

Discrete Fluctuations and Their Influence on Kinetics of Reactions

Daniel Ben-Avraham¹

Received November 10, 1986; revision received February 5, 1987

We study the fluctuations arising from the discrete particle nature of the reactants in chemical processes, which we term *discrete fluctuations*. It is shown how the magnitude of discrete fluctuations is formally obtained from the Van Kampen Ω -expansion of the master equation for the process in question. It is claimed that discrete fluctuations are, at times, an important factor in determining the anomalous kinetics of reaction systems. We specialize to diffusion-limited reactions in systems below their upper critical dimensionality. Some variations of the two-species annihilation process $A + B \rightarrow \text{inert}$, as well as some other examples, are presented and analyzed. Many of these examples prove our point about the dramatic influence of discrete fluctuations on the reaction kinetics. Our theoretical scaling predictions are backed by extensive Monte Carlo simulations.

KEY WORDS: Reaction kinetics; diffusion-limited reactions; two-species annihilation; Van Kampen's Ω -expansion; discrete fluctuations.

1. INTRODUCTION

The anomalous kinetics of reactions in systems that cannot be described by mean-field rate equations have attracted an ever-increasing interest in recent years.⁽¹⁻⁹⁾ Anomalous kinetics result from many different causes. Among the most studied cases are diffusion-limited reactions.⁽⁴⁻⁹⁾ In low space dimensionalities reaction rates become anomalous due to the diffusive motion of the reactants and because of various sources of dominant fluctuations, which are disregarded in the mean-field rate equations. Much physical insight was gained from research on even the simplest reaction schemes, such as irreversible one-species annihilation,^(5,7,10) $A + A \rightarrow \text{inert}$,

¹ Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215.

or two-species annihilation,^(5,6) $A + B \rightarrow \text{inert}$. From these we have learned that basically two ingredients suffice to fully explain the anomalous reaction rates. One is the scaling of the volume explored by a reactant particle with time, which is provided by random walk theory (diffusive motion). The other is the existence of spatial fluctuations in the concentration of the reactants, as emphasized especially by Kang and Redner.⁽¹¹⁾

The purpose of this paper is to draw attention to yet another possible source of fluctuations, which, though unimportant in the simple systems mentioned above, are indispensable for the understanding of the anomalous kinetics of some other, equally simple, systems. These are the fluctuations arising from the discrete nature of the reactant particles. We term them, for brevity, *discrete fluctuations*. Discrete fluctuations play an important role in determining the kinetics of various reactions. We define discrete fluctuations and show how to calculate their magnitude using Van Kampen's Ω -expansion⁽³⁾ in Section 2. The question of the relevance of discrete fluctuations is discussed in Section 3, and some simple examples of such cases are presented and analyzed in Sections 3 and 4. Finally, a further recent example (of n -species annihilation⁽¹²⁾) is recalled, and a discussion is included in Section 5.

2. DISCRETE FLUCTUATIONS AND THE VAN KAMPEN Ω -EXPANSION

Discrete fluctuations are those fluctuations arising from the particlelike nature of the reactants. In order to clarify this statement, suppose that all the physical conditions required for the validity of a mean-field rate equation are met, but drop the assumption that we can use a continuous concentration variable rather than the actual *number* of particles in each given state. The fluctuations arising, as a result, are discrete fluctuations.

As a simple example consider the irreversible one-species annihilation process^(5,7,10)



A mean-field rate equation describing the process is

$$\dot{c}_A(t) = -k \cdot c_A^2(t) \quad (2.2)$$

where $c_A(t)$ is the concentration of A particles at time t , k is the rate at which (2.1) occurs, and the overdot denotes differentiation with respect to time. If we keep all the physical conditions that are assumed in writing Eq. (2.2), but require a description of the system in terms of N_A , the number of A particles, we would have to replace the rate equation by a master

equation on the probability $P(N_A; t)$ of having N_A of the A particles at time t ,

$$\frac{\partial P(N_A; t)}{\partial t} = \Omega k \cdot \left[\frac{1}{2} \frac{N_A + 2}{\Omega} \frac{N_A + 1}{\Omega} P(N_A + 2; t) - \frac{1}{2} \frac{N_A}{\Omega} \frac{N_A - 1}{\Omega} P(N_A; t) \right] \quad (2.3)$$

Here Ω is the volume of the system. The first term in the rhs denotes the rate of increase of $P(N_A; t)$ as a result of a single $A + A \rightarrow$ inert reaction taking place, and is proportional to the probability of having $N_A + 2$ particles. The second term represents the rate of decrease of $P(N_A; t)$ due to a single reaction taking place. From $P(N_A; t)$ derived from Eq. (2.3) one can calculate the expected $N_A(t)$, which turns out to coincide, as required, with $c_A(t)\Omega$. But we also find fluctuations of $N_A(t)$ around its expected value, which are the result of the discrete nature of the system.

