

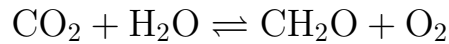
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# 1 Disordered Kinetics

## 1.1 Relaxation in the carbon cycle

Recall again the carbon cycle:

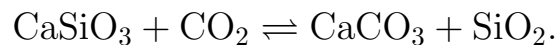


The back reaction—respiration—is a process of *degradation* or *decay*.

That is, microbes feed on organic detritus, slowly returning it to the atmosphere as  $\text{CO}_2$ .

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  $\text{CaSiO}_3$ :



Left-to-right, such reactions schematically represent the uptake of  $\text{CO}_2$  from the atmosphere and its transformation to dissolved  $\text{HCO}_3^-$  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

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

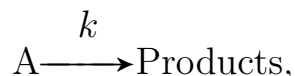
where  $\omega$  is called is the “attempt frequency” or “frequency factor.”

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  $\omega$  is the frequency at which the fluctuations lead to reaction.

### 1.2.2 First order decay

Consider the reaction



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  $\Delta t$ , we have

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

and therefore

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

Letting  $\Delta t \rightarrow dt$ , 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 occurring 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

$$c = N/V,$$

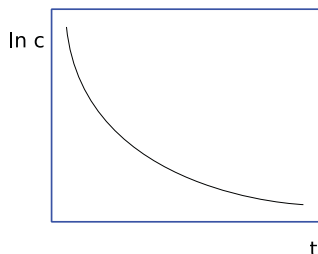
or equivalently, a weight fraction, and then infers  $k$  from

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

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 of 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

$$\frac{dc}{dt} = -k_n c^n, \quad n \geq 1$$

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

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

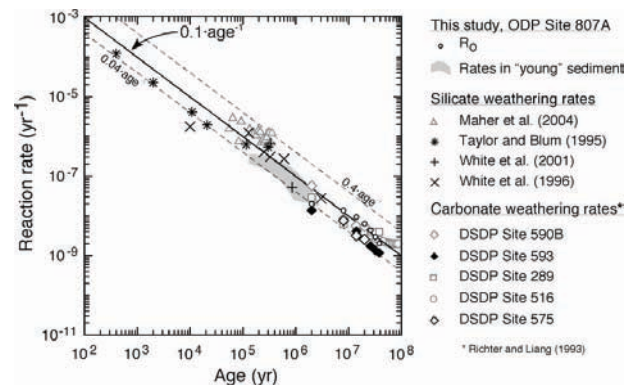
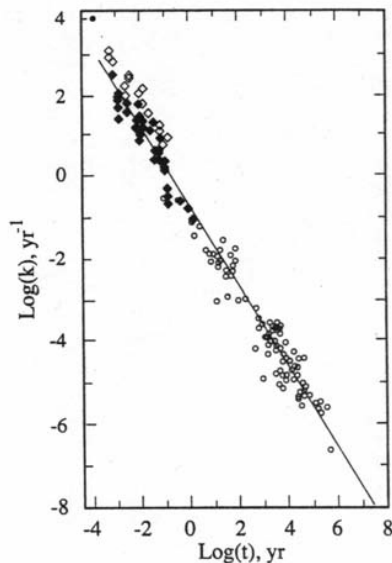
Such a relation is broadly consistent with the sublinear decay of  $\log c(t)$ . However it leaves open the interpretation of  $n$ .

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  $k_{\text{eff}}$  that decreases with time like

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

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  $n$ th-order kinetics, we would find

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

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 *microscopic*: at the scale of the typical bug’s universe (which has a radius of about 10  $\mu\text{m}$ ), or a pore in a sedimentary rock (a few  $\mu\text{m}$ ’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—intrinsic 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

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

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

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

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

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

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 coefficient.

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



Setting

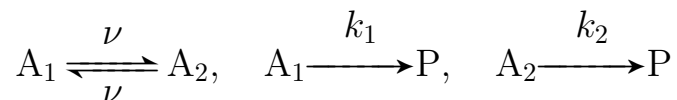
$$A_1 = [A_1], \quad A_2 = [A_2], \quad \text{and} \quad c = A_1 + A_2$$

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,



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  $\nu \rightarrow 0$ , we recover the “biexponential” model above.

