

On Zhurkov's Approach to the Strength of Solids

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Synopsis

Two modifications to the Zhurkov kinetic concept of static (creep) rupture is discussed: (a) solids where the common pole τ_0 is much larger than that associated with a vibrational frequency of bonded atoms in the solid and (b) materials where a common pole does not occur. Both cases are discussed within the Zhurkov framework. The activation thermodynamics and the association with transition state theory are revealed.

INTRODUCTION

The mechanisms and the laws governing the failure of brittle solids and polymers have features in common, and understanding of the phenomena can lead to the successful development of accelerated tests for such materials. For long duration performance of materials the designer needs to have data on how long his choice of material can be expected to last in a given situation. Real time tests are clearly impractical in both time and money, and the obvious solution to the problem is to use an acceptable accelerated test to predict lifetime.

The time dependence of the strength of solids and its connection with the mechanism of failure was studied by Zhurkov¹ and his co-workers. His phenomenological approach to delayed failure (creep rupture) is also known as kinetic rate theory. In the Soviet Union the Zhurkov method is unquestioned² while in the West it has been suspect, leading to questioning of the method with such comments as ". . . a good bit of discretion is often required to force the data to intersect at a pole."³ The purpose of the present communication is to minimize the discretion.

The Zhurkov method has modifications under certain conditions which have not been recognized. In some materials the common pole τ_0 which is obtained from $\log \tau$ vs. σ data at several temperatures is much larger than $\tau_0 \sim 10^{-13}$ s obtained with materials that conform to the usual Zhurkov method. Zhurkov associated τ_0 with the vibrational frequency of the bonded atoms in the solid. In other instances, experimental data do not result in a common pole at all. The discussion below shows how these materials can be brought into the Zhurkov framework.

From an applied viewpoint the primary value of the Zhurkov method is that it may be used to devise accelerated testing of materials. Here such tests are outlined for creep rupture within the usual method and its modifications. Elsewhere,⁴ it has been shown that accelerated tests for composites under static, dynamic, and cyclic loads are also possible.

THE ZHURKOV METHOD

Zhurkov developed his creep rupture method by successfully applying his relationships to a variety of materials (metals and nonmetals) and their time dependence of strength under unidirectional tension.

The relationship and definitions of Zhurkov are

$$\tau = Ae^{-\alpha\sigma} \quad (\text{at constant temp}) \quad (1)$$

$$\tau = \tau_0 e^{U^*/kT} \quad (\text{at fixed } \sigma) \quad (2)$$

where τ = time to rupture, α = const, A = const, σ = applied uniaxial stress, τ_0 = const, $U^* = U_0 - \gamma\sigma$ (energy), U_0 = an activation energy, γ = const, k = Boltzmann's constant, T = absolute temperature.

When a material behaves according to eqs. (1) and (2), τ_0 is considered to be the period of natural oscillations, i.e., $\tau_0 = 1/\nu$, where ν is the vibrational frequency of the bonded atoms (i.e., $\sim 10^{-13}$ s); U_0 is the activation energy of the elementary act of failure in the absence of stress; γ is a coefficient that depends on the structure of the material. Equations (1) and (2) are related through

$$\alpha = \gamma/kT \quad (3a)$$

$$A = \tau_0 \exp(U_0/kT) \quad (3b)$$

Figure 1 shows a schematic of results obtained by applying eq. (1) to creep rupture data. Such results are typical of those obtained by Zhurkov for a variety

