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## APPLICATION OF RATE THEORY TO ACCELERATED DURABILITY TESTING OF STRUCTURAL ADHESIVES

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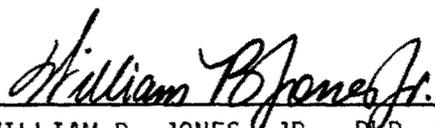
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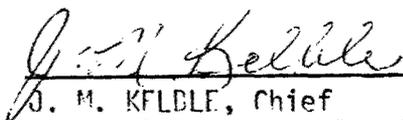


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## PREFACE

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I. INTRODUCTION

1.1 Discussion of Problem

Advanced polymeric adhesive bonded systems are emerging as strong candidates for production commitments in primary structures. Building on experience with metals, conventional design and analysis procedures of adhesive systems usually neglect the influence of environment and aging on predictions of the useful life of an adhesive bonded structure. However, in common with most polymeric and elastomeric materials, adhesives and adhesive bonded joints can experience significant changes in their mechanical response, failure properties and dimensional stability due to the combined effects of cure shrinkage and residual stresses, absorbed moisture and thermal environments and chemical/structure aging. These effects complicate efforts to project and demonstrate the durability characteristics of adhesive bonded structures during design, development and full-scale structural certification testing. Implementation of more stringent structural integrity policies which increase the emphasis placed on proven life-cycle durability prior to production acceptance of component parts provides further impetus for resolution of environmental and chemical/structural aging effects on adhesive systems.

The effects of aging and environment on polymeric or elastomeric materials are almost always deleterious. The environments considered to be most detrimental include ultraviolet and gamma irradiation; exposure to cleaning solvents, oxygen, ozone, moisture, and temperature; and mechanical loading history. The sensitivity of adhesives and adhesive bonded systems in particular, to these environments and their interactions is not fully understood and additional clarification and definition is required.

Mechanical response properties of adhesives and adhesive bonded structures as a function of physical environment, mechanical loading history and age are required to provide an adequate design data base. A basic understanding of failure (fracture) mechanisms and changes in the mode of failure due to aging, environment and load history is also lacking. This understanding must be established before laboratory simulation tests can be designed which will accurately predict in-service failure modes and mechanisms.

Determination of mechanical response and failure behavior of adhesive systems is further complicated by the fact that adhesive materials exhibit nonlinear viscoelastic and viscoplastic behavior under normal use conditions. Mechanical response properties are dependent upon the state of damage which exists in the adhesive system as well as the history of the environment and loading.

In addition, a predictive service life methodology requires sufficient testing replication to statistically assess analytical serviceability models, test data reliability and service life predictions.

External loading and environmental history as well as the internal system parameters of adhesive systems are subject to random variations.

However, most current structural analyses typically assume linear, elastic behavior, and are deterministic with uncertainties reflected in design safety factors or margins of safety which are not based on mathematical models describing the interplay between the various uncertainties. Probabilistic concepts need to be incorporated into structural analysis procedures.

Also, the general level of analysis may not permit identification of problem areas which have not been previously recognized by the designer/analyst. For example, no analysis method or approach has been demonstrated to interrelate or translate the results of one durability history to another history. Analysis support for judging the adequacy of repair actions is also needed.

## 1.2 Scope and Approach of Report

Based on the observations of the previous section, the development of a rational design and analysis methodology for making accurate service life predictions is a critical need if extensive and expensive repair or replacement of component parts, or rejection of a component or design for lack of an adequate initial service life prediction is to be avoided. This report summarizes the development of a rational methodology for accelerated aging and testing of polymeric adhesives and adhesive bonded joints. It is not entirely possible to discuss characterization of mechanical response (e.g., modulus and compliance) and failure (e.g., microcrack formation and growth, vacuole formation, damage accumulation) separately since the mechanical response depends on the state of damage within the adhesive system. Furthermore, a "correct" constitutive theory should be capable to describing material response behavior up to failure.

For our purposes herein aging is broadly classified in three categories:

1. Physical Aging
2. Chemical Aging
3. Structural Aging

Physical aging is reversible and for amorphous plastics and other glassy materials below  $T_g$  is associated with gradual relaxation towards an equilibrium state (Struik, 1977)<sup>1</sup>. These effects are reversible by heating above the glass transition temperature,  $T_g$ , in the absence of load. Moisture diffusion into and out of unstressed polymeric materials is another example of physical aging.

Chemical aging is irreversible and is associated with processes which permanently alter polymer morphology. These include continuing post-cure cross-linking, thermal degradation, oxidative cross-linking, irradiation, etc.

Structural, or mechanical aging as it is sometimes called, refers to damage accumulation or loss of residual strength due to a previous loading history (e.g., cyclic fatigue). These degradation effects are partially reversible for thermosetting plastics since some healing takes place when the material is allowed to recover under no load. Annealing thermoplastics near their melt temperature,  $T_m$ , reverses the effects of previous mechanical degradation.

Unfortunately the three categories of aging cannot be treated separately in a meaningful aging program due to synergistic effects.

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<sup>1</sup>Names and dates in parenthesis refer to references listed at the end of this report.

A systems approach to accelerated aging is adopted in that an attempt is made to identify critical material structure parameters and to relate these critical parameters through structure-property relationships to overall system performance. Primary attention is given to the effects of time, moisture, temperature and load history. The application of absolute reaction rate theory concepts is explored as a scientific basis for establishing an accelerated testing methodology. Some of the more dominant processes occurring during cure and aging of epoxy resin adhesives are identified and potential techniques for separating and monitoring the associated activation energies of these mechanisms with aging, environment and load history are discussed. Suggestions are also made for incorporating aging effects into appropriately rigorous constitutive models.