When mixing is fast relative to the decay reactions, i.e., when  $\nu \gg k_1$  and  $\nu \gg k_2$ ,  $A_1 \simeq A_2$  at long times  $t \gg \nu^{-1}$  and the aggregate system  $A_1 + A_2$  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

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

Assuming first-order kinetics,

$$\frac{d}{dt}c_k(k)dk = -kc_k(k)dk,$$

and therefore

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

The total concentration evolves as

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

Forming the probability density

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

we obtain the normalized decay

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

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

$p(k)dk$  = initial fraction of material decaying at rates between  $k$  and  $k + dk$ .

As an example, suppose [7]

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

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  $k \ll a^{-1}$ , another way of interpreting a power law decay of  $c(t)$ : instead of inferring the order  $n$  of the kinetics from  $\alpha$ , as in Section 1.2.3, we may merely view it as deriving from a power-law decay of the random rate distribution  $p(k)$ .

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

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

Comparing with the data shown in Section 1.2.3, we see good agreement at long times if  $\alpha \approx 0.2$ .

## 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  $j = 1, 2, \dots$ , 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  $M$  weakly interacting, similarly prepared, subsystems labeled by the index  $s$ .

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

We define the Boolean variable

$$I_{js} = \begin{cases} 1 & \text{if the } j\text{th channel is open in subsystem } s \\ 0 & \text{else.} \end{cases}$$

The  $j$ th channel is

- open with probability  $P_j$ ; and
- closed with probability  $1 - P_j$ .

Define

$$Q_s = \text{set of open channels in subsystem } s.$$

When a channel is closed, it does not contribute to the relaxation. Then the total rate  $W_s$  at which a subsystem  $s$  relaxes is

$$W_s = \sum_{j \in Q_s} \lambda_j.$$

Relaxation of the concentration  $c_s(t)$  in subsystem  $s$  then follows

$$\frac{c_s(t)}{c_s(0)} = \exp \left( - \sum_{j \in Q_s} \lambda_j t \right).$$

The normalized concentration  $c(t)$  in the entire macroscopic body is the average over the  $M$  subsystems:

$$c(t) = \frac{1}{M} \sum_s \frac{c_s(t)}{c_s(0)}.$$

Then the relaxation  $c(t)$  of the entire macroscopic body—i.e., relaxation averaged over the ensemble of subsystems—is a sum over the subsystems:

$$c(t) = \frac{1}{M} \sum_s \exp \left( - \sum_{j \in Q_s} \lambda_j t \right).$$

The entire system therefore relaxes at a distribution of rates given by  $W_s$ .

We rewrite the sums in terms of the Boolean variable  $I_{js}$ :

$$c(t) = \frac{1}{M} \sum_s \exp \left( - \sum_j \lambda_j I_{js} t \right)$$

For large  $M$ , the sum over  $s$  is equivalent to an ensemble average over the subsystems  $s$ :

$$c(t) = \left\langle \exp \left( - \sum_j \lambda_j t \right) \right\rangle_s$$

Since the rates implied by the sum over  $j$  vary from subsystem to subsystem, we see that we have a discrete representation of the random rate model. However we now have access to an alternative representation.

First, we convert the sum to a product:

$$c(t) = \left\langle \prod_j e^{-\lambda_j t} \right\rangle_s$$

Assuming each channel is independent of the others, the average of the product is equal to a product of averages:

$$c(t) = \prod_j \langle e^{-\lambda_j t} \rangle_s \tag{3}$$

We next address the average over  $s$ , bringing back the index variable  $I_{js}$  for clarity:

$$\begin{aligned} \langle e^{-\lambda_j t} \rangle_s &= \text{Prob}(\text{channel } j \text{ closed}) \cdot e^0 + \text{Prob}(\text{channel } j \text{ open}) \cdot e^{-\lambda_j t} \\ &= \frac{1}{M} \left[ \left( M - \sum_s I_{js} \right) + \sum_s I_{js} e^{-\lambda_j t} \right] \end{aligned}$$

