A CHEMICAL KINETICS APPROACH TO THE DURATION-OF-LOAD PROBLEM IN WOOD[1]

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ABSTRACT

The theory of absolute rates of chemical processes is presented as an appropriate conceptual framework for understanding the creep-rupture phenomena of duration of load (DOL) and rate of loading (ROL). The theory predicts the following experimentally observed phenomena:

(1) The logarithm of the time to failure under constant deadload stress increases linearly as the stress level is decreased.
(2) The rupture strength in a linear-ramp ROL experiment increases with the logarithm of the rate of stressing.

Moreover, the equations derived to describe these phenomena contain the same parameters. These parameters are defined physical quantities that describe the creep characteristics of the material. It is possible to predict how long a material will support a constant deadload stress (DOL behavior) from measurements of apparent rupture strength as a function of the rate of stressing in a linear-ramp loading experiment (ROL behavior).

Rupture of Douglas-fir in bending is selected as an example, and the experimental results from ROL-behavior experiments are used to predict DOL behavior. The theory adequately describes the experimentally observed results.

Keywords: Creep rupture, duration of load, rate of loading, bending rupture, Douglas-fir, absolute reaction rates, stress-strain behavior, tensile strength, modulus of rupture.

INTRODUCTION

Wood (Gerhards 1977), paper (Rance 1953), and textile fibers (Hearle and Morton 1962) all exhibit time-dependent rupture behavior. Any of these materials, loaded to a constant stress level considerably below its normal breaking stress, will nevertheless break—if that stress is maintained over a long enough time. This phenomenon has been called the duration-of-load (DOL) phenomenon. Researchers have empirically found that, for these materials under constant deadload stress, the logarithm of the time to failure varies inversely as the stress level. A second time-dependent rupture phenomenon exhibited by wood (Gerhards 1977), paper (Rance 1953), and textile fibers (Hearle and Morton 1962) can be called the rate-of-loading (ROL) phenomenon. The measured strength of the material increases as the rate at which the material is stressed increases. If the applied stress is increased linearly with time (linear ramp loading), the rupture strength increases with the logarithm of the rate of stressing.

The purpose of this paper is to demonstrate that the theory of absolute rates of chemical processes provides an appropriate conceptual framework for under-

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standing these creep-rupture phenomena. This theory predicts the experimentally observed behavior for both phenomena. It also provides the mathematical formalism connecting DOL and ROL behavior. Using this connection, one can predict how long a material will support a constant deadload stress (DOL behavior) from measurements of strength as a function of rate of stressing in a linear-ramp loading experiment (ROL behavior).

The bending of Douglas-fir is selected as an example, and the experimental results from ROL-behavior experiments alone are used to predict DOL behavior.

THEORETICAL BACKGROUND

A serious mathematical difficulty arises in the interpretation of the stress-strain behavior of a material at the point on the stress-strain curve that corresponds to failure or rupture. Up to that point, one can follow continuously the changes that take place as a result of elastic or viscoelastic response. Rupture, however, represents a discontinuity that cannot be avoided. No continuous set of variables describes both the state before and the state after rupture. One cannot even use thermodynamics (at least not reversible thermodynamics) to describe the rupture process because of the discontinuity and the need to define both starting and final states in consistent terms. Thus one can never describe a breaking process with the same degree of mathematical rigor that one can describe either an elastic deformation or a viscous flow. This mathematical difficulty seriously interferes with a fundamental understanding of rupture phenomena.

THE CHEMICAL KINETICS APPROACH

The chemical kinetics approach is one way of dealing with this mathematical difficulty. The kinetics approach makes the assumption that rupture is determined completely by the magnitude and nature of the deformation preceding rupture and that the elucidation of the role of creep in processes leading to failure is the essential problem.

The guiding principle behind the chemical kinetics approach to an understanding of rupture is the idea that the straining process itself is, or contains within it, a process of failure that becomes unstable at a time (pre)determined by the straining process, thus ending in rupture.

In order to examine the role of creep in fundamental terms, it is helpful to follow the methods used by Eyring and his coworkers (Glasstone et al. 1941; Tobolsky et al. 1943). They extended the theory of absolute rates of chemical reactions to describe the phenomena of viscosity and viscoelasticity.