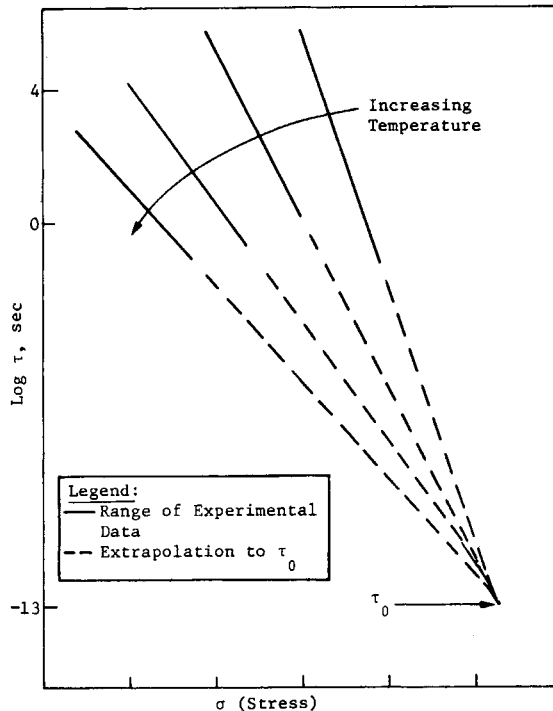


Fig. 1. Application of Zhurkov's Eq. (1): (—) range of experimental data; (---) extrapolation to τ_0 .

of materials. From such results, the constants A and σ are obtained at each temperature that is studied.

Figure 2 shows a schematic of results obtained by applying eq. (2) to such data where the slopes equal $U^*/2.303k$. A U^* is obtained for each σ . Then a plot of U^* vs. σ yields $U^* = -\gamma\sigma + U_0$, where the slope is γ and the intercept U_0 . It should be noted that γ may also be obtained from eq. (3a).

Data similar to Figures 1 and 2 for viscose fiber may be found in Chap. 1 of Ref. 2 and are analyzed in complete accord with the Zhurkov method.

Thus for an accelerated test of creep rupture, at some temperature of interest, three or four points at relatively high stresses (short rupture times) will permit predictions of results at much lower stresses, i.e., at much lower times to rupture. Such data taken at two or three easily accessible temperatures should predict results for desired stress at, say, very low temperatures. Such applications are the claimed usefulness of the method, and have indeed been applied to many materials.²

MODIFIED ZHURKOV BEHAVIOR

In Chap. 1 of Ref. 2 the time dependence of the strength of celluloid at four temperatures (20°C, 70°C, 85°C, 100°C) is presented (without discussion) in a figure similar to Figure 1 here. However, the pole τ_0 occurs near 5×10^{-4}

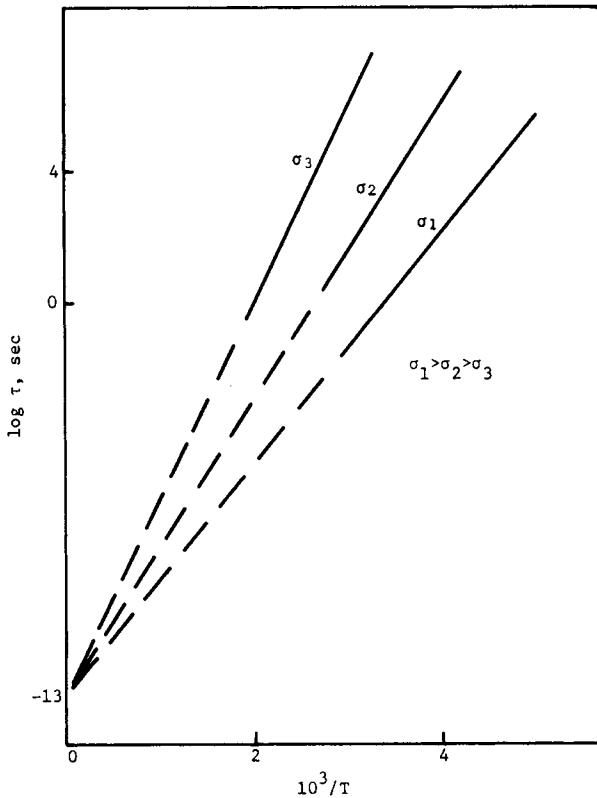


Fig. 2. Application of Zhurkov's eq. (2).

s—some 9 orders of magnitude removed from normal vibrational frequencies for well-behaved Zhurkov materials. From this data then, eq. (3b) is $A = 5 \times 10^{-4} \exp(U_0/RT)$. Here and below, R will be used rather than k , and the energy terms will be in calories.

The data for celluloid were replotted as in Figure 2. From the slopes the U^* were obtained as a function of σ . As before (previous section), this yields $U^* = -\gamma\sigma + U_0$. For celluloid the results are $U^* = -5.9\sigma + 62$ (kcal). Application of eq. (3a) using the α 's obtained from the original data gave values of γ only some 20–40% of 5.9. Clearly celluloid does not behave “normally” for the Zhurkov method, where the γ from eq. (3a) or (3b) yield the same value.