Using the definition of  $P_j$  we thus have, for large  $M$ ,

$$\langle e^{-\lambda_j t} \rangle_s = (1 - P_j) + P_j e^{-\lambda_j t}$$

Substituting this expression into equation (3), we find that the system relaxes according to

$$c(t) = \prod_j [(1 - P_j) + P_j e^{-\lambda_j t}]. \quad (4)$$

### 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

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

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  $j$ th channel is open.

When the correlation time of opening and closing of the  $j$ th channel is long compared to  $\lambda_j^{-1}$ , 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:

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

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

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

The decay function (4) then becomes

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

To simplify further, define the density of rates

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

Then

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

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:

- $\rho(\lambda)d\lambda$  is the average number of (open) channels with an individual rate between  $\lambda$  and  $\lambda + d\lambda$ .
- $p(k)dk$  is the overall probability that the total rate of relaxation is between  $k$  and  $k + dk$ .

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,

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

where in the second relation we have suppressed the normalizing factor  $c(0)$ . What  $\rho(\lambda)$  is associated with  $c(t)$ ?

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

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

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

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

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

$$\rho(\lambda) = \frac{1}{\lambda} \mathcal{L}^{-1} \left( \frac{\alpha}{a+t} \right) = \frac{\alpha}{\lambda} e^{-a\lambda}.$$

We find that  $p(k)$  and  $\rho(\lambda)$  are equal only if  $\alpha = 1$ .

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

$$k_{\text{eff}}(t) = \frac{-1}{c} \frac{dc}{dt} = \frac{\int_0^\infty k p(k) e^{-kt} dk}{\int_0^\infty p(k) e^{-kt} dk}$$

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

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

where we have taken  $\lambda$  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

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

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  $p(k)dk$  according to

$$p(k)dk = \sum_{N_1} \sum_{N_2} \dots P(N_1, N_2, \dots) \delta \left( k - \sum_j N_j \lambda_j \right) dk, \quad (7)$$

showing that the total “macroscopic” rate  $k$  is a weighted average of the “microscopic” rates  $\lambda_j$ .

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

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

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

### 1.7.1 Inverse Laplace transform

To gain an understanding of how a particular decay process works, one would like to know either the rate distribution  $p(k)$  or  $\rho(\lambda)$ .

For practical purposes,  $p(k)$  is often a more sensible quantity to work with. In principal, we may obtain an estimate of it from the inverse Laplace transform of  $c$ :

$$p(k) = \mathcal{L}^{-1} [c(t)].$$

The inverse is exact, but the problem is unfortunately *ill posed*, meaning that small amounts of noise in  $c(t)$  can lead to large differences in  $p(k)$ . Conversely, significantly different rate distributions  $p(k)$  can produce effectively the same  $c(t)$ .

Such inverse problems may be solved, however, by the method of *regularization*. The idea is to narrow the space of possible solutions to those for which  $p(k)$  is “smooth,” i.e., those for which

$$\left\| \frac{dp}{dk} \right\|^2$$

is small, while simultaneously minimizing the squared error

$$\|\hat{c} - c\|^2$$

where  $\hat{c}$  is the decay function predicted by the smooth estimate of  $p(k)$ .

One also wants to constrain the inverse problem so that  $\int p(k)dk = 1$ .

There are a variety of ways to perform such a constrained regularized inversion, but we do not discuss them here.

Instead we note that, in a surprisingly wide range of circumstances,  $p(k)$  turns out to be the lognormal distribution [10]

$$p(k) = \frac{1}{k} \frac{1}{2\pi\sigma^2} \exp\left[-\frac{(\ln k - \mu)^2}{2\sigma^2}\right],$$

which has parameters  $\mu$  and  $\sigma$ .

