

STOCHASTIC MODEL OF REVERSIBLE BIMOLECULAR REACTION EQUILIBRIUM

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A reversible bimolecular reaction, $A + B \rightleftharpoons C + D$, is studied as a Markov process discrete in time on using the number of reaction events scale. A stationary probability distribution corresponding to reaction equilibrium is derived, and on its basis relations for the mean and variance of the number of particles of the product in equilibrium are analyzed. The results referred to the scale of the number of reaction events are compared with those referred to the laboratory time scale.

The probability model of a reversible bimolecular reaction, based on common postulates of the stochastic theory of chemical reaction rates¹⁻³, was studied in detail in the laboratory time scale by Darvey, Ninham and Staff⁴ who found a solution for the mean value and variance of the number of reactant particles in equilibrium, Darvey and Ninham⁵ and Oppenheim and others⁶ who analyzed the transition of the stochastic into deterministic description outside equilibrium. The present work deals with the study of a reversible bimolecular reaction in the scale of reaction events, *i.e.* the reaction is modelled as a Markov process discrete in time. The reaction events scale, which is in comparison with the laboratory time scale somewhat artificial, represents an internal (*i.e.* independent of an external time standard) time scale of the reaction system. The description of the reaction equilibrium in this scale leads to a stationary probability distribution, on the basis of which the states of the system can be classified from the point of view of the mean number of events between returns into a given state. Relations for the mean and variance of the number of product particles in equilibrium together with a proof of the limiting transition of the stochastic into deterministic description of the reaction equilibrium are obtained simply by algebraic means.

Reaction Model

We shall consider a reversible bimolecular reaction, $A + B \rightleftharpoons C + D$, proceeding in a closed system of constant unit volume and constant temperature. The number, N_x , of particles of component $X = A, B, C, D$ in the system is considered as a random

variable. We shall assume for simplicity that the reactants are present in the system in a stoichiometric ratio, *i.e.* $N_A : N_B = N_C : N_D = 1$. The state of the system will be characterized by the number, N_C , of product particles. When the system is in the state $N_C = i$, then $N_A = N_B = N - i$ and $N_C = N_D = i$, where $2N$ means the (constant) total number of particles in the system. The number of possible states of the system is $N + 1$ ($N_C = 0, 1, 2, \dots, N$).

The basic postulate of the stochastic description of the reaction is the following: The probability that in a system in which there are $N_A = N_B = N - i$ particles A and B, and $N_C = N_D = i$ particles C and D, an arbitrarily chosen particle A reacts during the time interval $(t, t + \Delta t)$, $\Delta t \rightarrow 0$, with any particle B to give the products, is $k_1(N - i) \Delta t$; the probability that an arbitrarily chosen particle C reacts during the same interval with any particle D to recover the reactants is $k_2 i \Delta t$ (here the constants k_1, k_2 are identical with the rate constants of the deterministic chemical kinetics^{2,4}). — This postulate leads to the common stochastic description of the reaction in the laboratory time scale²⁻⁵. By eliminating the time parameter we obtain the description of the reaction in the scale of reaction events (a reaction event will be understood as reacting of one pair of reactants, A and B, or products, C and D); this method was used recently in describing a reversible first-order reaction⁷.

When the system is in the state i , then by a next reaction event it passes into the state $i + 1$ or $i - 1$. It follows from the mentioned postulate that the probability that the system passes from the state i by a next reaction event into the state $i + 1$ is given by

$$p_{i,i+1} = K(N - i)^2 / [i^2 + K(N - i)^2], \quad (1)$$

and the probability that it passes into the state $i - 1$ is

$$p_{i,i-1} = i^2 / [i^2 + K(N - i)^2], \quad (2)$$

where $K = k_1/k_2$ is the equilibrium constant of the reaction. The reaction under study can be hence modelled by a Markov chain defined by a stochastic matrix of constant transition probabilities, $\mathbf{P} \equiv \|p_{ij}\|$, where

$$p_{ij} = \begin{cases} K(N - i)^2 / [i^2 + K(N - i)^2] & \text{for } j = i + 1, \\ i^2 / [i^2 + K(N - i)^2] & \text{for } j = i - 1, \\ 0 & \text{in other cases } (0 \leq i, j \leq N). \end{cases} \quad (3)$$

