12.086 / 12.586 Modeling Environmental Complexity
Fall 2008

Lecture notes for 12.086/12.586, Modeling Environmental Complexity

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December 1, 2008

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1.1   Relaxation in the carbon cycle

Recall again the carbon cycle:

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$
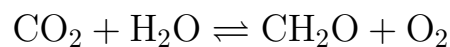
The back reaction—respiration—is a process of *degradation* or *decay*.

That is, microbes feed on organic detritus, slowly returning it to the atmosphere as CO_2.

A good example is the fate of leaves after they fall off trees. Another is the decay of marine detritus as it falls to the bottom of the sea, and degrades in sediments.

An example of another kind of decay is the *weathering* or *dissolution* of silicate minerals, here represented schematically as $CaSiO_3$:

$$CaSiO_3 + CO_2 \rightleftharpoons CaCO_3 + SiO_2.$$
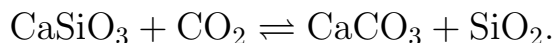
Left-to-right, such reactions schematically represent the uptake of CO_2 from the atmosphere and its transformation to dissolved HCO_3^- during weathering of silicate rocks, and its eventual precipitation and burial in the oceans as carbonate minerals.

We say that processes of decay and weathering represent *relaxation*, in that some quantity slowly diminishes, either until it vanishes or until some irreducible fraction is obtained.

1.2 Relaxation rate constants

What sets the rates of relaxation?

1.2.1 Arrhenius kinetics

Classical equilibrium chemical kinetics predicts reaction rate constants k in terms of activation energies E_a.

The activation energy is a potential barrier that is surmounted by a sufficient thermal fluctuation.

Define
$$\beta = \frac{1}{k_B T}$$

where T is temperature and k_B is Boltzmann's constant.

Arrhenius kinetics predicts the rate constant

$$k = \omega e^{-\beta E_a},$$

where ω is called is the "attempt frequency" or "frequency factor."

In the classical interpretation of Arrhenius kinetics, the fraction of reactant molecules with a kinetic energy greater than E_a is given by the Boltzmann factor $\exp(-\beta E_a)$.

In this essentially phenomenological characterization, the temperature defines the characteristic size of a thermal fluctuation, E_a is the energy barrier that must be overcome by the fluctuation, and ω is the frequency at which the fluctuations lead to reaction.

1.2.2 First order decay

Consider the reaction

$$A \xrightarrow{k} \text{Products},$$
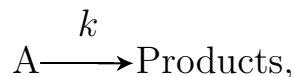
signifying the disappearance or extinction of A with rate constant k.

The meaning of the rate constant k is that, in a small interval of time $\Delta t \ll k^{-1}$,

$$P(\text{an arbitrary molecule reacts}) \simeq k\Delta t.$$

This probability applies to each molecule independently.

Thus if we have N molecules of A at time t, after a small time Δt, we have

$$N(t + \Delta t) = N(t) - kN\Delta t$$

and therefore

$$\frac{N(t + \Delta t) - N(t)}{\Delta t} = -kN.$$

Letting $\Delta t \to dt$, we have the *first-order decay*

$$\frac{dN}{dt} = -kN$$

with solution

$$N(t) = N(0)e^{-kt}.$$

1.2.3 Aging

In investigations of naturally occuring chemical decays within the carbon cycle, it is often difficult to measure k directly. Instead one measures, say, a concentration c per unit volume V such as
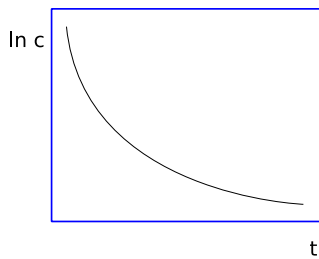
$$c = N/V,$$

or equivalently, a weight fraction, and then infers k from

$$k = -\frac{d \log c}{dt} = -\frac{1}{c}\frac{dc}{dt},$$

which is easily obtained from the slope of $\log c(t)$ on a semilog plot.

Such data may be obtained, e.g., from the decay of leaves, the degradation or organic matter in mud or sediment, or the dissolution of minerals.

