TIME OF PERSISTENCE OF A PARTICLE IN SELECTED STATE DURING REVERSIBLE FIRST-ORDER CONVERSION. APPLICATION TO CRYSTAL GROWTH AND DISSOLUTION

Milan ŠOLC and Jiří HOSTOMSKÝ

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received March 4th, 1980

The distribution of the total time of persistence of a particle in a state A was derived both in an exact and an approximate form on the basis of a probability model of the conversion $A \rightleftarrows B$. The result was applied to the probability description of a change in size of one-dimensional crystals in a double crystallizer. The time change of the distribution of the crystal sizes can be described by the Fokker–Planck equation for diffusion with a diffusion coefficient proportional to the square of the sum of values of the growth and dissolution rate constants.

We shall consider a particle that can exist in two states, A and B, passing reversibly from one to the other. We shall assume that the infinitesimal probability of transition of the particle from the state A to B or *vice versa* in the time interval t to $t + \Delta t$, where $\Delta t \to 0$, is equal to $k\,\Delta t$, where k is independent of time (the particle is memoryless). The conversion proper is considered an instantaneous event. This model forms the basis of a stochastic description of the chemical reaction $A \rightleftharpoons B$ with a unit equilibrium constant, and was used in calculating the distribution of the number of conversions of A to B and B to A (*i.e.*, number of elementary reaction events) of one particle and in the ensemble of particles in a finite time interval[1,2]. The present paper is devoted to the derivation of the distribution of the total time of persistence in a selected state (namely in A). The solution of this problem relates not only to the probability characteristics of chemical conversion of the given type, but also to the description of certain macroscopic systems such as a double crystallizer[3].

Distribution of the Total Time of Persistence of a Particle in State A

We assume that the particle is in the state A at time $t = 0$. In the time interval $(0; \tau\rangle$, this particle either remains in this state, or undergoes an odd number of transitions (it will be in the state B at time τ), or undergoes an even number of transitions (it will be in the state A at time τ). The total number of transitions of the particle is described by the Poisson distribution[1]: the probability that the number of transitions in $(0; \tau\rangle$ is m is equal to $\exp(-k\tau)\,(k\tau)^m/m!$.

The probability that the particle remains in $(0; \tau\rangle$ unchanged and persists in the state A for a time s to $s + \mathrm{d}s$ is given as

$$\exp(-k\tau)\,\delta(s-\tau)\,\mathrm{d}s\,, \tag{1}$$

where $\delta(s-\tau)$ is the Dirac function (δ distribution). The probability that the particle undergoes $2j-1$ transitions ($j \geqq 1$) in $(0;\tau\rangle$ and persists in state A for a total time s to $s + \mathrm{d}s$ is given as

$$k^{2j-1}\exp(-k\tau)\int_{s_1+s_3+\ldots s_{2j-1}=s}^{s+\mathrm{d}s}\ldots\int \mathrm{d}s_1\,\mathrm{d}s_3\ldots\mathrm{d}s_{2j-1}\,\cdot$$
$$\cdot\int_{s_2+s_4+\ldots s_{2j-2}=0}^{\tau-s}\ldots\int \mathrm{d}s_2\,\mathrm{d}s_4\ldots\mathrm{d}s_{2j-2}=k^{2j-1}\exp(-k\tau)\,s^{j-1}(\tau-s)^{j-1}\,\mathrm{d}s/((j-1)!)^2\,, \tag{2}$$

where $s_i > 0$ is the time interval between $i-1$ and i-th transition. The probability that the particle undergoes $2j$ transitions ($j \geqq 1$) in the interval $(0;\tau\rangle$ and persists in the state A for the total time s to $s + \mathrm{d}s$ is given as

$$k^{2j}\exp(-k\tau)\int_{s_1+s_3+\ldots s_{2j-1}=0}^{s}\ldots\int \mathrm{d}s_1\,\mathrm{d}s_3\ldots\mathrm{d}s_{2j-1}\,\cdot$$
$$\cdot\int_{s_2+s_4+\ldots s_{2j}=\tau-s-\mathrm{d}s}^{\tau-s}\ldots\int \mathrm{d}s_2\,\mathrm{d}s_4\ldots\mathrm{d}s_{2j}=k^{2j}\exp(-k\tau)\,s^{j}(\tau-s)^{j-1}\,\mathrm{d}s/j!(j-1)! \tag{3}$$

(Integrals in (*2*) and (*3*) are Dirichlet integrals or their differential forms.)

