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Stochastic Approach to the Random Activation Energy Model with a Rate-Determining Step. Universal Behavior for the Probability of Concentration Fluctuations

Marcel O. Vlad,*,†,‡ Stefan Müller,§ and John Ross†

Department of Chemistry, Stanford University, Stanford, California 94305-5080, Center of Mathematical Statistics, Casa Academiei Romane, Calea 13 Septembrie 13, Bucharest 5 Romania, and Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Unversitätsplatz 2, D-39106 Magdeburg, Germany

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We study the concentration fluctuations for a reversible overall reaction with a rate-determining step occurring in a system with static disorder described in terms of the random activation energy model. We assume that the rates of the forward and backward reactions can be expressed as products of random rate coefficients times concentration dependent factors, which can also depend on nonrandom quasiequilibrium constants such as adsorption coefficients or Michaelis−Menten constants. Further, we take the activation energies of the forward and backward processes to have a random component ΔE, which is selected from a frozen Maxwell−Boltzmann distribution. We derive a stochastic evolution equation for the joint probability density of the reaction extent ξ and of the random component ΔE of the activation barrier. The solution of this stochastic evolution equation leads to a general expression for the probability density $\mathscr{P}(\xi,t)$ of the reaction extent ξ at time t. For a long time, the probability density $\mathscr{P}(\xi,t)$ of concentration fluctuations approaches its stationary value $\mathscr{P}_{\rm st}(\xi)$, according to a universal power scaling law, which is independent of the detailed kinetics of the process $\mathscr{P}(\xi,t) \approx \mathscr{P}_{\rm st}(\xi) + t^{-\alpha}C(\xi)$ as $t \to \infty$, where α is a fractal exponent between 0 and 1 and $C(\xi)$ is a concentration dependent amplitude factor. A similar behavior is displayed by systems approaching a nonequilibrium steady state. We generalize our analysis to multiple overall reactions and to systems with dynamic disorder and develop methods for extracting kinetic information from experimental data.

1. Introduction

The random activation energy model is a popular approach for describing the kinetics of rate processes in systems with static disorder.[1] This model is based on the assumption that the activation energies of the rate coefficients have random components selected from certain probability laws, typically frozen Maxwell−Boltzmann distributions. The random activation energy model is essentially a statistical process with multiplicative noise, which leads to serious mathematical difficulties. For this reason, most studies in this field are based on the assumption that the concentration fluctuations can be neglected. However, the study of concentration fluctuations for random activation energy systems with linear kinetics shows that the coupling of concentration fluctuations with the fluctuations of the rate coefficient leads to an intermittent behavior,[2] which suggests that for disordered systems the concentration fluctuations play a more important role than in ordinary chemical kinetics.

In this article, we study the interaction between the ordinary concentration fluctuations and the fluctuations of the rate coefficients described by the random activation energy model for nonlinear reaction systems described by a single overall reaction. We show that for such systems the long-time behavior of the probability of concentration fluctuations and its moments and cumulants is described by universal power laws in time with scaling exponents that are independent of the detailed kinetics of the process. The structure of the paper is the following. In section 2, we give a general formulation of the problem. In section 3, we derive general stochastic evolution equations for static disordered kinetics and show that their solutions are related to the solutions of stochastic evolution equations for chemical systems with a single overall reaction and without disorder. In section 4, we study the asymptotic behavior for static disordered systems. In section 5, we investigate the generalization of our approach for systems with multiple overall reactions and dynamic disorder. Finally in section 6, we analyze the theoretical and experimental implications of our theory.

2. Formulation of the Problem

We consider a complex chemical process with a rate-determining step,[3] which can be represented by a single overall reaction

$$\sum_{u=1}^{S} \nu_u^{+} A_u \rightleftarrows \sum_{u=1}^{S} \nu_u^{-} A_u \tag{1}$$

We assume that the forward and backward reaction rates $r_\pm$, corresponding to the overall process (eq 1), can be represented as[3−4]

$$r_\pm = k_\pm g_\pm(\mathbf{A},\mathbf{K}) \tag{2}$$

where $g_\pm(\mathbf{A},\mathbf{K})$ are complicated functions of the concentration

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* Author to whom correspondence may be addressed. E-mail: marceluc@standord.edu.
† Stanford University.
‡ Casa Academiei Romane.
§ Otto-von-Guericke-Universität Magdeburg.

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vector **A** and of the vector of **K** of quasiequilibrium constants, such as adsorption coefficients or Michaelis−Menten constants

$$k_{\pm} = \mathscr{A}_{\pm} \exp\left(-\frac{E_{\pm} + \Delta E_{\pm}}{k_B T}\right) \tag{3}$$

are activated overall rate coefficients, $\mathscr{A}_{\pm}$ are pre-exponential factors, $E_{\pm}$ and $\Delta E_{\pm}$ are deterministic and random components of the activation energies, respectively, k_B is Boltzmann's constant, and T is the temperature of the system. According to the theory of reactions with one rate-determining step,[3−4] the rate coefficients $k_{\pm}$ of the forward and backward reactions fulfill the condition

$$k_+/k_- = (K_{eq})^{1/\sigma*} \tag{4}$$

where $\sigma*$ is the stoichiometric number of the rate-determining step and K_{eq} is the equilibrium constant of the overall reaction 1, which is nonrandom. From eqs 3 and 4, it follows that

$$\Delta E_+ = \Delta E_- = \Delta E \tag{5}$$

because otherwise the equilibrium constant K_{eq} would be random.

The composition of the system can be represented in terms of a single chemical variable, the intensive reaction extent ξ of the overall reaction 1. We have

$$d\xi = dA_u/(\nu_u^- - \nu_u^+) \tag{6}$$

By use of the Schroedinger analogy for the chemical master equation,[5] it follows that the composition fluctuations can be described by the following chemical Hamiltonian operator

$$\mathrm{H}_{\mathrm{disordered}}\left[\xi,\frac{\partial}{\partial\xi}\right].... = k_+\left[1 - \exp\left(-\Omega^{-1}\frac{\partial}{\partial\xi}\right)\right][g_+(\xi,\mathbf{K})...] + k_-\left[1 - \exp\left(+\Omega^{-1}\frac{\partial}{\partial\xi}\right)\right][g_-(\xi,\mathbf{K})...] \tag{7}$$

where

$$g_-(\xi,\mathbf{K}) = g_{\pm}(\mathbf{A}(0) + \xi[\nu_u^- - \nu_u^+],\mathbf{K}) \tag{8}$$

and Ω is the system size.

We assume[1,6] that the random component ΔE of the activation energies is selected from an exponential probability density

$$P(\Delta E)d\Delta E = \beta \exp(-\beta\Delta E)d\Delta E \quad \text{with} \quad \int_0^\infty P(\Delta E)d\Delta E = 1 \tag{9}$$

where the factor $\beta = 1/\langle\Delta E\rangle$ is in general a function of the system temperature T which obeys the constraint

$$\alpha = \beta k_B T = (k_B T)/\langle\Delta E\rangle < 1 \tag{10}$$

If $\beta = 1/(k_B T_*)$ with $T_* > T$, then eq 9 corresponds to a frozen Maxwell−Boltzmann distribution corresponding to the temperature T_*.

Given the above assumptions, the purpose of the present article is to evaluate the probability density $P(\xi,t)$ of concentration fluctuations at time t and to evaluate its asymptotic behavior in the thermodynamic limit and/or for a long time.