Stationary Probability Distribution

It follows from the properties of the matrix \mathbf{P} and from the theory of Markov chains⁸ that the reaction can be considered as a finite, irreducible periodic chain. All states

of the system are persistent: the system, once in the state i , returns into this state again, and the mean number of events between returns into this state is finite. If we denote the probability that the system passes from the state i after m reaction events into the state j by the symbol $p_{ij}^{(m)}$, then obviously

$$p_{ii}^{(m)} \begin{cases} > 0 & \text{for } m \text{ even,} \\ = 0 & \text{for } m \text{ odd,} \end{cases} \quad (4)$$

i.e. the states are periodic with a period equal to 2. From the theory of periodic Markov chains⁸ it follows further that

$$\lim_{m \rightarrow \infty} p_{ij}^{(2m)} = \begin{cases} 2u_j & \text{for } |i-j| \text{ even or zero,} \\ 0 & \text{for } |i-j| \text{ odd,} \end{cases} \quad (5a)$$

$$\lim_{m \rightarrow \infty} p_{ij}^{(2m+1)} = \begin{cases} 2u_j & \text{for } |i-j| \text{ odd,} \\ 0 & \text{for } |i-j| \text{ even or zero.} \end{cases} \quad (5b)$$

Here $u_j = 1/\mu_j$, where μ_j denotes mean number of reaction events between returns into the state j , represents a stationary probability distribution: The probability that the system, once in the state i , passes after a large number of reaction events into the state j is in the limit for $m \rightarrow \infty$ independent of the original state, i , and of the number, m , of reaction events (more exactly, it depends only on whether $|i-j|$ and m are even or odd). The distribution u_j fulfils the relation

$$u_j = \sum_{i=0}^N u_i p_{ij}, \quad (6)$$

which expresses the condition for the distribution characterizing the macroscopic equilibrium to be stationary. On introducing the transition probabilities (3) into Eq. (6) we obtain a system of equations

$$u_j = \frac{K(N-j+1)^2}{(j-1)^2 + K(N-j+1)^2} u_{j-1} + \frac{(j+1)^2}{(j+1)^2 + K(N-j-1)^2} u_{j+1} \quad (7)$$

with $0 \leq j \leq N$ (we set $u_{-1} = u_{N+1} \equiv 0$). This can be solved by induction to give

$$u_j = \left[K^{j-1} \binom{N-1}{j-1} + K^j \binom{N-1}{j} \right] u_0, \quad 0 \leq j \leq N. \quad (8)$$

(Here, as well as in further equations the terms $\binom{N-1}{-1}$ and $\binom{N-1}{N}$ are set equal

to zero.) Since u_j represents a probability distribution,

$$\sum_{i=0}^N u_i = 2 u_0 \sum_{i=0}^{N-1} K^i \binom{N-1}{i} = 1 \quad (9)$$

and hence

$$u_j = \left[K^{j-1} \binom{N-1}{j-1} + K^j \binom{N-1}{j} \right] / 2 \sum_{i=0}^{N-1} K^i \binom{N-1}{i}, \quad 0 \leq j \leq N. \quad (10)$$

Obviously $u_j(K) = u_{N-j}(1/K)$. The stationary probability distribution in the scale of reaction events is formally different from that in the laboratory time scale. Let $P_{ij}(\tau)$ be the probability that in a system in which i particles C were present at time $\tau = 0$ j particles C will be present at time τ ; then⁴

$$\lim_{\tau \rightarrow \infty} P_{ij}(\tau) \equiv P_j = K^j \binom{N}{j} / \sum_{i=0}^N K^i \binom{N}{i}. \quad (11)$$

This difference is a result of another way of describing the reaction and choosing a time scale. In the scale of reaction events, the time of persisting of the system in the state j (expressed by the number of events) is independent of j and equal to unity. In the laboratory time scale, the mean time, \bar{t}_j , of persisting of the system in the state j , expressed in common time units, depends on j as follows:

$$\begin{aligned} \bar{t}_j &\equiv \int_0^{\infty} t \cdot \exp \{ - [k_1(N-j)^2 + k_2j^2] t \} [k_1(N-j)^2 + k_2j^2] dt = \\ &= 1 / [k_1(N-j)^2 + k_2j^2]. \end{aligned} \quad (12)$$