At this stage one might become discouraged because of the complexity of the master equation (2.3). Luckily, there exists an elegant formal procedure for systematically approximating the solution of Eq. (2.3). This is known as the Van Kampen Ω -expansion. Using Van Kampen's notation,⁽³⁾ we now sketch the Ω -expansion for the one-species annihilation process. The number of particles is rewritten as

$$N_A = \Omega\phi + \sqrt{\Omega}\xi \quad (2.4)$$

The variable ϕ will later be shown to correspond to the concentration $c_A(t)$, and ξ is a measure for the variations from this function. The scaling of these fluctuations with $\sqrt{\Omega}$ is a fact justified *a posteriori* by the consistency of the expansion. The probability function $P(N_A; t)$ is replaced by $\Pi(\xi; t)$. Thus, from (2.4),

$$\left. \frac{\partial P}{\partial t} \right|_{N_A} = \frac{\partial \Pi}{\partial t} - \sqrt{\Omega}\phi \frac{\partial \Pi}{\partial \xi} \quad (2.5)$$

Also,

$$\left. \frac{\partial N_A}{\partial \xi} \frac{\partial P}{\partial N_A} \right|_t = \sqrt{\Omega} \left. \frac{\partial P}{\partial N_A} \right|_t = \frac{\partial \Pi}{\partial \xi} \quad (2.6)$$

This is used to Taylor-expand $P(N_A + 2; t)$ around $P(N_A; t)$. Upon making this expansion and the variables substitution, one gets an equation involving powers of $\Omega^{k/2}$ ($k = 1, 0, -1, -2, \dots$). Collecting like powers of Ω , one finds that the coefficients of the terms diverging like $\Omega^{1/2}$ yield

$$\dot{\phi} = -k \cdot \phi^2 \quad (2.7)$$

This is exactly like the mean-field rate equation (2.2) for $c_A(t)$, showing that $\phi(t)$ is indeed identified with $c_A(t)$. The coefficients of the terms with Ω^0 yield a Fokker–Planck equation:

$$\frac{\partial \Pi}{\partial t} = 2k \cdot \frac{\partial}{\partial \xi} (\phi \xi \Pi) + k \cdot \frac{\partial^2}{\partial \xi^2} (\phi^2 \Pi) \quad (2.8)$$

We have now reached our goal. Equation (2.8) enables us to calculate the expected value of the discrete fluctuations. Indeed, multiplying (2.8) by ξ^2 and integrating over ξ , we have

$$\partial \langle \xi^2 \rangle / \partial t = -2k \cdot \phi \langle \xi^2 \rangle + 2k \cdot \phi^2 \quad (2.9)$$

which together with (2.7) yields

$$\langle \xi^2 \rangle = \frac{2}{3} \phi (1 - \phi^3 / \phi(0)^3) + \langle \xi^2(0) \rangle \quad (2.10)$$

Recalling the meaning of ϕ and ξ from Eq. (2.4), we see that this can be interpreted in terms of the fluctuations in the particle number and the expected particle number itself,

$$\begin{aligned} & \langle (N_A - \langle N_A \rangle)^2 \rangle \\ &= \frac{2}{3} \langle N_A \rangle \{ 1 - [\langle N_A \rangle / \langle N_A(0) \rangle]^3 \} + \langle [N_A(0) - \langle N_A(0) \rangle]^2 \rangle \end{aligned} \quad (2.11)$$

To summarize, consideration of the discrete nature of the particles leads to the prediction of fluctuations in the expected particle number, which are not predicted by the mean-field rate equations. The Van Kampen Ω -expansion provides us with a formal way of evaluating these discrete fluctuations. In the following sections we will discuss reaction schemes where discrete fluctuations play a significant role in determining the kinetics of the system.