3. Stochastic Evolution Equation Approach to Static Disordered Kinetics

We introduce the joint probability

$$\mathscr{B}(\xi,\Delta E;t)d\xi d\Delta E \quad \text{with} \quad \int_0^\infty \int_0^\infty \mathscr{B}(\xi,\Delta E;t)d\xi d\Delta E = 1 \tag{11}$$

of the reaction extent ξ and of the random component ΔE of the energy barriers at time t and the conditional probability

$$\mathscr{R}(\xi|\Delta E;t)d\xi \quad \text{with} \quad \int_0^\infty \mathscr{R}(\xi|\Delta E;t)d\xi = 1 \tag{12}$$

The simplest version of the random activation energy model assumes static disorder; that is, a fluctuation of the energy barrier, once it occurs, lasts forever. Under these circumstances, the probability density of ΔE is time invariant and given by eq 9. It follows that

$$\mathscr{R}(\xi|\Delta E;t)d\xi = \mathscr{B}(\xi,\Delta E;t)d\xi/P(\Delta E) \tag{13}$$

Considering a given random fluctuation ΔE of the energy barriers an evolution equation for the conditional probability density $\mathscr{R}(\xi|\Delta E;t)$ can be derived in terms of the chemical Hamiltonian (eq 7)

$$\frac{\partial}{\partial t}\mathscr{R}(\xi|\Delta E;t) = -\Omega^{-1}\mathrm{H}_{\mathrm{disordered}}\left[\xi,\frac{\partial}{\partial\xi}\right]\mathscr{R}(\xi|\Delta E;t) \tag{14}$$

From eqs 3, 4, and 7, we notice that the chemical Hamiltonian (eq 7) can be expressed as

$$\mathrm{H}_{\mathrm{disordered}}\left[\xi,\frac{\partial}{\partial\xi}\right].... = \chi(\Delta E)\mathrm{H}_{\mathrm{ordered}}\left[\xi,\frac{\partial}{\partial\xi}\right].... \tag{15}$$

where

$$\chi(\Delta E) = \exp(-\Delta E/k_B T) \tag{16}$$

is a random transparence factor and

$$\mathrm{H}_{\mathrm{ordered}}\left[\xi,\frac{\partial}{\partial\xi}\right].... = \mathscr{A}_- \exp\left(-\frac{E_-}{k_B T}\right) \times \left\{(K_{eq})^{1/\sigma*}\left[1 - \exp\left(-\Omega^{-1}\frac{\partial}{\partial\xi}\right)\right][g_+(\xi,\mathbf{K})...] + \left[1 - \exp\left(+\Omega^{-1}\frac{\partial}{\partial\xi}\right)\right][g_-(\xi,\mathbf{K})...]\right\} \tag{17}$$

is the chemical Hamiltonian corresponding to a system without disorder for which $\Delta E = 0$.

By combining eqs 13−17, we can derive the following evolution equation for the joint probability density $\mathscr{B}(\xi,\Delta E;t)$

$$\frac{1}{\chi(\Delta E)}\frac{\partial}{\partial t}\mathscr{B}(\xi,\Delta E;t) = -\Omega^{-1}\mathrm{H}_{\mathrm{ordered}}\left[\xi,\frac{\partial}{\partial\xi}\right]\mathscr{B}(\xi,\Delta E;t) \tag{18}$$

By assuming that the fluctuations of the energy barriers are independent of the initial fluctuations of the reaction extent ξ at $t = 0$, the initial condition for the evolution eq 18 is

$$\mathscr{B}(\xi,\Delta E;0) = P(\Delta E)\mathscr{P}^0(\xi) \tag{19}$$

Now we consider a system for which the fluctuations of the energy barriers do not exist, that is, $\Delta E = 0$. Such a system is described by the evolution equation

$$\frac{\partial}{\partial t}\mathscr{P}_{\text{ordered}}(\xi;t) = -\Omega^{-1}\mathrm{H}_{\text{ordered}}\left[\xi,\frac{\partial}{\partial \xi}\right]\mathscr{P}_{\text{ordered}}(\xi;t) \quad (20)$$

with the initial condition

$$\mathscr{P}_{\text{ordered}}(\xi;0) = \mathscr{P}^{0}(\xi) \quad (21)$$

where $\mathscr{P}_{\text{ordered}}(\xi;t)$ is the probability density of the reaction extent ξ at time t. Equation 20 is a standard chemical master equation without disorder, which has been extensively studied in the literature. In some cases, such as first-order reaction networks or simple irreversible nonlinear kinetics, exact analytical solutions are available. Otherwise an asymptotic solution can be derived in the thermodynamic limit by means of the eikonal (Wentzel−Kramers−Brillouin) approximation.[5] The eikonal approximation leads to the following expression for the probability density $\mathscr{P}_{\text{ordered}}(\xi;t)$

$$\mathscr{P}_{\text{ordered}}(\xi;t) = \mathscr{Z}(t)^{-1}\exp[\Omega\mathscr{J}(\xi;t)] \quad \text{as} \quad \Omega \to \infty \quad \text{with} \quad \xi = \text{constant} \quad (22)$$

where

$$\mathscr{Z}(t) = \int \exp[\Omega\mathscr{J}(\xi;t)]d\xi \quad (23)$$

is a nonequilibrium chemical partition function and $\mathscr{J}(\xi;t)$ is a chemical action, which is the solution of the Hamilton−Jacobi equation

$$\frac{\partial}{\partial t}\mathscr{J}(\xi;t) + \mathrm{H}_{\text{ordered}}\left[\xi,\frac{\partial}{\partial \xi}\mathscr{J}(\xi;t)\right] = 0 \quad (24)$$

By comparing eqs 18 and 19 with eqs 20 and 21, we notice that they have exactly the same structure. We notice that we can express the solution of eqs 20 and 21 in terms of the solution of eqs 18 and 19. We have

$$\mathscr{B}(\xi,\Delta E;t) = \mathscr{P}_{\text{ordered}}(\xi;t\chi(\Delta E))P(\Delta E) \quad (25)$$

We are interested in the evaluation of the probability

$$\mathscr{P}_{\text{disordered}}(\xi;t)d\xi \quad \text{with} \quad \int\mathscr{P}_{\text{disordered}}(\xi;t)d\xi = 1 \quad (26)$$

of the reaction extent ξ at time t for disordered systems. We obtain

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \int_0^\infty \mathscr{B}(\xi,\Delta E;t)d\Delta E = \int_0^\infty \mathscr{P}_{\text{ordered}}(\xi;t\chi(\Delta E))P(\Delta E)d\Delta E \quad (27)$$

We insert eqs 9 and 16 into eq 27 and use the integration variable $\theta = t\chi(\Delta E)$, resulting in

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\mathscr{P}_{\text{ordered}}(\xi;\theta)\, d\theta = \mathscr{P}_{\text{ordered}}(\xi;t) - t^{-\alpha}\int_0^t \theta^{\alpha}\frac{\partial}{\partial\theta}\mathscr{P}_{\text{ordered}}(\xi;\theta)\, d\theta \quad (28)$$