Results for plant-matter decay throughout North America are shown here [10]:

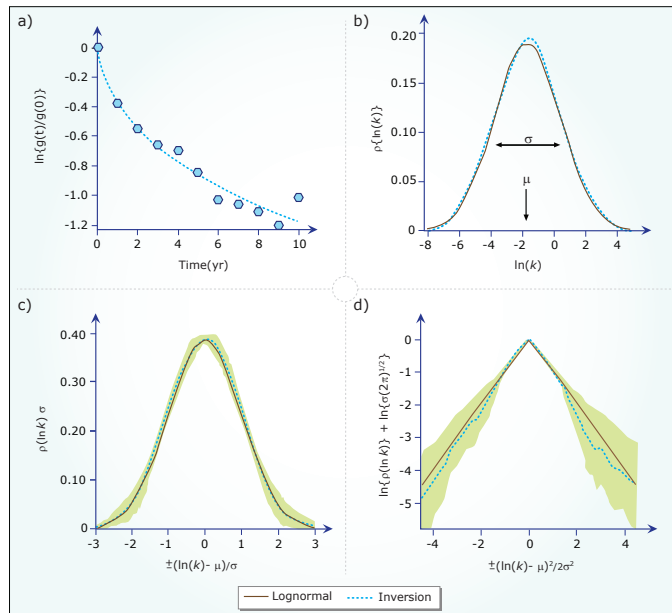


Figure by MIT OpenCourseWare.

### 1.7.2 Lognormal distribution

To see why  $p(k)$  is often lognormal, we examine some of its properties.

First, consider the new random variable

$$x = \ln k.$$

The pdf  $\rho(x)$  is given by

$$\begin{aligned}\rho(x) &= p[k(x)] \frac{dk}{dx} \\ &= \frac{1}{e^x \sqrt{2\pi\sigma^2}} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right] e^x \\ &= \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]\end{aligned}$$

We therefore see that the random variable  $x = \ln k$  has a Gaussian distribution with mean

$$\mu = \langle \ln k \rangle$$

and variance

$$\sigma^2 = \text{Var}(\ln k)$$

To see why the lognormal is ubiquitous, we consider the following model of decay [11].

Suppose that degradation of a particular organic compound (i.e., a “microscopic” unit) occurs only after  $N$  distinct local conditions have been satisfied.

For the problem of decaying organic matter, examples of such conditions include the

- water content
- pH
- nutrient concentration
- microbial community
- oxidizing agent
- concentration and type of organic matter, etc.

If any condition is not satisfied, then degradation of the compound fails to occur.

Let  $p_i$  be the probability that the  $i$ th condition in such a list is satisfied.

Assuming that the  $p_i$ 's are independent, the probability  $P$  that a degradation "event" occurs in a given time is

$$P = p_1 p_2 \dots p_N.$$

$P$  is the probability per unit time that an individual micro-unit vanishes, given a particular set of probabilities  $p_i$ .

Another micro-unit may, however, be associated with a different set of  $p_i$ 's, leading, then, to a different  $P$ . Thus the distribution of  $P$  would seem to depend on the particular distribution of each  $p_i$ .

However it does not. To see why, write

$$\ln P = \ln p_1 + \ln p_2 + \dots + \ln p_N.$$

So long as the random variables  $\ln p_i$  are well behaved (i.e., their first and second moments exist), the central limit theorem tells us that, for  $N$  large,

$$\ln P \text{ is Gaussian, with variance } \sigma^2 = \sum_i \text{var}(\ln p_i).$$

Identifying the rate constant  $k$  with the probability  $P$  per unit time of degradation, we thus find that  $k$  is lognormal.

Consequently the universality of the lognormal rate distribution derives from the central limit theorem.

Specifically, while additive processes produce Gaussian distributions, multiplicative processes produce lognormals.

Montroll and Shlesinger [11] distinguish the two cases with popular sayings. For the additive Gaussian case:

*foot bone 'tached to the leg bone, leg bone 'tached to the knee bone,  
knee bone 'tached to the thigh bone, thigh bone 'tached to the hip  
bone. ....*

Then with some variation in the length of each type of bone in a large population, heights of individuals are Gaussian. An entertaining version of this concept can be found by viewing this [video](#).