It is worth mentioning the usefulness of expressing discrete fluctuations as a function of the expected number of particles, rather than as an explicit function of time as in Eq. (2.11). The reason is that the explicit time scale is very sensitive to *other* fluctuation sources, such as the diffusive motion of the particles (which was *not* discussed in this section), so that it is more meaningful to represent discrete fluctuations as a function of the actual concentration, without bothering about the proper time scale.

3. THE RELEVANCE OF DISCRETE FLUCTUATIONS: SOME BASIC EXAMPLES

We have seen that discrete fluctuations in the particle number always exist. The question is, then, when do these fluctuations become important

to the extent that they influence the reaction rate significantly? It is hard to answer this question in a general way. However, in many cases the answer is self-evident. Van Kampen's Ω -expansion provides us with a formal way for evaluating the magnitude of discrete fluctuations. In some cases it is enough to compare these discrete fluctuations to other fluctuation sources, such as spatial fluctuations in concentration, thus obtaining the answer to whether discrete fluctuations are relevant or not. We recall^(5,6) in the following the example of two-species annihilation, for which spatial fluctuations in concentration play the most significant role. We then introduce some variations to this process, for which discrete fluctuations become as relevant as, or even more relevant than, spatial fluctuations in concentration, and study these models.

3.1. Two-Species Annihilation

The irreversible process of two-species annihilation



is a good example showing the essential physical considerations that are *usually* sufficient to predict the anomalous kinetics of a diffusion-limited reaction. Let us reproduce^(5,11) the reasoning done for the solution of this process. Consider the case in which there are initially the same concentrations of A and B particles, $c_A(0) = c_B(0) = c(0)$. We focus our attention on a domain of linear size l . In this domain there are initially of the order of $c(0) \pm [c(0) l^d]^{1/2}$ of the A and B particles. The uncertainty in the number of particles is due to their random distribution. These fluctuations are, in fact, spatial fluctuations in concentration. After a time of the order $t \sim l^2$, the particles in the domain would have had the chance to mix and interact with each other. This scaling of time with length is due to the diffusion mechanism, and t is a measure of the time that it would take a random walker to get across the domain of linear size l . After this time t , then, there would be left in the domain of the order of $[c(0) l^d]^{1/2}$ particles of the species that was initially in the majority. The concentration would then be

$$c(t) \sim [c(0) l^d]^{1/2} / l^d \sim [c(0)]^{1/2} t^{-d/4} \quad (3.2)$$

This is to be compared with the prediction of the mean-field rate equations that $c(t) = 1/[kt + 1/c(0)]$. The decay of the concentration is anomalous for low space dimensionalities, and the mean-field limit is reached when $d = 4$ (upper critical dimensionality). Note that in the derivation of (3.2) the conservation law for the particle number difference

$$N_A(t) - N_B(t) = \text{const} \quad (3.3)$$

has implicitly been used.

Let us now analyze discrete fluctuations and see why it was not necessary to include them in the reasoning leading to (3.2). We write a master equation for $P(N_A, N_B; t)$, the probability of having N_A of the A particles and N_B of the B particles at time t ,

$$\frac{\partial P(N_A, N_B; t)}{\partial t} = \Omega k \cdot (E_A E_B - 1) \frac{N_A N_B}{\Omega \Omega} P(N_A, N_B; t) \quad (3.4)$$

Here E_A is a raising operator defined by $E_A f(N_A) = f(N_A + 1)$, and E_B is the analogous raising operator for N_B . We now apply the Van Kampen formalism and substitute

$$N_A = \Omega \phi_A + \sqrt{\Omega} \xi_A \quad (3.5a)$$

$$N_B = \Omega \phi_B + \sqrt{\Omega} \xi_B \quad (3.5b)$$

and

$$P(N_A, N_B; t) = \Pi(\xi_A, \xi_B; t) \quad (3.5c)$$

After going through the stages sketched in Section 2, we find that the coefficients of the singular $\Omega^{1/2}$ terms give the mean field rate equations

$$\dot{\phi}_A = \dot{\phi}_B = -k \cdot \phi_A \phi_B \quad (3.6)$$

From the Ω^0 terms we get the Fokker-Planck equation

$$\begin{aligned} \frac{\partial \Pi}{\partial t} = k \cdot & \left[\left(\frac{\partial}{\partial \xi_A} + \frac{\partial}{\partial \xi_B} \right) (\phi_B \xi_A + \phi_A \xi_B) \Pi \right. \\ & \left. \frac{1}{2} \left(\frac{\partial}{\partial \xi_A} + \frac{\partial}{\partial \xi_B} \right)^2 \phi_A \phi_B \Pi \right] \end{aligned} \quad (3.7)$$