From eq 28, we can evaluate the moments $\langle\xi^m(t)\rangle_{\text{disordered}}$ of the intensive reaction extents for the disordered system. We obtain

$$\langle\xi^m(t)\rangle_{\text{disordered}} = \alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\langle\xi^m(\theta)\rangle_{\text{ordered}}\, d\theta = \langle\xi^m(t)\rangle_{\text{ordered}} - t^{-\alpha}\int_0^t \theta^{\alpha}\frac{\partial}{\partial\theta}\langle\xi^m(\theta)\rangle_{\text{ordered}}\, d\theta \quad (29)$$

where $\langle\xi^m(t)\rangle_{\text{ordered}}$ are the moments of the intensive reaction extent for the system without disorder. In Appendix A, we derive similar expressions for the cumulants $\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}}$ of the intensive reaction extents

$$\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}} = \alpha^m t^{-\alpha m}\sum_{n=1}^{m}\sum_{\substack{n_1,\dots,n_n\\ \Sigma_w n_w = n}}\frac{(-1)^{n-1}(n-1)!}{\prod_w n_w!}\prod_{w=1}^{m}\times \left\{\int_0^t(\theta_w)^{\alpha-1}\langle\xi^{n_w}(\theta_w)\rangle_{\text{ordered}}\, d\theta_w\right\} = \sum_{n=1}^{m}\sum_{\substack{n_1,\dots,n_n\\ \Sigma_w n_w = n}}\frac{(-1)^{n-1}(n-1)!}{\prod_w n_w!}\prod_{w=1}^{m}\left\{\langle\xi^{n_w}(t)\rangle_{\text{ordered}} - t^{-\alpha}\times \int_0^t(\theta_w)^{\alpha}\frac{\partial}{\partial\theta_w}\langle\xi^{n_w}(\theta_w)\rangle_{\text{ordered}}\, d\theta_w\right\} \quad (30)$$

In conclusion, in this section we have derived exact expressions for the time dependence of the probability density of the intensive reaction extent in a static disordered system and its moments and cumulants. These results are used in the following section for the analysis of the asymptotic behavior of concentration fluctuations in the thermodynamic limit and for a long time.

4. Asymptotic Behavior

We start out by studying the asymptotic behavior of concentration fluctuations in the thermodynamic limit. We consider large system sizes and arbitrary and finite times and introduce the extensive reaction extent

$$\Xi = \Omega\xi \quad (31)$$

In Appendix B, we show that for systems without disorder in the thermodynamic limit the cumulants $\langle\langle\Xi^m(t)\rangle\rangle_{\text{ordered}}$ of the extensive reaction extent all tend to 0 in the thermodynamic limit and the concentration fluctuations are nonintermittent.

For disordered systems in the thermodynamic limit, the probability of concentration fluctuations does not obey the eikonal scaling; however, it can be represented as a superposition of eikonal distributions. We have

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\mathscr{Z}(\theta)^{-1}\exp[\Omega\mathscr{J}(\xi;\theta)]\, d\theta \quad (32)$$

Since the eikonal scaling does not hold anymore for disordered systems, the cumulants $\langle\langle\Xi^m(t)\rangle\rangle_{\text{disordered}}$ of the extensive reaction extent are in general no longer proportional to the size of the system. By use of a method similar to the one presented in Appendix A, it is possible to derive a general formal expression for the cumulant of order m. However due to the complexity of this expression, it is hard to derive the scaling conditions for the cumulants as a function of the system size in the thermodynamic limit. Nevertheless, it is possible to evaluate these scaling conditions step by step. We come to

$$\langle\langle\Xi(t)\rangle\rangle_{\text{disordered}} \sim \Omega\alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\left(\frac{\partial\mathscr{E}(x;t)}{\partial x}\right)_{x=0} d\theta \quad \text{as} \quad \Omega \to \infty \quad (33)$$

$$\langle\langle \Xi^2(t)\rangle\rangle_{\text{disordered}} \approx \Omega\alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\left(\frac{\partial^2\mathcal{E}(x;t)}{\partial x^2}\right)_{x=0} d\theta + \Omega^2\left\{\left[\alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\left(\frac{\partial\mathcal{E}(x;t)}{\partial x}\right)_{x=0} d\theta\right]^2 - \alpha t^{-\alpha}\times \int_0^t \theta^{\alpha-1}\left[\left(\frac{\partial^2\mathcal{E}(x;t)}{\partial x^2}\right)_{x=0}\right]^2 d\theta\right\} \quad \text{as} \quad \Omega\to\infty, \text{etc.} \tag{34}$$

where $\mathcal{E}(x;t)$ is an adjoint stochastic potential introduced in Appendix B.

From eqs 33 and 34, it follows that for disordered systems the relative fluctuation of order two

$$\zeta^{(2)}_{\text{disordered}}(t) = \frac{\langle\langle \Xi^2(t)\rangle\rangle_{\text{disordered}}}{\langle\langle \Xi(t)\rangle\rangle^2_{\text{disordered}}} \tag{35}$$

tends toward a constant value as $\Omega \to \infty$

$$\zeta^{(2)}_{\text{disordered}}(t) \to 1 - \left\{\int_0^t \theta^{\alpha-1}\left[\left(\frac{\partial^2\mathcal{E}(x;t)}{\partial x^2}\right)_{x=0}\right]^2 d\theta\right\}\Bigg/ \left\{\alpha t^{-\alpha}\left[\int_0^t \theta^{\alpha-1}\left(\frac{\partial\mathcal{E}(x;t)}{\partial x}\right)_{x=0} d\theta\right]^2\right\} \quad \text{as} \quad \Omega\to\infty \tag{36}$$

It follows that for disordered systems in the thermodynamic limit the concentration fluctuations are intermittent. Here and in the following the term intermittent has the usual meaning from statistical mechanics and theory of turbulence; that is, it means that in a limit of the thermodynamic type, the relative fluctuations of different orders of the stochastic variables that describe the process do not tend toward 0.

The next step of our analysis is to study the scaling behavior of concentration fluctuations for arbitrary system sizes and a long time, $t \to \infty$. In Appendix C, we show that for a long time the probability density of concentration fluctuations tends toward the time-independent value $\mathcal{P}_{\text{ordered}}(\xi;\infty)$ according to a self-similar negative power law

$$\mathcal{P}_{\text{disordered}}(\xi;t) \approx \mathcal{P}_{\text{ordered}}(\xi;\infty) + t^{-\alpha}C(\xi) \quad \text{as} \quad t\to\infty \tag{37}$$

where $C(\xi)$ is an amplitude factor evaluated in Appendix C in terms of the eigenvalues of the chemical Hamiltonian (eq 17). An alternative but equivalent expression for $C(\xi)$ can be evaluated from eq 28. We get

$$C(\xi) = -\int_0^\infty \theta^\alpha \frac{\partial}{\partial\theta}\mathcal{P}_{\text{ordered}}(\xi;\theta)\, d\theta \tag{38}$$

Similar asymptotic expressions can be derived for moments and cumulants. We obtain

$$\langle \xi^m(t)\rangle_{\text{disordered}} \approx \langle \xi^m(\infty)\rangle_{\text{ordered}} - t^{-\alpha}\int_0^\infty \theta^\alpha \frac{\partial}{\partial\theta}\langle \xi^m(\theta)\rangle_{\text{ordered}}\, d\theta \quad \text{as} \quad t\to\infty \tag{39}$$

$$\langle\langle \xi^m(t)\rangle\rangle_{\text{disordered}} \approx \sum_{n=1}^m \sum_{\substack{n_1,\ldots,n_n \\ \sum_w n_w = n}} \frac{(-1)^{n-1}(n-1)!}{\prod_w n_w!}\prod_{w=1}^m \times \left\{\langle \xi^{n_w}(\infty)\rangle_{\text{ordered}} - t^{-\alpha}\int_0^\infty (\theta_w)^\alpha \frac{\partial}{\partial\theta_w}\langle \xi^{n_w}(\theta_w)\rangle_{\text{ordered}}\, d\theta_w\right\} \approx \langle\langle \xi^m(\infty)\rangle\rangle_{\text{ordered}} \quad \text{as} \quad t\to\infty \tag{40}$$