On the other hand, lognormal distributions characterize processes whose successful execution follows Franklin's proverb:

*for the want of a nail the shoe was lost, for the want of a shoe the horse was lost, for the want of a horse the rider was lost. . .*

A musical version is [here](#).

### 1.7.3 Relation to $k_{\text{eff}}(t)$

Recall that the observational data suggest an aging of the effective rate constant such that

$$k_{\text{eff}}(t) \simeq 0.2 \times t^{-1}.$$

In principle, we should expect that this result would follow from

$$k_{\text{eff}}(t) = \frac{-1}{c} \frac{dc}{dt} = \frac{\int_0^\infty k \Lambda(k; \mu, \sigma) e^{-kt} dk}{\int_0^\infty \Lambda(k; \mu, \sigma) e^{-kt} dk}$$

where  $\Lambda(k; \mu, \sigma)$  is the lognormal pdf

$$\Lambda(k; \mu, \sigma) = \frac{1}{k\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(\ln k - \mu)^2}{2\sigma^2}\right]$$

We can estimate the required integrals when the variance  $\sigma^2$  is large. First, change the variable of the lognormal to  $\kappa = k/e^\mu$  (i.e., express  $k$  in units of its median  $e^\mu$ ):

$$\Lambda_\kappa(\kappa) = \frac{1}{\kappa\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(\ln \kappa)^2}{2\sigma^2}\right].$$

Taking logs on both sides,

$$\ln \Lambda_\kappa(\kappa) = -\ln \kappa - \frac{(\ln \kappa)^2}{2\sigma^2} - \frac{\ln(2\pi\sigma^2)}{2}.$$

When the second term is much smaller than the first, i.e., when

$$|\ln \kappa| \ll 2\sigma^2$$

we have

$$\Lambda_\kappa(\kappa) \propto \frac{1}{\kappa} \quad \Rightarrow \quad \Lambda(k) \propto \frac{1}{k}$$

showing that a lognormal distribution is remarkably similar to a simple power law.

For practical purposes we suppose that the power law holds between values  $k_{\min}$  and  $k_{\max}$  and vanishes elsewhere.

Then our expression for  $k_{\text{eff}}$  becomes

$$k_{\text{eff}}(t) = \frac{\int_{k_{\min}}^{k_{\max}} e^{-kt} dk}{\int_{k_{\min}}^{k_{\max}} k^{-1} e^{-kt} dk}.$$

Noting that the exponential integral

$$E_1(k_{\min}t) = \int_{k_{\min}}^{\infty} k^{-1} e^{-kt} dk$$

we have

$$k_{\text{eff}}(t) = \frac{1}{t} \left( \frac{e^{-k_{\max}t} - e^{-k_{\min}t}}{E_1(k_{\max}t) - E_1(k_{\min}t)} \right)$$

At long times  $t \gg k_{\max}^{-1}$  we can neglect the terms involving  $k_{\max}$  so that

$$k_{\text{eff}}(t) = \frac{1}{t} \left( \frac{e^{-k_{\min}t}}{E_1(k_{\min}t)} \right)$$

If times are not so long so that  $t \ll k_{\min}^{-1}$ , the numerator is effectively unity and we can employ the asymptotic expansion [12]

$$E_1(k_{\min}t) = -\gamma - \ln k_{\min}t$$

where  $\gamma = 0.5772\dots$  is Euler's constant. Then

$$k_{\text{eff}}(t) \sim \frac{1}{t} \left( \frac{1}{-\gamma - \ln k_{\min}t} \right), \quad k_{\max}^{-1} \ll t \ll k_{\min}^{-1}.$$

We see that  $k_{\text{eff}}(t)$  is not a pure power law but instead contains a logarithmic correction.

