

Stress dependent activation entropy for dynamic fatigue of pristine silica optical fibers

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Subcritical crack growth in fused silica is treated as a stress assisted chemical reaction between water and strained bonds at the crack tip. In this work, the kinetics of the reaction is modeled by assuming the stress reduces the energy barrier of the activated complex by affecting both the activation enthalpy and entropy, where the stress dependence can take different forms. This theory is compared with dynamic fatigue data obtained for pristine fused silica optical fiber. The experiments were conducted in both distilled water and pH 7 buffer solution, and the results are found to be similar. The fatigue parameters were found by fitting to three different forms for the stress dependence; the activation enthalpy and entropy were then determined from the fatigue parameters. It is found that stress increases the activation entropy, whichever kinetic form is used, and thereby reduces the activation energy barrier height. The activation enthalpy is also stress dependent, but stress tends to increase the enthalpy contribution to the barrier height. The results show subcritical crack growth in high strength silica is dominated by entropy effects. © 2001 American Institute of Physics. [DOI: 10.1063/1.1361245]

I. INTRODUCTION

Fatigue in silica glass, i.e., strength degradation under stress, is the result of subcritical crack growth.^{1,2} It has been found that the apparent activation energy for fatigue in silica glass is stress dependent.³⁻⁵ However, the rate process is controlled by the activation free energy rather than the apparent activation energy;⁶ the stress dependence of the activation entropy therefore should have some effect on fatigue. Few studies on the activation entropy for fatigue have been published. The activation entropy was first found to be stress dependent for fatigue of a porous alumina by Avigdor and Brown.⁷ Scanlan⁸ later proposed a theory indicating both the activation enthalpy and entropy for the slow crack growth in fused silica should depend on stress. He reexamined crack growth rate data for silica glass of Wiederhorn and Bolz³ to verify his theory.⁸ Inness, Kurkjian, and Brownlow⁹ showed that the activation entropy term for static fatigue of silica optical fiber exists by reanalyzing Kao's data,⁴ but they did not consider the stress dependence of the entropy. The data associated with these studies on activation entropy were not detailed enough to understand the entropy effects on fatigue, since the stress dependence of activation entropy was either ignored, or different mathematical forms for the stress dependence were not discussed.

This article is intended to identify the role of the activation entropy in the fatigue of fused silica by measuring the activation enthalpy and entropy together with a thorough consideration of the implications of assuming different stress forms. A theory for the fatigue rate of silica glass will be proposed and compared with experimental data. In contrast with static fatigue tests, which were used to study activation

entropy in all the earlier work, we have used an experimentally more convenient dynamic fatigue technique, which can generate extensive fatigue data within a reasonable time. The material used for this study is "pristine" silica optical fiber, which exhibits high strength with an extremely narrow strength distribution.¹⁰ The small scatter in strength improves the accuracy of the fatigue data obtained, and makes the estimates of the fatigue parameters more accurate.

II. THEORY

The well-known subcritical crack growth model has been commonly used to describe the fatigue of ceramic materials.¹¹ Under mode I loading, a crack of length c locally amplifies the applied stress, σ_a , resulting in a stress intensity given by

$$K_I = \sigma_a Y \sqrt{c}, \quad (1)$$

where Y is a parameter which describes the crack shape and loading geometry. When the stress intensity factor exceeds a critical value, K_{IC} , the crack grows catastrophically and causes failure. The mechanism for subcritical crack growth is stress assisted chemical reactions between the solid and reactive environmental species, most commonly water.^{1,12} A mathematical form for the stress dependence of the resulting crack growth is needed in order to estimate the lifetime of the material under stress. Various kinetics models describing the relationship between the slow crack growth rate and the stress intensity have been proposed in the literature.¹³ We will consider here three of the more commonly used models. First, the empirical power law^{14,15} is widely used for its mathematical simplicity and assumes the crack growth velocity, \dot{c} , is

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$$\dot{c} = A_1 \left(\frac{K_I}{K_{IC}} \right)^{n_1} \quad \text{model 1;} \quad (2)$$

the second model, based on simple chemical kinetics, is given by^{2,3}

$$\dot{c} = A_2 \exp\left(n_2 \frac{K_I}{K_{IC}} \right) \quad \text{model 2;} \quad (3)$$

and the third model is a simplification^{13,16} of a chemical potential model¹⁷

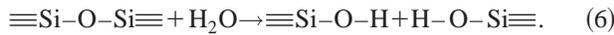
$$\dot{c} = A_3 \exp\left(n_3 \left(\frac{K_I}{K_{IC}} \right)^2 \right) \quad \text{model 3.} \quad (4)$$