A somewhat different analysis of the celluloid data reveals thermodynamic functions not apparent in the discussion of the previous section. From eq. (1), for any fixed τ , the constant A may be obtained as a function of temperature. The results are presented in Figure 3 from which $A = 5.6 \times 10^{-34} \exp(63,400/RT)$. The preexponential factor is 30 orders of magnitude from that obtained above (i.e., 5×10^{-4}). With Zhurkov materials (previous section) the preexponential factors do not differ for a similar analysis. The energy terms ($U_0 \approx 62 \approx 63.4$ kcal) are in good agreement considering the fact that data was extracted from the rather small figure of Ref. 2.

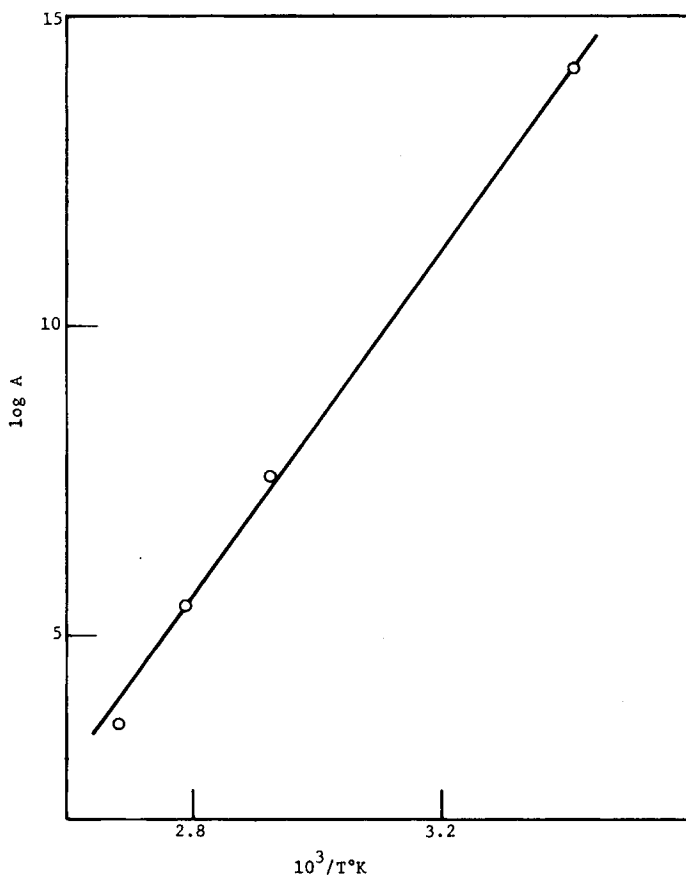


Fig. 3. The constant A for celluloid.

Using the value $\tau_0 = 5 \times 10^{-4}$ and A 's from Figure 3 and inserting these into eq. (3b), $A = \tau_0 \exp(U'_0/RT)$ (where the prime is to distinguish from the above determined U_0), U'_0 may be obtained as a function of temperature shown in Figure 4, where $U'_0 = -130T + 62,000$ cal. It appears then that $U'_0 = -130T + U_0$. It should be noted here that this is of the form $\Delta F = \Delta H - T\Delta S$.

For these two different A 's, i.e., $A = 5 \times 10^{-4} \exp(U'_0/RT)$ and $A = 5.6 \times 10^{-34} \exp(U_0/RT)$, Zhurkov's eq. (1) yields two equations, which must be resolved:

$$\tau = 5 \times 10^{-4} e^{U'_0/RT} e^{-\alpha\sigma} \tag{1a}$$

$$\tau = 5.6 \times 10^{-34} e^{U_0/RT} e^{-\alpha\sigma} \tag{1b}$$

Substituting for $U'_0 = -130T + U_0$

$$\ln \tau = -130/R + U_0/RT - \alpha\sigma + \ln \tau'_0 \tag{1a'}$$

where τ'_0 should be the 5×10^{-4} value, and

$$\ln \tau = U_0/RT - \alpha\sigma + \ln(5.6 \times 10^{-34}) \tag{1b'}$$

Equating and solving for τ'_0 ,

$$\tau'_0 = \tau_0 e^{130/R} = 5.6 \times 10^{-34} (3.27 \times 10^{28}) = 1.83 \times 10^{-5}$$

in reasonable agreement with 5×10^{-4} , considering the available data.

