

diative continuum observed by Raksit et al.⁴⁹

Concluding Remarks

In this Account, we have shown how neutralized ion beam techniques complement the more traditional methods of spectroscopy to obtain a substantial body of information on the simplest polyatomic radical, H₃. In particular, the combination of optical and neutralized ion beam techniques has allowed for the determination of excited-state lifetimes by time resolved emission experiments. Further, the existence of a unique metastable excited state, first identified in nonoptical neutralized ion beam experiments, has provided access to the absorption and photoionization spectra of the radical. Considering the generality of neutralized ion beam techniques, future work in this area can be expected to obtain information on an almost limitless number of chemically interesting species. Additionally, the vertical nature of the neutralization process allows regions of a neutral potential energy surface not readily

accessed conventionally, such as a transition state,⁵⁸ to be probed directly by the appropriate choice of the precursor ion. In particular, emission spectra for species such as H₃O and H₂F, which have yet to be observed by conventional methods, may be obtainable by the techniques outlined in this Account. Further, as metastable states of the perdeuterated analogues, D₃O and D₂F, can be produced by ion beam neutralization,⁵⁹ their absorption and photoionization spectra should be similarly obtainable through application of the techniques that have been so successfully applied to H₃.

We are grateful to the National Science Foundation for support through the Materials Science Center (NSF Grant DMR-82-17227A03) at Cornell University and NSF Grant CHE-8520267.

Registry No. H₃, 12184-91-7.

(58) Collings, B. A.; Polanyi, J. C.; Smith, M. A.; Stolow, A.; Tarr, A. *W. Phys. Rev. Lett.* **1987**, *59*, 2251.

(59) See, for example: Raksit, A. B.; Jeon, S. J.; Porter, R. F. *J. Phys. Chem.* **1986**, *90*, 2298.

Rate Processes with Dynamical Disorder

ROBERT ZWANZIG

Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, Maryland 20892

Received November 15, 1989 (Revised Manuscript Received February 26, 1990)

Simple and effective methods for solving problems in nonequilibrium statistical mechanics are scarce and valuable. In the absence of elementary textbooks in this area, such methods tend to be reinvented many times. I review here one particular example: a method for treating rate processes when a rate constant is replaced by a random function of time (hence "dynamical disorder"). In particular, the rate constant is taken to be a function of some control variable which may either jump between discrete values according to exponential waiting time distributions, or else fluctuate according to a Langevin equation. Generalizations of the method are described. The method usually leads to a decay in time that is nonexponential. My emphasis will be on the method, with just enough about its applications to show how general and useful it can be.

The class of problems for which this method is effective are conveniently called "rate processes with dynamical disorder". But to set the stage it will be helpful first to discuss rate processes with *static* disorder. A typical rate equation, for the concentration

C of some species undergoing chemical reaction, is

$$\frac{dC}{dt} = -k(B)C \quad (1)$$

where $k(B)$ is a rate constant that depends on a barrier height B ,

$$k(B) = k_0 \exp(-B/kT) \quad (2)$$

In a widely discussed example, due to Frauenfelder and co-workers,¹ the reaction is ligand binding to myoglobin. They claim that different conformational substrates have different barriers to rebinding; the probability of finding a barrier with height B in the interval dB is $\rho(B)dB$. Then the average time dependence of the concentration is

$$\langle C(t) \rangle = C(0) \int dB \rho(B) e^{-k(B)t} \quad (3)$$

In this example of static disorder, the course of the reaction clearly is no longer exponential in time.

While this illustration makes use of a particular pair of variables, the concentration C and the barrier height B , a much more general point of view is possible. C may denote any physical quantity that satisfies a rate equation, B may be any "control variable", and $k(B)$ may be any function of B . This general point of view is taken in much of what follows.

When B is a random function of time, $B(t)$, one has *dynamical* disorder. The time-dependent solution of the rate equation is

(1) Austin, R. H.; Beeson, K. W.; Eisenstein, L.; Frauenfelder, H.; Gunsalus, I. C. *Biochemistry* **1975**, *14*, 5355.