For finite system sizes, the relative fluctuations tend toward constant values at long times and the concentration fluctuations are intermittent

$$\zeta^{(m)}_{\text{disordered}}(t) = \frac{\langle\langle \xi^m(t)\rangle\rangle_{\text{disordered}}}{[\langle\langle \xi(t)\rangle\rangle_{\text{disordered}}]^m} \to \frac{\langle\langle \xi^m(\infty)\rangle\rangle_{\text{ordered}}}{[\langle\langle \xi(\infty)\rangle\rangle_{\text{ordered}}]^m} \quad \text{as} \quad t\to\infty \tag{41}$$

However, if both the system size and the time tend to infinity, the relative fluctuations tend to 0 and the concentration fluctuations are nonintermittent

$$\zeta^{(m)}_{\text{disordered}}(t) \to 0 \quad \text{as} \quad t\to\infty \quad \text{and} \quad \Omega\to\infty \tag{42}$$

In conclusion, in this section we have derived asymptotic scaling laws for the probability density of concentration fluctuations and its moments and cumulants for static disordered systems. For large system sizes and arbitrary times, the probability density of concentration fluctuations does not obey eikonal scaling and the concentration fluctuations are intermittent. For a long time and arbitrary system sizes the probability density of concentration fluctuations and its moments and cumulants approach time-invariant values according to negative power scaling laws and the fluctuations are also intermittent. For both large system sizes and times, the probability density of concentration fluctuations obey eikonal scaling and the fluctuations are nonintermittent.

5. Generalizations

In our derivations in sections 3 and 4, we have assumed that the system evolves toward a state of chemical equilibrium. It is easy to check that all equations derived in sections 3 and 4 also hold in the more general case where some constraints are present that prevent the system from reaching chemical equilibrium and instead the system approaches a nonequilibrium steady state.

A second generalization is a complex chemical process with many rate-determining steps, which can be represented by a set of R overall reactions[3−4]

$$\sum_{u=1}^S \nu^+_{uw}A_u \rightleftarrows \sum_{u=1}^S \nu^-_{uw}A_u \; w = 1, ..., R \tag{43}$$

We assume that the forward and backward reaction rates $r_\pm{}^{(w)}$ corresponding to the overall process (eq 1) can be represented as

$$r_\pm{}^{(w)} = k_\pm{}^{(w)}g_\pm{}^{(w)}(\mathbf{A},\mathbf{K}) \tag{44}$$

where $g_\pm{}^{(w)}(\mathbf{A},\mathbf{K})$ are complicated functions of the concentration vector $\mathbf{A}$ and of the vector of $\mathbf{K}$ of quasiequilibrium constants, such as adsorption coefficients or Michaelis−Menten constants

$$k_\pm{}^{(w)} = \mathcal{A}_\pm{}^{(w)}\exp\left(-\frac{E_\pm{}^{(w)} + \Delta E_\pm{}^{(w)}}{k_B T}\right) \tag{45}$$

are activated overall rate coefficients, $\mathcal{A}_\pm{}^{(w)}$ are pre-exponential factors, $E_\pm{}^{(w)}$ and $\Delta E_\pm{}^{(w)}$ are deterministic and random components of the activation energies, respectively, and other symbols have the same significance as before. According to the theory of multiple rate-determining steps,[3−4] the rate coefficients $k_\pm{}^{(w)}$ of the forward and backward reactions fulfill the conditions

$$k_+{}^{(w)}/k_-{}^{(w)} = (K_{\mathrm{eq}}^{(w)})^{1/\sigma_w{}^*} \tag{46}$$

where σ_w* is the stoichiometric number of the wth rate-determining step and $K_{\mathrm{eq}}^{(w)}$ is the equilibrium constant of the wth overall reaction 1, which is nonrandom. From eqs 45 and 46, we come to a set of conditions similar to eq 5

$$\Delta E_+{}^{(w)} = \Delta E_+{}^{(w)} = \Delta E^{(w)} \tag{47}$$

because otherwise the equilibrium constants $K_{\mathrm{eq}}^{(w)}$ would be random.

The composition of the system can be represented in terms of R chemical variables, the intensive reaction extents ξ_w of the overall reactions 43. We have

$$dA_u = \sum_{w=1}^{R} (\nu_{uw}{}^- - \nu_{uw}^+)\, d\xi_w \tag{48}$$

The composition fluctuations can be described by a compound chemical Hamiltonian operator

$$\mathrm{H}_{\mathrm{disordered}}[\xi,\nabla_\xi].... = \sum_{w=1}^{R} \mathrm{H}_{\mathrm{disordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right].... \tag{49}$$

where $\xi = (\xi_1, \xi_2, ...)$

$$\mathrm{H}_{\mathrm{disordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right] = k_+{}^{(w)}\left[1 - \exp\left(-\Omega^{-1}\frac{\partial}{\partial \xi_w}\right)\right] \times [g_+{}^{(w)}(\xi,\mathbf{K})...] + k_-{}^{(w)}\left[1 - \exp\left(\Omega^{-1}\frac{\partial}{\partial \xi_w}\right)\right][g_-{}^{(w)}(\xi,\mathbf{K})...] \tag{50}$$

are chemical Hamiltonians attached to overall reactions (eq 43) and

$$g_\pm(\xi,\mathbf{K}) = g_\pm(\mathbf{A}(0) + [\nu_{uw}^- - \nu_{uw}^+]\xi,\mathbf{K}) \tag{51}$$

By analogy with eq 15, the chemical Hamiltonians attached to the different overall reactions can be represented as

$$\mathrm{H}_{\mathrm{disordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right].... = \chi_w(\Delta E^{(w)})\mathrm{H}_{\mathrm{ordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right]... \tag{52}$$

where

$$\chi_w(\Delta E^{(w)}) = \exp(-\Delta E^{(w)}/k_{\mathrm{B}}T) \tag{53}$$

are random transparence factors attached to the overall reactions (eq 43) and

$$\mathrm{H}_{\mathrm{ordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right].... = \mathcal{A}_-{}^{(w)} \exp\left(-\frac{E_-{}^{(w)}}{k_{\mathrm{B}}T}\right) \times \left\{(K_{\mathrm{eq}}^{(w)})^{1/\sigma_w{}^*}\left[1 - \exp\left(-\Omega^{-1}\frac{\partial}{\partial \xi_w}\right)\right][g_+{}^{(w)}(\xi,\mathbf{K})...] + \left[1 - \exp\left(+\Omega^{-1}\frac{\partial}{\partial \xi_w}\right)\right][g_-{}^{(w)}(\xi,\mathbf{K})...]\right\} \tag{54}$$

are individual chemical Hamiltonians attached to the overall reactions (eq 43) for a system without disorder. The total chemical Hamiltonian for a system without disorder is given by

$$\mathrm{H}_{\mathrm{ordered}}[\xi,\nabla_\xi].... = \sum_{w=1}^{R} \mathrm{H}_{\mathrm{ordered}}^{(w)}\left[\xi,\frac{\partial}{\partial \xi_w}\right].... \tag{55}$$