According to the kinetic theory of matter, all atoms and molecules are in motion. This molecular motion, when analyzed in terms of statistical mechanics, provides a description of the macroscopic motion. In a solid, for example, the motion of its component molecules is more restricted than in a liquid; and in a liquid, more restricted than in a gas. In a solid, each atom or molecule or group of molecules can be pictured as sitting at the bottom of a potential energy well (Fig. 1). At equilibrium, a molecule in its well appears quite satisfied where it is. But that does not mean that it does not move from that site. Because it is in constant motion, it can occasionally surmount the energy barrier and get to a new position of minimum energy. In a solid this jumping of an energy barrier is less frequent than in a liquid, and on the average there are just as many jumps to the left
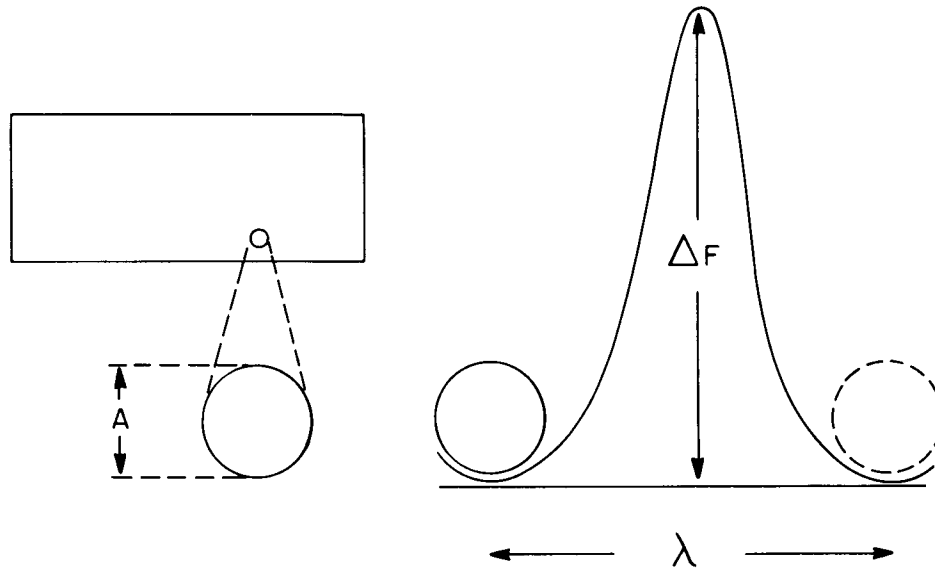
Fig. 1. For a material with no external stress, the potential energy barrier is symmetrical, and the tendency of the force center to jump the barrier is the same from either direction. The number of jumps right per unit time equals $\dfrac{kT}{h} \exp\left(\dfrac{-\Delta F}{RT}\right)$ and the net number of jumps per unit time equals 0. A = Cross section of the force center. ΔF = Height of the energy barrier. λ = Distance between jumps.

direction as there are to the right, so that there is no net movement of the solid or parts of the solid.

The kinetic theory of absolute rates tells us that the number of jumps per unit time in, say, the right direction, ν_+, is given by

$$\nu_+ = \frac{kT}{h} \exp\left(\frac{-\Delta F}{RT}\right)$$

ΔF is the energy of activation needed for jumping, or the height of the potential energy barrier. Boltzmann's constant is given by k, Planck's constant by h, the absolute temperature by T, and the gas constant by R.

The number of jumps per unit time in the opposite direction

$$\nu_- = \frac{kT}{h} \exp\left(\frac{-\Delta F}{RT}\right)$$

is identical, so that, on the average, there are just as many jumps to the left as there are to the right: so that no net motion occurs.

The situation changes when, superimposed upon this symmetrical energy barrier, we apply an external mechanical stress, f, on the material. The tendency of the molecules to jump the barrier in one direction is different from the tendency to jump the barrier in the reverse direction.