Let $p_\tau(s)\,\mathrm{d}s$ denote the probability that the particle persists in state A for a total time s to $s + \mathrm{d}s$ in the interval $(0;\tau\rangle$. The probability density follows from expressions (*1*)–(*3*) (by summing and replacing the summation variable j by $j+1$) in the form

$$p_\tau(s)=\exp(-k\tau)\{\delta(s-\tau)+k\sum_{j=0}^{\infty}[k^2s(\tau-s)]^j/(j!)^2+$$
$$+k^2s\sum_{j=0}^{\infty}[k^2s(\tau-s)]^j/j!(j+1)!\}=\exp(-k\tau)[\delta(s-\tau)+kI_0(2ku)+$$
$$+k(s/u)I_1(2ku)]\,,\quad 0<s\leqq\tau\,, \tag{4}$$

where I_0 and I_1 denote modified Bessel functions[4] of the order 0 and 1, and $u = [s(\tau-s)]^{1/2}$. It can easily be shown (by integrating the sums in (*4*) term by term) that the density $p_\tau(s)$ is normalized, *i.e.*, its integral from 0 to τ is equal to 1.*

---

* The integration of $\delta(s-\tau)$ is to be understood as $\int_0^{\tau+}\delta(s-\tau)\,\mathrm{d}s = 1$.

The mean time of persistence of the particle in state A is given as

$$E_\tau(s) \equiv \int_0^\tau s p_\tau(s)\,\mathrm{d}s = \tau \exp(-k\tau)\left[\exp(k\tau)/2 + \sinh(k\tau)/2k\tau\right] =$$

$$= (\tau/2)\left[1 + (1 - \exp(-2k\tau))/2k\tau\right]. \tag{5}$$

(This can be derived also in the following way: the probability that the particle undergoes m transitions in $(0; \tau\rangle$ is[1] $\exp(-k\tau)(k\tau)^m/m!$. With m ($m \geqq 0$) transitions, the particle is in the state A on the average for a time $\tau/2$ or $(m+2)\,\tau/(2m+2)$ for m odd or even, respectively. Hence, $E_\tau(s) = \tau \exp(-k\tau)\left[1 + (1/2)\,k\tau + (2/3)\,(k\tau)^2/2! + \ldots\right]$, which is identical with Eq. (*5*).)

The second term in brackets in the final expression for $E_\tau(s)$ decreases to zero with increasing $k\tau$ and expresses *1*) the vanishing influence of the initial condition (exponential term) and *2*) the fact that for an even number of conversions the state A is, on the average, more probable than B (factor $1/2k\tau$).

A numerical calculation of $p_\tau(s)$ shows that this one-peak density is generally asymmetrical with respect to the position of the maximum (Fig. 1). For $k\tau \gg 1$, the functions I_0 and I_1 can be replaced, in the region of the maximum, by the first term of their asymptotic expansion[5] and the density $p_\tau(s)$ can be approximated by

$$p_\tau(s) = (2k/\pi\tau^3)^{1/2}(s + \tau/2)\exp\left[-2k(s - \tau/2)^2/\tau\right] \tag{6}$$

with a maximum at $s_m \approx (\tau/2)(1 + 1/2k\tau)$ equal to $p_\tau(s_m) \approx (2k/\pi\tau)^{1/2}(1 + 1/8k\tau)$, with the mean $E_\tau(s) \approx s_m$ and dispersion $D_\tau^2(s) \approx (\tau/4k)(1 - 1/4k\tau)$. The values of s_m and $p_\tau(s_m)$ calculated from Eq. (*4*) and approximation (*6*) do not differ for

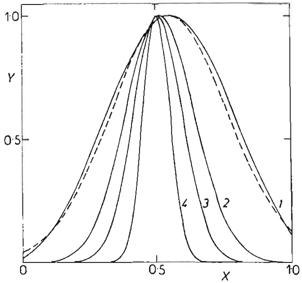

FIG. 1

Reduced Probability Density of the Total Time of Persistence in State A

Values of $k\tau$: *1* 5, *2* 15, *3* 30, *4* 100; $X = s/\tau$, $Y = p_\tau(s)/p_\tau(s_m)$. Solid curves correspond to the exact density (*4*), dashed curve to the approximation (*6*). For $k\tau > 15$, the approximation (*6*) coincides with the exact density.

$k\tau > 5$ by more than 1%. It is apparent from Fig. 1 that the approximation (*6*) is satisfactory for $k\tau > 5$ practically in the whole interval $(0; \tau\rangle$.

In the limit for $k\tau \to \infty$, it is possible to approximate $p_\tau(s)$ by the normal density

$$p_\tau(s) = (2k/\pi\tau)^{1/2} \exp\left[-2k(s - \tau/2)^2/\tau\right] \tag{7}$$

with the mean $E_\tau(s) = s_m = \tau/2$, maximum $p_\tau(s_m) = (2k/\pi\tau)^{1/2}$, and dispersion $D_\tau^2(s) = \tau/4k$. Numerical calculations show that this approximation is satisfactory already for $k\tau > 50$.

The mean time of persistence of the particle in the state A (or B) between the i-1 and i-th transition is $1/k$. The term $k\tau$ can hence be interpreted as the mean number of transitions of the particle in the interval $(0; \tau\rangle$. Our numerical calculations show that when the mean number of transitions is equal to several tens, the probability density of the total time of persistence of the particle in the state A can satisfactorily be described by a normal distribution with the center at $\tau/2$.

