rightarrow k_1 = k_2 \Rightarrow [S]_e = [R]_e = 1/2$$

Inserting these conclusions in (2) yields:

$[S](t) = (1/2)(1 + e^{-2kt}), [R](t) = (1/2)(1 - e^{-2kt}), t \ge 0$

Because of the symmetry of the graphs of the functions from above with respect to the demy-axis $y = 1/2$, we have:

$$1/4 = (1/2)(1 - e^{-2kt_{1/2}}) \Leftrightarrow t_{1/2} = \ln 2/2k = t^*.$$

Maximizing over k the kinetic energy $E(t, k) = 2k^2 \exp(-4kt)$, for positive fixed t, we obtain:

$$\frac{\partial E}{\partial k} = 2(2k - 4k^2 t)e^{-4kt} = 0, \ t_{E,\max} = 1/(2k) > t_{1/2} \Rightarrow \qquad (7)$$
$$\max_{t\in(0,\infty)} E(t) = 2k^2 e^{-2} < 2k^2 = E(0).$$

Relation (7) reflects the hyperbolic dependence between t and k.

(ii) Assume firstly that: $2k \le 1$. Consider the modified Jukovsky's analytic transformation on the complex plane with zero deleted:

$J(z, 2k) = 1/z + 2k z, |z| < 1$

Then a simple computation shows that $2k < 1$ implies that this function is univalent in the unit disk U. It follows that $J(\cdot, 2k)$ satisfies the requirements of Theorem 14.13[6] (Theorem on the area; see also[4]). Application of this result yields:

$|2k| = 2k \leq 1.$

It follows that $2k = 1$ is the maximal possible value such that $J(\cdot, 2k)$ to be univalent in the unit disk. This leads to a minimal value for $t_{1/2} = \ln 2/(2k) = \ln 2$, $t_{E,\max|(0,\infty)} = 1/(2k) = 1$, under the same requirement on $J(\cdot, 2k)$. Of coarse, smaller values for the same times occur in case of $2k > 1$. However, a very large 2k is unrealistic at the initial time and leads to exceeding the total kinetic energy consumed after its maximum is attained. Application of the above reasoning for $J(\cdot, 1/(2k))$, shows that $1/(2k) = 1 = 2k$ is the largest value of $1/(2k)$, and the smallest value of 2k, for which the transformation $J(\cdot, 1/(2k))$ is univalent, in the second case: $2k > 1$. This case must be considered because of inconveniences of a large k mentioned above. Here is another argument of considering $2k = 1$ as optimal value. If we define the even function $g(x) = \exp(-4kx^2)$, then $h(x) = g(x) / \left(\int_R g \right)$ is a probability density of a distribution function associated to a random variable. This random variable has a normal Gauss (0, 1) distribution if and only if $k = 1/2$. Finally observe that the matrix A of the differential system (1) is symmetric, with eigenvalues 0, - 2k, and by Caylay-Hamilton Theorem, it satisfies the basic relation:

$$A^2 = -2kA \Rightarrow A^n = (-2k)^{n-1} A = (-1)^{n-1} A,$$
$$\|A^n\| = \|A\| = 1 \Leftrightarrow 2k = 1$$

That is we have the last relation if and only if the norm of the matrix A is one. In this case, A applies the normalized eigenvector $\vec{v} = (1/\sqrt{2}, -1/\sqrt{2})$ **associated to $\lambda = -2k = -1$ into its opposed vector. Moreover, we have:**

$$A = \frac{1}{2}\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}, \text{ and } -A, \exp(-tA), (t > 0)$$

is a symmetric positive semi-definite matrix of norm one, respectively positive definite matrix of norm e^t The vector $\vec{v}$ is a fixed point for $-A$ and for $h(A)$, whenever h is analytic in a domain containing the set $\{0, 1\} = \sigma(-A)$. Moreover, we have:

$(-A)^2 = -A,$

which means that $-A$ is a projector if and only if $2k = 1$.

Theorem 2.2

For any initial data, the solution of (3) is:

$$[S]-[S]_e = \frac{1}{2}\left[([A]_e - [A]_0)\exp\left(-\frac{k_{-1}}{[A]_e}t\right) + ([S]_0 - [R]_0)\exp(-k_{-1}t)\right];$$
$$[R]-[S]_e = \frac{1}{2}\left[([A]_e - [A]_0)\exp\left(-\frac{k_{-1}}{[A]_e}t\right) - ([S]_0 - [R]_0)\exp(-k_{-1}t)\right] \quad (8)$$
$$[A]-[A]_e = ([A]_0 - [A]_e)\exp\left(-\frac{k_{-1}}{[A]_e}t\right),$$
$$[S]_e = [R]_e, k_1[A]_e = k_{-1}[R]_e$$

Proof

The equation in $[A]$ can be solved separately, replacing $[S] + [R]$ by $1 - [A]$. Subtraction and addition of the first two equations lead to simple equations in $[S] - [R]$, $[S] + [R]$.