We notice that in general the total Hamiltonian $\mathrm{H}_{\mathrm{disordered}}[\xi,\nabla_\xi]$.... cannot be expressed in a simple way in terms of $\mathrm{H}_{\mathrm{ordered}}[\xi,\nabla_\xi]$..... This is possible only if

$$\Delta E^{(1)} = ... = \Delta E^{(R)} = \Delta E \tag{56}$$

and

$$\chi_1(\Delta E^{(1)}) = ... = \chi_R(\Delta E^{(R)}) = \chi(\Delta E) = \exp(-\Delta E/k_BT) \tag{57}$$

that is, if the fluctuations of the energy barriers are collective and controlled by a single random component of the activation energies. If the conditions (eqs 56 and 57) are fulfilled, then eqs 49 and 57 lead to a condition similar to eq 15

$$\mathrm{H}_{\mathrm{disordered}}[\xi,\nabla_\xi]..... = \chi(\Delta E)\mathrm{H}_{\mathrm{ordered}}[\xi,\nabla_\xi]..... \tag{58}$$

In this case, the theory developed in sections 3 and 4 can be easily extended for multiple overall reactions. We get the following expression for the probability density of concentration fluctuations

$$\mathscr{P}_{\mathrm{disordered}}(\xi;t) = \alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}\mathscr{P}_{\mathrm{ordered}}(\xi;\theta)\, d\theta = \mathscr{P}_{\mathrm{ordered}}(\xi;t) - t^{-\alpha}\int_0^t \theta^{\alpha}\frac{\partial}{\partial \theta}\mathscr{P}_{\mathrm{ordered}}(\xi;\theta)\, d\theta \tag{59}$$

which has the same structure as eq 28 with the difference that the intensive reaction extent ξ is replaced by the vector of intensive reaction extents ξ.

If for systems without disorder for a long time the probability of concentration fluctuations evolves toward a stationary value, then the results about the large size and time behavior derived in section 4 can be easily extended for multiple overall reactions. For large size and arbitrary time as well as for long time and arbitrary size for a disordered system the concentration fluctuations are intermittent. For large sizes and finite time, the eikonal approximation does not hold. For a long time, the probability density approaches its stationary value according to a negative power law. If both the time and the system size are large, then the eikonal approximation holds and the concentration fluctuations are nonintermittent.

Another generalization corresponds to the case where the fluctuations of the energy barriers are dynamic, that is, the fluctuations of the energy barrier are random functions of time. We consider the case of multiple overall reactions with collective fluctuations, which includes the model of a single rate-determining step as a particular case. If the fluctuating component ΔE of the activaton energy barriers is a random function of time, the same is true for the transparency factor

$$\chi(t) = \exp[-\Delta E(t)/(k_{\mathrm{B}}T)] \tag{60}$$

It is convenient to introduce a random, intrinsic time scale, $\theta(t)$, which obeys the stochastic evolution equation

$$d\theta(t)/dt = \chi(t), \theta(t) = \int_0^t \chi(t')\, dt' \tag{61}$$

From eqs 58 and 61, it follows that, for a given realization $\chi(t)$ of the transparency factor, the conditional probability density of concentration fluctuations $\mathscr{P}_{\mathrm{disordered}}(\xi|\chi)$ is the solution of the master equation

$$\frac{\partial}{\partial\theta(t)}\mathscr{P}_{\text{disordered}}(\xi|\chi) = -\Omega^{-1}\mathrm{H}_{\text{ordered}}[\xi,\nabla_{\xi}]\mathscr{P}_{\text{disordered}}(\xi|\chi) \tag{62}$$

which has the same structure as the evolution equation for the probability density $\mathscr{P}_{\text{ordered}}(\xi)$ corresponding to a system without disorder

$$\frac{\partial}{\partial t}\mathscr{P}_{\text{ordered}}(\xi) = -\Omega^{-1}\mathrm{H}_{\text{ordered}}[\xi,\nabla_{\xi}]\mathscr{P}_{\text{ordered}}(\xi) \tag{63}$$

It follows that the unconditional probability density of concentration fluctuations for a disordered system, $\mathscr{P}_{\text{disordered}}(\xi;t)$, can be expressed as

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \langle\mathscr{P}_{\text{ordered}}(\xi;\theta(t))\rangle = \langle\mathscr{P}_{\text{ordered}}(\xi;\int_0^t \chi(t')\,dt')\rangle \tag{64}$$

where $\langle...\rangle$ is a dynamic average taken over all possible values of the random function $\chi(t)$.

To evaluate the dynamic average in eq 64, we represent $\mathscr{P}_{\text{ordered}}(\xi;\theta)$ as an inverse Fourier transform

$$\mathscr{P}_{\text{ordered}}(\xi;\theta) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi\,\exp(-i\varpi\theta)\bar{\mathscr{P}}_{\text{ordered}}(\xi;\varpi) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi\int_0^{\infty} dx\,\exp(i\varpi(x-\theta))\mathscr{P}_{\text{ordered}}(\xi;x) \tag{65}$$

where

$$\bar{\mathscr{P}}_{\text{ordered}}(\xi;\varpi) = \int_0^{\infty}\exp(i\varpi\theta)\mathscr{P}_{\text{ordered}}(\xi;\theta)\,d\theta \tag{66}$$

is the direct Fourier transform of $\mathscr{P}_{\text{ordered}}(\xi;\theta)$. In eq 65 we have taken into account that $\mathscr{P}_{\text{ordered}}(\xi;t < 0) = 0$. Equation 64 becomes

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \left\langle\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi \times \exp(-i\varpi\int_0^t \chi(t')\,dt')\int_0^{\infty} dx\,\exp(i\varpi x)\mathscr{P}_{\text{ordered}}(\xi;x)\right\rangle \tag{67}$$

We represent the stochastic properties of the transparence factor $\chi(t)$ in terms of the characteristic functional

$$\mathscr{J}[q(t')] = \langle\exp(i\int_0^t q(t')\chi(t')\,dt')\rangle \tag{68}$$

where $q(t')$ is a test function conjugated to the transparence factor $\chi(t')$. By assuming that in eq 67 the dynamic average and the integrals commute, we come to

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi\,\mathscr{J}[q(t') = -i\varpi]\int_0^{\infty} dx\,\exp(i\varpi x)\mathscr{P}_{\text{ordered}}(\xi;x) \tag{69}$$

Equation 69 is the generalization of eqs 28 and 59, for systems with dynamic disorder. Unlike eqs 28 and 59, in general, eq 69 does not lead to universal relaxation laws for a long time. To investigate the asymptotic of the probability of concentration fluctuations, we need a more detailed knowledge of the dynamic fluctuations of the random energy barriers.

In conclusion, in this section, we have investigated different generalizations of our approach. The results for a single overall reaction approaching equilibrium also hold for processes approaching a nonequilibrium stationary state or for multiple overall reactions with collective fluctuations of the energy barriers. It is also possible to derive general expressions of the probability of concentration fluctuations for systems with dynamic disorder. Concerning the possible experimental occurrence of the various types of disorder considered here, we emphasize that we are not aware of any experimental studies for which the collective fluctuations described in this section have been observed. We think that such collective fluctuations may exist, especially for processes where the fluctuations of the energy barriers are caused by the fluctuations of the same external random parameter, such as a random electromagnetic field.

6. Experimental Implications

Since most experiments on disordered kinetics deal with macroscopic (average) concentrations or reaction extents, the analysis in this section is focused on the study of average values. For a single overall reaction, the average intensive reaction extent can be evaluated from eqs 29 and 39

$$\langle\xi(t)\rangle_{\text{disordered}} = \langle\xi(t)\rangle_{\text{ordered}} - t^{-\alpha}\int_0^t \theta^{\alpha}\frac{\partial}{\partial\theta}\langle\xi(\theta)\rangle_{\text{ordered}}\,d\theta \approx \langle\xi(\infty)\rangle_{\text{ordered}} - t^{-\alpha}B \quad \text{as} \quad t\rightarrow\infty \tag{70}$$

with

$$B = \int_0^{\infty} t^{\alpha}\frac{\partial}{\partial t}\langle\xi(t)\rangle_{\text{ordered}}\,dt = \int_0^{\infty} t^{\alpha}r_{\text{ordered}}(t)\,dt \tag{71}$$

where $r_{\text{ordered}}(t) = r_+ - r_-$ is the net reaction rate for a system without disorder, expressed as a function of time.

