Increasing Velocity, Determining the Values at Equilibrium and Remarkable Rate Constants in Inter–Conversion Processes Revisited

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Abstract

Inter-conversion processes of labile molecules obey similar laws to those of reversible chemical reactions. The main purpose of this review article is to recall and improve and correct previous results on this subject. Namely, one corrects a result on the relationship between two rate constants, in the case when an intermediate state is involved. One proves that by increasing velocity, the concentrations of the main species at equilibrium are equal. This assertion seems to be true in both cases: when an intermediate state is involved and in the opposite case. In the latter case, one characterizes the property of being a projector for the linear transform defined by the matrix of the differential system which governs the process. Namely, one proves that this transform is a projector if and only if the rate constants have a common value. This value is ½ and equals the equal values of the concentrations at equilibrium.

Keywords: inter-conversion; equilibrium; optimal solutions; increasing velocity; Schwarz inequality; remarkable rate constants; projector

1 Introduction

In this case study, we improve some results from [1]. The inter–conversion processes of labile molecules are governed by similar differential systems as those related to linear reversible chemical reactions (see [1] and also [2], as well as the references therein). The first purpose of the present mini - review paper is to show that in some "optimal" cases, at equilibrium (in the sense of the linear differential systems), a physical equilibrium occurs too. In fact, the concentrations of the main species at equilibrium are equal. The second aim of this work is to determine remarkable rate constants of the process. In order to determine the special rate constants, an additional condition is necessary. In case of no intermediate sate, we found that a suitable such condition is that the linear (symmetric) operator defined by the matrix of the corresponding differential system is a projector. Our methods do not involve measurements, but only mathematical notions and results. Thus, the notions of an eigenvalue, symmetric matrices, as well as that of a projector are applied, in order to obtain remarkable values of the rate constants in terms of linear operators. The connection with elementary theory of real and complex functions [3] is also pointed out and/or applied. The rest of the paper is organized as follows. Section 2 deals with the subjects mentioned above, in the case of two main species, with or/and without an intermediate state. Section 3 gives the proofs of the results of Section 2 and their methods. Section 4 concludes the paper.

2 The results

Inter-conversion processes of configurationally labile molecules isolated from all external influences are similar to the first order reversible chemical reactions, as described below. Starting from this behavior, governed by the corresponding linear system of differential equations with constant coefficients, we will show that under some natural conditions of increasing the mean of the velocity, one deduces that the concentrations at equilibrium (when $t \to \infty$) verify the equalities

$$[R]_e = [S]_e = \frac{1}{2}$$

and the two rate constants are equal: $k_1 = k_2 := k$. Under additional assumption, we infer that the remarkable common value for the rate constants is $k = \frac{1}{2}$ (see Theorem 2.1). Namely, we prove that the operator defined by the matrix of the differential system involved has norm one (and it is also a projector) if and only if

$$k = \frac{1}{2}\left(= [R]_e = [S]_e\right)$$

We start by recalling the general law of inter – conversion process (or linear reversible reaction), under some initial data assumptions:

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

Here *S*, *R*, as well as $[S]$, $[R]$ are the concentrations of the main species at a current point $t \in [0,\infty)$, k_1, k_2 being the rate constants. Notations $[R]_e$, $[S]_e$ are used for the concentrations at equilibrium, (when $t \to \infty$). 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 rate constants k_1, k_2 is an important and quite difficult task.

By addition of equations, one obtains that the derivative of $[S]+[R]$ is vanishing everywhere, hence $[S]+[R]=C$, where $C>0$ is constant. By the initial conditions, this constant equals one. Thus $[S]+[R]\equiv 1.$ Both rate constants appearing below are positive numbers. Derivation in the second equation leads to

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

The first main problem is to show that the optimal values at equilibrium are equal. In the present paper, we determine the values at equilibrium and remarkable rate constants of (1), also considering a particular case, when the inter-conversion occurs through an achiral intermediate governed by (3).

$$\begin{aligned}
&S \xrightarrow{k_{-1}} A \xrightarrow{k_1} R; \\
&S \xleftarrow[k_1]{} A \xleftarrow[k_{-1}]{} R; \\
&\frac{d[S]}{dt} = k_1[A] - k_{-1}[S]; \\
&\frac{d[R]}{dt} = k_1[A] - k_{-1}[R]; \\
&\frac{d[A]}{dt} = k_{-1}([S]+[R]) - 2k_1[A]; \\
&[k_1[A]_e = k_{-1}[S]_e = k_{-1}[R]_e \Rightarrow [S]_e = [R]_e.
\end{aligned} \tag{3}$$