(Following the work of Jakus, Ritter, and Sullivan,¹³ we have normalized the stress intensity factor to its critical value, K_{IC} , for simplicity.) The parameters in the kinetics models, the n_i ($i=1,2,3$) represent the sensitivity of the chemical reaction to stress (stress corrosion susceptibility parameter), and the A_i depend on the environment and material. It is not clear which of these kinetics models best describes the fatigue of silica.¹⁸ However, to clarify our development of a general kinetics model, we can write these three models in one form with a generalized function of normalized stress intensity, $f(K)$, where $K = K_I/K_{IC}$

$$\dot{c} = A_i \exp(n_i f(K)) \quad (5)$$

in which $f(K)$ takes the form $\ln K$, K , and K^2 for models 1, 2, and 3, respectively.

Fatigue in silica glass is well known to result from the chemical reaction between strained siloxane bonds and ambient moisture^{1,19,20}



Such a reaction can be characterized by absolute reaction rate theory,²¹ also known as transition state theory, (e.g., Moore and Pearson²²). This theory assumes that the reactants form a short-lived activated complex which is situated at the top of an energy barrier. The rate of the reaction is then given by the velocity at which the activated complex travels over the top of this barrier.⁶ According to this theory, the rate constant of a chemical reaction, k_r , is⁶

$$k_r = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^*}{RT} \right), \quad (7)$$

where κ is the transmission coefficient which represents the probability of the activated complex passing over the energy barrier and decomposing to form the products (κ is usually taken as unity), k_B and h are the Boltzmann and Planck constants, and ΔG^* is the free energy change from the initial to the activated state, i.e., the height of the energy barrier.

The free energy barrier of the reaction has both activation enthalpy and entropy contributions, $\Delta G^* = \Delta H^* - T\Delta S^*$. An entropic term is expected because the reactants are more disordered than the activated complex; This difference in randomness results in an entropy decrease which represents a barrier to the reaction.²² It is generally assumed that the stress reduces the activation energy by decreasing the activation enthalpy.²¹ The influence of stress on the activation entropy is seldom considered, but it is reasonable to

expect it to be a significant effect. Scanlan⁸ did discuss this subject but only in terms of a simple exponential stress dependence, i.e., model 2. However, we will show that the interpretation of results can depend on the assumed form of the stress dependence. We therefore develop a more general theory here. The activation enthalpy, $\Delta H^*(K)$, and the activation entropy, $\Delta S^*(K)$, can be written as:

$$\Delta H^*(K) = \Delta H_0^* - b_H f(K), \quad (8)$$

$$\Delta S^*(K) = \Delta S_0^* + b_S f(K). \quad (9)$$

ΔH_0^* and ΔS_0^* are the activation enthalpy and entropy at zero applied stress. For simplicity, we assume the form of the stress dependence of both entropy and enthalpy is the same, namely, $f(K)$, though their sensitivity to K is different (i.e., $b_H \neq b_S$). The signs of the terms containing b_H and b_S are chosen such that if these parameters are positive, increasing K would decrease the barrier height and so increase the crack growth rate. The crack growth rate in silica glass can be related to the rate constant by

$$\dot{c} = c_0 k_r g(a_{\text{OH}^-}), \quad (10)$$

where c_0 is the increase in crack length per breaking bond at the crack tip; $g(a_{\text{OH}^-})$ is a monotonically increasing function of the hydroxyl activity. It is included in Eq. (10) because it has been suggested that fatigue of silica glass is dominated by reaction with hydroxyl ions, rather than molecular water, since the fatigue rate increases with pH.^{23,24} Though not essential for the development of our theory, it will be assumed that $g(a_{\text{OH}^-})$ is proportional to a power of the concentration of hydroxyl ions, C_{OH} , i.e.,

$$g(a_{\text{OH}^-}) = \alpha C_{\text{OH}}^m, \quad (11)$$

where m is the reaction order, and α is the constant of proportionality which will depend on the units of concentration and the assumed standard state.