We then meet a very interesting problem: plots of $\log c(t)$ vs t are often sublinear, like

One way of interpreting such a plot is to suggest that the reaction kinetics are not first order, but instead of order n such that

$$\frac{dc}{dt} = -k_n c^n$$

where k_n is a different rate constant and the power n suggests something like the need for an n-body collision for the extinction of a particular molecule.

Separating variables above, we obtain

$$c^{-n}dc = -k_n dt \quad \Rightarrow \quad c \propto t^{\frac{1}{1-n}}, \quad n > 1,$$

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Such a relation is broadly consistent with the sublinear decay of $\log c(t)$. However it leaves open the interpretation of n.

If instead we restrict ourselves to first-order kinetics, we note that the concave upward appearance of $\log c(t)$ suggests a kind of effective rate constant k_{eff} that decreases with time like

$$k_{\text{eff}}(t) = -\frac{\mathrm{d}\log c}{\mathrm{d}t}. \tag{1}$$

Such a relation implies that the effective first-order rate constant depends on the age of the material that is decaying.

Much data has been obtained for $k_{\text{eff}}(t)$ [1,2]:
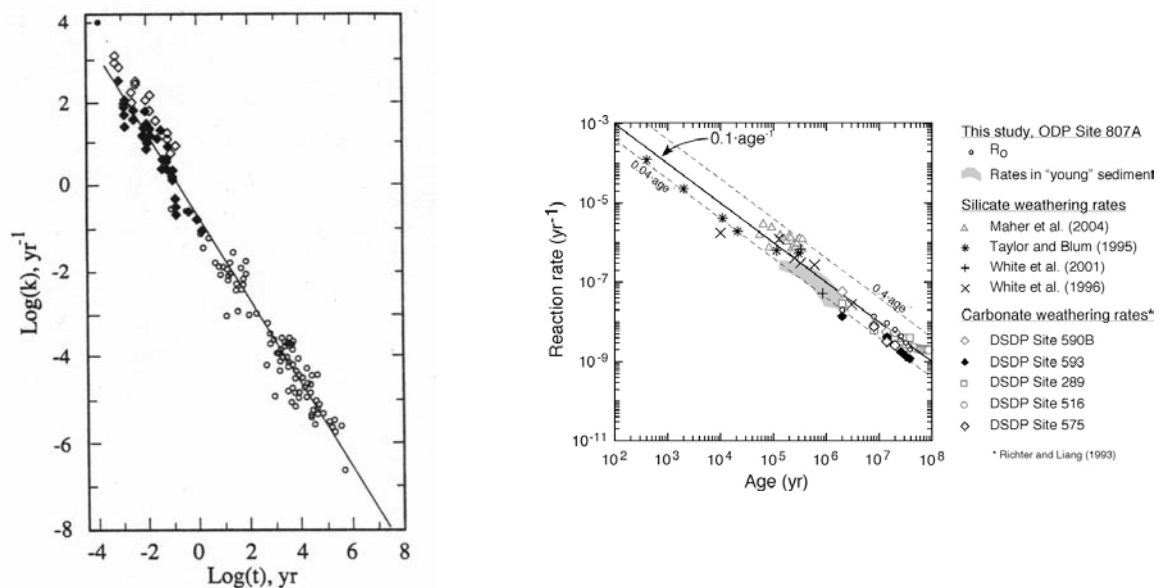
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These data are for the decay of organic matter (left) and mineral dissolution. Both are roughly consistent with the power law

$$k_{\text{eff}} = 0.2 \times t^{-1}$$

at time scales that span orders of magnitude, from days to millions of years. At least at first glance, it seems entirely remarkable that both problems quantitatively yield the same aging effect.

If we were to again assume nth-order kinetics, we would find

$$k_{\text{eff}}(t) \simeq \frac{1}{n-1} \times t^{-1} \quad \Rightarrow \quad n \simeq 6.$$

We know of no way to justify the ubiquity of 6th-order kinetics.

Thus we must turn to other interpretations of the aging effect.

1.2.4 Rationalizing the aging effect

Broadly speaking, the causes are thought to be either *intrinsic* or *extrinsic*.