Robert Zwanzig was born in Brooklyn, NY, on April 9, 1928. He received a B.S. in Chemistry from the Polytechnic Institute of Brooklyn in 1948, an M.S. from the University of Southern California in 1950, and a Ph.D. from the California Institute of Technology in 1952. After holding positions at Yale University, The Johns Hopkins University, and the National Bureau of Standards, he became a research professor at the University of Maryland, where he was named Distinguished Professor of Physical Science in 1976. In 1988 he moved to the National Institutes of Health, where he is currently chief of the section on theoretical biophysics in the National Institute of Diabetes and Digestive and Kidney Diseases. He is a member of the National Academy of Science and has received the Peter Debye award in Physical Chemistry and the Irving Langmuir award in Chemical Physics from the American Chemical Society. His research deals with a variety of theoretical problems in chemical physics.

$$C(t) = C(0) \exp\left[-\int_0^t ds k(B(s))\right] \quad (4)$$

and clearly involves the entire history of B in the interval between 0 and t . If B fluctuates very rapidly, then we may reasonably expect that $k(B(s))$ can be replaced by its time average $\langle k \rangle$, and exponential decay is recovered,

$$C(t) \cong C(0) \exp(-\langle k \rangle t) \quad (5)$$

If B fluctuates very slowly, we may reasonably expect that eq 3, the static disorder result, is correct. The problem is how to handle the intermediate cases, where the fluctuations are neither very slow nor very fast.

Examples

This is a brief list of some places in which questions of dynamical disorder have arisen. It is not intended to be comprehensive, but only to show a variety of applications.

(1) **Theory of Spectral Line Shapes.** While this is not strictly a rate process, the spirit is similar. A time correlation function $C(t)$ satisfies the equation $dC(t)/dt = i\omega(t) C(t)$, and the frequency $\omega(t)$ is a random function of time. Anderson² treated this problem in a quite general way in 1954, although others had the right idea earlier.³

(2) **Self-Diffusion in Water.** Singwi and Sjolander⁴ studied a dynamical model in which a water molecule jumps randomly between states; in one state, its motion is oscillatory about an equilibrium position, and in the other state, its motion is diffusive.

(3) **Gated Diffusion.** Szabo, Shoup, Northrup, and McCammon⁵ treated a model of diffusion-controlled reactions where the reaction occurs only at the surface of an object. The reactivity, expressed by a boundary condition, fluctuates in time, or the "gate" opens and closes.

(4) **Protein Dynamics.** Agmon and Hopfield⁶ presented a model theory for ligand rebinding in myoglobin, in which the rate constant depends on a protein coordinate, and the time dependence of that coordinate is described by Brownian motion of a harmonic oscillator.

(5) **Fluorescence Depolarization.** Szabo⁷ considered a class of problems where the nonradiative decay constant of a fluorophore may depend on its orientation, local environment, and electronic state. These fluctuate because of rotational, conformational, and state-to-state dynamics.

(6) **Dynamical Percolation.** Harrison and Zwanzig⁸ gave an approximate treatment of a random walk on a lattice in which the lattice bonds open and close randomly in time.

(7) **Barrierless Relaxation.** Bagchi and Fleming⁹ considered models of relaxation in which a particle

(2) Anderson, P. W. *J. Phys. Soc. Jpn.* 1954, 9, 316.

(3) Slichter, C. P. *Principles of Magnetic Resonance*, 2nd ed.; Springer-Verlag: Berlin, 1978. Appendix F contains early history of the procedure.

(4) Singwi, K. S.; Sjolander, A. *Phys. Rev.* 1960, 119, 863.

(5) Szabo, A.; Shoup, D.; Northrup, S. H.; McCammon, J. A. *J. Chem. Phys.* 1984, 77, 4484.

(6) Agmon, N.; Hopfield, J. J. *J. Chem. Phys.* 1983, 78, 6947.

(7) Szabo, A. *J. Chem. Phys.* 1984, 81, 150.

(8) Harrison, A. K.; Zwanzig, R. *Phys. Rev.* 1985, A32, 1072.

(9) Bagchi, B.; Fleming, G. R. *J. Phys. Chem.* 1990, 94, 9.

undergoes Brownian motion on a potential surface until it reaches a reactive sink.

In all of these examples, the main point is that some property that is decisively important to a rate process is fluctuating in time.