Prior to the specific discussion of accelerated testing of epoxy adhesive systems an overview of structural analysis and service life predictive analysis methodologies is first presented to emphasize the importance of and to place in proper perspective the role of accelerated testing.

An Appendix contains additional supporting documentation and development of important concepts of reaction rate theory.

Finally, no attempt has been made to establish historical precedence for the references cited nor to provide an all-inclusive bibliography. Rather, references are cited which emphasize particular concepts and provide particular background information. Since little accelerated aging of any predictive value to epoxy adhesive systems has been conducted most references, examples, and extrapolations are drawn from other areas.

## II. OVERVIEW OF STRUCTURAL DESIGN AND ANALYSIS METHODOLOGY

Structural design and analysis procedures for adhesive bonded structures should optimize structural performance from a maintenance and serviceability (i.e., durability) point of view. Overall costs should be minimized through trade-offs between initial costs, recurring costs, maintenance strategies and structural performance. Accomplishment of these objectives requires, in particular:

1. Accurate descriptions of loads and environments throughout the anticipated useful life of the adhesive bonded structure.
2. Accurate characterization of material response and failure (fracture) properties for each material and each bonded component under laboratory conditions representative of field use conditions.
3. Accurate predictions of stresses, strains and deflections throughout the bonded system due to the prescribed loads and environments.
4. Accurate predictions of system distress or damage accumulation due to the prescribed loads and environments.
5. Accurate relations between system distress and system performance.
6. Verification and evaluation of system performance predictive models under field use conditions.
7. Modification and re-evaluation of predictive models as required.

A representative design and analysis methodology for adhesive bonded structures consists of the five phases shown schematically in Figure 1.