Equation 70 is a generalization of similar types of asymptotic laws derived for special types of reaction kinetics. Negative power laws of the type (eq 70) have been derived in the literature both for relaxation processes as well as for first-order, irreversible reactions in disordered systems.[1] More recently, similar scaling laws have been derived for reversible, first-order kinetics[7] as well as for nonlinear, one-variable reaction kinetics in disordered systems.[8] Equation 70 describes all these situations as particular cases.

An important factor for experimental applications is the time necessary for reaching the scaling asymptotic regime described by eq 70. If the scaling regime is reached very close to the stationary regime, the experimental study of the scaling regime can be very difficult. Fortunately this is not the case. Experimental data reported in the literature[1] show that the time necessary for reaching the scaling regime is of the order of magnitude of the reaction half time. The same conclusion can be reached by simple numerical computations for isolated, irreversible reactions of first and second order. By use of simple analytic expressions for the average concentrations derived in our previous publications,[7−8] we have done simple numerical computations which show that, for an irreversible reaction of first order, the time necessary for reaching the scaling regime varies between 0.8 and 1.4 half times, depending on the numerical value of the scaling exponent α; extreme values of α, close to 0 or unity, lead to shorter times necessary for reaching the scaling regime, whereas values of α close to 0.5 lead to longer times. The behavior for second-order reactions is a bit more complicated; in this case, both the half time and the time necessary for reaching the scaling regime decrease with the increase of the initial concentration of the reacting species but in different proportions. There is no simple relation between these two times; nevertheless, the time necessary for reaching the scaling regime has the same order of magnitude for the reaction half time.

The time-dependent factor of the asymptotic kinetic law (eq 70) is universal; that is, for a long time, the power law $\sim t^{-\alpha}$ is independent of the kinetics of the process. The amplitude factor B, however, depends on the kinetics of the process. Unfortunately, it is hard to extract the kinetic information from the amplitude factor B. In the following, we come up with simple rules in the particular case of single species, irreversible ($K_{\text{eq}} \rightarrow \infty$), noncatalytic overall reactions with a single determining step. We assume that the overall reaction can be represented as

$$\nu\text{A} \rightarrow \text{Products} \tag{72}$$

and that the kinetics of the process can be represented by the mass action law and the rate of the process is given by

$$r_{\text{ordered}} = kA^n \tag{73}$$

where k is the nonrandom part of the rate coefficient. Since in general the reaction is not elementary, the reaction order n need not be equal to the stoichiometric coefficient ν. We solve the deterministic kinetic equation and use the integral kinetic equation for expressing the reaction the reaction rate r_{ordered} as a function of time. We obtain

$$r_{\text{ordered}}(t) = k(A_0)^n[1 - (1-n)(A_0)^{-(1-n)}kt]^{-n/(1-n)}\, h\left(\frac{(A_0)^{1-n}}{(1-n)k} - t\right) \quad \text{for} \quad n < 1 \tag{74}$$

$$r_{\text{ordered}}(t) = A_0 k \exp(-kt) \quad \text{for} \quad n = 1 \tag{75}$$

$$r_{\text{ordered}}(t) = k(A_0)^n[1 + (n-1)(A_0)^{n-1}kt]^{-n/(n-1)} \quad \text{for} \quad n > 1 \tag{76}$$

where $A_0 = A(0)$ and $h(x)$ is the Heaviside step function. We notice that for $n < 1$ the asymptotic scaling law is approached after a finite, although usually long, time. From eqs 74–76, we come to

$$B = k^{-\alpha}(A_0)^{1+\alpha(1-n)} \frac{\Gamma(1+\alpha)\Gamma\left(\frac{1}{1-n}\right)}{(1-n)^{1+\alpha}\Gamma\left(1+\alpha+\frac{1}{1-n}\right)} \quad \text{for} \quad n < 1 \tag{77}$$

$$B = k^{-\alpha}A_0\Gamma(1+\alpha) \quad \text{for} \quad n = 1 \tag{78}$$

$$B = k^{-\alpha}(A_0)^{1+\alpha(1-n)} \frac{\Gamma(1+\alpha)\Gamma\left(\frac{1}{n-1} - \alpha\right)}{(n-1)^{1+\alpha}\Gamma\left(\frac{n}{n-1}\right)} \quad \text{for} \quad n > 1 \quad \text{and} \quad \frac{1}{n-1} > \alpha \tag{79}$$

We suggest the following procedure for extracting kinetic information from experimental data. The procedure starts with the evaluation of the scaling exponent α. If the random activation energy model is correct, then the scaling exponent α may be dependent on temperature but must be independent of the initial concentration A_0. A first experimental consistency test of the model is the fact that repeated experiments at the same temperature but with different initial concentrations A_0 leads to the same exponent α. If this is the case, the plot ln B vs ln A_0 must be a straight line with a slope $1 + \alpha(1 - n)$. From this slope, we can evaluate the reaction order n. From B, α, and n, we can evaluate the nonrandom part k of the rate coefficient by using eqs 77–79.

The experimental study of the variation of the scaling exponent with temperature, $\alpha = \alpha(T)$, leads to information about the distribution of the random energy barriers. If $\alpha(T)$ is a linear function of the absolute temperature, then the random component ΔE of the energy barriers is distributed according to a Maxwell–Boltzmann energy law[1,9,10]

$$P(\Delta E)\, d\Delta E = (k_B T_*)^{-1} \exp(-\Delta E/(k_B T_*))\, d\Delta E \tag{80}$$

"frozen" at a constant characteristic temperature

$$T_* = 1/(\partial\alpha/\partial T) \tag{81}$$

If the scaling exponent $\alpha = \alpha(T)$ is a nonlinear function of temperature, then the distribution of energy barriers, although still exponential, is not characterized by a constant characteristic temperature.

If the distribution of energy barriers is not exponential, then the universal scaling law (eq 70) is not valid anymore. In this case, it is of interest to evaluate the distribution of energy barriers from experimental data. For an arbitrary distribution of energy barriers $P(\Delta E)\, d\Delta E$, eq 27 is replaced by

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \int_0^\infty \mathscr{P}_{\text{ordered}}(\xi;t\chi(\Delta E))P(\Delta E)\, d\Delta E = \int_0^1 \mathscr{P}_{\text{ordered}}(\xi;t\chi)\rho(\chi)\, d\chi \tag{82}$$

where

$$\rho(\chi) = \int_0^\infty \delta[\chi - \exp(-\Delta E/(k_B T))]P(\Delta E)\, d\Delta E = \frac{k_B T}{\chi}P[k_B T \ln(1/\chi)] \tag{83}$$

is the probability density of the transparence factor χ. From eq 82 we get the following expression for the average integral kinetic law

$$\langle\xi(t)\rangle_{\text{disordered}} = \int_0^1 \langle\xi(t\chi)\rangle_{\text{ordered}}\rho(\chi)\, d\chi \tag{84}$$