Combining Eqs. (7)–(11), the crack growth velocity is given by

$$\dot{c} = c_0 \frac{k_B T}{h} \alpha C_{\text{OH}}^m \exp\left(\frac{-\Delta H_0^*}{RT} + \frac{\Delta S_0^*}{R} \right) \times \exp\left[\left(\frac{b_H}{RT} + \frac{b_S}{R} \right) f(K) \right]. \quad (12)$$

Comparing Eq. (12) with Eq. (5), the fatigue parameters can be expressed in terms of fundamental thermodynamic parameters

$$A_i = c_0 \frac{k_B T}{h} \alpha C_{\text{OH}}^m \exp\left(\frac{-\Delta H_0^*}{RT} + \frac{\Delta S_0^*}{R} \right), \quad (13)$$

$$n_i = \frac{b_H}{RT} + \frac{b_S}{R}. \quad (14)$$

Even though the form of $f(K)$ is uncertain, this analysis shows that if the activation entropy for fatigue of silica is stress dependent, then the n_i should have a temperature independent term [Eq. (14)]. Scanlan found this same result but assuming a simple exponential kinetics form (model 2).⁸ However, here we show this is a general result for any rea-

sonable kinetic form. In most published work, only one kinetic form is assumed for data analysis, consequently any conclusions drawn may depend on that form being correct. We use all three models to determine which conclusions are general and which depend on the validity of the assumed kinetics form.

In this work, the temperature dependence of the fatigue parameters, the n_i and A_i , will be examined in order to study the stress dependence of the activation enthalpy and entropy. The same experiments were conducted in two testing solutions: distilled water and pH 7 buffer solution, in an attempt to understand the contribution of hydroxyl ion concentration on the activation enthalpy and entropy. All three kinetics models will be used to analyze dynamic fatigue data because it is not known which model best describes the fatigue of silica glass. This also serves to determine which conclusions are dependent on the assumed kinetics form and which are more general in nature.

The material used in this work is pristine silica optical fiber, which is considered "flaw free."¹⁰ It thus might be argued that the theory derived above is not valid since the subcritical crack growth model assumes the material contains well defined sharp microcracks. This issue has been brought up in the past. Michalske, Smith, and Bunker²⁵ discuss the fatigue mechanisms in high strength silica fiber and concluded that the measured fatigue results can be described by the subcritical crack growth model if the crack growth rate increases exponentially with applied stress. However, they overlook the possibility that other models could also give good agreement between slow crack growth and fiber fatigue. Matthewson¹⁸ points out that even if the subcritical crack growth model is not strictly valid for pristine fiber, it is still a useful vehicle for describing trends with environmental effects. Considering the fatigue is controlled by crack propagation rather than crack initiation, the use of our theory to compare the experimental results of pristine optical fiber can therefore be justified.

III. EXPERIMENTAL PROCEDURES

Dynamic fatigue experiments were performed on a fused silica optical fiber, which has a 125 μm glass diameter and a 250 μm outer UV-curable acrylate coating diameter. The strength of the fiber was found using a two-point bend technique,^{26,27} which can measure the strength of many specimens simultaneously. The tests were conducted at five faceplate speeds: 0.1, 1, 10, 100, and 1000 $\mu\text{m/s}$,²⁸ at temperatures ranging from 30 to 80 $^\circ\text{C}$, controlled to ± 0.1 $^\circ\text{C}$. The experiments were conducted in both distilled water and pH 7 buffer solution. Twenty specimens were measured under each testing condition. All specimens were pre-equilibrated at room temperature in the testing solution for three days before performing the dynamic fatigue tests to ensure moisture has completely penetrated the polymer coating. Before starting the experiments, the samples were immersed in the testing solution at the test temperature for 5 min to ensure the fiber reached thermal equilibrium. This equilibration time is short to avoid zero stress aging which occurs rapidly at the higher temperature.²⁹