It should be noted that the $\exp(130/R)$ is an entropy of activation.⁵ This also follows from the analogy between U_0 and ΔF mentioned above. Then U_0 is the enthalpy of activation, ΔH^\ddagger , and

$$\tau = 5 \times 10^{-4} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} e^{-\alpha\sigma}$$

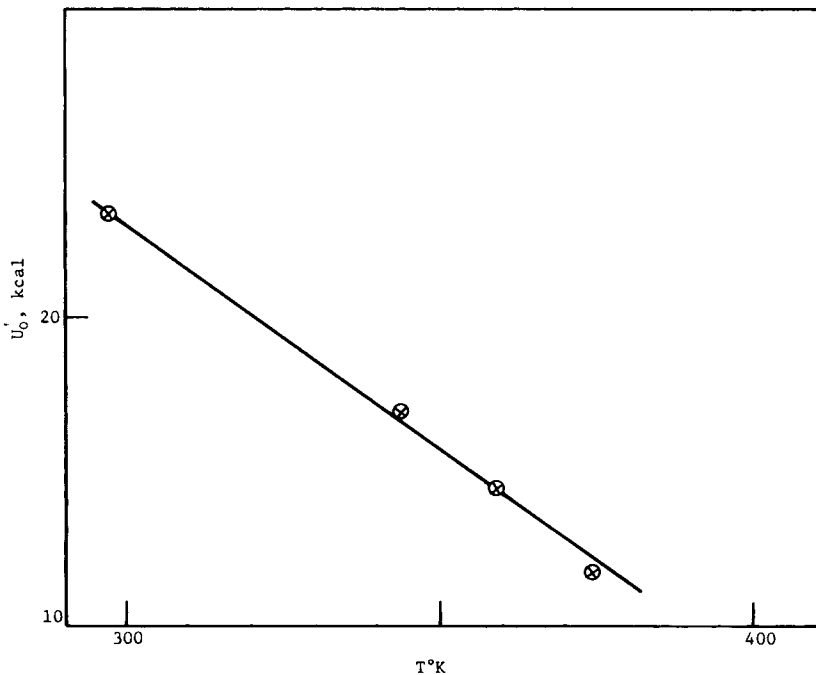


Fig. 4. Variation of the energy term in A (see text).

or

$$\tau = \tau_0 e^{\Delta F^\ddagger / RT} e^{-\alpha \sigma}$$

$$\tau = \tau_0 e^{(\Delta F^\ddagger - \gamma \sigma) / RT}$$

which is, of course, Zhurkov's eq. (2). Thus for "normal" Zhurkov materials (previous section), where U_0 is obtained by extrapolation of $U(\sigma)$ to $\sigma = 0$, U_0 is to be identified with the free energy of a standard state.

In air, Lucite⁶ and Delrin⁷ behave in a manner similar to celluloid, i.e., the pole depicted in Figure 1 is also some 9–10 orders of magnitude removed from Zhurkov type materials ($\tau_0 \sim 10^{-13}$). They can be assessed in the same manner as above for celluloid.

Accelerated tests for these kinds of materials can be carried out in the same manner as noted above for "normal" Zhurkov materials.

MODIFIED ZHURKOV BEHAVIOR—PARALLEL SLOPES

When Lucite and Delrin are tested under vacuum, the data for $\log \tau$ vs. σ do not intersect at a common τ_0 as depicted in Figure 1. A series of parallel lines for the various temperatures are observed. Similar results are observed for cellulose acetate and polystyrene for both air and vacuum tests.⁶

Figure 2 then is modified to Figure 5 when $\log \tau$ is considered as a function of temperature [Zhurkov's equation (2)].