Kinds of Dynamical Disorder

Two specific kinds of dynamical disorder are known to be easily handled by the methods to be described here.

The first is discrete disorder; $B(t)$ takes on only the discrete set of values $\{B_1, B_2, B_3, \dots\}$. Each value corresponds to a "state". Transitions or "jumps" between states occur at time intervals that are chosen from exponential waiting time distributions. Alternatively, as in writing a program for computer simulation, the probability of a jump from B_j to B_k in the small time interval dt is $w_{kj} dt$. This leads eventually to a master equation for the time dependence of the probability ρ_j that a given state is occupied:

$$\frac{\partial}{\partial t} \rho_j = \sum_k w_{jk} \rho_k - \sum_k w_{kj} \rho_j \quad (6)$$

The general theory of this kind of process is explained in many places, for example, by van Kampen¹⁰ in his textbook *Stochastic Processes in Physics and Chemistry*.

The second kind of disorder is continuous; $B(t)$ is determined by a Langevin equation, as in Brownian motion theory:

$$\frac{d}{dt} B(t) = -\lambda B(t) + F(t) \quad (7)$$

where λ is a decay rate and $F(t)$ is Gaussian white noise. In the prototypical Langevin equation, B is the momentum of a Brownian particle, λ is a friction coefficient (divided by the particle mass), and F is a fluctuating force on the particle. But many other dynamical processes may be described by equations of this kind. Along with the Langevin equation, one requires thermal equilibrium information about the first and second moments of B and $F(t)$,

$$\begin{aligned} \langle B \rangle_{\text{eq}} &= 0 & \langle B^2 \rangle_{\text{eq}} &= \theta & \langle F(t) \rangle_{\text{eq}} &= 0 \\ \langle F(t) F(t') \rangle_{\text{eq}} &= 2\lambda\theta \delta(t-t') \end{aligned} \quad (8)$$

The last equation is the fluctuation-dissipation theorem. This leads eventually to a Fokker-Planck equation for the probability distribution of B as a function of time, which will be written down later. The general theory of this kind of process is explained in many places, e.g., by van Kampen and by Risken¹¹ in his monograph *The Fokker-Planck Equation*.

Direct Approach

In a direct approach to calculating the average of $C(t)$, we start with the integrated form as in eq (4):

$$C(t) = C(0) \exp\left[-\int_0^t ds k(B(s))\right] \quad (9)$$

(10) van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, 1981. See especially pp 203-208 for his treatment of dynamical disorder in a jump model.

(11) Risken, H. *The Fokker-Planck Equation*; Springer-Verlag: Berlin, 1984. See especially Appendix A1 for a treatment of dynamical disorder in a Langevin model.

Consider first how this can be obtained with jump dynamics. For simplicity, only two states will be used: $k_1 = k(B_1)$ and $k_2 = k(B_2)$. If one starts out in state 1, and no jump has occurred during the time interval t , the integral in the exponent is just tk_1 . If one jump has occurred, at time t_1 , the integral is $t_1k_1 + (t - t_1)k_2$. If two jumps have occurred, at times t_1 and t_2 , the integral is $t_1k_1 + (t_2 - t_1)k_2 + (t - t_2)k_1$; and so on. To complete the calculation one must average each exponential over the waiting-time distribution for each time interval and then sum over all possible numbers of jumps that can occur between 0 and t . van Kampen shows how this can be done in a formal way, making use of Laplace transforms and matrix algebra; but the calculation is not a pleasant one, especially when there are many states.

When the direct approach is used for Langevin dynamics, i.e., starting with eq 7, the task is even more unpleasant. We still have the integral representation of $C(t)$, but now $B(t)$ is given by the solution of the Langevin equation,

$$B(t) = B(0)e^{-\lambda t} + \int_0^t dt' e^{-\lambda(t-t')} F(t') \quad (10)$$

Some of the time dependence comes from relaxation of the initial value $B(0)$, and some comes from the noise $F(t)$. This expression for $B(t)$ has to be put into $k(B)$, and then the time integral has to be done. Finally we have to perform Gaussian averages of what are generally extremely complicated nonlinear functions of the noise.

Unless one is willing to invest in a computer simulation to get the average, as was done by Henry and Hochstrasser,¹² the direct approach is essentially impractical.