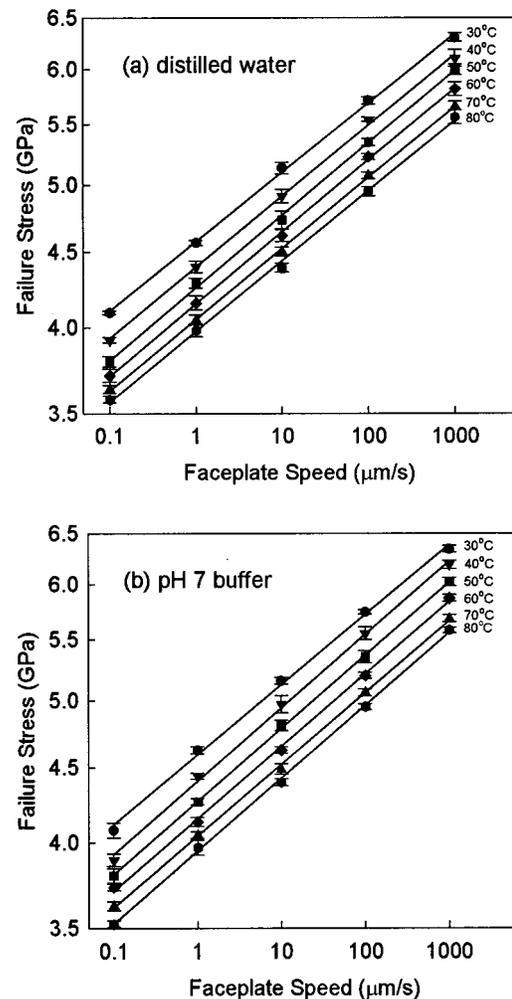


FIG. 1. The strength of fused silica optical fiber measured at various temperatures in (a) distilled water, and (b) pH 7 buffer solution, as a function of faceplate speed.

Unlike static fatigue, which can be used to obtain fatigue parameters graphically for any of the models [Eqs. (2)–(4)], the fatigue parameters generally need to be determined by numerical integration from dynamic fatigue data.¹³ A computer program was developed that integrates the fatigue equations and then fits the results to the experimental data to obtain the fatigue parameters. The program also calculates confidence intervals for the parameters which are essential for the work here. Reasonable values of certain parameters used in this procedure were assumed: the critical stress intensity factor $K_{IC} = 0.75$ $\text{MPa m}^{1/2}$, $Y = 1.16$, and the initial strength $\sigma_i = 12$ GPa. These values do not influence the estimates of the n_i ; they do influence the magnitude of the A_i , but the trends in the A_i with temperature are not affected. The conclusions we will draw from this work do not depend on the accuracy of these values.

IV. RESULTS AND DISCUSSION

A. Strength

The mean strength of the fiber at various temperatures is shown in Fig. 1 as a function of the faceplate speed. All error

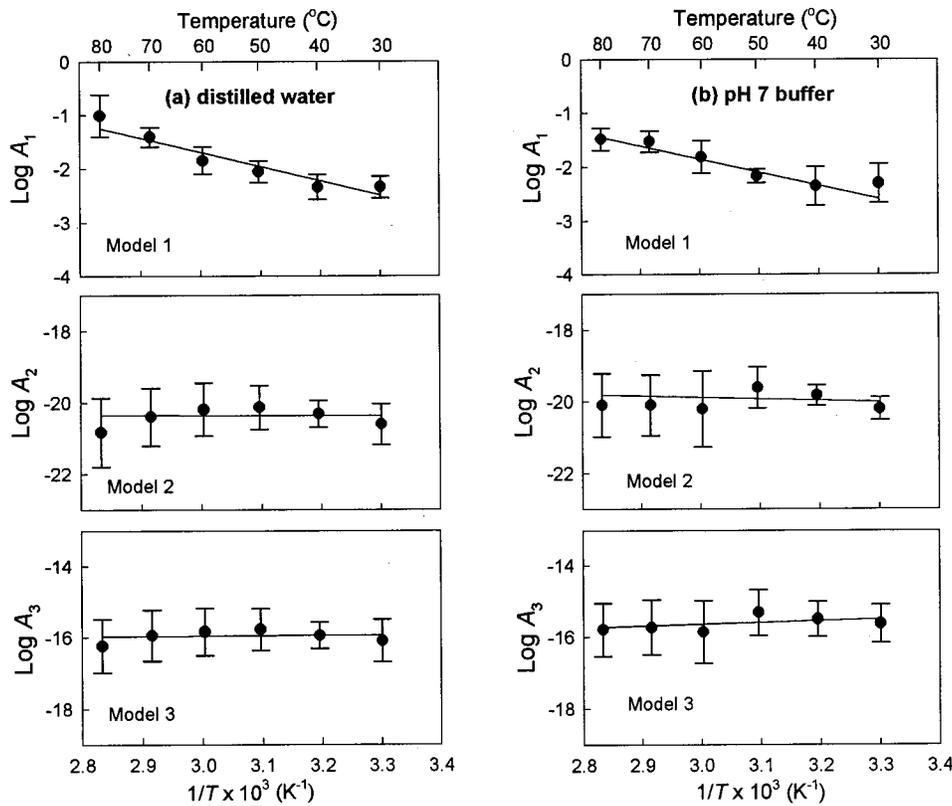


FIG. 2. The fatigue parameters, A_i (m/s), as a function of temperature measured in (a) distilled water, and (b) pH 7 buffer solution.

