Journal of Statistical Physics, Vol. 57, Nos. 1/2, 1989

The Elimination of Fast Variables in Complex Chemical Reactions. III. Mesoscopic Level (Irreducible Case)

J. A. M. Janssen[1,2]

Received October 20, 1988; revision received May 2, 1989

The master equation for a complex chemical reaction cannot always be reduced to a simpler master equation, even if there are fast and slow individual reaction steps. Nevertheless the elimination of intermediates can be carried out with the help of the Ω-expansion. This is illustrated with a well-known complex reaction: the dissociation of N_2O_5. It is shown that the intrinsic fluctuations in the N_2O_5 decay are larger than those implied by the master equation suggested by the macroscopic rate law.

KEY WORDS: Complex chemical reactions; intrinsic fluctuations; master equation; elimination of fast variables; Ω-expansion.

1. INTRODUCTION

In the preceding paper,$^{(1)}$ intrinsic fluctuations in complex chemical reactions were studied. I started with a detailed mesoscopic description in terms of the master equation that takes into account the fluctuations in the numbers of all reacting chemicals (including the intermediates). In some examples it was shown that, if one reaction step proceeds much faster than the others, it is possible to eliminate intermediates. In this way a reduced master equation was obtained, which gives a coarser description of the complex reaction.

Under which circumstances does a reduced master equation exist? Let us consider the following simple example:

$$X \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y \xrightarrow{k_3} Z \tag{1}$$

---

[1] Institute for Theoretical Physics, 3508 TA Utrecht, The Netherlands.

[2] Present address: Royal Netherlands Meteorological Institute, Department of Oceanography, 3730 AE De Bilt, The Netherlands.

It is assumed that k_2 and k_3 are much larger than k_1. Hence Y is a short-lived intermediate. Let Δt be a time interval that is much larger than the lifetime of a molecule Y, but much smaller than the lifetime of a molecule X: k_2^{-1}, $k_3^{-1} \ll \Delta t \ll k_1^{-1}$. During this time interval there is a probability $k_1 n \Delta t$ (n is the number of X molecules) that a molecule X forms a molecule Y. As Δt is much larger than the lifetime of the Y that has been created, this Y will either form an X and restore the original situation, or produce a Z. The probabilities for the transitions Y → X and Y → Z are $k_2(k_2+k_3)^{-1}$ and $k_3(k_2+k_3)^{-1}$, respectively. Hence there is a probability $k_1 n \Delta t\, k_3(k_2+k_3)^{-1}$ that the number of X molecules decreases by one. We conclude that (on a time scale on which the lifetime of Y is very small) the decay of X may be described by the following master equation:

$$\frac{\partial}{\partial t} p(n) = \frac{k_1 k_3}{k_2 + k_3} (E-1)\, np(n) \tag{2}$$

This is the coarse mesoscopic description of (1). It can also be obtained if one starts with the master equation for both X and Y and eliminates the intermediate Y in the standard way.(1,2)

It often happens that an intermediate may react via different reaction paths. In example (1), Y has two possible paths, Y → X and Y → Z. Eventually the intermediate will have chosen one of the paths, each one with a certain probability. Let us denote the probability for a reaction path i by π_i.

From the above discussion it is clear that the reduced master equation (2) could only be obtained because the probabilities π_1 and π_2 for the transitions Y → X and Y → Z are constant. One may check that the derivation also applies if the π_i depend on the number of X molecules, but that it breaks down if they depend on the number of Y molecules. Hence, one may expect that in this case a reduced master equation no longer exists.

In this paper we will investigate complex reactions with short-lived intermediates that may decay via different reaction paths. It will be shown explicitly that, if the π_i depend on the number of molecules of the intermediates, there does not exist a reduced master equation. However, it is still possible to eliminate intermediates by means of the Ω-expansion.(3)

2. ELIMINATION OF AN INTERMEDIATE BY MEANS OF THE Ω-EXPANSION

Consider the following complex reaction:

$$\mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Y}, \qquad 2\mathrm{Y} \xrightarrow{k_3} \mathrm{Z} \tag{3}$$

The net reaction is 2X → Z, and Y is a short-lived intermediate if $k_1 \ll k_2$, k_3. A single Y molecule may decay either unimolecularly according to Y → X, or bimolecularly in the process 2Y → Z. The probabilities with which both reaction paths are chosen depend on the total number of Y molecules. Hence, it is to be expected that it is impossible to describe the slow decay of X, 2X → Z, by a reduced master equation. I will show this explicitly in the following: I derive an equation that describes the fluctuations in X, and subsequently show that this equation cannot be obtained from a reduced master equation.