The notations $[S],[R],[A]$ are used for the current concentrations of the main species, respectively of the achiral intermediate [A], at a current point $t \in [0,\infty)$. One denotes by $[S]_e,[R]_e,[A]_e$ the values of the corresponding species at equilibrium (when $t \to \infty$); k_1, k_{-1} are the rate constants. Solving Cauchy problems related to the system is standard. The following case is considered:

$$[S]_0 = 1, \ \ [A]_0 = [R]_0 = 0,$$

where the index zero means that the corresponding concentration is considered at the initial moment $t_0 = 0$. By using elements of algebra, real and complex analysis, both significant rate constants related to the problem (1) are determined in Theorem 2.1 from below. In the sequel, by optimal values we mean those values for which the mean of the velocity of the inter–conversion process is maximal. In other words, our aim is to increase the velocity. We assume that we know an upper bound b for the rate constants k_1, k_2. The significance of the time moment $t_{1/2}$ is defined below.

Theorem 2.1. (i) *The general problem described by* (1) *leads to the following optimal values at equilibrium, respectively of the time-moment* $t_{1/2}$:

$$\begin{aligned}
&k_1 = k_2 := k, \quad [S]_e = [R]_e = \frac{1}{2}, \\
&[S](t) = \left(\frac{1}{2}\right)(1 + e^{-2kt}), \ [R](t) = \left(\frac{1}{2}\right)(1 - e^{-2kt}), \quad t \geq 0 \\
&t_{1/2} = \frac{\ln 2}{(2k)},
\end{aligned}$$

where $t_{1/2}$ is the time moment at which the half of the quantity $1/2$ obtained at equilibrium passes from state $[S]$ to state $[R]$.

(ii) *If* M_2 *is the matrix of the system* (1) *determined at point* (i), *then the linear operator defined by* $-M_2$ *is a projector if and only if* $k = \frac{1}{2}$. *In this case, the remarkable particular solution is*

$$[S](t) = \left(\frac{1}{2}\right)(1 + e^{-t}), \quad [R](t) = \left(\frac{1}{2}\right)(1 - e^{-t}), \quad t \geq 0, \ \ t_{1/2} = \ln 2\,.$$

Remark 2.1. Consider the modified Jukovsky's analytic transformation on the complex plane with zero deleted

$$J(z,2k)=\frac{1}{z}+2kz,\quad |z|<1, z\neq 0.$$

Then a simple calculation shows that $2k\leq 1$ implies that the function $J(\cdot,2k)$ is univalent in $U\backslash\{0\}, U:=\{z;\ |z|<1\}$. It follows that $2k=1$ is the maximal possible value such that $J(\cdot,2k)$ to be univalent in $U\backslash\{0\}$. This leads to a minimum value for

$$t_{1/2}=\frac{\ln 2}{(2k)}=\ln 2\,.$$

The conclusion is that the value $2k=1$ is a limit one, for which Jukovsky's application mentioned above is univalent in the open unit disk, with zero deleted. This cannot stand for a proof, but it is a method to guess the special value of $2k$ and its "geometric" meaning.

Remark 2.2. The solutions given by (i) of the above theorem, has the following properties: $[S]$ is strictly decreasing from 1 to $\frac{1}{2}$, $[R]$ is strictly increasing from 0 to $\frac{1}{2}$, hence the graphs of these two functions never meet. A common horizontal asymptote at $+\infty$ is the line $y=\frac{1}{2}$.

Next we assume that an intermediate state is involved. We consider an intermediate state [A] as described in (3), and assume that its role is to increase the velocity of the process. As in the case of Theorem 2.1, one assumes that we know an upper bound b_1 for the rate constants k_1, k_{-1}.