bars shown in this article represent a 95% confidence interval. As expected, the strength exhibits little scatter. The strengths measured in the two testing solutions do not show much difference indicating only water has diffused through

the polymer coating. In earlier work,³⁰ we have shown that bare fiber is weaker in pH 7 buffer than in water because the pH of water is lower than 7 due to dissolved carbon dioxide, and also because of the increase in the dissociation constant

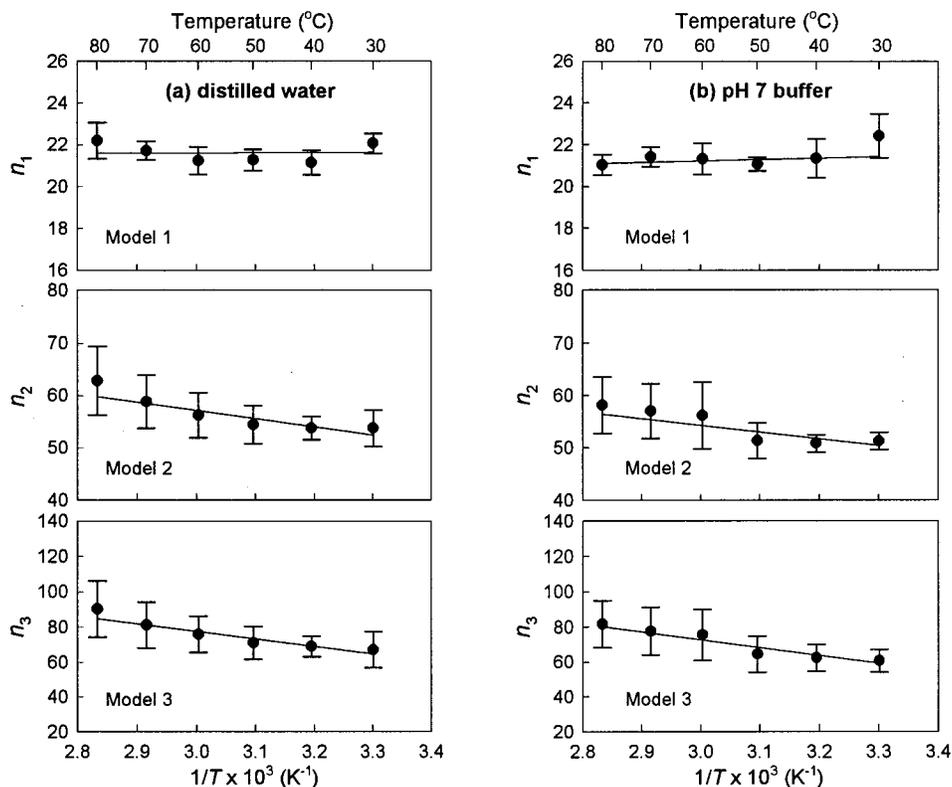


FIG. 3. The fatigue parameters, n_i , as a function of temperature measured in (a) distilled water, and (b) pH 7 buffer solution.