The master equation associated with (3) is given by

$$\begin{aligned}\frac{\partial}{\partial t} P(n, m) = k_1(E_n E_m^{-1} - 1)\, nP(n, m) \\ + k_2(E_n^{-1} E_m - 1)\, mP(n, m) \\ + k_3 \Omega^{-1}(E_m^2 - 1)\, m(m-1)\, P(n, m)\end{aligned} \tag{4}$$

The numbers of X and Y are denoted by n and m. The intermediate Y can be eliminated if k_2, $k_3 \gg k_1$. In order to ensure that the probabilities for the reaction paths Y → X and 2Y → Z are of the same order of magnitude, we furthermore assume $k_3 \gg k_2$. Actually, we have the stronger assumption that there exists a small parameter ε such that the different reaction constants are of different order in ε,

$$k_1 = \varepsilon^0 \kappa_1, \qquad k_2 = \varepsilon^{-1} \kappa_2, \qquad k_3 = \varepsilon^{-2} \kappa_3 \tag{5}$$

As k_3 is the largest reaction constant, it is tempting to look for a projection operator that obeys $\mathscr{P} k_3 \Omega^{-1}(E_m^2 - 1)\, m(m-1) = 0$. Such a projection operator, however, does not yield a meaningful reduced master equation, as it also eliminates slow mesoscopic time scales.(1) One way to circumvent this complication is by making a different separation of fast and slow terms. For the case of Eq. (4), however, this is not possible.

Nevertheless, it is still possible to perform the elimination of fast processes in (4) by making use of the Ω-expansion. Decompose the numbers n and m into a deterministic and a fluctuating part,

$$n = \Omega\varphi + \Omega^{1/2}\xi, \qquad m = \Omega\psi + \Omega^{1/2}\eta \tag{6}$$

Write the distribution $P(n, m)$ as a function of ξ and η, $\Pi(\xi, \eta)$. Expand the step operators according to

$$\begin{aligned}(E_n E_m^{-1} - 1) &= \Omega^{-1/2}\left(\frac{\partial}{\partial\xi} - \frac{\partial}{\partial\eta}\right) + \frac{1}{2}\Omega^{-1}\left(\frac{\partial}{\partial\xi} - \frac{\partial}{\partial\eta}\right)^2 + \cdots \\ (E_n^{-1} E_m - 1) &= \Omega^{-1/2}\left(-\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\right) + \frac{1}{2}\Omega^{-1}\left(-\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\right)^2 + \cdots \\ (E_m^2 - 1) &= 2\Omega^{-1/2}\frac{\partial}{\partial\eta} + 2\Omega^{-1}\frac{\partial^2}{\partial\eta^2} + \cdots\end{aligned} \tag{7}$$

Then the order-$\Omega^{1/2}$ terms yield the following rate equations:

$$\frac{d}{dt}\varphi=-\kappa_1\varphi+\varepsilon^{-1}\kappa_2\psi \tag{8}$$

$$\frac{d}{dt}\psi=\kappa_1\varphi-\varepsilon^{-1}\kappa_2\psi-2\varepsilon^{-2}\kappa_3\psi^2 \tag{9}$$

The order-Ω^0 terms yield an equation for the new density Π:

$$\begin{aligned}\frac{\partial}{\partial t}\Pi=&\kappa_1\left(\frac{\partial}{\partial\xi}-\frac{\partial}{\partial\eta}\right)\varphi\Pi+\frac{1}{2}\kappa_1\left(\frac{\partial}{\partial\xi}-\frac{\partial}{\partial\eta}\right)^2\varphi\Pi\\&+\varepsilon^{-1}\kappa_2\left(\frac{-\partial}{\partial\xi}+\frac{\partial}{\partial\eta}\right)\eta\Pi+\frac{1}{2}\varepsilon^{-1}\kappa_2\left(\frac{-\partial}{\partial\xi}+\frac{\partial}{\partial\eta}\right)^2\psi\Pi\\&+4\varepsilon^{-2}\kappa_3\frac{\partial}{\partial\eta}\eta\psi\Pi+2\varepsilon^{-2}\kappa_3\frac{\partial^2}{\partial\eta^2}\psi^2\Pi\end{aligned} \tag{10}$$