Intrinsic causes

- *Microbial degradation of organic matter.* It is commonly assumed that some organic compounds are metabolized slowly while others are metabolized quickly.

  In the jargon, the fast compounds are called *labile*, while the others are called *refractory* or *recalcitrant*.

  In this view, the slow decay of $k_{\text{eff}}(t)$ is interpreted as a labile-to-refractory cascade.

- *Mineral dissolution.* A similar rationale is invoked: due to local impurities or defects, some bits of mineral surface area dissolve faster than others.

Extrinsic causes Extrinsic causes are *environmental.*

The relevant environment is *microsopic*: at the scale of the typical bug's universe (which has a radius of about 10 μm), or a pore in a sedimentary rock (a few μm's again).

That is, the material undergoing decay can be somehow *inaccessible*:

- *Microbial degradation.* Association of organic matter with high-surface area clay-sized minerals may afford some protection from enzymatic hydrolysis, such that the least protected organic matter degrades first.

- *Mineral dissolution.* Tight pores or other effects of geometric confinement may make some minerals harder to access by sufficiently unsaturated fluids, providing a mechanism for a fast-to-slow cascade.

It seems obvious that all these factors—intrinic and extrinsic—play some role in the aging effect.

However it is hardly obvious why two entirely different systems—organic matter decay and mineral dissolution—should behave the same way, quantitatively.

Thus we seek a more fundamental perspective.

1.3   Disordered kinetics

Another perspective views the aging process as a consequence of *disordered kinetics* [3, 4].

In disordered kinetics, rate constants are not constant. They are instead rate coefficients that may vary.

There are two kinds of variation: *static* and *dynamic.*

- *Static disorder.* Fluctuations are "frozen" and last forever. The fluctuations typically manifest themselves as random initial conditions. An example would be the distribution of "lability" discussed above.

- *Dynamic disorder.* The environment changes as the reaction progresses, so that rate coefficients are random in time, due, e.g., to a changing climate.

Of course, any chemical system exhibits fluctuations at some microscopic scale due to thermal noise.

But in the usual thermodynamic or continuum limit, the relative mean-square

fluctuation of, say, the number N_V of molecules in a volume V scales like

$$\frac{\langle \tilde{N}_V^2 \rangle}{\langle N_V \rangle^2} \to 0 \text{ as } V \to \infty.$$

where $\tilde{N}_V = N_V - \langle N_v \rangle$. Thus we can ignore such thermal fluctuations in macroscopic systems.

We instead consider the qualitatively different case of relative fluctuations that do not vanish with increasing system size. These are called *intermittent.*

Consider again our first-order decay. In the absence of any intermittent fluctuations, we have

$$\dot{c} = -kc \qquad \Rightarrow \qquad \frac{c(t)}{c(0)} = e^{-kt}.$$

If instead we have fluctuations, $\dot{c}$ must instead be integrated over all possible random trajectories of $k = k(t)$, which yields

$$\frac{\langle c(t) \rangle}{c(0)} = \left\langle \exp\left(-\int_0^t k(t')\mathrm{d}t' \right) \right\rangle.$$

Note that

$$\frac{\langle c(t) \rangle}{c(0)} \neq e^{-\langle k \rangle t}$$

This situation applies equally to dynamical disorder, where $k = k(t)$ is some random function of time, and static disorder, where k is just a single random rate coeffient.

We conclude that $\langle c(t) \rangle$ potentially includes rich behavior that goes well beyond naive averaging of rate coefficients.

1.4   Random rate models

We now specialize to the case of static disorder, but first consider the conditions under which it may be assumed.

1.4.1   Preservation of static disorder

The simplest case of static disorder is a system with two components A_1 and A_2, such that

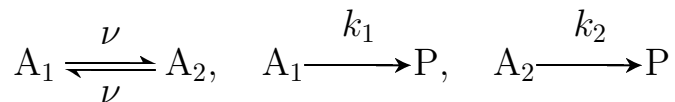$$A_1 \xrightarrow{k_1} P \quad \text{and} \quad A_2 \xrightarrow{k_2} P$$

Setting

$$A_1 = [A_1], \quad A_2 = [A_2], \quad \text{and} \quad c = A_1 + A_2$$

we have

$$c(t) = A_1(0)e^{-k_1 t} + A_2(0)e^{-k_2 t}$$

In geochemistry, such models of superposed exponential decays are called "multi-G" models [5].