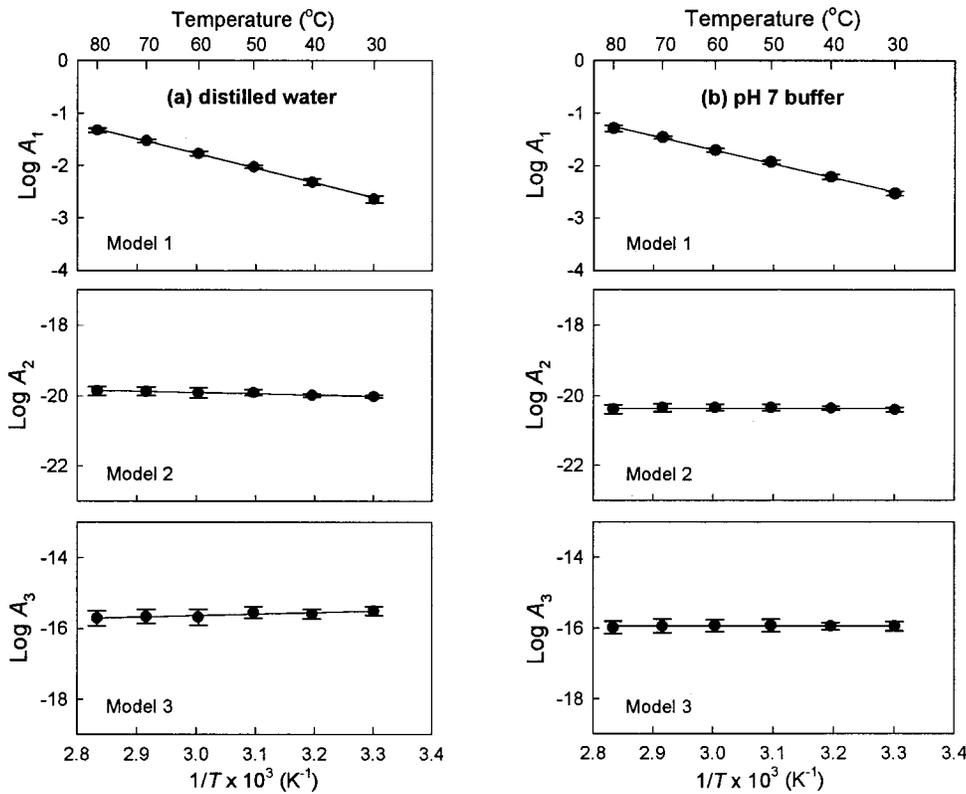


FIG. 4. The fatigue parameters, A_i (m/s), as a function of temperature measured in (a) distilled water, and (b) pH 7 buffer solution. These results are obtained by constraining the n_i to depend linearly on reciprocal temperature.

with temperature. Three days preconditioning time in the buffer solution at room temperature is insufficient for the pH controlling species to fully penetrate the coating of the fiber. The rate of diffusion of the buffering ions varies for different coatings; it has been shown that it can take months for the ions to start having an effect on the strength of coated fiber.³¹ The dilemma here is that zero stress aging resulting from reaction of water and silica could weaken the strength before the pH ions reach the fiber surface if given a very long preconditioning time. Nevertheless, the dynamic fatigue results obtained from the tests in pH 7 buffer solution can still be analyzed and compared with the results in distilled water.

B. Fatigue parameters

The fatigue parameters, the A_i and n_i , found by fitting the kinetics models to the dynamic fatigue data in Fig. 1, are shown as a function of temperature in Figs. 2 and 3. The values of the fatigue parameters obtained from the two testing solutions are similar and the trends with temperature are the same. This is further confirmation that the fiber in pH 7 buffer only sees the water and not the buffering ions.

Figures 2 and 3 show that n_1 does not change significantly with temperature, while A_1 shows approximately Arrhenius behavior. The empirical power law (model 1) usually assumes all the temperature dependence is in A_1 , which is the result obtained here. However, if the data are fitted to a model with more physical meaning (models 2 or 3), the temperature dependence is found to be predominately in n_i rather than in A_i , as shown in Figs. 2 and 3. However, the large error bars in these figures raise the question of whether the trends with temperature are real.

The confidence intervals for A_i and n_i were determined together with their variances and covariances. It has been shown that, because the two parameters are strongly correlated, the method for determining them gives significant uncertainty in their values even though the overall quality of fit is good.³² Since A_i and n_i are strongly correlated, the uncertainty in one parameter is greatly reduced if the other parameter is determined with higher precision. The theory presented above suggests that the n_i should be a linear function of $1/T$. By constraining the n_i to have this dependence, we are effectively fitting to all the data at all temperatures simultaneously which has the effect of greatly reducing the error bars in the A_i , as shown in Fig. 4. Despite applying the constraint, the trends with temperature remain unchanged. This shows that the trends shown in Figs. 2 and 3 are real, despite the large error bars.

C. Quality of fit

The residual sum of squares for the fit of the dynamic fatigue data to each model (Figs. 2 and 3) is compared in Fig. 5. The model which fits the data the best would have the smallest residual sum of squares. As shown in Fig. 5, model 3 fits the worst, and model 1 gives the best fit, while model 2 is somewhere in between. Figure 5 shows only the quality of fit to dynamic fatigue data; it does not necessarily correspond to the correctness of the model. Similar results for the quality of fit for the three models are found by Armstrong, Matthewson, and Kurkjian.³² However, they found that model 2 best describes how the fatigue parameters vary with