Finally, using this Fokker-Planck equation, we get equations for the fluctuation moments $\langle \xi^m \rangle$. The solution of the equations for the second moments can be cast into the form

$$\langle (N_A - \langle N_A \rangle)^2 \rangle = \frac{1}{3} \langle N_A \rangle \left[1 - \left(\frac{\langle N_A \rangle}{N_A(0)} \right)^3 \right] \quad (3.8a)$$

and

$$\langle (N_A - \langle N_A \rangle)^2 \rangle = \langle (N_B - \langle N_B \rangle)^2 \rangle = \langle (N_A - \langle N_A \rangle)(N_B - \langle N_B \rangle) \rangle \quad (3.8b)$$

when we assume, for convenience, that all the initial fluctuations are zero.

Indeed there develop discrete fluctuations, as anticipated. However, from Eq. (3.8b) we see that

$$\langle [(N_A - N_B) - (\langle N_A \rangle - \langle N_B \rangle)]^2 \rangle = 0 \tag{3.9}$$

This means that there are no fluctuations to the conservation law, Eq. (3.3). Recall that this is precisely the conservation law used in deriving the anomalous reaction rate of the system, Eq. (3.2). Thus, we are allowed to disregard discrete fluctuations because they do not affect any of the reasoning leading to (3.2).

Actually, the result (3.9) is trivial, and it could be derived by observing that the particle number difference $N_A - N_B$ is *locally* conserved, i.e., it is conserved for each single reaction that takes place, and therefore it cannot have any fluctuations. Nevertheless, we applied the Van Kampen formalism to provide one further example, and to give evidence of its accuracy.

3.2. Variations of the Two-Species Annihilation Process Affected by Discrete Fluctuations

Consider now the process⁽¹²⁾



where the two possibilities can occur with equal probabilities. If we let each of the two possibilities occur with the same rate k as in the original process, Eq. (3.1), it is represented by the master equation

$$\frac{\partial P(N_A, N_B; t)}{\partial t} = \Omega k \cdot [(E_A - 1) + (E_B - 1)] \frac{N_A}{\Omega} \frac{N_B}{\Omega} P(N_A, N_B; t) \tag{3.11}$$

The rate equations for this process are exactly the same as Eq. (3.6) for the $A + B \rightarrow \text{inert}$ process. Thus, for example,

$$\langle N_A(t) \rangle - \langle N_B(t) \rangle = \text{const} \tag{3.12}$$

is a conservation law (derived from the rate equations) analogous to (3.3). However, note that the conservation law (3.12) is stated in terms of the *average* quantities $\langle N_A \rangle$, $\langle N_B \rangle$. In fact, the particle number difference for the process in Eq. (3.10) is merely *globally* conserved, i.e., only on the average. Whenever a single $A + B \rightarrow A$ or $A + B \rightarrow B$ reaction takes place, the particle number difference $N_A - N_B$ changes by +1 or -1 (depending on which of the two possibilities occurs). Thus, $N_A - N_B$ is described by a perfect one-dimensional random walk, and

$$\langle [N_A(t) - N_B(t)]^2 \rangle = \text{number of reactions} = N(0) - N(t) \tag{3.13}$$

where $N(t) = N_A(t) + N_B(t)$ is the total number of particles in the system at time t . The Ω -expansion performed on Eq. (3.11) confirms these results.