Theorem 2.3

Assume that in (3) we have $[A]_0 = 1$. In this case, the non-trivial solution is:

$$[A]_e = [R]_e = [S]_e = 1/3, k_1 = k_{-1} := k,$$
$$[S](t) = [R](t) = 1/3\left(1 - e^{-3kt}\right),$$
$$[A](t) = (1/3)\left(1 + 2e^{-3kt}\right), t \geq 0. \quad (9)$$

The optimal solution corresponds to $k = 1/12$

$$[S](t) = [S](t) = (1/3)(1 - e^{-(1/4)t}),$$
$$[A](t) = (1/2)(1 + 2e^{-(1/4)t}), t \geq 0 \quad (10)$$

Proof

We must have $[S]_0 = [R]_0 = 0$, so that from (8), if $[A]_e \neq 0$, one obtains:

$$[S]-[S]_e = [R]-[R]_e = -[R]_e \exp(-k_{-1}t/[A]_e),$$
$$[A]-[A]_e = (1-[A]_e)\exp(-k_{-1}t/[A]_e), t \geq 0 \quad (11)$$

From (11) we infer that

$[S]$, $[R]$, hence $[S] + [R]$

are increasing with t, and $[A]$ is a decreasing function of t. We can write the system (3) as:

$$\frac{d([S]+[R])}{dt} = 2k_1[A] - 2k_{-1}[S],$$
$$\frac{d[A]}{dt} = 2k_{-1}[S] - 2k_1[A], [A]_0 = 1, ([S]+[R])(0) = 0$$

Observe that this is a Cauchy problem of type (1), Review

where:

$[R] \mapsto [S] + [R], [S] \mapsto [A], k_2 \mapsto 2k_1, k_1 \mapsto 2k_{-1}$

Following the proof of Theorem 2.1, we must have:

$$2k_1 = 2k_{-1} := 2k, [S]_e = [R]_e = [A]_e = 1/3 \Rightarrow$$
$$[S](t) = [R](t) = (1/3)(1 - e^{-3k_{-1}t}), \quad (12)$$
$$[A](t) = (1/3)(1 + 2e^{-3k_{-1}t})$$

These relations prove the first assertions (9) from the statement. The optimal is given by extending the kinetic energy function

$$(2e^{-6k_{-1}t} + 4e^{-6k_{-1}t}) = 6e^{-6k_{-1}t}$$

by parity to the real axes, and considering the attached distribution function:

$$f(x) = \frac{6e^{-6k_{-1}x^2}}{6 \cdot \int_R e^{-6k_{-1}t^2} dt} = \frac{e^{-6k_{-1}x^2}}{\sqrt{2\pi}(12k_{-1})^{-1/2}}$$

Then f is a (0, 1) distribution function if and only if $\sigma = (12k_{-1}) = 1 \Leftrightarrow k_{-1} = k_1 = 1/12$. These relations yield the normal (optimal) solutions (10).

Theorem 2.4

Assume that $[S]_0 = 1$. Then the only possible solution is:

$$2k_1 = 2k_{-1} := 2k, [S](t) - 1/3 = (1/2)[(1/3)e^{-3kt} + e^{-kt}],$$
$$[R](t) - 1/3 = (1/2)[(1/3)e^{-3kt} - e^{-kt}], [A](t) = (1/3)(1 - e^{-3kt}).$$

The optimal solution is:

$$k_1 = k_{-1} := k = 1/12, [S](t) - 1/3 = (1/2)[(1/3)e^{-(1/4)t} + e^{-(t/12)}],$$
$$[R](t) - 1/3 = (1/2)[(1/3)e^{-(1/4)t} - e^{-(t/12)}], [A](t) = (1/3)(1 - e^{-(1/4)t}), t \geq 0$$

Proof

Relations (8) and the present initial data yield:

$$[S] - [S]_e = \frac{1}{2}[[A]_e \exp(-k_{-1}t/[A]_e) + \exp(-k_{-1}t)];$$
$$[R] - [R]_e = \frac{1}{2}[[A]_e \exp(-k_{-1}t/[A]_e) - \exp(-k_{-1}t)]; \quad (13)$$
$$[A] - [A]_e = -[A]_e \exp(-k_{-1}t/[A]_e)$$

By similar arguments to those of Theorem 2.3, based on the proof of Theorem 2.1, on the system (3), $[S]$ + $[R]$ being decreasing, $[A]$ increasing, and relations (13), we have:

$$k_1 = k_{-1} := k, [A]_e = [S]_e = [R]_e = 1/3,$$
$$[S](t) - 1/3 = (1/2)[(1/3)e^{-3kt} + e^{-kt}],$$
$$[R](t) - 1/3 = (1/2)[(1/3)e^{-3kt} - e^{-kt}],$$
$$[A](t) = 1/3(1 - e^{-3kt})$$

As in the proof of theorem 2.3, the optimal solution is obtained for $k = k_{-1} = 1/12$. Now the conclusion follows.

CONCLUSIONS

A general mathematical method for solving the problems mentioned in the Abstract is proposed. No measuring procedure is involved. Determining constant rates requires optimality conditions motivated in Theorem 2.1, (ii) In all the cases considered above, these final values are equal one to each other. Hence, the concentrations of the states $[S]$, $[R]$ are equal at infinity. The molecules of the state $[R]$ are exactly mirror images of those in state $[S]$; this case models equilibrium between species. Connections to other fields appear partially in Theorem 2.1. Under natural constraints, both constant rates can be determined (Theorem 2.1, (ii), and the optimal solutions from the other theorems). The equality at equilibrium in all of the considered cases leads to the maximal values of their product. This is a consequence of the mean inequality.

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