1. Problem Definition.
2. Stress (Structural Response) Analysis.
3. Strength (Distress or Failure) Analysis.

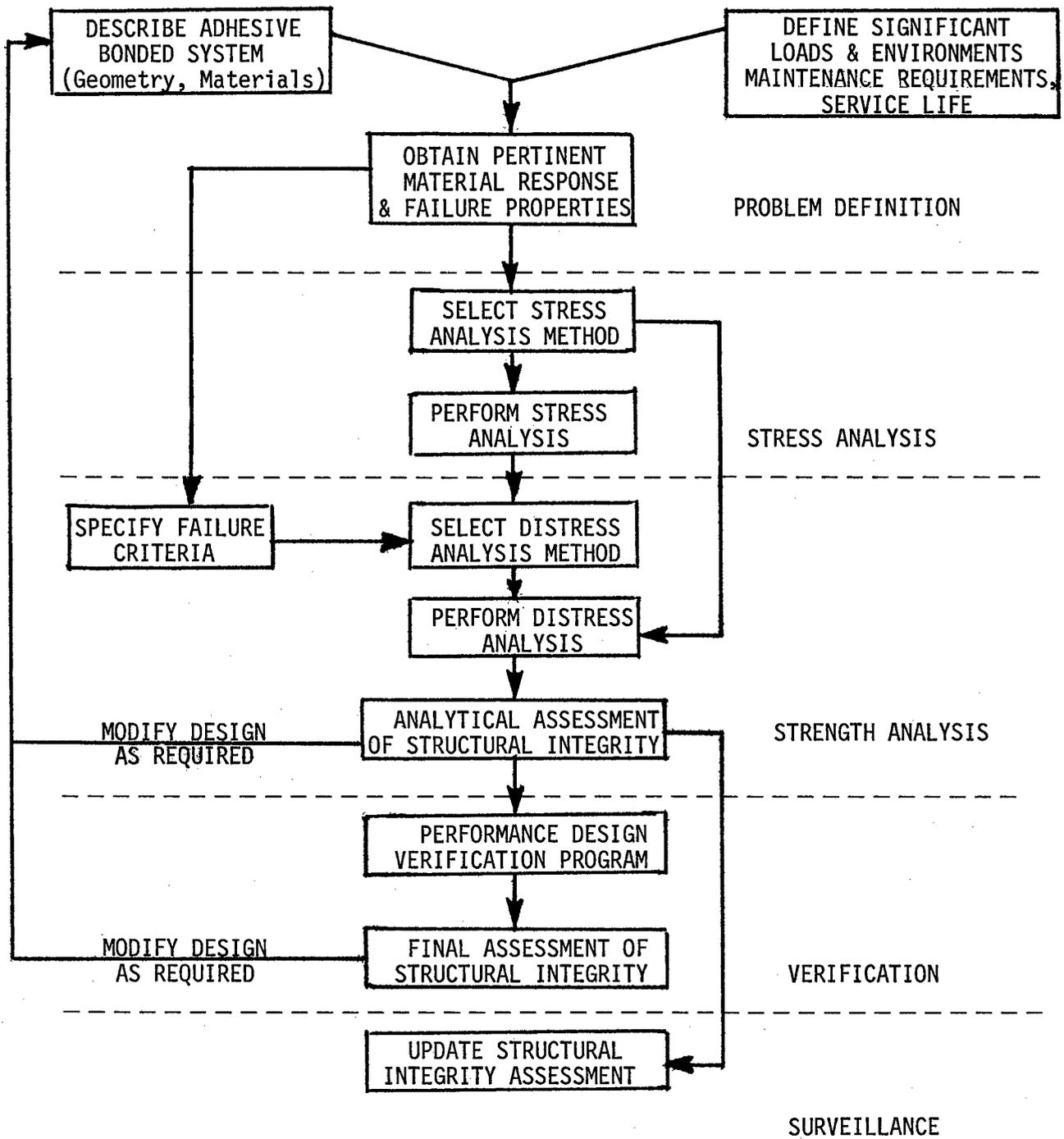


FIGURE 1 - ADHESIVE BONDED STRUCTURES DESIGN METHODOLOGY

4. Verification.

5. Surveillance.

The approach depicted in Figure 1 is typical, but may be modified for special types of analyses. The scope of analysis for a particular situation should be determined in early phases of the analysis so that data requirements can be clearly defined. Although the nature and precision of the data required depends upon the type of analyses to be performed, minimum requirements generally consist of:

1. Description of adhesive system and subsystem components.
2. Definition of loads and environments.
3. Adhesive and bonded joint response and failure properties.
4. Required service life.
5. Maintenance requirements.

In principle, the general level of analysis should permit identification of problem areas which arise and which have not been previously recognized by the designer/analyst. In particular, the analysis method or approach should be capable of: (1) interrelating or translating the results of one durability history to another history, and (2) accounting for a possible change in the critical failure mode with aging time. Analysis support for evaluating the adequacy of repair actions is also necessary.

In addition, the analysis, design and material characterization procedures should employ probabilistic concepts to account for inherent statistical variability. For example, sufficient test data replication is required to statistically assess material constitutive models, test data reliability, and service life predictive models. External loading and environmental histories, as well as internal system parameters (e.g.,

geometry, processing variables, material properties, etc.) are also subject to random variations. Thus, in contrast to deterministic analysis procedures in which uncertainties are reflected in design safety factors or margins of safety which are not based on mathematical models describing the interplay between the various uncertainties, probabilistic concepts should be incorporated to improve and to make structural integrity life predictions more physically realistic.

### III. OVERVIEW OF SERVICE LIFE PREDICTIVE ANALYSIS METHODOLOGY

#### 3.1 Introduction

The problem of estimating the useful service life of any physical system ultimately becomes one of assessing the likelihood that the system will continue to be able to perform its required functions as time passes. So long as the probability of operational success remains high, the system will be acceptable and will continue to be used. When the changes occurring with time cause the probability of system failure to rise above some acceptable limit, the useful life of the system is ended, and it must be repaired or replaced. Thus, the determination of the useful service life of an adhesive bonded structure requires estimation of the probability of system failure as a function of its age and environment.

The techniques for estimating system failure probability fall into two broad and frequently overlapping categories: empirical and analytical. The empirical approach involves the testing of a significant number of actual parts or their analogs at selected ages and environmental conditions and extrapolating the resulting failure rate data. In the analytical approach, the failure probability assessment is made through an evaluation of all of the failure-inducing and failure-resisting factors in the system under the environmental and loading conditions imposed during its lifetime.

The major difficulty with the strictly empirical approach is that real-time testing for evaluation of adhesive joints is not practical since the knowledge gained comes too late to impact on material selection or design considerations. The analytical approach, coupled with an accelerated

testing program, is more desirable since it provides more timely results which ultimately can become a part of the design decision process so that future systems can be developed to meet specific service life requirements. The problem here is in developing the analytical models relating the accelerated life behavior with the actual service conditions.

The service life analysis methodology is an extension of the reliability concepts and technology pursued in other disciplines, (see e.g., Zelen (1964), Bolotin (1969), Gertsbath and Kordonsky (1969), ASTM (1972), Freudenthal (1972), Mann, Schafer and Singpurwalla (1974), Witcraft (1975), Layton, Bennett and Breitling (1977)). The principal steps are:

1. Failure mode analysis to determine how each component in a system can fail to perform its required functions.
2. Failure mechanism analysis to determine the processes by which each failure mode can occur.
3. Stochastic analysis of each failure mechanism model to determine failure probability as a function of system age.
4. Combination of results of step (3) into an assessment of total system failure probability as a function of age.

A diagram of the information flow involved in the process is shown in Figure 2. The steps are more fully described in the following paragraphs.

### 3.2 Failure Mode Analysis

A thorough failure mode analysis is needed to identify and define all of the credible potential failure modes of the system. The failure mode analysis provides the basis for analyzing the system at the failure mechanism level and for combining the analytical results for each mechanism into a total assessment of the system. It consists of the following steps:

1. Preparation of a complete physical description of the system.

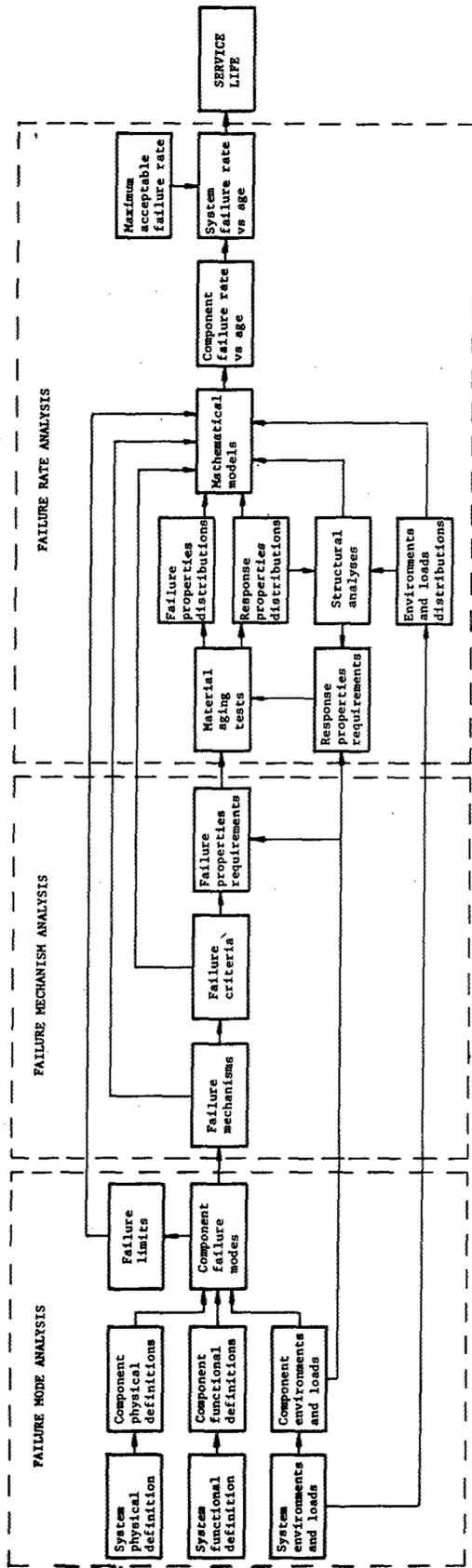


FIGURE 2. SERVICE LIFE ANALYSIS INFORMATION FLOW (AFTER WITCRAFT, 1975).

2. Preparation of a complete functional description of the system.
3. Preparation of complete physical and functional description of each of the system components and definitions of their environmental requirements.
4. Listings of the modes of failure of each of the components.

Steps (1) and (2) include a definition of the physical system and a summary of what the system is required to do. Steps (2) and (3) also imply a detailed description of the environments and loads the system experiences during its lifetime. Step (4) includes a definition of the limits of failure for each mode; that is, to what extent can the condition represented by a given failure mode be permitted to extend before the system must be considered to have failed.

A failure mode analysis normally proceeds from the basis that the system is initially in an unfailed state. That is, all components are produced in accordance with established procedures and specifications, and the system is assembled to initially meet all intended functions.

Furthermore, it is typically assumed that fabrication or processing defects do not cause an initial failure; however, the presence of initial flaws may contribute to subsequent age or environment related failures. For example, a poor bond between the adhesive and adherend may cause a premature failure (with time) but still not cause failure initially.

A failure mode analysis must also consider potential changes in the critical mode of failure due to aging or interactions with the environment. For example, experimental evidence has shown that an adhesive joint may fail cohesively in the adhesive shortly after manufacture whereas exposure to moisture at elevated temperatures degrades the bond-line integrity and leads to interfacial failures between the adherend and adhesive

at some later time. Thus, the initial cohesive failure mode has changed to an interfacial failure mode after interaction with the environment, and a failure mode analysis which did not consider this possibility would be inadequate and lead to erroneous conclusions regarding service life.

### 3.3 Failure Mechanism Analysis

A failure mechanism is the process by which the system is transformed from an unfailed state to a failed state as defined by the pertinent failure mode. Each failure mode has at least one and may have multiple failure mechanisms.

The failure mechanism is the level of definition at which probabilistic analysis of the service life of the system is performed. The credible mechanism or mechanisms for each failure mode must be defined with a description of how they relate to one another; that is, whether they are dependent or independent.

One of the initial requirements of a failure mechanism analysis is to establish, by way of experience, experiment or analysis, which stress or strain components actually limit the failure processes under the environmental and loading conditions pertinent to the system. This task dictates the material characteristics that must be measured to determine the pertinent failure properties.

One critical failure mechanism for adhesive bonded joints has been identified as fatigue.

### 3.4 Failure Rate Analysis

A mathematical model of a physical system is the vehicle by which the probability of failure by each of the failure mechanisms is assessed.

It relates all the pertinent input variables so that a unique "stress" level may be determined from a given set of variables. It also relates the resulting stress level to the "strength" corresponding to the particular failure mechanism of interest; thus, permitting an evaluation of the margin of safety between stress and strength for a given set of conditions. As used herein, stress and strength refer to the failure-inducing and failure-resisting factors related to a given mechanism, and are not necessarily material stresses and strengths in the mechanical sense. That is, one could be concerned with limiting deformations or strains depending upon the situation.

A model for each failure mechanism is required. For the physical stresses, models at more than one location in the system are frequently required, depending on the relative stress levels in the maximum stressed region. For correlated failure mechanisms, the mechanism models are combined to give a model for a probabilistic analysis of the system. Independent mechanisms may be analyzed separately and the results combined for system assessment.

The failure probability is then determined by a stochastic analysis of each of the mechanism models to determine the statistical distribution of the difference between the "stresses" and "strengths" for each mechanism. The fraction of this joint probability distribution function that is less than zero is the probability of failure by that mechanism.

A failure probability analysis requires determination of each of the input variables contributing to the system stresses, the statistical distribution of the stress-resisting (strength) factors for each failure mechanism, and any significant covariances between stress or strength variables.

The final analysis is most often carried out through an approximate solution of the mechanism mode. This approximate solution may be obtained using Monte Carlo simulation techniques or approximate closed form probabilistic techniques. The analysis is carried out for different assumed system ages and environments; inputting pertinent material property changes as determined experimentally, to generate the failure rate with age.