Simplified Model of Double Crystallizer

We shall consider two vessels, A and B, mutually connected. At a time $t = 0$, the first one contains a solution with N equal one-dimensional crystals of length x_0, while the other contains only the solution. In the time interval $(0; \tau\rangle$ the crystals pass from the vessel A to B and back; the conditions (temperature and concentration) are chosen such that the crystals in the vessel A grow at a linear rate $\varkappa_1$ and in the vessel B they dissolve at a linear rate $\varkappa_2$. Both rates are independent of time and size of the crystals and are positive. The probability of transition of a crystal from one vessel into the other in the interval $(t, t + \Delta t)$, $\Delta t \to 0$, is $k\,\Delta t$ and the mean time of persistence of a crystal in each of the vessels between two consecutive transitions is $1/k$. At a time τ an arbitrarily chosen crystal has a length x which can be expressed as $x = x_0 + \varkappa_1 s - \varkappa_2(\tau - s) = x_0 - \varkappa_2\tau + (\varkappa_1 + \varkappa_2)\,s$, where s is a random variable given by the density (*4*). We assume that $x_0 - \varkappa_2\tau > 0$ and that the rate of formation of new crystals is negligible, so that the total number of crystals is constant. The probability density of the crystal length at a time τ is given as

$$f(x, \tau) = p_\tau[(x - x_0 + \varkappa_2\tau)/(\varkappa_1 + \varkappa_2)]/(\varkappa_1 + \varkappa_2)\,, \tag{8}$$

where $x_0 - \varkappa_2\tau \leqq x \leqq x_0 + \varkappa_1\tau$ and $p_\tau(\ldots)$ is the density according to Eq. (*4*). The mean crystal length at a time τ is given as

$$E_\tau(x) = x_0 + (\varkappa_1 - \varkappa_2)\,\tau/2 + (\varkappa_1 + \varkappa_2)\left[1 - \exp(-2k\tau)\right]/4k \approx$$
$$\approx x_0 + (\varkappa_1 + \varkappa_2)/4k + (\varkappa_1 - \varkappa_2)\,\tau/2\,. \tag{9}$$

In the general case, the distribution of the crystal length at $t = 0$ is determined by the density $q(x_0)$, $a \leqq x_0 \leqq b$, $\int_a^b q(x_0)\,\mathrm{d}x_0 = 1$. We assume that $a - \varkappa_2\tau > 0$; then we have

$$f(x, \tau) = (\varkappa_1 + \varkappa_2)^{-1} \int_a^b p_\tau[(x - x_0 + \varkappa_2\tau)/(\varkappa_1 + \varkappa_2)]\, q(x_0)\,\mathrm{d}x_0\,. \qquad (10)$$

The mean crystal length at time τ is given as

$$E_\tau(x) = E(x_0) + (\varkappa_1 + \varkappa_2)\, E_\tau(s) - \varkappa_2\tau \approx$$

$$\approx E(x_0) + (\varkappa_1 - \varkappa_2)\,\tau/2 + (\varkappa_1 + \varkappa_2)/4k\,, \qquad (11)$$

where $E(x_0) = \int_a^b x_0\, q(x_0)\,\mathrm{d}x_0$ and $E_\tau(s)$ is given by Eq. (*5*). The dispersion of the crystal length at time τ is

$$D_\tau^2(x) \approx D^2(x_0) + \tau(\varkappa_1 + \varkappa_2)^2/4k - (\varkappa_1 + \varkappa_2)^2/16k^2 \qquad (12)$$

and $D^2(x_0)$ is the dispersion of the crystal length at $t = 0$. The approximate expressions in (*9*), (*11*), and (*12*) correspond to the replacement of the exact density $p_\tau(\ldots)$ by the approximation (*6*). Eqs (*11*) and (*12*) enable one to calculate $\varkappa_1$ and $\varkappa_2$ from the value of k and the first and second moments of the distribution of the crystal length at time τ.

In the limit for $k\tau \to \infty$, the probability density $f(x, \tau)$ is the solution of the Fokker–Planck diffusion equation[6]:

$$\partial f(x, \tau)/\partial\tau = -[(\varkappa_1 - \varkappa_2)/2]\,\partial f(x, \tau)/\partial x + [(\varkappa_1 + \varkappa_2)^2/8k)]\partial^2 f(x, \tau)/\partial x^2 \quad (13)$$

with the diffusion coefficient $(\varkappa_1 + \varkappa_2)^2/8k$.

REFERENCES

1. Šolc M.: Z. Phys. Chem. (Franfurt am Main) *92*, 1 (1974).
2. Vlad M.: Rev. Roum. Chim. *21*, 677 (1976).
3. Skřivánek J., Žáček S., Hostomský J., Vacek V. in the book: *Industrial Crystallization* (J. W. Mullin, Ed.), p. 173. Plenum Press, New York 1976.
4. Gradshteyn I. S., Ryzhik I. M.: *Table of Integrals, Series, and Products.* Academic Press, New York 1965.
5. Jeffreys H.: *Asymptotic Approximations*, p. 89. Oxford Univ. Press, London 1968.
6. Feller W.: *An Introduction to Probability Theory and Its Applications*, Vol. I, p. 358. Wiley, New York 1968.

Translated by K. Micka.