In some situations it is more realistic to imagine that A_1 and A_2 interact. For example,

$$A_1 \underset{\nu}{\overset{\nu}{\rightleftharpoons}} A_2, \quad A_1 \xrightarrow{k_1} P, \quad A_2 \xrightarrow{k_2} P$$

In terms of differential equations, we have

$$
\begin{aligned}
\dot{A}_1 &= -(k_1 + \nu)A_1 + \nu A_2 \\
\dot{A}_2 &= -(k_2 + \nu)A_2 + \nu A_1
\end{aligned}
$$

As $\nu \to 0$, we recover the "biexponential" model above.

When mixing is fast relative to the decay reactions, i.e., when $\nu \gg k_1$ and $\nu \gg k_2$, the aggregate system behaves as if there were just a single (average) rate coefficient $(k_1 + k_2)/2$:

$$c(t) = c(0) \exp\left[-\frac{1}{2}(k_1 + k_2)t\right].$$

We conclude that non-exponential decays occur for static disorder only when interactions among the decaying species are slow compared to the "intrinsic" decay rates.

1.4.2 Continuous superposition

A more general approach to static disorder without mixing follows from the assumption of a continuous distribution of rates.

Define

$$c_k(k,t)\mathrm{d}k \;=\; \text{concentration of reactants with rate coefficient}$$
$$\text{between } k \text{ and } k + \mathrm{d}k \text{ at time } t.$$

Assuming first-order kinetics,

$$\frac{\mathrm{d}}{\mathrm{d}t}c_k(k)\mathrm{d}k = -kc_k(k)\mathrm{d}k,$$

and therefore

$$c_k(k,t)\mathrm{d}k = c_k(k,0)e^{-kt}\mathrm{d}k.$$

The total concentration evolves as

$$c(t) \;=\; \int_0^\infty c_k(k,t)\mathrm{d}k$$
$$\;=\; \int_0^\infty c_k(k,0)e^{-kt}\mathrm{d}k.$$

Forming the probability density

$$p(k) = \frac{c_k(k,0)}{\int_0^\infty c_k(k,0)\mathrm{d}k}$$

we obtain the normalized decay

$$\frac{c(t)}{c(0)} = \int_0^\infty p(k)e^{-kt}\mathrm{d}k. \tag{2}$$

We call this the *random rate model* [6]. In geochemistry, it is called the *reactive continuum model* [7]. Mathematically, it represents the *Laplace transform* of $p(k)$.

Note that the probability

$p(k)\mathrm{d}k = $ initial fraction of material decaying at rates between k and $k + \mathrm{d}k$.

As an example, suppose [7]

$$p(k) = \frac{1}{\Gamma(\alpha)} k^{\alpha-1} e^{-ak}, \qquad \alpha > 0$$

where $\Gamma(\cdot)$ is the gamma function and a is a parameter. Insertion into the random rate model then yields

$$\frac{c(t)}{c(0)} = (a+t)^{-\alpha}.$$

Thus we see, for $k \gg a$, another way interpreting a power law decay of $c(t)$: instead of inferring the order n of the kinetics from α, as in Section 1.2.3, we may merely view it as deriving from the random rate distribution $p(k)$.

It is also of interest to consider the time dependent effective relaxation rate (1):

$$k_{\text{eff}}(t) = -\frac{\mathrm{d}\log c}{\mathrm{d}t} = \frac{\alpha}{t}$$

Comparing with the data shown in Section 1.2.3, we see good agreement if $\alpha \simeq 0.2$.

1.5 Random channel model

We now consider the problem of parallel relaxation from an entirely different point of view [8].

Assume that relaxation takes place locally, on a microscopic scale.