Let us try to generalize by not necessarily calling the jumping objects molecules, because elements larger than molecules might be involved in the motion. They might be groups of molecules, filaments, fibrils, etc. Let us just call them elements
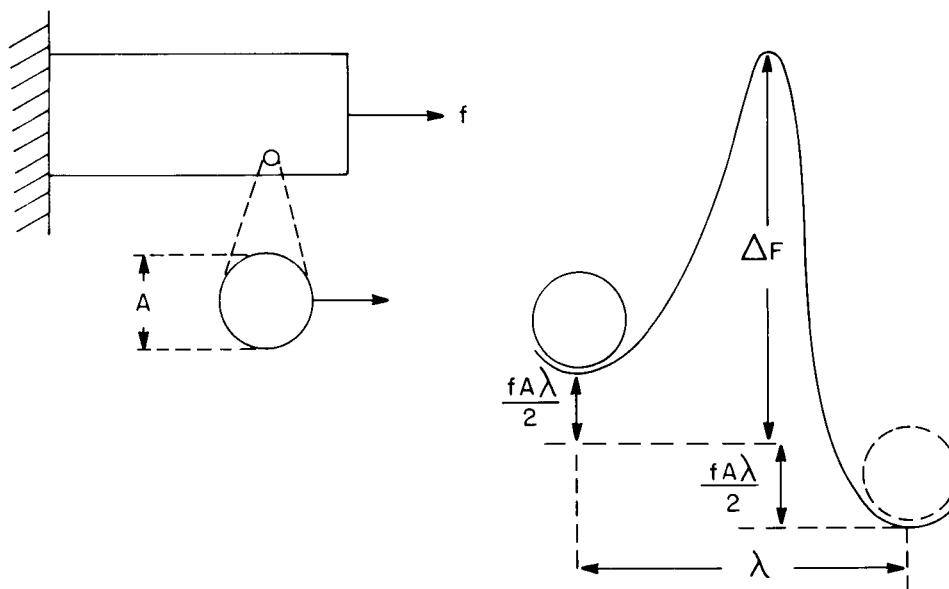
FIG. 2.   For a material under external stress, the potential energy barrier is distorted, and the tendency to jump the barrier in the direction of the applied stress is greater than in the opposite direction. The net number of jumps per unit time equals

$$\frac{kT}{h}\exp\left(\frac{-\Delta F}{RT}\right)\left[\exp\left(\frac{fA\lambda}{2kT}\right) - \exp\left(\frac{-fA\lambda}{2kT}\right)\right]$$

A = Cross section of the force center. ΔF = Height of the energy barrier. λ = Distance between jumps. f is the applied stress.

or force centers. The easiest case to envision is a tensile stress. Although a tensile stress is used for simplicity, the treatment is equally applicable to any generalized stress that has the unit's force per unit area and its appropriate response.

The additional force that the molecule or force center feels is the stress on the force center multiplied by A, the cross-sectional area of the force center. And if the distance between minimum potential energy troughs in the direction of the stress is given by λ, then the applied stress contributes an amount of mechanical work towards surmounting the energy barrier equal to

$$\frac{fA\lambda}{2}$$

This is equivalent to a symmetric distortion of the potential energy barrier to give it a form like that shown in Fig. 2. For this unsymmetric energy barrier the number of jumps per unit time in the right direction is given by

$$\nu_+ = \frac{kT}{h}\exp\left(\frac{-\Delta F}{RT}\right)\exp\left(\frac{fA\lambda}{2kT}\right)$$

The number of jumps per unit time in the reverse direction is given by

$$\nu_- = \frac{kT}{h}\exp\left(\frac{-\Delta F}{RT}\right)\exp\left(\frac{-fA\lambda}{2kT}\right)$$

The overall net tendency to jump the energy barrier is the number of jumps per unit time in one direction minus the number of jumps per unit time in the opposite direction;

$$\nu_+ - \nu_- = \frac{kT}{h} \exp\left(\frac{-\Delta F}{RT}\right)\left[\exp\left(\frac{fA\lambda}{2kT}\right) - \exp\left(\frac{-fA\lambda}{2kT}\right)\right]$$

Because the quantities A and λ always appear as a product, let's call that product δ. δ has the units of (m³) and represents the volume of the force center or moving element.

Then

$$\nu_+ - \nu_- = \frac{kT}{h} \exp\left(\frac{-\Delta F}{RT}\right)\left[\exp\left(\frac{f\delta}{2kT}\right) - \exp\left(\frac{-f\delta}{2kT}\right)\right]$$

$$\sinh X = \frac{e^x - e^{-x}}{2}$$

so

$$\nu_+ - \nu_- = \frac{2kT}{h} \exp\left(\frac{-\Delta F}{RT}\right)\sinh\left(\frac{f\delta}{2kT}\right)$$

The net number of jumps per unit time multiplied by the distance per jump, λ, gives a rate of dislocation of the element. And if we call that rate of local strain dislocation, $\frac{d\gamma}{dt}$, then

$$\frac{d\gamma}{dt} = (\nu_+ - \nu_-)\lambda = \frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right)\sinh\left(\frac{f\delta}{2kT}\right) \tag{1}$$

We will assign the function γ the boundary condition that $\gamma = 0$ when $t = 0$.