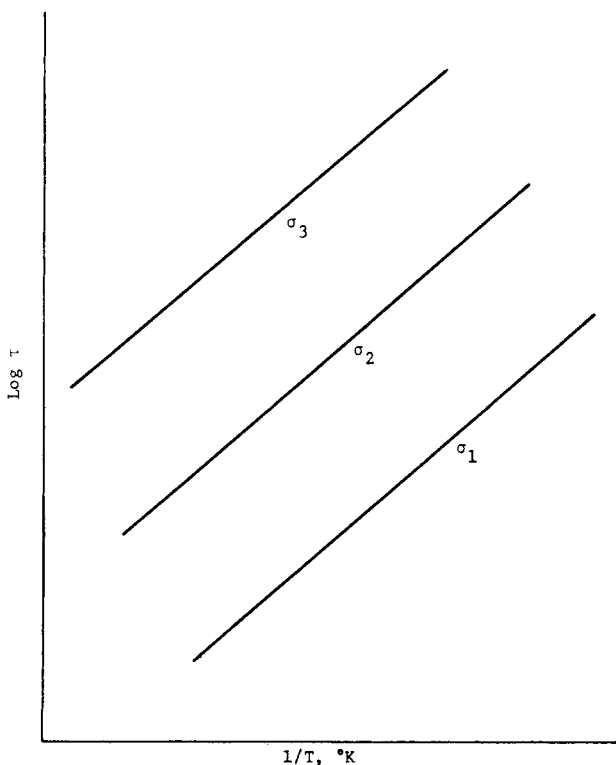


Fig. 5. Time to rupture as a function of temperature for materials showing parallel slopes for $\log \tau$ vs. σ .

The existence of parallel slopes for $\log \tau$ vs. σ may be understood by considering Figure 5:

$$\begin{aligned}\frac{d(\ln \tau)}{dT} &= -\frac{U^*}{kT^2} = \text{const} \\ \frac{\partial}{\partial \sigma} \left(\frac{d(\ln \tau)}{dT} \right) &= \frac{\partial}{\partial \sigma} \left(\frac{U_0 - \gamma \sigma}{kT^2} \right) = 0 \\ \frac{\partial}{\partial \sigma} U_0 &= 0 \quad (\text{from definitions above}) \\ \frac{\partial}{\partial \sigma} \left(\frac{d(\ln \tau)}{dT} \right) &= \frac{\partial}{\partial \sigma} \left(\frac{\gamma \sigma}{kT^2} \right) = 0 \\ \frac{\partial}{\partial \sigma} \left(\frac{\gamma \sigma}{kT^2} \right) &= \frac{1}{kT^2} \left(\sigma \frac{\partial \gamma}{\partial \sigma} + \gamma \right) = 0 \\ \sigma \frac{\partial \gamma}{\partial \sigma} + \gamma &= 0\end{aligned}$$

where either $\gamma = 0$ or $\gamma = f(\sigma)$.

The analysis below shows that $\gamma = 0$. However, in filled polymers such as graphite/epoxy composites, it has been shown elsewhere⁴ that $\gamma = f(\sigma)$.

Since $\log \tau$ vs. σ have parallel slopes, α is a constant, and for Lucite $\alpha = 3.36$, at any temperature. From results similar to those depicted in Figure 5, $U^* = 42.8$ kcal. An analysis similar to that depicted in Figure 3 yields

$$A = 8.2 \times 10^{-20} e^{U^*/RT}$$

An entropy term on the order of $e^{13.8/R}$ will bring the preexponential factor in line with a Zhurkov τ_0 .

Analysis for τ_0 vs. σ , shown in Figure 6, yields

$$\tau_0 = 8.2 \times 10^{-20} e^{-3.36\sigma}$$

Since $\alpha = 3.36$, then

$$\tau_0 = 8.2 \times 10^{-20} e^{-\alpha\sigma}$$

Inserting A into eq. (1) and τ_0 into (2) and equating their logarithms shows $U^* = U_0 - \gamma\sigma$, and since U^* is constant (see Fig. 5) it must be concluded that $\gamma = 0$ for materials showing parallel slopes for $\log \tau$ vs. σ at various temperatures.

Finally, for results showing parallel slopes, Zhurkov's equation (2) is simply

$$\tau = \tau_0 e^{U_0/RT}$$

This conclusion was reached earlier⁶ without detailed analysis. It has been shown⁷ that for such materials U_0 is essentially identical with the activation energies of thermal decomposition.