As (10) is a linear Fokker–Planck equation, one easily derives equations for the moments $\langle\xi^k\rangle$, $\langle\xi^l\rangle$, and $\langle\xi^n\eta^m\rangle$. From the equations for the first and second moments one finds the following equations for the variances and covariance:

$$\begin{aligned}\frac{d}{dt}\langle\langle\xi^2\rangle\rangle=&-2\kappa_1\langle\langle\xi^2\rangle\rangle+\kappa_1\varphi\\&+2\varepsilon^{-1}\kappa_2\langle\langle\xi\eta\rangle\rangle+\varepsilon^{-1}\kappa_2\psi\end{aligned} \tag{11}$$

$$\begin{aligned}\frac{d}{dt}\langle\langle\eta^2\rangle\rangle=&2\kappa_1\langle\langle\xi\eta\rangle\rangle+\kappa_1\varphi\\&-2\varepsilon^{-1}\kappa_2\langle\langle\eta^2\rangle\rangle+\varepsilon^{-1}\kappa_2\psi\\&-8\varepsilon^{-2}\kappa_3\psi\langle\langle\eta^2\rangle\rangle+4\varepsilon^{-2}\kappa_3\psi^2\end{aligned} \tag{12}$$

$$\begin{aligned}\frac{d}{dt}\langle\langle\xi\eta\rangle\rangle=&-\kappa_1\langle\langle\xi\eta\rangle\rangle+\kappa_1\langle\langle\xi^2\rangle\rangle-\kappa_1\varphi\\&+\varepsilon^{-1}\kappa_2\langle\langle\eta^2\rangle\rangle-\varepsilon^{-1}\kappa_2\langle\langle\xi\eta\rangle\rangle-\varepsilon^{-1}\kappa_2\psi\\&-4\varepsilon^{-2}\kappa_3\psi\langle\langle\xi\eta\rangle\rangle\end{aligned} \tag{13}$$

Inspection of (8), (9), and (11)–(13) shows that the variables ψ, $\langle\langle\eta^2\rangle\rangle$, and $\langle\langle\xi\eta\rangle\rangle$ vary faster than φ and $\langle\langle\xi^2\rangle\rangle$.

The distinction between fast and slow variables can be made more explicit if one performs the scaling

$$\psi=\varepsilon z,\qquad\langle\langle\eta^2\rangle\rangle=\varepsilon\zeta_1,\qquad\langle\langle\xi\eta\rangle\rangle=\varepsilon\zeta_2 \tag{14}$$

Equations (8), (9), and (11)–(13) transform under (14) into

$$\frac{d}{dt}\varphi = -\kappa_1\varphi + \kappa_2 z \tag{15}$$

$$\frac{d}{dt}z = \frac{1}{\varepsilon}(\kappa_1\varphi - \kappa_2 z - 2\kappa_3 z^2) \tag{16}$$

$$\frac{d}{dt}\langle\langle\xi^2\rangle\rangle = -2\kappa_1\langle\langle\xi^2\rangle\rangle + \kappa_1\varphi + \kappa_2\zeta_2 + \kappa_2 z \tag{17}$$

$$\frac{d}{dt}\zeta_1 = \frac{1}{\varepsilon}(\kappa_1\varphi - 2\kappa_2\zeta_1 + \kappa_2 z - 8\kappa_3 z\zeta_1 + 4\kappa_3 z^2) + 2\kappa_1\zeta_2 \tag{18}$$

$$\frac{d}{dt}\zeta_2 = \frac{1}{\varepsilon}(\kappa_1\langle\langle\xi^2\rangle\rangle - \kappa_1\varphi + \kappa_2\zeta_1 - \kappa_2\zeta_2 - \kappa_2 z - 4\kappa_3 z\zeta_2) - \kappa_1\zeta_2 \tag{19}$$