If we try now to argue along the same lines as for the $A + B \rightarrow \text{inert}$ process (Section 3.1), we should have to consider the discrete fluctuations in the conservation law $\langle N_A \rangle - \langle N_B \rangle = \text{const}$. Consider, again, a domain of linear size l . After a time $t \sim l^2$ the particles in the domain would have reacted with each other. Since $N_A - N_B$ is conserved (though only on the average), we still expect a contribution from spatial fluctuations in concentration of the order of $[N(0)]^{1/2}$. In addition, discrete fluctuations in $N_A - N_B$ would make a contribution of the *same* order of magnitude. Thus, the decay law for concentration will not differ qualitatively from (3.2). However, discrete fluctuations become as important as spatial fluctuations in concentration and their effect is measurable. A trivial effect, due to discrete fluctuations, is that starting with the same initial number of A and B particles in the system, the final state would consist of the order of $[N(0)]^{1/2}$ particles of one of the species, as opposed to the final state of the equivalent $A + B \rightarrow \text{inert}$ process, which would be depleted. The effect of discrete fluctuations is demonstrated in Fig. 1. This is a schematic plot of $N(t)$ and $N_A(t) - N_B(t)$ as a function of the number of reactions up to time t . The number of B particles is proportional to the gap between the two

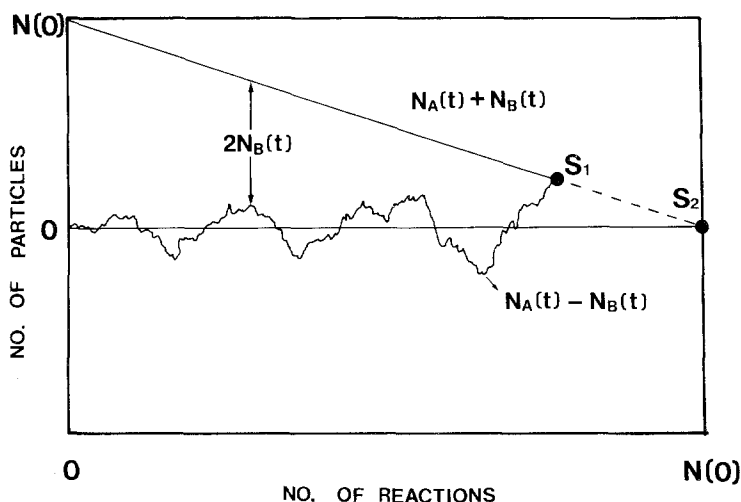


Fig. 1. Schematic representation of the $A + B \rightarrow \text{either A or B}$ process. Shown is the total number of particles $N(t) = N_A(t) + N_B(t)$ and the particle number difference $N_A(t) - N_B(t)$ as a function of the number of reactions. The process ends when the two curves meet at S_1 [or when $N_A(t) - N_B(t) = -N(t)$]. For the $A + B \rightarrow \text{inert}$ process $N_A(t) - N_B(t) = 0$, and the process goes on until the totally depleted state S_2 is reached.

curves, and the process ends when the two curves cross, with the system consisting of only A particles. Another possibility is that the process ends when the curve representing $N_A(t) - N_B(t)$ crosses the curve of $-N(t)$. In this case the final state of the system will consist of only B particles. Only the first possibility is shown in Fig. 1.

A more dramatic effect of discrete fluctuations is found in the two-species annihilation process with a correlated initial distribution⁽⁵⁾ of particles. Suppose that in the initial state the particles are deposited in pairs. That is, pairs of A and B particles (occupying adjacent sites) are randomly distributed in a lattice. If the process $A + B \rightarrow \text{inert}$ takes place, the argument leading to Eq. (3.2) fails. In a domain of linear size l there are initially *equal* amounts of A and B particles. After a time $t \sim l^2$ there is left an amount of particles of the order of unity. Thus, for the $A + B \rightarrow \text{inert}$ process with correlated initial conditions

$$c(t) \sim 1/l^d \sim 1/t^{d/2} \quad (3.14)$$

In contrast, consider the $A + B \rightarrow \text{either A or B}$ process with correlated initial conditions. After a time $t \sim l^2$ there would be left in the domain not of the order of unity, but of the order of $[c(0) l^d]^{1/2}$ particles of one of the species, generated by the discrete fluctuations in the particle number difference. Thus,

$$c(t) \sim [c(0)]^{1/2} / t^{d/4} \quad (3.15)$$

Discrete fluctuations in concentration *dominate* the process $A + B \rightarrow \text{either A or B}$ with correlated initial conditions, to the extent that the decay law for the process is qualitatively different than that for the analogous $A + B \rightarrow \text{inert}$ process. Numerical results of computer simulations of the various cases discussed above will now be presented.