The determination of failure rate at a given age involves:

1. Calculation of critical stress (strain) components at critical locations.
2. Combining these critical stress components into the pertinent stresses governing the failure criterion.
3. Integration of the rate of cumulative damage resulting from these stresses up to the age of interest over any desired loading or environmental history.

Aging and environmental effects are input through changes in the material response properties that determine the stress levels in the system and changes in the material failure properties. As an example, the simplest empirical law for life expectancy when there is a history of different loading and environmental conditions is Miner's linear cumulative damage law. Miner introduced the a priori "measure of damage",  $D$ , which is zero for the initial (undamaged) state of the material and is unity for complete failure. In terms of fatigue loading it is assumed that the damage caused by a given cycle is independent of the state of the structure at a given time and of the preceding history of the loading, and is simply added to the damage caused by the preceding cycles. Assuming the increment in the measure  $D$ , for a number of  $n_i$  cycles with stress  $S_i$ , to equal to

$$D_{S_i} = \frac{n_i}{N(S_i)} \quad (1)$$

where  $N(S_i)$  is the number of cycles to failure at stress  $S_i$ , the failure condition is obtained by summing the damage,

$$D = \sum_i D_{S_i} = \sum_i \frac{n_i}{N(S_i)} = 1 \quad (2)$$

It is often more convenient to work with an integral relationship, in which case, Equation (2) is replaced by

$$\int_0^{N_\ell} \frac{dn}{N(S)} = 1 \quad (3)$$

for continuous load histories. Equation (3) may be solved for the limiting number of cycles to failure,  $N_\ell$ .

Fracture mechanics considerations offer an alternate approach to fatigue failure of adhesive bonded joints, since fatigue failure is widely interpreted as the initiation and growth of cracks or defects to a critical size. Since the crack initiation phase at discontinuities which act as stress raisers occupies only a small portion of time when compared to the total failure life, prediction of service life can be obtained from a knowledge of the number of loading cycles required for a crack or flaw to grow to a critical size. Crack growth behavior is typically described in terms of an effective stress intensity factor,  $K_{eff}$ , or equivalently an effective strain energy release rate,  $G_{eff}$ .

Failure is taken, for example, at the point where a growing crack reaches a critical size or the cumulative damage as given by, say (2) or (3) reaches unity. Repetition of this analysis using system parameters and load paths selected at random from their populations gives the distribution of the cumulative damage at the selected age and environment. The

failure rate is then the fraction of that population that equals or exceeds one. The distribution of age at failure can be obtained by permitting the integration of the cumulative damage for each adhesive bonded joint to proceed until one of the stress locations indicates failure. This establishes the age at failure for the particular sample bonded joint, and repetitions of this process gives the estimated distribution for the population. The distribution of ages at first failure can be determined by selecting the minimum value from a substantial number of sample distributions of age at failure; thus permitting assessment of the expected time to first failure in a given population of adhesively bonded joints.

Combining the estimated failure rates by all of the failure modes provides an estimate of the total system failure rate as a function of its age and environment. Thus, once a maximum acceptable failure probability is established, the useful service life of the system can be determined.

### 3.5 Sensitivity Analyses

A critical item in the fabrication of adhesive bonded systems is the establishment of meaningful and realistic manufacturing tolerances and quality control limits for processing operations such as adherend surface preparation, adhesive thickness, and cure pressure and temperature. These limits can be established by systematically varying each of the input variables over its estimated range and then evaluating the impact of each parameter on the failure rate and expected service life. The life-limiting components and the particular failure modes involved can thus be determined. The magnitudes of changes in design, material properties, loading or environmental conditions required to effect desired changes in the service life can be established, and the areas where design requirements can be

safely relaxed in the interest of processing economy can be identified. This information can then be fed back into the system design process and the analyses repeated to arrive at a configuration to meet a specified system service life under the range of imposed environments and loads at minimal costs.

#### IV. DEGRADATION MECHANISMS OF EPOXY ADHESIVES

Depending upon the particular loading and environmental history epoxies experience all three types of aging behavior discussed in Section I. They also exhibit degradation mechanisms common to many polymers [see, e.g., Winslow (1977)], although in adhesive joints, load, temperature and moisture histories dominate structural response and failure.

In summarizing the degradation mechanisms of epoxies and adhesive joints it is convenient to consider the behavior above and below the glass transition temperature,  $T_g$ , separately, and in some instances the behavior of the neat resin separately from the adhesive joint. Epoxies are frequently undercured when put into service [see, e.g., Levy (1976,1977)]. As a result, continued cross-linking and resultant hardening is observed at temperatures above  $T_g$ . Oxidative cross-linking and thermal degradation (i.e., chain scission) are also evident at high temperatures.

The most serious environment for adhesive joints is the combined load-temperature-moisture environment. Epoxies typically show two transitions as may be determined from dynamic mechanical spectroscopy. The higher order, or first-order transition, occurs around  $T_g$  where the epoxy transitions from a rubber-like material to a glass-like material. Viscoelastic or time dependent behavior is still observed down to the second order or  $\beta$ -transition, where most side-chain motion is apparently frozen-in. Moisture acts primarily as a plasticizer although some hydrolytic chain scission has been observed at temperatures above  $T_g$  for particular epoxy systems. The extent of the polymer chain-plasticizer interaction is

determined by intermolecular forces such as dispersion forces, induction forces, dipole-dipole interactions and hydrogen bonding. As a plasticizer the primary physical effect of moisture absorption is the lowering of  $T_g$  by as much as 60°C and swelling of the bulk matrix.