The stationary probability distributions u_j and P_j are bound by the relation

$$P_j = u_j \bar{t}_j / \sum_{i=0}^N u_i \bar{t}_i. \quad (13)$$

For the distribution (10) we have $u_j/u_{j+1} < 1$ for $j(j+1) < K(N-j)(N-j-1)$, i.e. for $j < K^{1/2}N[(1 + (1-K)^2/4KN^2)^{1/2} - K^{1/2}]/(1-K) - \frac{1}{2}$. From this it follows that for sufficiently large values of N the largest term in Eq. (10) corresponds to the value of j_{\max} which is close to the deterministic number of particles C in equilibrium, $N_C^{\text{eq}} = K^{1/2}N/(1 + K^{1/2})$: $j_{\max} \approx N_C^{\text{eq}} - \frac{1}{2} + (1-K)/8K^{1/2}N - \dots$

Mean Value and Fluctuation of the Number of Particles in Equilibrium

If the system is originally in the state i , then the probability that it will attain after n reaction events the state j is $p_{ij}^{(n)}$. The mean number of particles C in the system after $2m$ reaction events is $\langle N_C \rangle_{2m,i} = \sum_{j=0}^N j p_{ij}^{(2m)}$, and after $2m + 1$ reaction events $\langle N_C \rangle_{2m+1,i} = \sum_{j=0}^N j p_{ij}^{(2m+1)}$. We now define the mean number of particles C in the system in the limit $m \rightarrow \infty$ as

$$\langle N_C \rangle_{\infty} \equiv \frac{1}{2} \left(\lim_{m \rightarrow \infty} \langle N_C \rangle_{2m,i} + \lim_{m \rightarrow \infty} \langle N_C \rangle_{2m+1,i} \right) = \sum_{j=0}^N j u_j. \quad (14)$$

The mean square number of particles C in the limit $m \rightarrow \infty$ can be defined analogously as

$$\langle N_C^2 \rangle_{\infty} \equiv \frac{1}{2} \left(\lim_{m \rightarrow \infty} \langle N_C^2 \rangle_{2m,i} + \lim_{m \rightarrow \infty} \langle N_C^2 \rangle_{2m+1,i} \right) = \sum_{j=0}^N j^2 u_j, \quad (15)$$

where

$$\langle N_C^2 \rangle_{2m,i} = \sum_{j=0}^N j^2 p_{ij}^{(2m)} \quad \text{and} \quad \langle N_C^2 \rangle_{2m+1,i} = \sum_{j=0}^N j^2 p_{ij}^{(2m+1)}.$$

The physical sense of these mean values can be explained as follows. Let us consider a large set of systems in which the reaction under study proceeds at equal conditions (equal N , temperature, volume and initial composition). Now either *a*) we choose at random n natural numbers $m_i > m$, $1 \leq i \leq n$, and select from the given set n systems in which m_1, m_2, \dots, m_n reaction events were realized from the beginning of the experiment, or *b*) we select $n/2$ systems in which $2m$ reaction events were realized and $n/2$ systems in which $2m + 1$ reaction events were realized. With increasing values of n and m , the mean values of N_C and N_C^2 for the set of n systems selected in the manner *a*) or *b*) will approach those given by Eqs (14) and (15).

From the mentioned equations and from the form of the distribution u_j it follows (we assume $K \neq 1$) that

$$\langle N_C \rangle_{\infty} = \sum_{j=0}^{N-1} j K^j \binom{N-1}{j}^2 / \sum_{j=0}^{N-1} K^j \binom{N-1}{j}^2 + \frac{1}{2}, \quad (16)$$

$$\begin{aligned} \langle N_C^2 \rangle_{\infty} &= \sum_{j=0}^{N-1} j^2 K^j \binom{N-1}{j}^2 / \sum_{j=0}^{N-1} K^j \binom{N-1}{j}^2 + \langle N_C \rangle_{\infty} = \\ &= K(N-1)(N-2\langle N_C \rangle_{\infty}) / (1-K) + \langle N_C \rangle_{\infty}. \end{aligned} \quad (17)$$