3.3. Numerical Results for Two-Species Annihilation

In order to test the various predictions made above, we performed several Monte Carlo simulations for the processes $A + B \rightarrow \text{inert}$ and $A + B \rightarrow \text{either A or B}$ with totally random as well as with pair-correlated initial distributions. The simulations of these four cases were performed on a one-dimensional lattice. A particle is represented by an occupied site on the lattice, and its diffusion is simulated by a random walk with a probability 1/2 of stepping to either one of the adjacent sites. A reaction takes place immediately upon collision of an A and a B particle. The two particles are then removed from the system for the $A + B \rightarrow \text{inert}$ process, whereas only one of the particles is removed, at random, for the

$A + B \rightarrow$ either A or B process. With each particle move, time is increased by $1/N(t)$. We used periodic boundary conditions.

In Fig. 2 we plot the results for all four cases as obtained from some typical runs. The lattice consists of 1,000,000 sites, and $N_A(0) = N_B(0) = 150,000$. Shown is $\ln[N_A(t)]$ against $\ln t$. The case of $A + B \rightarrow$ inert with a totally random initial distribution was used as a test for the reliability of our simulations. Its simulations show good agreement with results presented in the past^(5,11) and with the theoretical prediction of Eq. (3.2). The case of $A + B \rightarrow$ either A or B with a totally random initial distribution shows almost the same results. Curiously enough, the *combined* effect of spatial fluctuations in concentration and of discrete fluctuations is very much like that of fluctuations in concentration alone, even quantitatively.

The case of $A + B \rightarrow$ inert with a pair-correlated initial distribution shows the expected decay of concentration going as $1/t^{1/2}$ [Eq. (3.14)]. This is due to the absence of spatial fluctuations in concentration in the initial state. This situation is preserved as the process goes on by virtue of the conservation of the particle number difference. In contrast, in the case of $A + B \rightarrow$ either A or B with a pair-correlated initial distribution, in spite of the absence of spatial fluctuations in the initial state, concentration

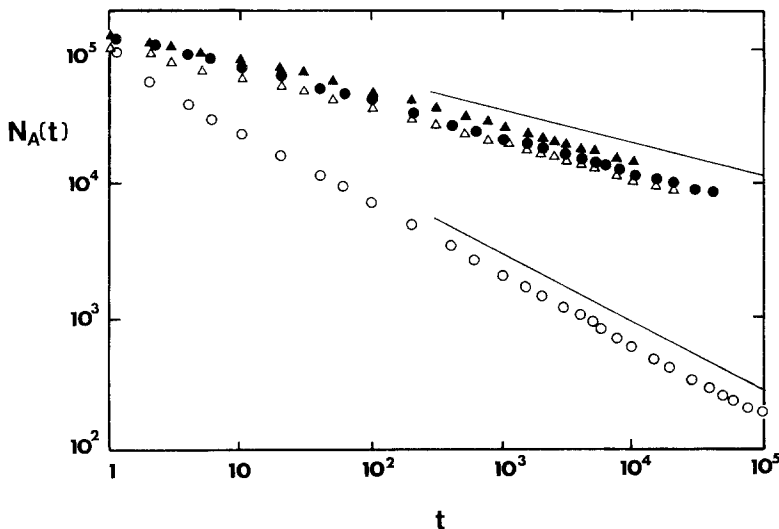
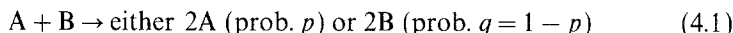


Fig. 2. Simulation results of the various two-species annihilation processes discussed in the text. Shown is $\ln N_A(t)$ against $\ln t$ for the $A + B \rightarrow$ inert process with (\bullet) a totally random and (\circ) with a pair-correlated initial distribution, and for the $A + B \rightarrow$ either A or B process with (\blacktriangle) a totally random and (\triangle) with a pair-correlated initial distribution. Solid lines with slope $-1/2$ and $-1/4$ are shown for comparison.

decays as $1/t^{1/4}$. Because of discrete fluctuations, the particle number difference is no longer locally conserved, resulting in the growing of spatial fluctuations as the process evolves. This is in agreement with our prediction, Eq. (3.15), and proves that discrete fluctuations can dominate the kinetics of the system. Indeed, discrete fluctuations play here the same role as spatial fluctuations in concentration when the initial distribution is totally random.