The absorption and desorption of moisture in epoxy resins is a diffusion controlled process with a strongly temperature dependent diffusion coefficient. For the neat resin in an unstressed state slow (near equilibrium) absorption and desorption of moisture constitutes a physical aging process. That is, the effects are reversible and softening of the matrix is recoverable by removal of excess water. However, under more rapid transient conditions the existence of a moisture concentration gradient even in unconstrained or unstressed samples leads to stress gradients due to volumetric swelling which causes microcracking and crazing of the matrix. This problem is further complicated for multiphase systems such as, for example, a system with scrim cloth and/or butadiene rubber filler. In this case, differential moisture absorption of the components can lead to high local stresses and subsequent matrix crazing or cracking.

The above effects are still further complicated by temperature excursions above and below the  $T_g$  and by loading. Temperature excursions above and below  $T_g$  affect the diffusion absorption and desorption coefficients and thus further increase internal stresses. Water molecules may also interact chemically during the post cure process at temperatures above  $T_g$ .

The effects of moisture, temperature and load are magnified in an adhesive joint, since moisture absorption and desorption are slower, temperature excursions and thermal equilibrium are achieved more rapidly

and the stress state is non-uniform with large stress gradients (mathematically infinite) occurring at the exposed adhesive/adherend interface.

The scenario of environmental degradation of adhesive bonded joints may thus be summarized in the following fashion. At temperatures below  $T_g$  moisture diffuses slowly into the adhesive which plasticizes the adhesive, thereby gradually lowering  $T_g$  of the epoxy and causing volumetric swelling of the adhesive. The volumetric swelling increases stresses already existing due to structural loading on the joint and residual cure shrinkage and thermal stresses. These increased stresses may cause crazing or cracking. A temperature excursion above  $T_g$  in the presence of moisture increases the moisture absorption rate and thus the above effects. Once above  $T_g$  the epoxy undergoes a post-cure reaction, which may be enhanced by the presence of moisture. The additional crosslinks that are formed, form in a local stress-free state even though the joint is under a macroscopic stress. High temperature excursions in a hot, dry environment cause moisture to leave the adhesive and a concentration gradient to develop in the interior of the adhesive, rather than at the free surface. For rapid heating this gradient is larger and more severe than the original absorption gradient.

The initial moisture absorption results in bulk compressive stress at the adhesive free surface and the adhesive/adherend interface which are superposed on the existing tensile and shear stress state existing in the joint. Moisture desorption on the other hand induces tensile stresses in the adhesive at its free surface and at the adhesive/adherent interface, which superposed on an existing tensile stress field may lead to failure or fracture. Thus, the critical environment is most likely the situation where moisture is leaving rather than entering the adhesive system. The

initial presence of moisture, by lowering  $T_g$  and plasticizing the epoxy resin, may degrade the strength and fracture characteristics of the adhesive system such that removal of the moisture increases stresses sufficient to cause failure or fracture before recovery of inherent material strength.

One additional concern is moisture diffusion along the adhesive/adherend bond interface. For improperly prepared metal adherend surfaces moisture may chemically react with the interface oxide layer on the metal and lead to a degraded interfacial bond with time. This effect has been observed in which lap shear specimens failed cohesively in the adhesive immediately after manufacture, but which failed adhesively between the adhesive and adherend after exposure to a hot, wet environment.

## V. DEVELOPMENT OF AGING CONSTITUTIVE THEORIES

In order to properly characterize and predict the aging behavior of adhesives and adhesive joints it is necessary to incorporate appropriate kinetic parameters describing aging and degradation mechanisms into the constitutive equations for the mechanical response, failure and fracture behavior. Ideally, a single constitutive theory describing the mechanical response up to failure is desirable; however, no such unified theory has yet been developed for any material. Thus, mechanical response, and failure and fracture characteristics are commonly discussed separately.

### 5.1 Mechanical Response

The mechanical response of viscoelastic material (linear or nonlinear) is determined by the loading and environmental histories. That is, for example, the stress response at time  $t$ ,  $S(t)$ , is given by

$$S(t) = \int_{s=0}^{\infty} e(t-s), \psi(t-s) \quad (4)$$

where  $e$  represents the (finite) strain history and  $\psi$  represents the environmental history. Assuming, for the purposes of discussion linear viscoelastic behavior, Equation (4) has the explicit integral representation

$$S(t) = \int_0^e K_1\{\psi(\tau), t-\tau\} de(\tau) + \int_0^\psi K_2\{\psi(\tau), t-\tau\} d\psi(\tau) \quad (5)$$

where  $K_1$  and  $K_2$  represent relaxation functions for the strain and environmental histories, respectively. If  $\psi$  represents, for example, only the temperature history,

$$\psi(t) = \int_0^\theta \alpha \, d\theta \quad (6)$$

then (5) simplifies to

$$S(t) = \int_0^t K_3\{\psi(\tau), t-\tau\} \frac{\partial}{\partial \tau} [e^{-\psi I}] \, d\tau \quad (7)$$

in which  $I$  represents the identity tensor. For a constant coefficient of thermal expansion,  $\alpha$ , Equation (4) reduces to the familiar form

$$S(t) = \int_0^t K\{\psi(\tau), t-\tau\} \frac{\partial}{\partial \tau} (e^{-\alpha\theta I}) \, d\tau \quad (8)$$

