THE FIRST PASSAGE TIME TO THE EQUILIBRIUM STATE OF A FIRST ORDER REACTION

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The first passage time to the state of exact equilibrium (the most probable stationary state) for a first order reaction is described in terms of the probability density and the first and second moments. For large systems, the first moment is proportional to the logarithm of the number of particles in the system, while the dispersion is independent of the size of the system.

We shall consider a closed system with N particles that can exist in two distinguishable forms, A and B. The probabilities of the conversions of A into B and of B into A in a time interval $(t, t + dt)$ are $k_1 \, dt$ and $k_2 dt$, respectively. The state of the system at time t is determined by the number of particles A at t, $N_A(t)$. The random variable $N_A(t)$ represents a stochastic process that serves as a model of the first order reaction

$$ A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B . $$
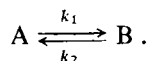
At a time t sufficiently remote from the instant of the system realization, the composition of the system is described by a stationary distribution[1-3] that characterizes the macroscopic equilibrium. The mean number of particles A at equilibrium is $\overline{N_A(\infty)} = N/(1 + k_1/k_2)$. The state $N_A(t) = \{N/(1 + k_1/k_2)\}$ ($\{..\}$ signifies the integer nearest the expression within the braces) is one of the highest stationary probability and is referred to as the state of exact equilibrium[4]. The attainment of a macroscopic equilibrium can be identified with the time of the first passage to the state $\{N/(1 + k_1/k_2)\}$. While the mean number of particles A, $\overline{N_A(t)}$, reaches the value $\overline{N_A(\infty)}$ only in the limit as $t \to \infty$, the mean first passage time to the state of exact equilibrium is finite and, as will be shown later, depends not only on the conversion probabilities k_1 and k_2, but also on the size of the system, N.

In this paper, we shall derive the distribution of the first passage times from state N to the state of exact equilibrium and its first and second moments for two extreme types of conversion, *viz.* $k_1 = k_2$ and $k_2 = 0$.

RESULTS

A Symmetrical Reversible Reaction: $k_1 = k_2 = k$

Let $N_A(0) = n$, $0 \leq n \leq N$, at time $t = 0$. The conditional probability that $N_A(t) = j$ at time t is[3]

$$P(j, t|n, 0) = \sum_{i=0}^{j} \binom{n}{i} \binom{N-n}{j-i} q^{N-n-j+2i} r^{n+j-2i}, \qquad (1)$$

where $q = [1 + \exp(-2kt)]/2$ and $r = [1 - \exp(-2kt)]/2$.

The probability that a system which at time $t = 0$ was in the state $N_A(0) = N$, N even, will pass for the first time to the state $N_A(t) = N/2$ (the state of exact equilibrium) in the interval $(t, t + dt)$ will be denoted by the symbol $f_{N,N/2}(t)\,dt$. The probability density $f_{N,N/2}(t)$ is given by the integral equation[5]

$$P(j, t|N, 0) = \int_0^t f_{N,N/2}(x)\, P(j, t-x|N/2, 0)\, dx, \quad j \leq N/2. \qquad (2)$$

This equation has been solved for $j = N/2$ using several approximations[4]. It will be shown now that, for $j = 0$, it is possible to obtain an exact solution and to derive exact expressions for the first and second moments of the density $f_{N,N/2}(t)$.

For $j = 0$, $n = N$ and $N/2$, Eq. (1) gives

$$P(0, t|N, 0) = r^N = [1 - \exp(-2kt)]^N/2^N \qquad (3)$$

$$P(0, t|N/2, 0) = (qr)^{N/2} = [1 - \exp(-4kt)]^{N/2}/2^N. \qquad (4)$$

Substituting Eqs (3) and (4) into (2), taking the Laplace transformation, using the convolution theorem and rearranging, we obtain the Laplace transform of the density $f_{N,N/2}(t)$:

$$\mathcal{L}_p\{f_{N,N/2}(t)\} = \int_0^\infty f_{N,N/2}(t) \exp(-pt)\, dt =$$

$$= B(p/4k + 1/2, N/2)/2^N\, B(N/2 + 1, N/2), \qquad (5)$$

where the beta function $B(x, y) = \Gamma(x)\,\Gamma(y)/\Gamma(x + y)$, the gamma function $\Gamma(x) = \int_0^\infty \exp(-u)\, u^{x-1}\, du$, and p is the complex transform variable. $\mathcal{L}_{p=0}\{f_{N,N/2}(t)\} = 1$ and thus $f_{N,N/2}(t)$ is normalized.