In this equation γ represents the microscopic strain (in actual displacement) so that $\frac{d\gamma}{dt}$ is the rate of dislocation or rate of creep deformation.

Equation (1) is equivalent to one that is sometimes called the hyperbolic sine law of viscous flow. If $f\delta \ll 2kT$, then the hyperbolic sine is equal to its argument, and the rate of strain is proportional to f, the stress. This is just a description of a Newtonian liquid, where the rate of strain is proportional to stress. Now it is reasonable that we should have an equation that applies to liquids as well as solids because we have not done anything yet to limit our discussion to solids. If we limit our discussion to solids, then we will limit ourselves to only those cases for which $f\delta \gg 2kT$. kT is the measure of thermal energy in the system; $f\delta$, a measure of the mechanical work involved. So we will be dealing with those cases for which the mechanical work involved to obtain movement or dislocation is large compared to the thermal energy of the material. Roughly, this corresponds to a system where large forces are required before movements occur, rather than, for example, in liquids. In ordinary liquids f is of the order of 0.1 Pa, while the molecular volume, δ, is of the order of 1×10^{-27} m³, i.e., $f\delta \ll 2kT$.

Equation (1) is equivalent in form to an equation used in the damage accumulation model (Gerhards and Link 1983) explanation of time-dependent rupture

phenomena. This equivalence is apparent if the variable of integration, γ, is replaced by its reduced variable, $\dfrac{\gamma}{\gamma_B}$, the ratio of creep deformation to critical creep deformation. The limits of integration in this form are 0 and 1, where unity corresponds to the level of "damage" that causes failure. Unlike the damage accumulation theory, however, all of the parameters used in Eq. (1) have defined physical interpretations. If indeed three characteristics of the material are known — 1) the volume of the moving element, δ, 2) the height of the potential energy barrier, ΔF, and 3) the ratio, $\dfrac{\gamma}{\lambda}$ (the localized strain)—then Eq. (1) contains no adjustable parameters.

In order to integrate Eq. (1), we make use of the critical assumption of the theory. This assumption is the creep-rupture hypothesis: there is an upper limit that the localized strain deformation can reach, γ_B, above which the material can no longer support the stress and the material fails or ruptures. This idea that there is a critical strain that determines rupture has a long history. Probably the first to suggest it was St. Venant (ca. 1855). But the first to suggest this creep-rupture hypothesis in terms of the limits of integration was Coleman (1956), and it is Coleman's formalism and treatment that is followed here with some modifications for our special purposes.

We may integrate Eq. (1) only if we know the functional dependence of the stress on time, f(t). We will consider only two cases in detail. For DOL behavior, we are concerned with the creep deformation that occurs under a stress that is invariant with time, f = constant. For ROL behavior, we are interested in the integration for the case where the stress increases linearly with time, f = αt; a so-called linear ramp, where α is the rate of stressing.

PREDICTION OF DOL BEHAVIOR

If the stress is constant over time, that is, at time t = 0 a constant stress is applied, the material will creep until a localized strain deformation is reached, γ_B; at which point in time, t_B, the specimen fails.

$$\int_0^{\gamma_B} d\gamma = \frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right) \sinh\left(\frac{f\delta}{2kT}\right) \int_0^{t_B} dt$$

$$\gamma_B = \left[\frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right) \sinh\left(\frac{f\delta}{2kT}\right)\right] t_B$$

$$\text{let } a = \frac{h\gamma_B}{kT\lambda} \exp\left(\frac{\Delta F}{RT}\right)$$

$$b = \frac{\delta}{2kT}$$

$$\text{then } t_B = \frac{a}{2} \operatorname{csch} fb$$

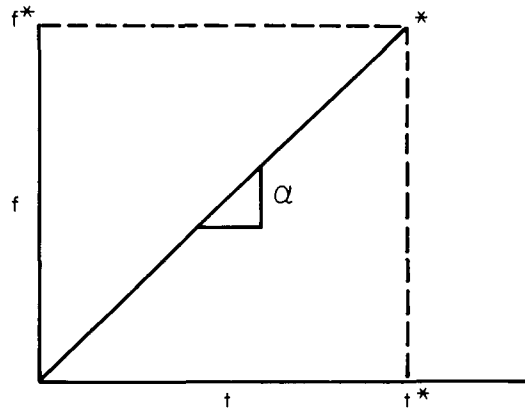$$\operatorname{csch} x = \frac{1}{\sinh x} \approx \frac{2}{e^x - e^{-x}}$$