The fast variables z, ζ_1, ζ_2 may be eliminated according to the standard scheme.(2) Equation (16) implies that z approaches the value Z determined by $\kappa_1\varphi - \kappa_2 Z - 2\kappa_2 Z^2 = 0$. Hence $z \rightarrow Z(\varphi)$, where

$$Z(\varphi) = -\tfrac{1}{4}\kappa_2\kappa_3^{-1} + (\tfrac{1}{16}\kappa_2^2\kappa_3^{-2} + \tfrac{1}{2}\kappa_1\kappa_3^{-1}\varphi)^{1/2} \tag{20}$$

Similarly, (18) and (19) imply that $\zeta_1 \rightarrow V(\varphi)$ and $\zeta_2 \rightarrow C(\varphi, \langle\langle\xi^2\rangle\rangle)$, where

$$V(\varphi) = [2\kappa_2 + 8\kappa_3 Z(\varphi)]^{-1}[\kappa_1\varphi + \kappa_2 Z(\varphi) + 4\kappa_3 Z(\varphi)^2] \tag{21}$$

$$\begin{aligned} C(\varphi, \langle\langle\xi^2\rangle\rangle) = {} & [\kappa_2 + 4\kappa_3 Z(\varphi)]^{-1} \\ & \times [\kappa_1\langle\langle\xi^2\rangle\rangle - \kappa_1\varphi - \kappa_2 Z(\varphi) + \kappa_2 V(\varphi)] \end{aligned} \tag{22}$$

Incidentally, (21), (20), and (14) imply

$$\langle\langle\eta^2\rangle\rangle = \frac{\kappa_2 + 3\kappa_3 Z(\varphi)}{\kappa_2 + 4\kappa_3 Z(\varphi)}\varepsilon Z(\varphi) < \psi \tag{23}$$

Hence the fluctuations in the intermediate Y are smaller than those induced by Poissonian statistics (sub-Poissonian fluctuations). For the reduced equations which describe the slow evolution of φ and $\langle\langle\xi^2\rangle\rangle$, one thus finds

$$\frac{d}{dt}\varphi = -\kappa_1\varphi + \kappa_2 Z(\varphi) = -2\kappa_3 Z(\varphi)^2 \tag{24}$$

$$\frac{d}{dt}\langle\langle\xi^2\rangle\rangle = -2\kappa_1\langle\langle\xi^2\rangle\rangle + \kappa_1\varphi + 2\kappa_2 C(\varphi, \langle\langle\xi^2\rangle\rangle) + \kappa_2 Z(\varphi) \tag{25}$$

With the use of (22) one may write (25) as

$$\frac{d}{dt}\langle\!\langle\xi^2\rangle\!\rangle = \frac{-8\kappa_1\kappa_3 Z(\varphi)}{\kappa_2+4\kappa_3 Z(\varphi)}\langle\!\langle\xi^2\rangle\!\rangle + 2\kappa_3 Z(\varphi)^2$$

$$\times\{1+\kappa_2[\kappa_2+8\kappa_3 Z(\varphi)][\kappa_2+4_3 Z(\varphi)]^{-2}\} \tag{26}$$

Equations (24) and (25) describe the stochastic behavior of the slow decay $2X\rightarrow Z$. The form of these equations suggests that they might be obtained via an Ω-expansion of a single-variable master equation. In the next section I will show that this is not the case.

3. NONEXISTENCE OF A REDUCED MASTER EQUATION

Consider the following one-variable master equation:

$$\frac{\partial}{\partial t}q(n) = (E-1)\,r(n)\,q(n) \tag{27}$$

If one puts in the usual way $n=\Omega\varphi+\Omega^{1/2}\xi$ and performs the Ω-expansion of (27), the $\Omega^{1/2}$ and Ω^0 terms yield the following equations:

$$\frac{d}{dt}\varphi = -R(\varphi) \tag{28}$$

$$\frac{\partial}{\partial t}\Pi(\xi, t) = R'(\varphi)\frac{\partial}{\partial\xi}\xi\Pi + \frac{1}{2}R(\varphi)\frac{\partial^2}{\partial\xi^2}\Pi \tag{29}$$

where

$$R(\varphi) = \lim_{\Omega\rightarrow\infty}\Omega^{-1}r(\Omega\varphi) \tag{30}$$