Assuming thermorheologically simple material behavior the influence of temperature history on the stress response is accounted for by time-temperature superposition and introduction of a time-temperature "shift function",  $a_T$ , which is a monotonic function of temperature and chosen so as to be unity at some reference temperature,  $T = T_R$ ;

$$S(t) = \int_0^t K\{\xi - \xi'; T_R\} \frac{\partial}{\partial \tau} (e^{-\alpha\theta}) \, d\tau \quad (9)$$

where  $\xi$  and  $\xi'$  are the temperature reduced time variable defined by

$$\xi - \xi' = \frac{t}{a_T} - \frac{\tau}{a_T} \quad (10)$$

for isothermal temperature fields, and

$$\xi - \xi' = \int_{\tau}^t \frac{dt'}{a_T[T(t')]} \quad (11)$$

for transient temperature fields.<sup>1</sup>

The shift function,  $a_T$ , may be developed from molecular considerations of free volume [see, e.g., Williams, Landel, Ferry (1955), Ferry (1971)], or from a continuum mechanics point of view [see, e.g., Morland and Lee (1960), Hunter (1961), Christensen and Naghdi (1967), Christensen (1971)]. Below  $T_g$ , the shift factor is usually found to obey an Arrhenius type relationship

$$\log a_T = \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (12)$$

where  $\Delta H$  is the activation energy and  $R$  is the universal gas constant. At temperatures above  $T_g$  many amorphous polymers obey the WLF relation [Williams, Landel and Ferry (1955)]

$$\log a_T = \frac{-8.86(T-T_2)}{101.6+T-T_2} \quad (13)$$

where  $T_g$  is approximately equal to  $T_2 + 50^\circ\text{C}$ , with an apparent activation energy,  $\Delta H_a$ , given by

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<sup>1</sup>In practice, the stress tensor given by (9) is decomposed into a sum of dilatational and deviatoric components and two relaxation functions are defined; one for dilatation, which is frequently assumed to be elastic, and one for shear.

$$\Delta H_a = R \frac{d \log a_T}{d(1/T)} \quad (14)$$

Now considering  $\psi$  to be a more general environmental history, the same general procedure may be followed [see, e.g., Stauffer, et al. (1971, 1972, 1973, 1975), Hufferd, et al. (1975, 1977a,b)]. The effects of the environmental history are defined in terms of a reduced variable, similar to temperature-reduced time [see, e.g., Hefty (1966), Fulmer (1967, 1968), Halpin (1968), Bartenev and Zuyev (1968), Rabotnov (1968), Ferry (1971), Kaelble, et al. (1971, 1974, 1975), Ishai (1975), Berens and West (1975), Wu and Ruhmann (1975), Weitsman (1977a,b)]. Starting from a reference temperature, chemical aging state and moisture level, the stress response may be written

$$\begin{aligned} S(t) = & \int_0^t K_1[\xi - \xi'; T_R, C_R, m_R] \frac{\partial}{\partial \tau} (e - \alpha\theta) d\tau \\ & + \int_0^t K_2[\xi - \xi'; T_R, C_R, m_R] \frac{\partial}{\partial \tau} C(\tau) d\tau \\ & + \int_0^t K_3[\xi - \xi'; T_R, C_R, m_R] \frac{\partial}{\partial \tau} m(\tau) d\tau \end{aligned} \quad (15)$$

where  $C_R$  and  $m_R$  are the reference chemical aging state and moisture content, respectively,  $C(t)$  and  $m(t)$  are chemical aging and moisture content histories, and  $\xi - \xi'$  may again be defined in terms of free-volume concepts [see, e.g., Ferry (1971), Kaelble (1971), Fulmer (1967, 1968)].

Most generally, the free volume,  $\psi_0$  may be written

$$\psi_0 = a_1 T + a_2 C + a_3 m + a_4 CT + a_5 mT + a_6 Cm + a_7 CmT \quad (16)$$

and the resulting shift factor relating the response  $\eta$  at a given temperature, chemical aging state, and moisture level to the corresponding response,  $\eta_0$ , at the reference state; i.e.,

$$\eta/\eta_0 = A \exp\left(\frac{\psi_0}{T-T_0}\right) \quad (17)$$

As a practical matter, it may not be possible to experimentally determine the combined effects of moisture, temperature and chemical aging on the free volume. In this case it may be acceptable to initially neglect these interactions by assuming  $a_4 = a_5 = a_6 = a_7 = 0$  in (16) so that the shift factor may be written

$$\begin{aligned} a_{T,C,m} &= \log \eta/\eta_0 = \log a_T + \log a_C + \log a_m \\ &= \log (a_T a_C a_m) \end{aligned} \quad (18)$$

and the reduced time  $\xi - \xi'$  becomes

$$\xi - \xi' = \int_0^t \frac{dt'}{a_T[T(t')] a_C[C(t')] a_m[m(t')]} \quad (19)$$

Although (19) ignores or neglects combined effects of moisture, temperature and chemical aging in the deviation of the appropriate shift functions from a molecular point of view, synergistic effects are still accounted for through the material response functions  $K_1, K_2$  and  $K_3$  in (15). The shift functions  $a_C$  and  $a_m$  may be defined analogously to (11).

The material response functions  $K_1$ ,  $K_2$  and  $K_3$  are determined from tests at various temperatures, chemical aging states and moisture levels from which the activation energies associated with these environmental variables are determined using (12) - (14). The aging response may then be determined as a perturbation of the non-aging response [see, e.g., Stauffer and Strauss (1973), Hufferd (1977a)].