Indirect Approach

In the last illustration of the direct approach, the main difficulty was to calculate averages of complicated functions of the noise. But this can be accomplished at a much earlier stage of the theory, by using probability distributions. We denote by $f(C, B; t)$ the probability distribution that the variables C and B have specified values at time t . This function satisfies a kind of Liouville (or conservation) equation, analogous to what one does in statistical mechanics.

There one starts with a phase space in which values of momentum p and position x specify a phase point. The number density of systems at the location (p, x) at time t is $f(p, x; t)$. Systems can be neither created nor destroyed, so f satisfies a conservation law, in which $\partial f / \partial t$ is minus the divergence of a flux vector, $-\nabla \cdot \vec{J} = -\partial J_p / \partial p - \partial J_x / \partial x$. The flux vector $\vec{J} = (J_p, J_x)$ is the product $f\vec{v}$ of the number density f and a velocity \vec{v} . In the usual case, the velocity in the x direction is $v_x = dx/dt = \partial H / \partial p$, and the velocity in the p direction is $v_p = dp/dt = -\partial H / \partial x$, where H is the Hamiltonian. In the present case, the momentum p is replaced by the variable C , and the position x is replaced by B . There is no Hamiltonian, but it is not needed anyway because we already know what the two velocities are. Then the appropriate Liouville equation is

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial C} \left(\frac{dC}{dt} f \right) - \frac{\partial}{\partial B} \left(\frac{dB}{dt} f \right) \quad (11)$$

or, on putting in the velocities explicitly,

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial C} (-k(B)Cf) - \frac{\partial}{\partial B} (-\lambda Bf + F(t)f) \quad (12)$$

The final term, containing time-dependent noise, makes this a stochastic Liouville equation.

What we would like to have is the average of f over the noise. This will be denoted by $g(C, B; t) = \langle f(C, B; t) \rangle_{\text{noise}}$. There is a standard procedure, found in many textbooks and review articles,¹³ for converting the stochastic Liouville equation into a Fokker-Planck equation for the noise-averaged distribution. A simple derivation is given in the Appendix. The result is

$$\frac{\partial g}{\partial t} = -\frac{\partial}{\partial C} (-k(B)Cg) - \frac{\partial}{\partial B} (-\lambda Bg) + \frac{\partial}{\partial B} \left(\lambda \theta \frac{\partial g}{\partial B} \right) \quad (13)$$

The second derivative comes from the average over Gaussian white noise.

What is really wanted is the full average of $C(t)$, taken over noise and also over the initial distributions of C and B . In typical applications, the initial distribution of C might be taken as perfectly sharp, and the initial distribution of B might be thermal equilibrium. In the work of Agmon and Hopfield, a displaced thermal equilibrium is used. The noise average has already been taken; the additional ensemble average gives

$$\langle C; t \rangle = \int dB \int dC C g(C, B; t) \quad (14)$$

There are occasions when it may be useful to look at fluctuations about the average, $\langle C^2; t \rangle - \langle C; t \rangle^2$. These can be defined in a similar way, but I will not pursue this here. It turns out to be convenient to do the above average in two separate stages. First, one does a partial average, over C for fixed B ,

$$\bar{C}(B; t) = \int dC C g(C, B; t) \quad (15)$$

Then the complete average is

$$\langle C; t \rangle = \int dB \bar{C}(B; t) \quad (16)$$

The reason for going through this apparently cumbersome procedure can be seen readily when one uses the Fokker-Planck equation to obtain an equation for the partial average. To do this, we simply multiply the Fokker-Planck equation by C and integrate by parts over C , leading to

$$\frac{\partial \bar{C}}{\partial t} = -k(B)\bar{C} + \lambda \theta \frac{\partial}{\partial B} \left(\frac{\partial \bar{C}}{\partial B} + \frac{B}{\theta} \bar{C} \right) \quad (17)$$

The first term on the right is a sink, describing loss of C by the rate process $k(B)$; the second term is a particular Smoluchowski operator, describing overdamped Brownian motion of a "harmonic oscillator" whose coordinate is B .