From (29) one obtains an equation for the variance:

$$\frac{d}{dt}\langle\!\langle\xi^2\rangle\!\rangle = -2R'(\varphi)\langle\!\langle\xi^2\rangle\!\rangle + R(\varphi) \tag{31}$$

We now compare (24) and (26) with (28) and (31). If one puts $R(\varphi)=2\kappa_3 Z(\varphi)^2$, then (24) and (28) coincide, and (26) becomes

$$\frac{d}{dt}\langle\!\langle\xi^2\rangle\!\rangle = -2R'(\varphi)\langle\!\langle\xi^2\rangle\!\rangle + R(\varphi)[1+S(\varphi)] \tag{32}$$

with

$$S(\varphi) = \kappa_2[\kappa_2+8\kappa_3 Z(\varphi)][\kappa_2+4\kappa_3 Z(\varphi)]^{-2} > 0 \tag{33}$$

Hence, (26) and (31) differ from each other, and the master equation (27) does not apply.

The solution of (32) [and hence of (26)] with initial condition $\langle\langle \xi^2 \rangle\rangle(0) = 0$ can easily be found,

$$\langle\langle \xi^2 \rangle\rangle(t) = R^2(\varphi(t)) \int_{\varphi(t)}^{\varphi_0} [1 + S(\varphi')]\, R^{-2}(\varphi')\, d\varphi' \tag{34}$$

$\varphi(t)$ is the solution of (28) with $\varphi(0) = \varphi_0$. From (34) we conclude that the fluctuations are larger than those implied by (27).

This enhancement of fluctuations can be understood as follows. Consider reaction (3), and suppose that in a certain time interval the reaction X → Y consumes more X than on average. Then, the number of Y molecules increases above their average value, the probability for the reaction X → Y diminishes, and the reaction 2Y → Z is favored. Consequently, less than the average amount of X molecules will be formed back by the reaction Y → X. This mechanism thus leads to an increase of fluctuations in the number of X molecules. On the other hand, it is also responsible for the relative small fluctuations in the number of Y molecules [cf. (23)].

Fluctuations can also be inhibited. Consider, e.g., the following complex reaction:

$$X \rightleftarrows 2Y, \qquad Y \rightarrow Z \tag{35}$$

If now in a certain time interval more X decay than on average, then (as the number of Y increases) the probability for the back reaction 2Y → X increases. Hence, more X will be formed back, and the fluctuations are inhibited.

Reaction (35) can be treated along the same lines as (3), but I will not do this. In the next section I consider an example of a real complex reaction.

4. DISSOCIATION OF N_2O_5

The dissociation of N_2O_5 obeys the following stoichiometric equation:

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \tag{36}$$

The reaction is complex, which is implied by the fact that the decay of N_2O_5 is governed by a linear law,

$$\frac{d}{dt}[N_2O_5] = -k[N_2O_5] \tag{37}$$

The following reaction mechanism, involving the intermediates NO_3 and NO, was proposed by Ogg$^{(4,5)}$:

$$
\begin{aligned}
&N_2O_5 \underset{2}{\overset{1}{\rightleftarrows}} NO_2 + NO_3 \\
&NO_2 + NO_3 \xrightarrow{3} NO_2 + NO + O_2 \qquad (38) \\
&NO + NO_3 \xrightarrow{4} 2NO_2
\end{aligned}
$$

If one denotes the concentrations of N_2O_5, NO_2, O_2, NO_3, and NO by x_1, x_2, x_3, x_4, and x_5, the rate equations can be written as

$$\frac{d}{dt}x_1 = -k_1x_1 + k_2x_2x_4 \tag{39}$$

$$\frac{d}{dt}x_4 = k_1x_1 - [(k_2 + k_3)x_2 + k_4x_5]x_4 \tag{40}$$

$$\frac{d}{dt}x_5 = (k_3x_2 - k_4x_5)x_4 \tag{41}$$

It is understood that x_2 and x_3 depend on the other variables according to $x_2 = C_2 - 2x_1 - x_4 - x_5$ and $x_3 = C_3 - \frac{1}{2}x_1 - \frac{1}{2}x_4 + \frac{1}{2}x_5$, where C_2 and C_3 are constants.