Now we represent the average integral kinetic law for a system without disorder, $\langle\xi(t)\rangle_{\text{ordered}}$ by an inverse Fourier transform (see also eqs 65 and 66)

$$\langle\xi(t)\rangle_{\text{ordered}} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi \exp(-i\varpi t)\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}}\, d\varpi \tag{85}$$

where

$$\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}} = \int_0^\infty \exp(i\varpi t)\langle\xi(t)\rangle_{\text{ordered}}\, dt \tag{86}$$

is the direct Fourier transform of the integral kinetic law for a system without disorder, $\langle\xi(t)\rangle_{\text{ordered}}$. In eq 85, we have taken into account that $\langle\xi(t < 0)\rangle_{\text{ordered}} = 0$. By combining eqs 84 and 85, we come to

$$\langle\xi(t)\rangle_{\text{disordered}} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\varpi \int_0^1 d\chi \times \exp(-i\varpi\chi t)\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}}\rho(\chi) \tag{87}$$

Next we introduce the characteristic function

$$\bar{\rho}(\sigma) = \int_0^{\infty} \exp(i\chi\sigma)\rho(\chi)\, d\chi = \int_0^{1} \exp(i\chi\sigma)\rho(\chi)\, d\chi \qquad (88)$$

of the probability density $\rho(\chi)$ of the transparence factor. In eq 88, we have taken into account that $\rho(\chi > 1) = 0$. By using eq 88, eq 87 becomes

$$\langle\xi(t)\rangle_{\text{disordered}} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \bar{\rho}(-\varpi t)\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}}\, d\varpi = \frac{1}{2\pi t}\int_{-\infty}^{+\infty} \bar{\rho}(\sigma)\left\langle\bar{\xi}\left(-\frac{\sigma}{t}\right)\right\rangle_{\text{ordered}} d\varpi \qquad (89)$$

Equations 84 and 89 are linear integral equations for the probability density $\rho(\chi)$ of the transparence factor and its characteristic function $\bar{\rho}(\sigma)$. By solving these equations numerically, we can evaluate the functions $\rho(\chi)$ and $\bar{\rho}(\sigma)$. Further on, by applying eq 83, we can compute the probability density of the random component of the energy barrier

$$P(\Delta E) = (k_B T)^{-1} \exp(-\Delta E/(k_B T))\rho[\exp(-\Delta E/(k_B T))] \qquad (90)$$

If experimental data are not accurate the evaluation of the functions $\rho(\chi)$ and $\bar{\rho}(\sigma)$ may not be possible. However, the first few moments of the transparency factor can still be evaluated from eq 89. We recall the moment expansion of the characteristic function $\bar{\rho}(\sigma)$

$$\bar{\rho}(\sigma) = 1 + \sum_{m=1}^{\infty} \frac{(i\sigma)^m}{m!}\langle\chi^m\rangle \qquad (91)$$

where

$$\langle\chi^m\rangle = \int_0^1 \chi^m \rho(\chi)\, d\chi \quad m = 1, 2, ... \qquad (92)$$

are the positive integer moments of the transparence factor and use a Taylor expansion of the average kinetic curve $\langle\xi(t)\rangle_{\text{disordered}}$

$$\langle\xi(t)\rangle_{\text{disordered}} = \langle\xi(0)\rangle + \sum_{m=1}^{\infty} \frac{t^m}{m!}\frac{d^m}{dt^m}\langle\xi(0)\rangle_{\text{disordered}} \qquad (93)$$

We insert eqs 91 and 93 into eq 89, resulting in

$$\langle\xi(0)\rangle - \frac{1}{2\pi}\int_{-\infty}^{+\infty}\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}}\, d\varpi + \sum_{m=1}^{\infty}\frac{t^m}{m!}\left[\frac{d^m}{dt^m}\langle\xi(0)\rangle_{\text{disordered}} - (-i)^m\langle\chi^m\rangle\frac{1}{2\pi}\int_{-\infty}^{+\infty}\varpi^m\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}} d\varpi\right] = 0 \qquad (94)$$

From eq 94, we obtain the following equations for the moments

$$\langle\chi^m\rangle = \frac{2\pi(-i)^{-m}}{\int_{-\infty}^{+\infty}\varpi^m\langle\bar{\xi}(\varpi)\rangle_{\text{ordered}}\, d\varpi}\frac{d^m}{dt^m}\langle\xi(0)\rangle_{\text{disordered}} \qquad (95)$$

An alternative set of equations for the moments can be obtained by applying a similar procedure to the integral eq 84

$$\langle\chi^m\rangle = \frac{\dfrac{d^m}{dt^m}\langle\xi(0)\rangle_{\text{disordered}}}{\dfrac{d^m}{dt^m}\langle\xi(0)\rangle_{\text{ordered}}} \qquad (96)$$

In conclusion, in this section we have investigated some experimental implications of our theory. We have introduced a consistency test for the validity of the random activation energy model in its simplest form, which assumes an exponential distribution of energy barriers. For simple kinetic models, we have introduced a simple procedure, which makes it possible to evaluate the kinetic parameters of the process, from the amplitude factor of the scaling law. For the case where the distribution of the energy barriers is not exponential, we have a general approach which makes it possible to evaluate the probability densities of the transparence factors and of the activation barriers from experimental data. We have also introduced a method for the direct evaluation of the moments of the transparence factors from experimental data.

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Appendix A

In this appendix, we evaluate the cumulants of the intensive reaction extent ξ. We introduce the cumulant generating function of the reaction extent for the disordered system

$$\mathscr{H}_{\text{disordered}}(\rho;t) = \ln\{\int\mathscr{P}_{\text{disordered}}(\xi;t)\exp(i\rho\xi)\, d\xi\} = \sum_{m=1}^{\infty}\frac{i^m}{m!}\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}} \qquad (A.1)$$

and the moment-generating function for the reaction extent for a system without disorder

$$\mathscr{G}_{\text{ordered}}(\rho;t) = \int\mathscr{P}_{\text{ordered}}(\xi;t)\exp(i\rho\xi)\, d\xi = 1 + \sum_{m=1}^{\infty}\frac{i^m}{m!}\langle\xi^m(t)\rangle_{\text{ordered}} \qquad (A.2)$$

Here ρ is the Fourier variable conjugated to the intensive reaction extent ξ, $\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}}$ are the cumulants of the reaction extent in the disordered system, and $\langle\xi^m(t)\rangle_{\text{ordered}}$ are the moments of the reaction extent in the ordered system. By combining eqs 28, A.1, and A.2, we come to

$$\begin{aligned}\mathscr{H}_{\text{disordered}}(\rho;t) &= \ln\{1 + \alpha t^{-\alpha}\int_0^t \theta^{\alpha-1}[\mathscr{G}_{\text{ordered}}(\rho;\theta) - 1]\, d\theta\} = \\ &-\sum_{m=1}^{\infty}\frac{(-\alpha t^{-\alpha})^m}{m}\prod_{w=1}^{m}\left\{\int_0^t(\theta_w)^{\alpha-1}\times\sum_{\epsilon_w=1}^{\infty}\frac{(i\rho)^{\epsilon_w}}{\epsilon_w!}\langle\xi^{\epsilon_w}(\theta_w)\rangle_{\text{ordered}}\, d\theta_w\right\} = \\ &-\sum_{m=1}^{\infty}\frac{(-\alpha t^{-\alpha})^m}{m}\sum_{\epsilon=m}^{\infty}\frac{(i\rho)^{\epsilon}}{\epsilon!}\sum_{\substack{\epsilon_1,...,\epsilon_1\\ \sum_w\epsilon_w=\epsilon}}\frac{\epsilon!}{\prod_w\epsilon_w!}\prod_{w=1}^{m}\times \\ &\{\int_0^t(\theta_w)^{\alpha-1}\langle\xi^{\epsilon_w}(\theta_w)\rangle_{\text{ordered}}\, d\theta_w\}\end{aligned} \qquad (A.3)$$

By changing the order of summation and the summation labels in eq A.3 and comparing the result with the expansion in eq A.1, we can compute the cumulants $\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}}$. We come to

$$\langle\langle\xi^m(t)\rangle\rangle_{\text{disordered}} = \sum_{n=1}^{m} (-1)^{n-1} \sum_{\substack{n_1,\ldots,n_n \\ \sum_w n_w = n}} \frac{(n-1)!}{\prod_w n_w!} \prod_{w=1}^{m} \times \left\{ \int_0^t \langle \xi^n{}_w(\theta_w)\rangle_{\text{ordered}}\, d\left(\frac{\theta_w}{t}\right)^{\alpha} \right\} \quad \text{(A.4)}$$

from which, integrating by parts, we obtain eq 30.