In fact, this equation appeared in the paper by Agmon and Hopfield that was cited earlier. B corresponds to their protein coordinate x , $k(B)$ is their ligand binding rate $k_0 \exp(-\alpha x)$, and the Langevin equation for x is obtained by dropping the acceleration term from the equation of motion of a damped noisy harmonic oscillator,

(12) Henry, E. R.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* 1987, 84, 6142.

(13) Chandrasekhar, S. *Rev. Mod. Phys.* 1943, 16, 1. Kittel, C. *Elementary Statistical Physics*; John Wiley and Sons: New York, 1958.

$$0 \cong -m\omega_0^2 x - \zeta \frac{dx}{dt} + F(t) \quad (18)$$

So one finds $\lambda = m\omega_0^2/\zeta$ and $\theta = kT/m\omega_0^2$. I will refer to eq 17 as an "Agmon-Hopfield" equation.

What has been gained? The horribly complex task of performing the noise average in the direct approach is replaced in the indirect approach by the task of solving a partial differential equation. (This is very much in the same spirit as evaluating Feynman path integrals by solving the Schrödinger equation!) But solving partial differential equations of the Agmon-Hopfield type is almost trivial nowadays, by a variety of efficient numerical methods. Rate processes with this kind of dynamical disorder can now be handled easily.

One should be aware that there are many processes that can lead to the same mathematical problem. Agmon and Hopfield had in mind for B a displaced real normal mode of a protein. But another scenario (suggested by Henry, Eaton, and Hochstrasser¹⁴) that illustrates my point is to suppose that the rate constant $k(B)$ has the standard Arrhenius form, where B is a local temperature that fluctuates according to a Langevin equation. For example, one might imagine that a ligand is dissociated by a laser pulse that deposits a lot of energy locally in the protein, raising the local temperature. As the local temperature falls (with some relaxation time, and the corresponding noise), the rate changes. The point is that C can be any property that obeys a rate equation, and $k(B)$ can be any function of any control variable B that decays and fluctuates according to a Langevin equation.

Indirect Approach. Jump Dynamics

The corresponding treatment of dynamical disorder for jump dynamics is quite simple. The control parameter is discrete, B_1, B_2, \dots , and the rate is $k_i = k(B_i)$. Dependence on B is replaced by dependence on the index i . The probability distribution $f(C, B; t)$ becomes $f_i(C; t)$. The probability per unit time of a transition from state i to state j is w_{ji} . The noise-averaged probability distribution is $g_i(C; t)$ and satisfies a "Liouville-master" equation,

$$\frac{\partial}{\partial t} g_i = -\frac{\partial}{\partial C} (-k_i C g_i) + \sum_j (w_{ij} g_j - w_{ji} g_i) \quad (19)$$

This is analogous to eq 13 in the case of Langevin dynamics. The last term on the right is a "master" operator in the present case and a "Smoluchowski" operator in the earlier case.

As before, the average $\langle C; t \rangle$ is found in two stages,

$$\begin{aligned} \bar{C}_i(t) &= \int dC C g_i(C; t) \\ \langle C; t \rangle &= \sum_i \bar{C}_i(t) \end{aligned} \quad (20)$$

The partially averaged C satisfies the analogue of eq 17,

$$\frac{\partial}{\partial t} \bar{C}_i = -k_i \bar{C}_i + \sum_j (w_{ij} \bar{C}_j - w_{ji} \bar{C}_i) \quad (21)$$

This equation is intuitively quite obvious: \bar{C} changes in time either because of decay or because of a change in state. The special case where there are only two states is almost trivial and can be worked out analyti-

cally. For problems where the number of possible states is reasonably small, say less than 100, this equation is easily solved numerically by finding eigenvalues and the right and left eigenvectors of the matrix on the right hand side of this equation.

Generalizations

While the preceding discussion was based on a simple chemical reaction scheme, it is really much more general. In the first place, the quantity called C may be a multicomponent vector, for example, the concentration of a diffusing species $C(r, t)$, where the index is the position r . In the second place, the rate constant called $k(B)$ may be a matrix or an operator acting on C . An example is the diffusion operator $-k(B) \rightarrow D(B)\nabla^2$. If the control variable B is discrete, then one has an equation describing state-dependent diffusion,

$$\frac{\partial}{\partial t} \bar{C}_i(R, t) = D_i \nabla^2 \bar{C}_i(R, t) + \sum_j (w_{ij} \bar{C}_j(R, t) - w_{ji} \bar{C}_i(R, t)) \quad (22)$$

This equation was discussed by van Kampen in connection with Singwi and Sjolander's treatment of self-diffusion in water.