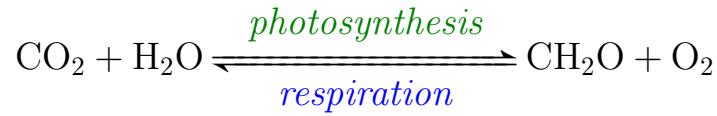
Empirical studies [13] suggest that  $-7 \lesssim \ln k_{\min} t \lesssim -3$ . Supposing an average value of  $-5$  we then find

$$k_{\text{eff}}(t) \simeq 0.2 \times t^{-1}$$

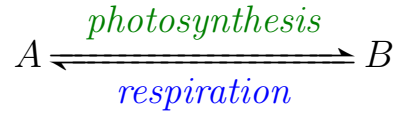
as found in the experimental data.

## 1.8 The elementary cycle $A \rightleftharpoons B$

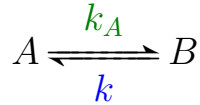
Consider again the carbon cycle:



Simplify it by writing



and now take the rates as

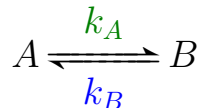


where

- $A \rightarrow B$  at a constant rate  $k_A$ .
- $B \rightarrow A$  at a *random* rate  $k$ .

### 1.8.1 Equilibrium ratio

The simplest case:  $B \rightarrow A$  at a deterministic rate  $k = k_B$ :



In terms of differential equations, we have

$$\begin{aligned} \dot{A} &= -k_A A + k_B B \\ \dot{B} &= k_A A - k_B B \end{aligned}$$



We find the equilibrium ratio

$$\frac{A}{B} = \frac{k_B}{k_A}.$$

Returning to the random rate  $k$ , we set

$$b(k)dk = \text{fraction of } B \text{ that reacts at a rate } k \text{ between } k \text{ and } k + dk.$$

$B$  is the sum of its parts:

$$\int_0^\infty b(k)dk = B.$$

$A$  is converted to a continuum of  $k$ -types of  $B$ :

$$A \rightarrow b(k)dk, \quad 0 \leq k \leq \infty,$$

with specified probability

$$p(k)dk, \quad 0 \leq k \leq \infty.$$

$A$  and  $b(k)$  change as

$$\begin{aligned} \dot{A} &= -k_A A + \int_0^\infty kb(k)dk. \\ \dot{b}(k) &= k_A p(k)A - kb(k). \end{aligned}$$

In steady state,

$$b(k) = \frac{k_A}{k} p(k)A.$$

The equilibrium ratio

$$\frac{A}{B} = \frac{A}{\int_0^\infty b(k)dk}.$$

Inserting the steady solution for  $b(k)$ ,

$$\frac{A}{B} = \frac{1}{k_A \int_0^\infty k^{-1} p(k)dk} = \frac{1}{k_A} \frac{1}{\langle k^{-1} \rangle}$$

Thus  $A/B$  is determined by the first negative moment  $\langle k^{-1} \rangle$  of the pdf  $p(k)$ .

The first negative moment of the lognormal is

$$\langle k^{-1} \rangle = \int_0^\infty k^{-1} \Lambda(k)dk = e^{-\mu + \sigma^2/2}.$$

Therefore

$$\frac{A}{B} = \frac{e^{\mu - \sigma^2/2}}{k_A}.$$

Note that when

$$\sigma = 0 \quad \text{and} \quad \mu = \log k_B$$

we recover the case of the single deterministic rate,

$$\frac{A}{B} = \frac{k_B}{k_A}.$$

Interesting phenomena result from the *disordered* case  $\sigma > 0$ . To see why, suppose that we had *wrongly* assumed that  $B \rightarrow A$  at the *mean* rate

$$\langle k \rangle = \int_0^\infty k \Lambda(k) dk = e^{\mu + \sigma^2/2}.$$

We would then make the relative error

$$\begin{aligned} \frac{(A/B)_{\text{wrong}}}{(A/B)_{\text{true}}} &= \frac{\langle k \rangle}{1/\langle k^{-1} \rangle} \\ &= \langle k \rangle \langle k^{-1} \rangle. \end{aligned}$$

Inserting the expressions for the first positive and negative moments of the lognormal, we have

$$\left. \frac{(A/B)_{\text{wrong}}}{(A/B)_{\text{true}}} \right|_{\text{lognormal}} = e^{\sigma^2},$$

showing that the error in the equilibrium concentration ratio increases *exponentially* with  $\sigma^2$  when rates are lognormal.