The linear rate law (37) can be derived if one assumes that the first and fourth reaction steps are respectively much slower and much faster than the second and third steps. One then finds that x_4 and x_5 approach quasistationary values in a time that is much smaller than the decay time of x_1,

$$x_4 \to \frac{k_1x_1}{(k_2 + k_3)x_2 + k_4x_5} \qquad x_5 \to \frac{k_3}{k_4}x_2 \tag{42}$$

Hence, if one substitutes (42) into (39), one finds

$$\frac{d}{dt}x_1 = -2\frac{k_1k_3}{k_2 + 2k_3}x_1 \tag{43}$$

This result coincides with (37) and thus gives evidence for the Ogg mechanism (38).

The linear law (43) might suggest that the stochastic behavior of the N_2O_5 decay is governed by a master equation of the form

$$\frac{\partial}{\partial t}q(n) = k(E - 1)\,nq(n) \tag{44}$$

where $k = 2k_1k_3(k_2 + 2k_3)^{-1}$, and n denotes the number of N_2O_5 molecules. However, (44) reproduces the macroscopic equation (43), but it does not describe correctly the intrinsic fluctuations. The fluctuations will be calculated in the following sections, and it will turn out that they are larger than those implied by (44).

5. MESOSCOPIC TREATMENT OF N_2O_5 DECAY; ELIMINATION OF NO_3

The master equation associated with (38) reads

$$\begin{aligned}\frac{\partial}{\partial t} p(n_1, n_2, n_3, n_4, n_5) = {} & k_1(E_1 E_2^{-1} E_4^{-1} - 1)\, n_1 p \\ & + k_2 \Omega^{-1}(E_1^{-1} E_2 E_4 - 1)\, n_2 n_4 p \\ & + k_3 \Omega^{-1}(E_4 E_5^{-1} E_3^{-1} - 1)\, n_2 n_4 p \\ & + k_4 \Omega^{-1}(E_4 E_5 E_2^{-2} - 1)\, n_4 n_5 p \qquad (45)\end{aligned}$$

This equation describes the fluctuations in the numbers of molecules of all substances that are involved in reaction (38). It is my aim to derive a simpler equation that only describes the fluctuations in the number of N_2O_5 molecules. In this section the elimination of NO_3 ($\sim$ variable n_4) will be carried out. In the subsequent section I will deal with *NO* ($\sim$ variable n_5).

The master equation (45) is of the form

$$\frac{\partial}{\partial t} p = \mathbf{W}_1 p + (\mathbf{W}_2 + \mathbf{W}_3 + \mathbf{W}_4) p \qquad (46)$$

I assume $k_1 \ll k_2$, k_3, k_4, and apply the standard scheme for the elimination of fast variables (see refs. 1 and 2).

A suitable projection operator $\mathscr{P}$ should satisfy $\mathscr{P}(\mathbf{W}_2 + \mathbf{W}_3 + \mathbf{W}_4) = (\mathbf{W}_2 + \mathbf{W}_3 + \mathbf{W}_4)\mathscr{P} = 0$. The latter condition is obeyed by a $\mathscr{P}$ of the form

$$\mathscr{P} = \delta_{n_4,0} \sum_{n'_1 \cdots n'_5} K(n_1, n_2, n_3, n_4, n_5 \,|\, n'_1, n'_2, n'_3, n'_4, n'_5) \qquad (47)$$

The kernel K is determined by the condition $\mathscr{P}(\mathbf{W}_2 + \mathbf{W}_3 + \mathbf{W}_4) = 0$. If one writes out this condition, it turns out that $K(n \,|\, n')$ may be interpreted as the probability to end up in the point $n_1 \cdots n_5$ after $n'_4 - n_4$ steps (each step corresponds to a reaction 2, 3, or 4), given that $n'_1 \cdots n'_5$ is the starting point.