For these kinds of material behavior (i.e., parallel slopes) the accelerated tests are simpler to formulate since the temperature dependence can be obtained with fewer test points.

CONCLUSIONS

Zhurkov claimed that his equations were verified for both metals and non-metals. For nonmetals, at least, their modifications must be considered when

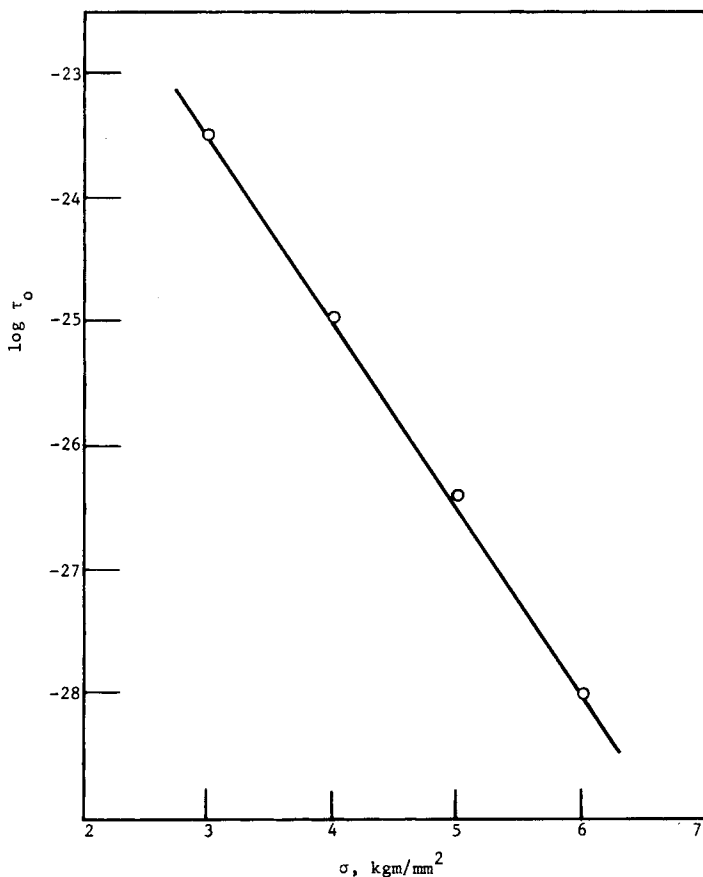


Fig. 6. τ_0 as a function of σ for Lucite.

undertaking data analysis by this method. However, the approach can be used to devise quite simple and time-saving accelerated tests, and it warrants more attention than it has received.

The discussion in the section on modified Zhurkov behavior most clearly indicates the kinetic rate theory basis of the approach. Zhurkov's energy term U_0 is to be associated with a standard state where this state is for $\sigma = 0$. This appears to be confirmed by the association of U_0 with the activation energy of thermal decompositions,⁶ where obviously $\sigma = 0$. (It would be instructive to study thermal decompositions of materials under load.) Since the Arrhenius rate constant is given by $k_T = Z \exp(-\Delta E/RT)$ the constant A in Zhurkov's eq. (1) appears to be $A = 1/k_T$ with $\tau_0 = 1/Z$. From absolute rate theory the rate constant is given by

$$k_r = (kT/h)e^{\Delta S^\ddagger/R}e^{-\Delta H^\ddagger/RT}$$

and Z , therefore, can be equated with $(kT/h) \exp(\Delta S^\ddagger/R)$. The $kT/h = \nu s^{-1}$ is associated with vibrations in an "activated complex." Then $\tau_0 = 1/\nu$, as defined by Zhurkov, ranges over $(1.6-1.2)10^{-13}$. These considerations imply the absence of an entropy term in "normal" Zhurkov materials as the analysis has

shown. For materials where $\tau_0 \neq 10^{-13}$, the entropy term appears to be contained within τ_0 .

Comparison of the behavior in air and in vacuum of Lucite⁶ and Delrin⁷ shows that for some polymers γ should be associated with surface phenomena, as suggested⁴ for the graphite/epoxy interface. If this conjecture is viable, then from studies of such materials it may be possible to determine the activation thermodynamics of crack growth. However, the true role of γ must await further work.

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