Relaxation results from passage through a "channel." We conceive of a channel as a sequence of events necessary for the decay of a microscopic unit of material.

Channels are labeled by the index $i = 1, 2, \ldots$, and are characterized by

$$\lambda_j = \text{relaxation rate in } j\text{th channel.}$$

1.5.1 Fixed rates

We divide a macroscopic body into many, weakly interacting subsystems.

The subsystems differ from each other in that they have different sets of *open* and *closed* channels. The jth channel is

- open with probability P_j; and

- closed with probability $1 - P_j$.

When a channel is closed, it does not contribute to the relaxation, so that the

$$\text{total relaxation rate} = \sum_j [\lambda_j P_j + 0 \cdot (1 - P_j)].$$

Relaxation of the entire macroscopic system is then

$$\frac{c(t)}{c(0)} = \left\langle \exp\left[-\sum_j \lambda_j t\right] \right\rangle,$$

where $\langle \cdot \rangle$ represents an average weighted by the probability each channel is open in the ensemble of subsystems.

Assuming each channel is independent of the others,

$$\frac{c(t)}{c(0)} = \prod_j \left\langle e^{-\lambda_j t} \right\rangle \tag{3}$$

$$= \prod_j \left[(1 - P_j) + P_j e^{-\lambda_j t} \right], \tag{4}$$

where the factor in parentheses represents the absence of relaxation due to closure of the channel.

1.5.2 Fluctuating rates

The preceding interpretation assumes channels remain open or closed forever.

We may instead allow the channels to open and close randomly, in response to, say, environmental fluctuations.

We can then define the fluctuating variable

$$\tilde{\lambda}_j(t) = \begin{cases} 0, & \text{channel } j \text{ closed at time } t \\ \lambda_j, & \text{channel } j \text{ open.} \end{cases}$$

Then

$$\frac{c(t)}{c(0)} = \left\langle \exp\left[-\sum_j \int_0^t \tilde{\lambda}_j(t')\mathrm{d}t'\right]\right\rangle.$$

If the probabilities per unit time of opening and closing are constant, we have a *random telegraph process* [9].

The probability P_j then represents the fraction of time the jth channel is open.

When the correlation time of opening and closing of the jth channel is long compared to λ_j^{-1}, open channels are genuinely "active" and we recover equation (4) assuming independence and the new interpretation of P_j.

1.5.3 Decay function

We rewrite the product (4) as:

$$\prod_j \left[(1 - P_j) + P_j e^{-\lambda_j t}\right] = \exp\left[\sum_j \log\left(1 - P_j + P_j e^{-\lambda_j t}\right)\right]$$

We assume that $P_j \ll 1$, corresponding in the fluctuating case to channels being almost always closed. Then

$$\log\left(1 - P_j + P_j e^{-\lambda_j t}\right) \simeq -P_j(1 - e^{-\lambda_j t}).$$

The decay function (4) then becomes

$$\frac{c(t)}{c(0)} = \exp\left[-\sum_j P_j(1 - e^{-\lambda_j t})\right].$$

To simplify further, define the density of rates

$$\rho(\lambda) = \sum_j P_j \delta(\lambda - \lambda_j).$$

Then

$$\frac{c(t)}{c(0)} = \exp\left[-\int_0^\infty \rho(\lambda)(1 - e^{-\lambda t})\mathrm{d}\lambda\right], \tag{5}$$

called the *random channel model* [6, 8].

1.6 Relation between random rates and random channels

At first glance, the random rate model (2) looks entirely different from the random channel model (5).

Moreover, $p(k)$ and $\rho(\lambda)$ differ:

- $\rho(\lambda)\mathrm{d}\lambda$ is the average number of (open) channels with an individual rate between λ and $\lambda + \mathrm{d}\lambda$.

- $p(k)\mathrm{d}k$ is the overall probability that the total rate of relaxation is between k and $k + \mathrm{d}k$.

Note also that $p(k)$ is a normalized probability density, while $\rho(\lambda)$ is an unnormalized number density.