Consider (45), and recall that the numbers of NO, NO_2, and NO_3

molecules are given by n_5, n_2, and n_4, respectively. The probabilities for the reactions 2, 3, and 4 are

$$\begin{aligned}\pi_2 &= \frac{k_2 n_2}{(k_2 + k_3) n_2 + k_4 n_5}\\ \pi_3 &= \frac{k_3 n_2}{(k_2 + k_3) n_2 + k_4 n_5}\\ \pi_4 &= \frac{k_4 n_5}{(k_2 + k_3) n_2 + k_4 n_5}\end{aligned} \tag{48}$$

Note that they do not depend on n_4. Hence, the elimination of this variable will not cause any complications.$^{(1)}$

The reduced probability q is defined by

$$q(n_1, n_2, n_3, n_5) = \sum_{n'} K(n_1, n_2, n_3, n_4 = 0, n_5 \,|\, n')\, p(n') \tag{49}$$

The lowest order of the standard scheme yields the following equation:

$$\begin{aligned}\frac{\partial}{\partial t} q = {} & k_1(E_1 E_2^{-1} E_3^{-1} E_5^{-1} - 1)\frac{k_3 n_1 (n_2 + 1)}{(k_2 + k_3)(n_2 + 1) + k_4 n_5} q\\ & + k_1(E_1 E_3^{-2} E_5 - 1)\frac{k_4 n_1 n_5}{(k_2 + k_3)(n_1 + 1) + k_4 n_5} q\\ & + \mathcal{O}(k_1^2)\end{aligned} \tag{50}$$

Let us now assume $k_4 \gg k_3$. Then the orders of magnitude of the terms on the right-hand side of (50) are widely different, and a further reduction seems possible. However, if one introduces the projection operator associated with the fast part of (50) and performs the elimination procedure, one does not arrive at a meaningful equation. The elimination of n_5 can only be properly achieved by means of the Ω-expansion.

6. Ω-EXPANSION: ELIMINATION OF NO

The Ω-expansion of (50) is cumbersome, but straightforward. I will not give all details of the calculation.

As the quantities $2n_1 + n_2 + n_5$ and $n_1 + 2n_3 - n_5$ remain constant in (50), we consider q only as function of n_1 and n_5. As usual, one puts

$$n_1 = \Omega \varphi_1 + \Omega^{1/2} \xi, \qquad n_5 = \Omega \varphi_5 + \Omega^{1/2} \eta \tag{51}$$

For n_2 one may put

$$n_2 = \Omega\varphi_2 + \Omega^{1/2}(-2\xi - \eta) \tag{52}$$

Expansion of the step operator yields for the $\Omega^{1/2}$ terms

$$\begin{aligned} \frac{d}{dt}\varphi_1 &= -\frac{k_1\varphi_1(k_3\varphi_2 + k_4\varphi_5)}{(k_2+k_3)\varphi_2 + k_4\varphi_5} \\ \frac{d}{dt}\varphi_5 &= \frac{k_1\varphi_1(k_3\varphi_2 - k_4\varphi_5)}{(k_2+k_3)\varphi_2 + k_4\varphi_5} \end{aligned} \tag{53}$$

and for the Ω^0 terms

$$\begin{aligned} \frac{\partial \Pi}{\partial t} = {} & \left(A\frac{\partial}{\partial\xi}\xi + B\frac{\partial}{\partial\xi}\eta + C\frac{\partial}{\partial\eta}\xi + D\frac{\partial}{\partial\eta}\eta\right)\Pi \\ & + \frac{1}{2}k_3\varphi_1\varphi_2\psi^{-1}\left(\frac{\partial}{\partial\xi} - \frac{\partial}{\partial\eta}\right)^2\Pi \\ & + \frac{1}{2}k_4\varphi_1\varphi_5\psi^{-1}\left(\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\right)^2\Pi \end{aligned} \tag{54}$$

with

$$\begin{aligned} \psi &= (k_2+k_3)\varphi_2 + k_4\varphi_5 \\ A &= \psi^{-2}[k_3(k_2+k_3)\varphi_2^2 + k_4(k_2+2k_3)\,\varphi_2\varphi_5 + 2k_2k_4\varphi_1\varphi_5 + k_4^2\varphi_5^2] \\ B &= \psi^{-2}k_2k_4\varphi_1(\varphi_2+\varphi_5) \\ C &= \psi^{-2}[-k_3(k_2+k_3)\varphi_2^2 + k_2k_4\varphi_2\varphi_5 + 2k_4(k_2+2k_3)\,\varphi_1\varphi_5 + k_4^2\varphi_5^2] \\ D &= \psi^{-2}k_4(k_2+2k_3)\,\varphi_1(\varphi_2+\varphi_5) \end{aligned} \tag{55}$$