4. THE "CONVERSION PROCESS"

Consider now the irreversible process in which upon reaction one of the species "converts" into the other



We can imagine A and B as representing different phases of a substance. For example, A could represent a water molecule and B a vapor molecule. Then Eq. (4.1) could describe a process in which a vapor molecule impinges on the water surface, with the result that it either sticks (with probability p) or bounces, knocking another water molecule out to the vapor phase (probability q). In the most general case the probabilities p and q might vary and have a dependence on parameters such as $N_A(t)$ or the interface shape, etc. Of course, Eq. (4.1) can hardly be counted as a model for phase transitions, since many other micromechanisms by which the equilibrium between the two phases could be maintained have not been taken into account. We merely suggested a possible interpretation of (4.1) which might be useful to keep in mind. Surely, one could find some other interpretations of (4.1) as a sociological or a biological process.

The master equation is

$$\begin{aligned} \frac{\partial P(N_A, N_B; t)}{\partial t} &= \Omega k \cdot [p(E_A^{-1} E_B - 1) + q(E_A E_B^{-1} - 1)] \\ &\times \frac{N_A}{\Omega} \frac{N_B}{\Omega} P(N_A, N_B; t) \end{aligned} \quad (4.2)$$

The Ω -expansion analysis yields the rate equations

$$\dot{c}_A(t) = -\dot{c}_B(t) = -k \cdot (p - q) c_A(t) c_B(t) \quad (4.2)$$

For p and q constants, we get for the fluctuations

$$\langle (N_A - \langle N_A \rangle)^2 \rangle = \frac{\langle N_A(t) \rangle}{|p - q|} \left(1 - \frac{\langle N_A(t) \rangle}{N_A(0)} \right), \quad p \neq q \quad (4.4a)$$

and

$$\langle (N_A - \langle N_A \rangle)^2 \rangle = \langle (N_B - \langle N_B \rangle)^2 \rangle = -\langle (N_A - \langle N_A \rangle)(N_B - \langle N_B \rangle) \rangle \quad (4.4b)$$

Note that, from (4.4b),

$$\langle \{ [N_A(t) + N_B(t)] - [\langle N_A(t) \rangle + \langle N_B(t) \rangle] \}^2 \rangle = 0$$

in agreement with the obvious *local* conservation of $N_A(t) + N_B(t)$. Actually, the “conversion” process can be analyzed without the aid of the Ω -expansion. We observe that upon each new reaction, $N_A(t)$ either increases by 1 (with probability p) or decreases by 1 (with probability q). Thus, $N_A(t)$ is described by a biased random walk,⁽¹³⁾ whose properties are well understood. In the case that p and q have a dependence on $N_A(t)$, the process maps to the much studied problem of a random walker in a potential field (e.g., Ref. 14).

The relevance of discrete fluctuations to the kinetics of the “conversion” process is most easily shown for the simplest case, where $p = q = 1/2$. In this case $N_A(t)$ performs an unbiased random walk with absorbing boundary points at $N_A(t) = 0$ and at $N_A(t) = N_A(0) + N_B(0)$. Clearly, the system evolves to a final state consisting of particles of only one of the species (A or B). In contrast, the mean-field rate equations for the “conversion” process with $p = q = 1/2$ are

$$\dot{c}_A(t) = \dot{c}_B(t) = 0 \quad (4.5)$$

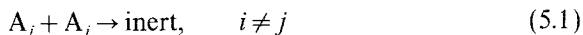
predicting that the initial state is stationary. Thus, we have presented an extreme example where discrete fluctuations are indispensable for the evolution of the system, and the process would not occur were it not for discrete fluctuations.

5. *N*-SPECIES ANNIHILATION AND DISCUSSION

While the examples of the $A + B \rightarrow$ either A or B and the “conversion” processes presented above demonstrated the relevance of discrete fluctuations to the kinetics of reactions, one might get the erroneous impression that a random choice between possible reaction channels is essential. Also, though the Van Kampen Ω -expansion was suggested as a formal method for the evaluation of discrete fluctuations, we could do as well with a simple-minded approach for each of our examples. We recall⁽¹²⁾ now the process of n -species annihilation as a further, nontrivial example of the effect of discrete fluctuations. There is no random choice between reaction channels in this process; nevertheless, discrete fluctuations are relevant to the kinetics of the system. Moreover, we were not able to find any sim-

ple-minded way for deriving the magnitude of the discrete fluctuations, but these were straightforwardly derived using Van Kampen's Ω -expansion.