The variance of the number of particles C in the limit $m \rightarrow \infty$, defined as $D^2\{N_C\}_\infty \equiv \langle N_C^2 \rangle_\infty - \langle N_C \rangle_\infty^2$, is given by

$$D^2\{N_C\}_\infty = [K(N - \langle N_C \rangle_\infty)^2 - \langle N_C \rangle_\infty^2 - K(N - \langle N_C \rangle_\infty) + \langle N_C \rangle_\infty]/(1 - K). \quad (18)$$

Eq. (16) shows that $\langle N_C \rangle_\infty$ is different from the deterministic value of N_C^{eq} . We shall derive two important inequalities for the lower and upper limit of the stochastic mean value of $\langle N_C \rangle_\infty$ and the upper limit of the variance (18). From the Cauchy inequality (for $N > 1$),

$$\left[\sum_{j=0}^{N-1} jK^j \binom{N-1}{j} \right]^2 < \sum_{j=0}^{N-1} j^2 K^j \binom{N-1}{j}^2 \sum_{j=0}^{N-1} K^j \binom{N-1}{j}^2 \quad (19)$$

and from Eq. (17) it follows that

$$\langle N_C \rangle_\infty \geq [K^{1/2}N/(1 + K^{1/2})] [1 - (K^{1/2} - 1)/2NK^{1/2}] \quad \text{for } K \geq 1. \quad (20)$$

Further we consider the sum

$$s_N(K) = \sum_{j=0}^{N-1} [(2j+1) - K^{1/2}(2N-2j-1)] K^j \binom{N-1}{j}^2. \quad (21)$$

With the aid of Eq. (16) we find easily that $\text{sign } s_N(K) = \text{sign} [\langle N_C \rangle_\infty - N_C^{\text{eq}}]$. For small values of N , the sum $s_N(K)$ can be expressed as

$$\begin{aligned} s_1(x^2) &= 1 - x, & s_2(x^2) &= (1 - x)^3, & s_3(x^2) &= (1 - x)^5 + 2x^2(1 - x), \\ s_4(x^2) &= (1 - x)^7 + 6x^2(1 - x)^3 + 8x^3(1 - x), & & & & (22) \\ s_5(x^2) &= (1 - x)^9 + 12x^2(1 - x)^5 + 32x^3(1 - x)^3 + 30x^4(1 - x), \end{aligned}$$

where $x = K^{1/2}$. These equations suggest that $s_N(K)$ has the same sign as the term $1 - K^{1/2}$, i.e. it is negative for $K > 1$ and positive for $K < 1$. It can be proved by induction that this applies for any natural number N . Namely

$$\begin{aligned} s_{N+1}(K) - (1 - K^{1/2})^2 s_N(K) &= \sum_{j=0}^N \left\{ (2j+1) \left[\binom{N}{j}^2 - \binom{N-1}{j}^2 \right] - \right. \\ &\left. - (4N - 2j + 1) \binom{N-1}{j-1}^2 \right\} - K^{1/2} \left\langle (2N - 2j + 1) \left[\binom{N}{j}^2 - \binom{N-1}{j-1}^2 \right] - \right. \end{aligned}$$

$$- (2N + 2j + 1) \binom{N-1}{j} \Big\} K^j = 2(1 - K^{1/2}) \sum_{j=1}^{N-1} \binom{N-1}{j} \binom{N-1}{j-1} K^j \quad (23)$$

and hence

$$s_{N+1}(K) = (1 - K^{1/2})^2 s_N(K) + 2(1 - K^{1/2}) \sum_{j=1}^{N-1} \binom{N-1}{j} \binom{N-1}{j-1} K^j. \quad (24)$$

The first term on the right-hand side of Eq. (24) has the same sign as $s_N(K)$, the second the same as $1 - K^{1/2}$. For $K > 1$ and $N = 1$, we have $s_1(K) < 0$ (cf. Eq. (22)) and hence by induction $s_N(K) < 0$ for any natural N . Analogously for the case $K < 1$. As a result,

$$s_N(K) \leq 0 \quad \text{for } K \geq 1. \quad (25)$$

From this and the definition (21) we obtain finally

$$\langle N_C \rangle_\infty \leq K^{1/2} N / (1 + K^{1/2}) = N_C^{\text{eq}} \quad \text{for } K \geq 1. \quad (26)$$