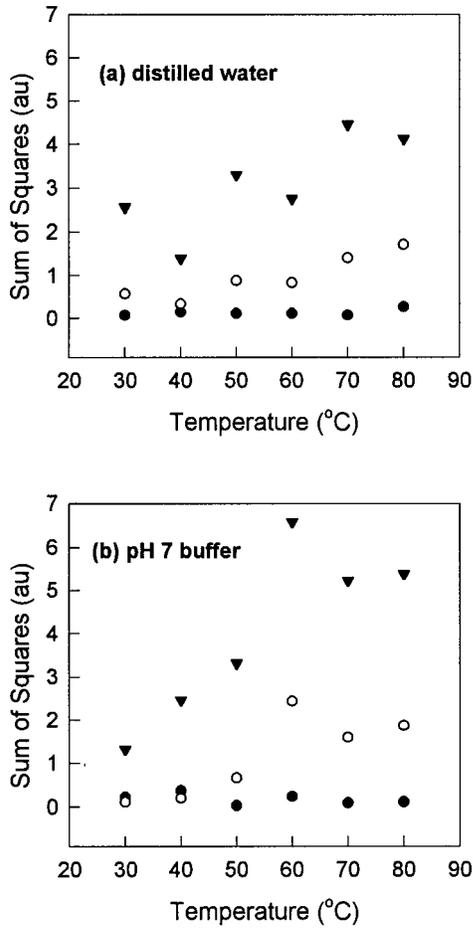


FIG. 5. Residual sum of squares measured in (a) distilled water, and (b) pH 7 buffer solution for Model 1 (●), Model 2 (○), and Model 3 (▼).

humidity. The fact that the residual sum of squares in Fig. 5 is smallest for model 1, therefore, does not mean it best describes the overall fatigue behavior.

D. Activation enthalpy and entropy at zero stress

The activation energy is usually obtained from an Arrhenius plot. However, by analyzing the temperature dependence of the fatigue parameters instead of the raw strength data, we can determine the activation enthalpy and entropy separately rather than an overall apparent activation energy.

Examination of Eq. (13) shows that the activation enthalpy and entropy extrapolated to zero stress, ΔH_0^* and $\Delta S_{0,app}^*$, can be calculated from the slope and intercept of a line fitted to $(\ln A_f - \ln T)$ vs $1/T$, where

$$\text{slope} = \frac{-\Delta H_0^*}{R}; \quad (15)$$

$$\text{intercept} = \ln \frac{c_0 k_B}{h} + \ln(\alpha C_{OH}^m) + \frac{\Delta S_0^*}{R}. \quad (16)$$

For the calculations in this article, c_0 is assumed to be 2.5 \AA , the same value used by Scanlan.⁸ However, the absolute value of the term $\ln(\alpha C_{OH}^m)$ is not known. Therefore, we can only calculate the apparent zero stress activation entropy, $\Delta S_{0,app}^*$, defined by

$$\Delta S_{0,app}^* = \Delta S_0^* + R \ln(\alpha C_{OH}^m). \quad (17)$$

(Approximate values for ΔH_0^* and $\Delta S_{0,app}^*$ can be obtained from the regression lines in Fig. 2 since the term of $\ln T$ is small. However, our results do account for the $\ln T$ term for precision.)

Table I summarizes the values of ΔH_0^* and $\Delta S_{0,app}^*$ found for the three kinetics models. The values obtained for the two testing solutions are the same within experimental errors; this is expected as discussed earlier. The activation enthalpy calculated using model 1 is $\sim 48 \text{ kJ/mol}$, but is effectively zero if calculated using models 2 and 3. The apparent activation entropy for model 1 is positive, but is negative for models 2 and 3. Since the value of αC_{OH}^m is unknown, we cannot interpret this difference between models. However, it has often been assumed^{8,9} that this term is unity (i.e., $\Delta S_0^* = \Delta S_{0,app}^*$), which cannot be justified.

E. Stress dependence of the activation parameters

The parameters, b_H and b_S , which quantify the stress dependence of the activation enthalpy and entropy, are calculated from the slope and intercept of the regression lines in Fig. 3. The results are shown in Table II. Once again, the results in the two testing solutions are similar. The b_H for model 1 is effectively zero, i.e., the activation enthalpy is roughly constant with stress. However, b_H is negative for models 2 and 3, i.e., the activation enthalpy increases with increasing stress. This means the results found for different kinetics models are not the same in this regard. This illustrates that analyzing fatigue data using only one kinetic form can lead to conclusions that are only valid for that particular form and may not be generally true. It is important to distinguish which conclusions are dependent on the kinetic form and which are not. This can only be done by considering a number of different models, as we have done here.