There is a corresponding rotational problem, where C depends on the orientation of a molecule, and the orientation changes by rotational diffusion. This is one of the ways Szabo treated fluorescence depolarization.

A final example is the study of dynamical percolation by Harrison and Zwanzig, in which C is the multidimensional probability of finding a random walker at a particular lattice site. The state of all bonds in a lattice (individually open or closed) is the multidimensional control variable B ; w_{ij} describes transitions between states of the entire lattice (bonds opening and closing); and $-k(B)$ is a random walk operator that depends on the state of the lattice.

The preceding review considered two specific kinds of dynamics, involving either jumps between discrete states or Brownian motion of a continuous variable. It is possible to generalize this also. (See, for example, the review by Bagchi and Fleming.⁹) Suppose that the dynamics of the control variable can be described by an equation for the probability distribution $\rho(B; t)$,

$$\frac{\partial}{\partial t} \rho(B; t) = \mathcal{L} \rho(B; t) \quad (23)$$

in which \mathcal{L} is some dynamical operator. A trivial example is the simplest relaxation time approximation,

$$\frac{\partial}{\partial t} \rho = -\frac{1}{\tau} (\rho - \rho_{\text{eq}}) \quad (24)$$

where $1/\tau$ is the rate of relaxation to the equilibrium distribution $\rho_{\text{eq}}(B)$. Then the Liouville equation for the joint probability distribution $g(C, B; t)$ is

$$\frac{\partial}{\partial t} g = -\frac{\partial}{\partial C} [-k(B)g] + \mathcal{L} g \quad (25)$$

The partial average $\bar{C}(B, t)$ obeys the equation

$$\frac{\partial}{\partial t} \bar{C} = -k(B)\bar{C} + \mathcal{L} \bar{C} \quad (26)$$

Whatever scheme is used to describe dynamical disorder, all that is required is that \mathcal{L} operates on functions of B only.

(14) Henry, E. R.; Eaton, W. A.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* 1986, 83, 8982.

I thank Attila Szabo for helpful comments.

Appendix

There are many treatments of the transition from a Langevin equation to the corresponding Fokker-Planck equation. The following one appeals to me as pedagogically simple.

The starting point is the stochastic Liouville equation for $f(C,B;t)$ as in eq 12,

$$\frac{\partial}{\partial t} f = -Lf - \frac{\partial}{\partial B} F(t) f \quad (\text{A1})$$

in which L is an abbreviation for the operator

$$L = \frac{\partial}{\partial C} (-k(B)C) + \frac{\partial}{\partial B} (-\lambda B) \quad (\text{A2})$$

Integration over time leads to the operator equation $f(C,B;t) =$

$$e^{-tL} f(C,B;0) - \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial B} F(s) f(C,B;s) \quad (\text{A3})$$

By iterating, one can develop a series expansion of f in powers of F . This is substituted in the last term of eq A1,

$$\frac{\partial}{\partial t} f(C,B;t) = -Lf(C,B;t) - \frac{\partial}{\partial B} e^{-tL} F(t) f(C,B;0) + \frac{\partial}{\partial B} \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial B} F(t) F(s) f(C,B;s) \quad (\text{A4})$$

Now we average over Gaussian white noise. The average $\langle f(C,B;t) \rangle$ is $g(C,B;t)$. Because the initial distribution $f(C,B;0)$ does not contain any effects of noise, the average $\langle F(t) f(C,B;0) \rangle$ is first order in the noise and

vanishes. Then we need only the average $\langle F(t) F(s) f(C,B;s) \rangle$.