The mean value $\langle N_C \rangle_\infty$ with respect to inequalities (20) and (26) fulfils the inequality

$$N_C^{\text{eq}} [1 - (K^{1/2} - 1) / 2NK^{1/2}] \leq \langle N_C \rangle_\infty \leq N_C^{\text{eq}} \quad \text{for } K \geq 1. \quad (27a)$$

In the laboratory time scale, it is possible to derive analogously

$$N_C^{\text{eq}} [1 + (K^{1/2} - 1) / 2NK^{1/2}] \geq \langle N_C \rangle_{\tau \rightarrow \infty} \geq N_C^{\text{eq}} \quad \text{for } K \geq 1, \quad (27b)$$

where $\langle N_C \rangle_{\tau \rightarrow \infty} \equiv \sum_{j=0}^N j P_j$ is the mean number of particles C corresponding to the stationary distribution in the time scale. This mean value can be interpreted in analogy with that in the reaction events scale as follows. a) We choose n real numbers $T_i > \tau$, $1 \leq i \leq n$, and from the above-mentioned set select n systems in which the reaction proceeded during the times T_1, T_3, \dots, T_n , or b) we select n systems in which the reaction proceeded during the same time τ . With increasing n and τ the mean number of particles in the set of n systems selected in the manner a) or b) will approach the value of $\langle N_C \rangle_{\tau \rightarrow \infty}$.

It is obvious that for $N \rightarrow \infty$ the ratio of both sides of the inequalities (27a,b) tends to one, and $\langle N_C \rangle_\infty$ as well as $\langle N_C \rangle_{\tau \rightarrow \infty}$ approach with increasing number of particles in the system the deterministic number of particles C in equilibrium, N_C^{eq} . It follows further from Eq. (18) and from the inequalities (20) and (26) that

$$\begin{aligned} D^2 \{N_C\}_\infty &< K^{1/2} N / (1 + K^{1/2})^2 + (1 + K) / 2(1 + K^{1/2})^2 < \\ &< N_C^{\text{eq}} / (1 + K^{1/2}) + \frac{1}{2} \quad \text{for } K \geq 1 \end{aligned} \quad (28)$$

so that the variance of the number of particles C is of the same order of magnitude as N or smaller. Since $D^2\{N_C\}_\infty = D^2\{N_A\}_\infty$ the inequality (28) is invariant with respect to the substitution of K for K^{-1} .

The probability that the system persists during the time interval $(t, t + \tau)$ in the state j is equal to $\exp[-(k_1(N-j)^2 + k_2j^2)\tau]$ and is largest for the state j_0 , where j_0 is the nearest integer to $KN/(1+K)$. If we consider this probability as a measure of the stability of the state then in the most stable state ($N_C = j_0$) there is a larger (for $K > 1$) or smaller (for $K < 1$) number of particles C than would correspond to the deterministic equilibrium and to the stochastic mean value in the scale of reaction events:

$$j_0 \geq N_C^{\text{eq}}, \quad \langle N_C \rangle_\infty \quad \text{for } K \geq 1. \quad (29)$$

(If $N > (1+K)/2 K^{1/2}$, then the same inequality can be derived from (27b) for $\langle N_C \rangle_{\tau \rightarrow \infty}$.) Only for $K = 1$ and N even, the state corresponding to the deterministic equilibrium is the most stable one.