The n -species annihilation process involves a system with n species A_1, A_2, \dots, A_n initially present with equal concentrations. Any two different species react irreversibly



For $n=2$ the process degenerates to the two-species annihilation process, $A + B \rightarrow \text{inert}$ (Section 3). For $n \rightarrow \infty$, the restriction that a species does not interact with itself is neglected, and the process parallels the one-species annihilation process, $A + A \rightarrow \text{inert}$ (Section 2). Thus, for the range of finite $n > 2$, the model interpolates between these two important reaction schemes. A *global* conservation law can be derived from the mean-field rate equations

$$\prod_{j=2}^n (c_{A_1} - c_{A_j}) / c_{A_1}^{n-2} = \text{const} \quad (5.2)$$

A_1 is arbitrarily chosen and Eq. (5.2) can in fact be rewritten, singling out any one of the A_j . A simple-minded argument based on this conservation law and which invokes spatial fluctuations in concentration (as for the two-species annihilation process in Section 3.1) does not yield satisfactory results, and one is led to consider the effect of discrete fluctuations.

The physical picture is as follows. The n species in a domain of linear size l react until one of the species is eliminated, leaving only $n-1$ species in the domain. By analyzing discrete fluctuations (using Van Kampen's Ω -expansion), we realize that after one of the species is eliminated there remain in the domain of the order of $[c_A(0) l^d]^{(n-2)/(n-1)}$ particles of each of the remaining $n-1$ species. Note that for $n > 3$ this is larger than the particle number difference

$$N_{A_i}(0) - N_{A_j}(0) \sim [c_A(0) l^d]^{1/2}$$

arising from spatial fluctuations in concentration. Now the $n-1$ remaining species react until another species in the domain is eliminated. Substituting $n-1$ for n , we see that there would then remain of the order of

$$[c_A(0) l^d]^{[(n-2)/(n-1)](n-3)/(n-2)} = [c_A(0) l^d]^{(n-3)/(n-1)}$$

particles of the $n-2$ remaining species. The same reasoning goes on until we are left with only three species in the domain. Then, for the first time, spatial fluctuations in concentration become of the same order of magnitude as discrete fluctuations. By the time the third species is eliminated, we are left (by either kind of fluctuation-dominated mechanism) with of the order of $[c_A(0) l^d]^{1/(n-1)}$ particles of each of the remaining two species. Now, for the last stage, spatial fluctuations are the

only relevant ones, and we are left with of the order of $[c_A(0)l^d]^{1/2(n-1)}$ particles of the last species in the domain. Since the whole process described above takes place at a time $t \sim l^2$, we have

$$c(t) \sim c(0)^{1/2(n-1)} t^{-(d/2)[1-1/2(n-1)]} \quad (5.3)$$

This was confirmed by extensive numerical simulations. Equation (5.3) interpolates, as expected, between the known results for one-species annihilation (for $n \rightarrow \infty$) and two-species annihilation (for $n = 2$).

In conclusion, we have emphasized the role of discrete fluctuations in determining the anomalous kinetics of reaction processes. We showed how the Van Kampen Ω -expansion provides us with a formal elegant way for evaluating their order of magnitude. Some simple examples of processes in which discrete fluctuations are relevant were presented and studied in Sections 3 and 4. We also reviewed the n -annihilation process, which is a nontrivial example of a case where discrete fluctuations are highly relevant, and for which Van Kampen's Ω -expansion proves to be most useful in providing us with their order of magnitude. One of the most interesting open questions is to find a rule for deciding when discrete fluctuations are relevant and when can we safely ignore them.

ACKNOWLEDGMENTS

It is a pleasure to thank S. Redner and F. Leyvraz for their interest and their help throughout all stages of this work. I acknowledge the support of the Weizmann Fellowship and partial support of grants from the U. S. Army Research Office, which made this work possible.

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