As shown in Table II, the b_S term is nonzero for all the models, indicating the activation entropy indeed is stress dependent. The positive sign of b_S implies that the activation

TABLE I. The activation enthalpy and entropy extrapolated to zero stress for the three kinetics models measured in distilled water and pH 7 buffer solution.

Environment		Model 1	Model 2	Model 3
Distilled water	ΔH_0^* (kJ/mol)	48 ± 8	-2 ± 14	-4 ± 9
	$\Delta S_{0,app}^*$ (kJ/mol K)	0.05 ± 0.03	-0.46 ± 0.04	-0.38 ± 0.03
pH 7 buffer solution	ΔH_0^* (kJ/mol)	44 ± 8	5 ± 16	-12 ± 9
	$\Delta S_{0,app}^*$ (kJ/mol K)	0.03 ± 0.02	-0.43 ± 0.05	-0.4 ± 0.03

TABLE II. The coefficients of the stress dependence of the activation enthalpy and entropy, b_H and b_S .

Environment		Model 1	Model 2	Model 3
Distilled water	b_H (J/mol)	$(0.7 \pm 9.9) \times 10^4$	$(-1.3 \pm 0.3) \times 10^5$	$(-3.5 \pm 0.6) \times 10^5$
	b_S (J/mol K)	$(1.8 \pm 0.3) \times 10^2$	$(8.7 \pm 1.1) \times 10^2$	$(1.7 \pm 0.2) \times 10^3$
pH 7 buffer solution	b_H (J/mol)	$(5.5 \pm 9.1) \times 10^4$	$(-1.1 \pm 0.4) \times 10^5$	$(-3.7 \pm 0.6) \times 10^5$
	b_S (J/mol K)	$(1.6 \pm 0.3) \times 10^2$	$(7.7 \pm 1.2) \times 10^2$	$(1.7 \pm 0.2) \times 10^3$

entropy increases with increasing stress for all three kinetics models. We can therefore conclude that the stress dependence of activation entropy is generally important, and this is true whichever kinetics model is assumed. Such stress dependence is consistent with the previous results for slow growth of macroscopic cracks in silica glass,⁸ and for static fatigue of porous alumina in water.⁷

It is known that the rate of a reaction is determined by the activation energy barrier (the free energy of activation), and not necessarily by the activation enthalpy alone.⁶ Our results show that stress reduces the activation barrier height by increasing the activation entropy. Although typically assumed, the stress does not reduce the enthalpy contribution to the barrier height; indeed, for the more physically reasonable exponential models, the enthalpy contribution increases the barrier height. However, the overall effect is a lowering of the barrier since the effect on entropy dominates. This implies that stress dependent subcritical crack growth, at least in fused silica, is dominated by entropy effects rather than enthalpy.

V. CONCLUSIONS

A generalized chemical kinetics theory for the fatigue rate of silica glass is proposed. Results for the dynamic fatigue of a polymer coated fused silica optical fiber were compared with the theory. The fatigue experiment was conducted in both distilled water and pH 7 buffer solution at temperatures ranging from 30 to 80 °C using a dynamic two-point bend technique. The strength data were then fitted to three different crack growth kinetics models to determine the fatigue parameters, A_i and n_i ($i = 1 \dots 3$). The activation enthalpy and entropy are determined from the temperature dependence of A_i and n_i .

No significant difference was found between the behavior measured in pH 7 buffer solution and distilled water. This is because only water penetrates the fiber coating on the time scale of the experiments. Results for bare fiber in pH 7 and water, when the pH ions can immediately reach the fiber surface, are expected to be different because the neutral pH of water changes with temperature.

It is found that the activation entropy is stress dependent, as proposed in the theory. The activation entropy increases with increasing applied stress for all three kinetics models. The stress dependent activation entropy has a dominant contribution to the activation energy barrier.

The stress dependence of the activation enthalpy varies for the different kinetics models considered. However, in all cases, the stress does not reduce the activation enthalpy. Indeed, for some forms of the kinetics model, stress increases the enthalpy barrier.

The results indicate that some conclusions drawn from fatigue data depend on the assumed form of the kinetic model. It is therefore not appropriate to assume just one kinetic model, because the conclusions might be misleading. It is advisable to use several forms in order to establish the generality of any conclusions.

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