To appreciate the difference between the two, recall from Section 1.4.2 that, in the context of the random rate model,

$$p(k) = \frac{1}{\Gamma(\alpha)}k^{\alpha-1}e^{-ak} \qquad \Rightarrow \qquad \tilde{c}(t) = (a + t)^{-\alpha}.$$

What $\rho(\lambda)$ is associated with $\tilde{c} = c/c(0)$?

Taking the logarithm and differentiating both sides of the random channel model, we obtain

$$-\frac{\mathrm{d}\log\tilde{c}}{\mathrm{d}t} = \int_0^\infty \lambda\rho(\lambda)e^{-\lambda t}\mathrm{d}\lambda.$$

The LHS is identical to our previous expression (1) for $k_{\text{eff}}(t)$. The RHS is the Laplace transform of $\lambda\rho(\lambda)$. Therefore

$$\rho(\lambda) = \frac{1}{\lambda}\mathcal{L}^{-1}[k_{\text{eff}}(t)]. \tag{6}$$

For the above example of $p(k)$, we found $k_{\text{eff}} = \alpha/t$ in Section 1.4.2. In that case,

$$\rho(\lambda) = \frac{1}{\lambda}\mathcal{L}^{-1}[\alpha/t] = \frac{\alpha}{\lambda},$$

which bears only a slight resemblance to $p(k)$ for small α.

We can obtain a general relation between $p(k)$ and $\rho(\lambda)$ by noting that

$$k_{\text{eff}}(t) = \frac{-1}{c}\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{-\int_0^\infty kp(k)e^{-kt}\mathrm{d}k}{\int_0^\infty p(k)e^{-kt}\mathrm{d}k}$$

where we have merely substituted the random rate model (2) for c. Substitution into (6) then yields

$$\rho(\lambda) = \frac{1}{\lambda}\mathcal{L}^{-1}\left[\frac{\int_0^\infty kp(k)e^{-kt}\mathrm{d}k}{\int_0^\infty p(k)e^{-kt}\mathrm{d}k}\right],$$

where we have takent λ conjugate to t in the inverse Laplace transform.

From these observations we see that each model is essentially a reinterpretation of the other.

To better understand the connection, we require the probability distribution

$$P(N_1, N_2, \ldots) = P(N_1 \text{ channels of type 1, } N_2 \text{ channels of type 2, } \ldots),$$

which in an appropriate limit is Poissonian [6], expressed in terms of the averages $\langle N_1 \rangle$, $\langle N_2 \rangle$, etc.

In this interpretation, each channel has a very small probability of being open. By defining the total rate of relaxation

$$k = \sum_j N_j \lambda_j,$$

we find the probability $p(k)\mathrm{d}k$ according to

$$p(k)\mathrm{d}k = \sum_{N_1}\sum_{N_2}\ldots P(N_1, N_2, \ldots)\, \delta\left(k - \sum_j N_j \lambda_j\right)\mathrm{d}k, \qquad (7)$$

showing that the total "macroscopic" rate k is a weighted average of the "microscopic" rates λ_j.

Now recall that our overall goal is to evaluate the average decay function

$$\langle\tilde{c}\rangle = \langle e^{-kt}\rangle.$$

We now see two interpretations of the average $\langle\cdot\rangle$:

- $\langle\cdot\rangle$ is an average over all possible rates k randomly drawn from $p(k)$.

- $\langle\cdot\rangle$ is an average over all possible rates k randomly drawn from $p(k)$ as computed by (7).

The two models are thus physically equivalent.

The differences are a matter of formal expression and interpretation:

- *Random channels*: $\langle e^{-kt}\rangle$ derives from fluctuations of individual microscopic contributions to the decay process.

- *Random rates*: $\langle e^{-kt}\rangle$ derives from fluctuations of the total macroscopic decay rate.

In the context of the present discussion, the utility of each model will be determined by the extent to which it provides an understanding of the *mechanisms* that produce the observed aging effects discussed in Section 1.2.3.

1.7 Universal random rate distribution

- Forney's inversion yields a universal random rate distribution $p(k)$.

- The resulting random rate model is approximated by the exponential integral.

- The model predicts $k_{\text{eff}}(t) \simeq 0.2/t$.

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