The mean time of the first passage to the state $N/2$ is

$$\bar{\tau} = -\mathrm{d}\mathscr{L}_p\{f_{N,N/2}(t)\}/\mathrm{d}p\big|_{p=0} = (1/2^{N+2}k) \cdot$$
$$\cdot \left[\mathrm{B}(p/4k + 1/2, N/2)/\mathrm{B}(N/2 + 1, N/2)\right]\left[\psi(p/4k + 1/2) - \right.$$
$$\left. - \psi(p/4k + 1/2 + N/2)\right]\big|_{p=0} = (1/2k)\sum_{i=0}^{N/2-1} 1/(2i + 1), \qquad (6)$$

where the function $\psi(x) = \mathrm{d}\ln\Gamma(x)/\mathrm{d}x$. For large N, the right-hand side approaches the expression $(1/4k)(\ln N + C + \ln 2)$, where $C = 0.5772..$ is the Euler constant, a result which was obtained previously[4]. The dispersion of the first passage times to the state $N/2$ is

$$D^2(\tau) = \overline{\tau^2} - \bar{\tau}^2 = \mathrm{d}^2\mathscr{L}_p\{f_{N,N/2}(t)\}/\mathrm{d}p^2\big|_{p=0} - \bar{\tau}^2 =$$
$$= (1/2k)^2\sum_{i=0}^{N/2-1} 1/(2i + 1)^2 . \qquad (7)$$

For large N, the dispersion tends to $\pi^2/32k^2$ and hence is independent of N.

An explicit form for the density $f_{N,N/2}(t)$ is obtained by the inverse transformation of Eq. (5):

$$f_{N,N/2}(t) = \left[k/2^{N-2}\,\mathrm{B}(N/2 + 1, N/2)\right]\exp\left(-2kt\right)\left[1 - \exp\left(-4kt\right)\right]^{N/2-1} . \qquad (8)$$

This represents a one-peak density with the maximum at the point $t_{max} = (1/4k)\ln(N - 1)$. For large N, this density can be expressed in the transformed form[6]

$$f_{N,N/2}(t) \approx \left[4k/(2\pi)^{1/2}\right]\exp\left[-z - (1/2)\exp\left(-2z\right)\right], \qquad (9)$$

$z = 2kt - (1/2)\ln N$, $z \geqq -(1/2)\ln N$. The shape of this curve does not change with increasing N, but the position of the maximum shifts linearly with the logarithm of N to higher values of t.

An Irreversible Reaction: $k_1 = k$, $k_2 = 0$

At time $t = 0$, the system contains N independent particles A with the common exponential lifetime distribution $\mathrm{Prob}\{\text{lifetime A} \leqq t\} = 1 - \exp(-kt)$. The change in the number of particles A, $N_A(t)$, with time represents a linear death process[7], which serves as a model of, for example, the radioactive decay[8,9]. The first passage time to the state of exact equilibrium is defined as the time at which the last particle A disappears (the population lifetime). The probability that there will be no particle A in the system at time t is

$$P(0, t|N, 0) = \left[1 - \exp(-kt)\right]^N . \qquad (10)$$

The probability density of the disappearance time of A from the system, $f_{N,0}(t)$, is obtained by solving the integral equation

$$P(0, t|N, 0) = \int_0^t f_{N,0}(x) P(0, t - x|0, 0)\, dx\,. \qquad (11)$$

Since $P(0, t - x|0, 0) = 1$ (no new particles A are formed in the system), the solution of Eq. (11) is

$$f_{N,0}(t) = dP(0, t|N, 0)/dt = kN \exp(-kt)\left[1 - \exp(-kt)\right]^{N-1}\,, \qquad (12)$$

and the mean disappearance time of the last particle A from the system is

$$\bar{\tau} = \int_0^\infty t f_{N,0}(t)\, dt = (1/k) \sum_{i=0}^N 1/i\,. \qquad (13)$$

For large N, the right-hand side of the equation tends to the expression $(1/k)(\ln N + C)$. The dispersion of the disappearance times for a population of particles A is

$$\overline{\tau^2} - \bar{\tau}^2 = \int_0^\infty t^2 f_{N,0}(t)\, dt - \bar{\tau}^2 = (1/k^2) \sum_{t=1}^N 1/i^2\,. \qquad (14)$$

For large N, the right hand side approaches the expression $\pi^2/6k^2$.

Equation (13), which can be rewritten in the form

$$\frac{\text{mean population lifetime}}{\text{mean individual lifetime}} = 1 + (1/2) + (1/3) + \ldots(1/N) \approx \ln N + C\,,$$

holds for independent memoryless particles such as the atoms of radioactive elements, energized polyatomic molecules with rapid intramolecular redistribution of the vibrational energy or electronically excited states of molecules and atoms for which the probability of disappearance in the interval $(t, t + dt)$ is independent of t (even in these cases, however, the exponential memoryless particle lifetime distribution is just a good approximation to the reality[10-12]).

In both the cases solved here, the first passage time to the state of exact equilibrium is described by a probability density with a sharp maximum at a time proportional to the logarithm of the number of particles in the system and a width independent of the size of the system. The mathematical limit $t \to \infty$ that appears in the definition of the equilibrium quantities may, for large N, be identified with t-values of the order of $\bar{\tau}$, i.e. values remote from the instant of the system realization by the $\ln N$ multiple of the relaxation time of the reaction.

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