From (54) one obtains the following equations for the variances and covariance:

$$\begin{aligned} \frac{d}{dt}\langle\langle\xi^2\rangle\rangle &= -2A\langle\langle\xi^2\rangle\rangle - 2B\langle\langle\xi\eta\rangle\rangle \\ &\qquad + k_3\psi^{-1}\varphi_1\varphi_2 + k_4\psi^{-1}\varphi_1\varphi_5 \\ \frac{d}{dt}\langle\langle\eta^2\rangle\rangle &= -2C\langle\langle\xi\eta\rangle\rangle - 2D\langle\langle\eta^2\rangle\rangle \\ &\qquad + k_3\psi^{-1}\varphi_1\varphi_2 + k_4\psi^{-1}\varphi_1\varphi_5 \\ \frac{d}{dt}\langle\langle\xi\eta\rangle\rangle &= -(A+D)\langle\langle\xi\eta\rangle\rangle - B\langle\langle\eta^2\rangle\rangle - C\langle\langle\xi^2\rangle\rangle \\ &\qquad - k_3\psi^{-1}\varphi_1\varphi_2 + k_4\psi^{-1}\varphi_1\varphi_5 \end{aligned} \tag{56}$$

If one investigates Eq. (53) and (56), one finds (as $k_4 \gg k_3$) that φ_5, $\langle\!\langle \eta^2 \rangle\!\rangle$, and $\langle\!\langle \xi\eta \rangle\!\rangle$ are fast and φ_1 and $\langle\!\langle \xi^2 \rangle\!\rangle$ slow. In a time of order k_4^{-1} the fast variables approach quasistationary values,

$$\begin{aligned} \varphi_5 &\to \frac{k_3}{k_4}\varphi_2 \\ \langle\!\langle \eta^2 \rangle\!\rangle &\to \frac{k_3}{k_4}\varphi_2 \\ \langle\!\langle \xi\eta \rangle\!\rangle &\to \frac{-2k_3}{k_4}\langle\!\langle \xi^2 \rangle\!\rangle - \frac{k_2 k_3}{k_4(k_2+2k_3)}\varphi_2 \end{aligned} \tag{57}$$

Hence, in the quasistationary state the fluctuations in the number of NO molecules have the Poissonian property $\langle\!\langle n_5^2 \rangle\!\rangle = \langle n_5 \rangle$. With the help of (57) the fast variables may be eliminated. It follows that the slow variables evolve according to

$$\frac{d}{dt}\varphi_1 = -2\frac{k_1 k_3}{k_2+2k_3}\varphi_1 \tag{58}$$

$$\frac{d}{dt}\langle\!\langle \xi^2 \rangle\!\rangle = -4\frac{k_1 k_3}{k_2+2k_3}\langle\!\langle \xi^2 \rangle\!\rangle + 2\frac{k_1 k_3}{k_2+2k_3}\varphi_1\left[1+\left(\frac{k_2}{k_2+2k_3}\right)^2\right] \tag{59}$$

Equation (58) was already derived in (43). Equation (59), which describes the fluctuations in the number of N_2O_5 molecules, implies that the stochastic behavior of the N_2O_5 decay cannot be described by the master equation (44); (44) underestimates the magnitude of the fluctations, as may be verified by solving (58) and (59) explicitly.

ACKNOWLEDGMENTS

I am indebted to Prof. N. G. van Kampen for discussions and critical reading of the manuscript. This work was part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM).

REFERENCES

1. J. A. M. Janssen, *J. Stat. Phys.*, this issue, preceding paper.
2. N. G. van Kampen, *Phys. Rep.* **124**:69 (1985).
3. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1983).
4. S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).
5. R. A. Ogg, Jr., *J. Chem. Phys.* **15**:337, 613 (1947).