### 1.8.2 Turnover time and age

Reference: [14]

Define

- *turnover time*: the mean time taken by the reaction  $B \rightarrow A$ .

- the mean *age* of  $B$ : the mean time each bit of a population of  $B$  has spent being  $B$ .

We imagine that we can probe the reservoir of  $B$  and determine the time that each molecule has spent being  $B$  since it was “born” by the reaction  $A \rightarrow B$ .

**Age distribution** The *age distribution* is

$$p_a(\tau)d\tau = \text{fraction of } B \text{ with age between } \tau \text{ and } \tau + d\tau,$$

where

$$\int_0^{\infty} p_a(\tau)d\tau = 1.$$

The mean age  $a$  is

$$a = \int_0^{\infty} \tau p_a(\tau)d\tau.$$

**Exit-time distribution** The *exit time* is the age of a bit of  $B$  when it is transformed to  $A$ .

The *exit time distribution*  $p_\varepsilon(\tau)$  is the age distribution of  $B$  when  $B \rightarrow A$ :

$$p_\varepsilon(\tau)d\tau = P(B \rightarrow A \text{ after waiting a time between } \tau \text{ and } \tau + d\tau).$$

$p_\varepsilon(\tau)$  is also called the *transit time*, *residence time*, and *first-passage time* distribution. It too integrates to unity:

$$\int_0^{\infty} p_\varepsilon(\tau)d\tau = 1.$$

The *turnover time* is the *mean exit time*  $\varepsilon$ , where

$$\varepsilon = \int_0^{\infty} \tau p_\varepsilon(\tau)d\tau.$$

In general,  $p_\varepsilon(\tau) \neq p_a(\tau)$  and  $a \neq \varepsilon$ .

Consider, e.g., human populations:

- The mean exit time  $\varepsilon \simeq 70$  yr.
- The mean age  $a \simeq 30$  yr.

Biogeochemical cycles typically exhibit the opposite behavior, with differences measured in orders of magnitude.

Consider, e.g, marine organic carbon:

- The turnover time  $\varepsilon \simeq 14$  yr.
- The mean age  $a \simeq 5000$  yr.

**Survival function and its relation to age and exit time** Define the flux

$$J(\tau) = \text{mass with age } \leq \tau \text{ that reacts from } B \rightarrow A \text{ per unit time.}$$

Assume a steady input and output flux  $J_0$  to and from the  $B$ -state. Then

$$J_0 - J(\tau) = \text{the total reactive flux with age } > \tau.$$

Divide by  $J_0$  to obtain the dimensionless *survival function*

$$S(\tau) = 1 - \frac{J(\tau)}{J_0}.$$

$S(\tau)$  is an *impulse response*: it gives the fraction of  $B$  that survives a time  $> \tau$  as species  $B$ .

We can also write it in terms of the exit time distribution:

$$S(\tau) = \int_{\tau}^{\infty} p_{\varepsilon}(\tau') d\tau'$$

Take derivatives on both sides, we find the exit time distribution

$$\boxed{p_{\varepsilon}(\tau) = -\frac{dS}{d\tau}}. \quad (8)$$

Consequently the turnover (mean exit) time is

$$\begin{aligned}\varepsilon &= - \int_0^\infty \tau \frac{dS}{d\tau} d\tau \\ &= -\tau S(\tau) \Big|_0^\infty + \int_0^\infty S(\tau) d\tau\end{aligned}$$

where we have integrated by parts. We find

$$\boxed{\varepsilon = \int_0^\infty S(\tau) d\tau.}$$

The mass  $B$  at any particular moment in time contains contributions that were “born” at all past times, weighted by the fraction that remains.