Reaction with Unit Equilibrium Constant

For $k_1 = k_2 = k$ ($K = 1$), the stationary probability distribution u_j given by Eq. (10) reduces to

$$u_j = \left[\binom{N-1}{j-1} + \binom{N-1}{j} \right] / 2 \binom{2N-2}{N-1} \quad (30)$$

and the quantities $\langle N_C \rangle_\infty$ and $\langle N_C^2 \rangle_\infty$ defined by Eqs (14) and (15) can be immediately evaluated:

$$\langle N_C \rangle_\infty = N/2, \quad \langle N_C^2 \rangle_\infty = (N^3 - N^2 - 1)/2(2N - 3), \quad (31), (32)$$

so that the coefficient of variation of the number of particles C for $m \rightarrow \infty$ is given by

$$CV\{N_C\}_\infty \equiv (\langle N_C^2 \rangle_\infty - \langle N_C \rangle_\infty^2)^{1/2} / \langle N_C \rangle_\infty = [(N^2 - 2)/N^2(2N - 3)]^{1/2}, \quad (33)$$

which with increasing value of N approaches $(2N)^{-1/2}$. Thus, we obtain the value of the coefficient of variation in the laboratory time scale⁴ ($CV\{N_C\}_{\tau \rightarrow \infty} = (2N - 1)^{-1/2}$) only as a limiting case for large values of N since the stationary probability distributions in the scale of reaction events and in the laboratory time scale are different. With respect to (13), we have $P_j = u_j \bar{i}_j k N^3 / (2N - 1)$ so that $P_j \approx u_j$ for such values of $j = N/2 + i$ for which $4i^2/N^2 \ll 1$. Since \bar{i}_j in the time scale depends on j and is largest for $j = N/2$ ($\bar{i}_{N/2} = 2/kN^2$), i. e. for the state corresponding to the stochastic mean value, $CV\{N_C\}_\infty > CV\{N_C\}_{\tau \rightarrow \infty}$.

The mean number of reaction events between returns into the state $N/2$ (N even), $\mu_{N/2} = 1/u_{N/2}$, can be expressed with the aid of the Stirling formula as

$$\mu_{N/2} \approx \frac{1}{2}(\pi N)^{1/2}. \quad (34)$$

For comparison, in the case of a first-order reaction, $A \rightleftharpoons B$, in a system with a total number of particles $N_A + N_B = N$ (hence with the same number of possible states as the envisaged bimolecular reaction system) and with a unit equilibrium constant we have⁷ $\mu_{N/2} \approx (\pi N/2)^{1/2}$.

The mean number of reaction events between returns into the states $i = 0$ and $i = N$ is

$$\mu_0 = \mu_N \approx 2^{2N-1}/(\pi N)^{1/2}. \quad (35)$$

The mean values, $\mu_{N/2}$ and $\mu_0 = \mu_N$, increase with the total number of particles. To estimate roughly the mean recurrence time of the state $N/2$, $\tau_{N/2}$, we proceed as follows: The mean time corresponding to one reaction event in a system which is close to the state 0 or N is about $1/kN^2$, and the mean time corresponding to one reaction event in a system close to the state $N/2$ is about $2/kN^2$. Hence, the mean recurrence time of the state $N/2$ fulfils the relation $\sqrt{\pi/2}kN^{3/2} < \tau_{N/2} < \sqrt{\pi}kN^{3/2}$. Analogously, for the mean recurrence time of the state 0 or N we have $2^{2N-1} : \sqrt{\pi}kN^{5/2} < \tau_0, \tau_N < 2^{2N}/\sqrt{\pi}kN^{5/2}$. Whereas $\tau_{N/2}$ decreases with increasing total number of particles in the system, τ_0 and τ_N increase rapidly.

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REFERENCES

1. Bharucha-Reid A. T.: *Elements of the Theory of Markov Processes and their Applications*. McGraw-Hill, New York 1960.
2. McQuarrie D. A.: *J. Appl. Prob.* 4, 413 (1967).
3. McQuarrie D. A.: *Advan. Chem. Phys.* 15, 149 (1969).
4. Darvey I. G., Ninham B. W., Staff P. J.: *J. Chem. Phys.* 45, 2145 (1966).
5. Darvey I. G., Ninham B. W.: *J. Chem. Phys.* 46, 1626 (1967).
6. Oppenheim I., Shuler K. E., Weiss G. H.: *J. Chem. Phys.* 50, 460 (1969).
7. Šolc M.: *Z. Physik. Chem., Neue Folge* 83, 64 (1973).
8. Feller W.: *An Introduction to Probability Theory and its Applications*. Wiley, New York 1957.

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