FIG. 3.   In a linear-ramp rate-of-loading (ROL) test the applied stress (f) increases linearly with time (t) up to failure (*).

$$= 2e^{-x} \quad \text{if} \quad x \gg 1$$

$$t_B = a \exp(-bf)$$

$$f = \frac{1}{b} \ln a - \frac{1}{b} \ln t_B \tag{2}$$

Equation (2) is the well-verified relationship between stress, f, and the logarithm of the time required to break. This equation is most often seen by wood engineers as an empirical relationship between stress (normalized, and expressed as a percent) and the common log t.

This, then, is the first of two important predictions of the chemical kinetics approach, that for a material under constant deadload stress, the logarithm of the time to failure varies inversely as the stress level.

$$f \sim \ln \frac{1}{t_B}$$

PREDICTION OF ROL BEHAVIOR

The result of the integration of Eq. (1) changes if instead of a constant deadload stress we consider a stress that varies with time. The simplest type of time-dependent stress to consider is a linear ramp; one for which the stress is increased linearly with time, at a rate of stress application, α (Fig. 3).

$$f = \alpha t$$

In this case the sample fails at a time, t^*, corresponding to a stress, f^*.

$$\frac{d\gamma}{dt} = \frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right) \sinh[bf(t)]$$

$$\int_0^{\gamma_B} d\gamma = \frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right) \int_0^{t^*} \sinh(b\alpha t) \, dt$$

$$\gamma_B = \frac{2kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right) \left[\frac{1}{\alpha b}(\cosh \alpha bt^* - \cosh 0)\right]$$

but $\alpha t^* = f^*$
and if $bf^* \gg 1$

$$\cosh 0 \ll \cosh bf^* = \frac{e^{bf^*}}{2}$$

$$\gamma_B = \frac{kT\lambda}{h} \exp\left(\frac{-\Delta F}{RT}\right)\frac{1}{\alpha b} \exp(bf^*)$$

$$\exp(bf^*) = \left[\frac{h\gamma_B}{kT\lambda} \exp\left(\frac{\Delta F}{RT}\right)\right]\alpha b$$

$$\exp(bf^*) = a\alpha b$$

$$f^* = \frac{1}{b} \ln ab + \frac{1}{b} \ln \alpha \tag{3}$$

Equation (3) is the second important prediction of the kinetic approach amply verified experimentally. That prediction is that the breaking stress (in a linear-ramp ROL experiment) increases as the logarithm of the rate of loading.

SIGNIFICANCE OF THE DERIVED EQUATIONS

We have two equations, Eqs. (2) and (3), that predict 1) the dependence of breaking time on stress in a constant deadload experiment and 2) the dependence of breaking stress on the rate of loading in a linear-ramp ROL experiment.

$$(2) \qquad\qquad f = \frac{1}{b} \ln a - \frac{1}{b} \ln t_B$$

$$(3) \qquad\qquad f^* = \frac{1}{b} \ln ab + \frac{1}{b} \ln \alpha$$

The only parameters in Eqs. (2) and (3) are the quantities a and b. These quantities are, in turn, relatable to material properties. For example, since $b = \delta/2kT$, it provides an immediate estimate of the volume of the moving element, δ. On the other hand, because

$$a = \frac{h\gamma_B}{kT\lambda} \exp\left(\frac{\Delta F}{RT}\right)$$

the value of a can provide a measure of the height of the potential energy barrier, ΔF, only if the ratio γ_B/λ, can be estimated from the additional measurement of the critical strain, i.e., the strain at failure.

If the theory is valid, when one plots f versus $\ln t_B$ or plots f^* versus $\ln \alpha$, straight lines result. Moreover, the slope of the line given by Eq. (2) is negative that given by Eq. (3).

We see that f and f^* and t_B and α are all experimental quantities. The only other quantities in these equations are a and b, so that if one could evaluate the quantities