Theorem 2.2. *Assume that* $[S]_0-[R]_0\neq 0$. *Then the solution of* (3) *is*

$$[S](t)=\frac{1}{2}\Big(\frac{2k_1}{k_{-1}+2k_1}-\Big([A]_0-\frac{k_{-1}}{k_{-1}+2k_1}\Big)e^{-(k_{-1}+2k_1)t}+([S]_0-[R]_0)e^{-k_{-1}t}\Big),$$

$$[R](t)=\frac{1}{2}\Big(\frac{2k_1}{k_{-1}+2k_1}-\Big([A]_0-\frac{k_{-1}}{k_{-1}+2k_1}\Big)e^{-(k_{-1}+2k_1)t}-([S]_0-[R]_0)e^{-k_{-1}t}\Big),$$

$$[A](t)=\Big([A]_0-\frac{k_{-1}}{k_{-1}+2k_1}\Big)e^{-(k_{-1}+2k_1)t}+\frac{k_{-1}}{k_{-1}+2k_1} \tag{4}$$

In the next result, by optimal solution we mean that solution which maximizes the velocity mean of the process which occurs in the intermediate state $[A]$, in terms of the relationship between k_1 and k_{-1}.

Theorem 2.3. *Assume that* $[S]_0=1,\ [A]_0=[R]_0=0$. *Then the only optimal solution is obtained for* $k_{-1}=2k_1:=k$ *and is given by*

$$[S](t)=\frac{1}{2}\Big(\frac{1}{2}+\frac{1}{2}e^{-2kt}+e^{-kt}\Big)$$

$$[R](t)=\frac{1}{2}\Big(\frac{1}{2}+\frac{1}{2}e^{-2kt}-e^{-kt}\Big)$$

$$[A](t)=\frac{1}{2}(1-e^{-2kt}), t\geq 0$$

In particular, we have $[A]_e=\frac{1}{2}, [R]_e=[S]_e=\frac{1}{4}$.

Remark 2,3.

The matrix of the system (3) is not symmetric for $k_{-1} = 2k_1$. That matrix would be symmetric if and only if $k_1 = k_{-1}$. The latter equality, used in [1], seems to be not realistic and contradicts the relation $k_{-1} = 2k_1$ proved below.

3 Proofs and related methods

Proof of Theorem 2.1. (i) Looking for the optimal solution of (1), we observe that maximizing the absolute value of the velocity is equivalent to maximizing the square of the velocity. For any number

$$t_0 > 0,$$

maximizing the mean of the square of the velocity on the interval $[0, t_0]$ means, thanks to (2), to find an upper bound for

$$\frac{1}{t_0} k_1^2 \int_0^{t_0} \exp(-2(k_1 + k_2)t)dt \le \frac{b^2}{t_0} \int_0^{t_0} \exp(-2(k_1 + k_2)t)dt$$

(recall that $0 < k_1 \le b$). We maximize the above integral, from the point of view of relationship between the two rate constants. Due to Schwarz inequality, one deduces

$$\int_0^{t_0} \exp(-2k_1 t)\exp(-2k_2 t)dt \le \left(\int_0^{t_0} \exp(-4k_1 t)dt \right)^{\frac{1}{2}} \left(\int_0^{t_0} \exp(-4k_2 t)dt \right)^{\frac{1}{2}} .$$

and, as it is well–known, equality occurs (that is maximum is attained, and the integral in the left-hand side is maximal) if and only if and only if there exists a scalar c_0 such that

$$\exp(-2k_1 t) = c_0 \exp(-2k_2 t)$$

for all $t \in [0, t_0]$. The last relation may be rewritten as

$$\exp(2(k_2 - k_1)t) = c_0 = \text{const.}, \quad \forall t \in [0, t_0].$$

This may be true if and only if $k_2 - k_1 = 0$, $c_0 = 1$, that is

$$k_1 = k_2 =: k, c_0 = 1.$$

From the last equality (1), also using $[S] + [R] \equiv 1$, this leads to $[S]_e = [R]_e = \frac{1}{2}$. Under the optimality assumptions mentioned at point (i), to find the values of the rate constants, we observe that one of the eigenvalues of the matrix M_2 of the linear differential system (1) is zero, and the other one is