For a steady state in which  $J_0$  is the steady “input” flux to  $B$  and  $B_0$  is the steady mass of  $B$ , the contributions to  $B_0$  are integrated over the survival function, scaled by  $J_0$ :

$$B_0 = J_0 \int_0^\infty S(\tau) d\tau.$$

Thus the turnover time is simply

$$\boxed{\varepsilon = B_0/J_0},$$

which could have been inferred immediately from dimensional analysis.

In steady state, the dimensional survival flux  $J_0 - J(\tau)$  must be balanced by  $B_0 p_a(\tau)$ , the mass per unit time that passes the “age barrier” at  $t$  to become just older than  $t$ :

$$J_0 - J(\tau) = B_0 p_a(\tau).$$

In the analogy with human populations, this statement is akin to observing that the death rate of people older than, say, 65, must be balanced in steady state by the rate at which the younger population crosses the 65-year age barrier.

Dividing the expression above by  $J_0$ , we obtain

$$S(\tau) = \varepsilon p_a(\tau).$$

Therefore the age distribution

$$\boxed{p_a(\tau) = \frac{1}{\varepsilon} S(\tau).}$$

**Example: single decay rate  $k_0$**  In this case the survival function is

$$S(\tau) = e^{-k_0\tau}.$$

The exit time distribution is

$$p_\varepsilon(\tau) = -\frac{dS}{d\tau} = k_0 e^{-k_0\tau}$$

and the turnover time is

$$\varepsilon = k_0^{-1}.$$

The age distribution is

$$p_a(\tau) = \frac{S(\tau)}{\varepsilon} = k_0 e^{-k_0\tau}.$$

Thus  $a(\tau) = \varepsilon(\tau) \propto e^{-\tau/\varepsilon}$ , a very special case!

**Disordered rates** The mean age is

$$\begin{aligned} a &= \frac{1}{\varepsilon} \int_0^\infty \tau S(\tau) d\tau \\ &= \frac{1}{\varepsilon} \int_0^\infty \tau d\tau \int_0^\infty p(k) e^{-k\tau} dk \\ &= \frac{1}{\varepsilon} \int_0^\infty dk p(k) \int_0^\infty d\tau \tau e^{-k\tau} \\ &= \frac{1}{\varepsilon} \int_0^\infty dk k^{-2} p(k) \end{aligned}$$

and therefore

$$a = \frac{1}{\varepsilon} \langle k^{-2} \rangle.$$

Similar calculations yield the turnover time:

$$\begin{aligned} \varepsilon &= -\int_0^\infty \tau \frac{dS}{d\tau} d\tau \\ &= \int_0^\infty \tau d\tau \int_0^\infty k p(k) e^{-k\tau} dk \\ &= \int_0^\infty dk k p(k) \int_0^\infty d\tau \tau e^{-k\tau} \\ &= \int_0^\infty dk k^{-1} p(k). \end{aligned}$$

Consequently

$$\varepsilon = \langle k^{-1} \rangle.$$

**The lognormal case** When  $p(k)$  is lognormal, computation of the first and second negative moments readily yield the turnover time

$$\varepsilon = e^{-\mu+\sigma^2/2}$$

and the mean age

$$a = e^{-2\mu+2\sigma^2}/\varepsilon = e^{-\mu+3\sigma^2/2}.$$

Consequently

$$a = \varepsilon e^{\sigma^2},$$

showing that the ratio of the mean age to the turnover time grows exponentially with  $\sigma^2$ .

**Marine organic carbon** Consider again marine organic carbon:

- Primary productivity is about  $J_0 = 50$  Gt/yr.
- The oceans contains about  $B_0 = 700$  Gt organic C.
- Thus the turnover time  $\varepsilon = B_0/J_0 \simeq 14$  yr.
- The mean age  $a \simeq 5000$  yr.

If we may assume that marine respiration rates are lognormally distributed, then

$$\sigma = \sqrt{\ln(a/\varepsilon)} \simeq 2.4.$$

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