Here is where the two properties "Gaussian" and "white" are used. The average of any product of an odd number of Gaussian random variables will vanish. The average of a product of an even number of Gaussian random variables, for example, $\langle F_1 F_2 F_3 F_4 \rangle$, can be found by taking all possible pairings of the variables, for example, $\langle F_1 F_2 \rangle \langle F_3 F_4 \rangle + \langle F_1 F_3 \rangle \langle F_2 F_4 \rangle + \langle F_1 F_4 \rangle \langle F_2 F_3 \rangle$. Next we use the "white noise" property: $\langle F(t_1) F(t_2) \rangle$ is proportional to the δ function $\delta(t_1 - t_2)$,

$$\langle F(t_1) F(t_2) \rangle = 2\lambda\theta \delta(t_1 - t_2) \quad (\text{A5})$$

Consider now the average $\langle F(t) F(s) f(C,B;s) \rangle$. The first noise factor $F(t)$ can be paired with the second, $F(s)$, or it can be paired with noise factors contained in $f(C,B;s)$. But $f(C,B;s)$ can depend on $F(s')$ only for those times s' that are earlier than s . This pairing leads to $\delta(t-s')$ and requires that a time t that is later than s must be equal to a time s' that is earlier than s . Thus there are no contributions from such pairings, and only the first pairing, of $F(t)$ and $F(s)$, will contribute. Then for present purposes we can write $\langle F(t) F(s) f(C,B;s) \rangle = \langle F(t) F(s) \rangle \langle f(C,B;s) \rangle$. This introduces $2\lambda\theta \delta(t-s)$ and removes both the operator $e^{-(t-s)L}$ and the time integral. The time integral from 0 to ∞ picks up half of the δ function and removes the factor 2. The result is the Fokker-Planck equation,

$$\frac{\partial}{\partial t} g = -Lg + \lambda\theta \frac{\partial^2}{\partial B^2} g \quad (\text{A6})$$

which is eq 13.

Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry

P. E. MCGOVERN* and R. H. MICHEL

Museum Applied Science Center for Archaeology, University Museum, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received December 6, 1989 (Revised Manuscript Received February 2, 1990)

Royal purple, 6,6'-dibromoindigotin (DBI, structure III in Figure 1, X = Br), is the most renowned of ancient dyes.¹ Even before Nero issued a decree in the first century A.D. that gave the emperor the exclusive right

Patrick E. McGovern was born in Corpus Christi, TX, in 1944. His academic background combined the physical sciences, archaeology, and history: an A.B. in Chemistry from Cornell University and a Ph.D. in Near Eastern Archaeology and Literature from the Oriental Studies Department of the University of Pennsylvania. Since 1979, he has been a Research Scientist in the Museum Applied Science Center for Archaeology (MASCA), where he has been engaged in a wide range of research in archaeological chemistry, including radiocarbon dating, cesium magnetometer surveying, colorant analysis of ancient glasses, pottery technology, and organic analysis of vessel contents and dyes.

Rudolph H. Michel was born in Landau, Germany, in 1925 and came to the U.S. in 1936. He was trained as a physical organic chemist, receiving his B.S. from the City College of New York and his Ph.D. from the University of Notre Dame. He investigated various aspects of polymer chemistry, including the syntheses of many new materials, in his professional career at E. I. du Pont de Nemours & Co., from which he retired as a Research Fellow in 1985. Soon afterward and continuing to the present, he volunteered his considerable chemical expertise to begin a new "career" in archaeochemical research at MASCA.

to wear royal purple garments, the association of this dye with royalty and high ecclesiastics was well established. As one example, biblical texts² incorporating Iron Age traditions prescribed that the tabernacle curtains and the high priest's vestments were to be dyed with royal purple.

The sociopolitical and religious significance of royal purple was closely tied to its economic value. In some periods, it was worth as much as 10-20 times its weight in gold.³ This circumstance can be traced to the fact that the precursors of DBI, which convert to the dye in air and light (see Figure 1), are found in nature only in the hypobranchial secretions of certain marine mollusks (Figure 2).⁴ As many as 10 000 animals are

(1) Brunello, F. *The Art of Dyeing in the History of Mankind*; Neri Pozza Editore: Venice, 1973; pp 13, 57, 79.

(2) See: Exod. 26:1, 31; 28:4-6; 39:1, 28-29. 1 Kings 5:1-12; 7:13-14; 9:10-14, 26-28; 10:11, 22. 2 Chron. 2:7, 14; 3:14. Ezek. 27:7, 16, 24.

(3) Born, W. *Ciba Rev.* 1937, 1, 106-111, 124-128.