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

the associated eigenvector for the latter being $\bar{v}_2 = \left(-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)$. The normalized eigenvector $\bar{v}_1$ corresponding to the eigenvalue $\lambda_1 = 0$ is $\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)$ since $k_1 = k_2$ leads to the fact that the matrix of the system (1) is symmetric. It follows that the range of the linear symmetric operator defined by M_2 is the one-dimensional subspace generated by $\bar{v}_2$. The value of the moment time $t_{1/2}$ defined by

$$\frac{1}{4}=[R]_{t_{1/2}}$$

follows from (2), also using the basic equality $k_1=k_2$. In fact, the following equality should be verified by $t_{1/2}$:

$$\frac{1}{4}=\frac{1}{2}\left(1-\exp(-2kt_{1/2})\right)\Leftrightarrow t_{1/2}=\frac{\ln 2}{2k}.$$

Thus the proof of the assertions at point (i) is finished. To prove (ii), observe that in the case of an optimal solution, the matrix M_2 of the differential system (1) is symmetric. Its eigenvalues are $0,-2k$. The characteristic equation is $\lambda(\lambda+2k)=0$. By Cayley-Hamilton Theorem, M_2 satisfies the basic relation:

$$M_2^2=-2kM_2 \Leftrightarrow (-M_2)^2=-2kM_2$$

On the other hand, by definition, $-M_2$ defines a projector if and only

$$(-M_2)^2=-M_2$$

Comparing the last two relations, we get $2k=1$, as claimed. Then the matrix M_2 becomes

$$\mathrm{M}_2=\frac{1}{2}\begin{pmatrix}-1 & 1\\ 1 & -1\end{pmatrix}$$

and $(-M_2)$ is a symmetric positive semi-definite matrix of norm one. The vector $\bar{v}_2$ is a fixed point for $-M_2$. The set $\{0,1\}=\sigma(-M_2)$ is the spectrum of $-M_2$. For this special value $\mathrm{k}=1/2$, also using the results (i), the assertions of the statement (ii) follows. This concludes the proof. □

Proof of Theorem 2.2.

The equation in $[A]$ can be solved separately, eliminating the other unknowns of the system (one replaces $[S]+[R]$ by $1-[\mathrm{A}]$). This leads to a first order linear differential equation in the unknown $[\mathrm{A}]$. Solving this equation, we find the desired explicit expression for $[\mathrm{A}]$. Then standard arguments (such as subtraction and addition of the first two equations) lead to simple equations in the unknowns $[S]-[R],\ [S]+[R]$. The conclusion follows by addition and subtraction of these last mentioned relations, via elementary computations. □

Proof of Theorem 2.3.

From the point of view of optimum relationship between k_1 and k_{-1} appearing in (4), in order to maximize the mean of the velocity in state $[A]$ on an interval $[0,t_0]$, we have to maximize

$$I=\int_0^{t_0} e^{-(k_{-1}+2k_1)t}dt=\int_0^{t_0} e^{-k_{-1}t}e^{-2k_1t}dt\le\left(\int_0^{t_0} e^{-2k_{-1}t}\,dt\right)^{1/2}\left(\int_0^{t_0} e^{-4k_1t}\,dt\right)^{1/2}$$

because of Schwarz inequality (see also the proof of Theorem 2.1. and use the inequality given by hypothesis $k_{-1} \leq b_1 = const.$). As it is well known, the maximum value of I is attained if and only if when the relation between integrals becomes an equality, and this is happening if and only if there exists a constant c such that

$$e^{-k_{-1}t} = ce^{-2k_1 t}, t \in [0, t_0]$$

The last equality is equivalent to

$$e^{(2k_1 - k_{-1})t} = c, , t \in [0, t_0] \Leftrightarrow 2k_1 - k_{-1} = 0, c = 1$$

Inserting the equality $2k_1 = k_{-1}$ into (4), the conclusion follows. □

4 Conclusions

We have proved that in all the cases appearing in the theorems involving optimal solutions, the concentrations states at equilibrium $[R]_e, [S]_e$ are equal. In particular, we have not only an equilibrium at infinity in the sense of differential systems, but also an equilibrium of the concentrations of the main species. In case of no intermediate state, one also proves that the rate constants are equal. Under the same assumption, remarkable value for the rate constants are proposed in terms of the operator defined by the matrix of the corresponding differential system. Namely, the common value of the concentrations at equilibrium equals the common value of the rate constants (cf. Sections 2, 3). We have corrected the result from [1] on the case of an intermediate state. It seems that in this case, for a maximal velocity at intermediate state, we should have $2k_1 = k_{-1}$..

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