Appendix B

We introduce the characteristic function of the extensive reaction extent $\Xi = \Omega\xi$

$$G_{\text{ordered}}(b;t) = \langle \exp(i\Xi b)\rangle = \int \exp(i\Omega\xi b)\mathscr{P}_{\text{ordered}}(\xi;t)\, d\xi \quad \text{(B.1)}$$

and evaluate it in the eikonal approximation. We insert eq 22 into eq B.1 and evaluate the integral by using the steepest descent approximation. We obtain

$$G_{\text{ordered}}(b;t) = \mathscr{L}^{-1} \int \exp(i\Omega\xi b) \exp\{\Omega[i\xi b + \mathscr{J}(\xi;t)]\}d\xi \approx \exp[\Omega\psi(ib;t) + \mathscr{O}(\Omega^0)] \quad \text{as} \quad \Omega \to \infty \quad \text{with} \quad \xi = \text{constant} \quad \text{(B.2)}$$

where

$$\psi(ib) = ib\mathscr{E}(ib) + \mathscr{J}((ib)) \quad \text{(B.3)}$$

and

$$\mathscr{E}(x;t) = -[\partial\mathscr{J}(\xi;t)/\partial\xi]^{(-1)}$$

$$-\partial\mathscr{J}(\mathscr{E}(x;t);t)/\partial\mathscr{E}(x;t) = x; x = ib \quad \text{(B.4)}$$

is the inverse function of $-\mathscr{J}(\xi;t)/\partial\xi$. The cumulants $\langle\langle\Xi^m(t)\rangle\rangle_{\text{ordered}}$ can be evaluated by expanding $\ln G_{\text{ordered}}(b;t)$ in a Taylor series. We have

$$\ln G_{\text{ordered}}(b;t) = \sum_{m=1}^{\infty} \frac{(ib)^m}{m!} \langle\langle\Xi^m(t)\rangle\rangle_{\text{ordered}} \quad \text{(B.5)}$$

By combining eqs B.2, B.3, and B.5, we come to

$$\langle\langle\Xi^m(t)\rangle\rangle_{\text{ordered}} \approx \Omega\partial^m\mathscr{E}(0;t)/\partial x^m \quad \text{as} \quad \Omega \to \infty \quad \text{with} \quad \xi = \text{constant} \quad \text{(B.6)}$$

We notice that for systems without disorder the relative fluctuations of different orders

$$\zeta^{(m)}_{\text{ordered}}(t) = \frac{\langle\langle\Xi^m(t)\rangle\rangle_{\text{ordered}}}{\langle\langle\Xi(t)\rangle\rangle^m_{\text{ordered}}} \approx \Omega^{-(m-1)} \left\{ \frac{\partial^m\mathscr{E}(0;t)/\partial x^m}{[\partial(0;t)/\partial x]^m} \right\} \to 0 \quad \text{as} \quad \Omega \to \infty \quad \text{(B.7)}$$

tend to 0 in the thermodynamic limit; that is, for systems without disorder, the fluctuations are nonintermittent.

Appendix C

In this Appendix, we consider the more general case of a system with many overall reactions and with collective fluctuations of the energy barrier. The case of a single overall reaction considered in section 4 is included as a particular case.

The time dependence of the probability of concentration fluctuations in the ordered system is given by

$$\mathscr{P}_{\text{ordered}}(\xi;t) = \sum_u f_u(\xi) \exp(-\Omega\lambda_u t) + \int \varphi_u(\xi,\lambda) \exp(-\Omega\lambda t) d\lambda \quad \text{(C.1)}$$

where λ_u and λ are the eigenvalues from the discrete and continuous spectrum of the chemical Hamiltonian. The smallest discrete eigenvalue is $\lambda_0 = 0$, and simple; all other eigenvalues, discrete or continuous, have positive real parts; these restrictions ensure that for large amounts of time the state probability evolves toward a time-independent value. For systems with detailed balance, the eigenvalues are discrete and real. Multiple eigenvalues may occur, but they are rather unlikely and are therefore neglected in eq 1. By inserting eq C.1 into eq 28, we come to

$$\mathscr{P}_{\text{disordered}}(\xi;t) = \sum_u f_u(\xi)\{\exp(-\Omega\lambda_u t) + (\Omega\lambda_u t)^{-\alpha}\gamma(\alpha + 1, \Omega\lambda_u t)\} + \int \varphi_u(\xi,\lambda)[\exp(-\Omega\lambda t) + (\Omega\lambda t)^{-\alpha}\gamma(\alpha + 1, \Omega\lambda t)]\, d\lambda \quad \text{(C.2)}$$

where $\gamma(x,y)$ is the incomplete γ function. By use of the asymptotic properties of the incomplete gamma function, it follows that

$$\mathscr{P}_{\text{disordered}}(\xi;t) \approx \mathscr{P}_{\text{ordered}}(\xi;\infty) + t^{-\alpha}C(\xi) \quad \text{as} \quad t \to \infty \quad \text{(C.3)}$$

where

$$C(\xi) = \Gamma(\alpha + 1)[\sum_u (\Omega\lambda_u)^{-\alpha} f_u(\xi) + \int (\Omega\lambda)^{-\alpha}\varphi(\lambda,\xi)\, d\lambda] \quad \text{(C.4)}$$

and $\Gamma(x)$ is the complete gamma function. A similar analysis can be carried out for the moments and the cumulants.

The contribution of multiple eigenvalues, if they exist, can be analyzed in a similar way. A discrete eigenvalue $\lambda_u^{(m)}$ with multiplicity m leads to contributions to $\mathscr{P}_{\text{ordered}}(\xi;t)$ containing exponential terms modulated by polynomials

$$f_u^{(m)}(\xi)t^x \exp(-\Omega\lambda_u^{(m)}t) \quad x = 0, \ldots, m - 1 \quad \text{(C.5)}$$

Such terms lead to contributions to $\mathscr{P}_{\text{disordered}}(\xi;t)$ which scale as $t^{-\alpha}$ as $t \to \infty$. We have

$$\alpha t^{-\alpha} \int_0^t \theta^{\alpha-1} f_u^{(m)}(\xi)\theta^x \exp(-\Omega\lambda_u^{(m)}\theta)\, d\theta = \alpha t^{-\alpha}\gamma(\alpha + x, \Omega\lambda_u^{(m)}t) \approx t^{-\alpha}\alpha\Gamma(\alpha + x) \quad \text{as} \quad t \to \infty \quad \text{(C.6)}$$

which, once again, leads to the asymptotic law C.3.

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