## 5.2 Failure and Fracture

Considerably more work has been done on failure and fracture directly within the framework of rate theory as presented in Appendix A [see, e.g., Krausz and Eyring (1975), Graham and Robinson (1969, 1970), Zhurkov (1965), Knauss (1963, 1965), Smith et al. (1973), Prevorsek and Lyons (1964), DeVries et al. (1971a,b), Robinson (1973), Kaelble et al. (1975), Halpin (1968), Bartenev and Zuyev (1968), Hefty (1966), Ishai (1975), Berens and West (1975), Coleman (1956), Tobolsky and Eyring (1943), Bueche (1955, 1957), Halpin and Polley (1967)]. In general, all approaches are essentially equivalent [Henderson (1970), Robinson (1973)], and the time to failure may be written in the form

$$t_f = \tau_0 \exp \left[ - \left( \frac{V - W(\sigma)}{kT} \right) \right] \quad (20)$$

where  $V$  represents the activation energy for the process and  $W(\sigma)$  is the stored elastic energy associated with the loading history. Assuming elastic behavior,  $W(\sigma)$  is often written  $W(\sigma) = \sigma\lambda$  where  $\lambda$  is the activation volume. In using (20) it is necessary to evaluate  $\tau_0$  and  $V$  as a function of environmental history from tests conducted at various times under differing

environmental conditions. For most polymeric materials  $\tau_0$  is inversely proportional to absolute temperature.

## VI. SUMMARY AND RECOMMENDATIONS

Considerable evidence has been gathered in recent years demonstrating the influence of temperature, aging and moisture on the mechanical response and failure of epoxy resins and adhesive bonded joints [see, e.g., Levy (1976, 1977), Kaelble, et al. (1974, 1975), Hefty (1966), Ishai (1975), Berens and West (1975), Wu and Ruhmann (1975), Weitsman (1977a,b), Levi (1977), Bascomb and Lockhart (1978), Marceau, et al. (1978), DeLollis (1977), Vaughan (1976), Macosko (1977), Ishai (1969), Katz (1977), Althof and Brockman (1977), Brockman (1976), Lewis and Natarajan (1976), Moehlenpah, et al. (1970), Vaughan (1976), Jones, et al. (1974), Kaelble, et al. (1975), May and Adsit (1976), Lewis, et al. (1972), Schjelderup and Jones (1978), Reinhart, et al. (1975), Vinson, et al. (1977), Marceu and McMillan (1976), Drzal, L. T. (1977), Kaelble (1977), Jones and Mahoney (1977), Brussat, et al. (1977), Renton (1978), Romanko (1977-1978)].

The important considerations in developing an accelerated testing program for structural adhesives are to identify the dominant mechanisms associated with curing and environmental aging. Separate these if possible, to determine associated activation energies and kinetic parameters as described in Appendix A, and incorporate the kinetic models in the constitutive models as described in Section V.

Epoxy resins are characterized by viscosity, melting point, hydroxyl number, percent unsaturation, active and bound chlorine and molecular weight distribution. Cure mechanisms are most easily identified by DSC. Epoxide equivalent or functionality can be identified by IR analysis.

Epoxies may be titrated with a standard base, after adding a hydrogen halide. In general, functionality increases with molecular weight of the fractions and if the average functionality is adjusted by blending, variations in distributions of functionality may account for differences in physical properties among various batches of resins and adhesives.

Thermal stability of adhesives is chiefly affected by the structure of the epoxy resin, type of curing agent, chlorine content and cure schedule. At high temperatures thermal and oxidative degradation may be expected. Oxidative degradation is limited by the diffusion rate of oxygen and may be determined by measurements of free and bound oxygen. Antioxidants offer some protection against oxidative degradation at room temperature, but the life may be shortened as the temperature is increased. The increase in cross-link density due to oxidation may be measured by NMR techniques and gas chromatography may offer some potential in identifying species. Thermal degradation may be estimated by measurements of weight gains and losses, even in the presence of moisture.

If the aging reaction is of the free radical type, then the reaction can be accelerated by gamma irradiation and measured by ESR.

Considering adhesive bonded joints, the instability of the interphases in liquid environments may be predicted from thermodynamic considerations. The thermodynamic work of adhesion,  $W_A$ , in an inert mechanism, (e.g., dry air) and in the absence of chemisorption and interdiffusion may be expressed by

$$W_A = \gamma_x + \gamma_y - \gamma_{xy} \quad (21)$$

where  $\gamma_x$  and  $\gamma_y$  are the surface free energies of the two solid phases and

and  $\gamma_{xy}$  is the interfacial free energy. In the presence of a wetting liquid (denoted by the suffix "l") the work of adhesion  $W_{A\ell}$  is

$$W_{A\ell} = \gamma_{x\ell} + \gamma_{y\ell} - \gamma_{xy} \quad (22)$$

A positive value of  $W_A$  or  $W_{A\ell}$  indicates stability of the interface between the two phases x and y, while a negative value indicates a spontaneous tendency for the interface to dissociate. Thus, calculations of the parameter,  $W_{A\ell}$ , enables the environmental stability of the interface to be determined.

The change from a positive to a negative work of adhesion provides a driving force for the displacement of epoxy adhesive from aluminum. The result is the observed increased tendency for the failure mode to transition from a cohesive to an interfacial adhesive failure. A mechanism of this environmental failure is the penetration of water and dissociation of the epoxy-aluminum oxide interface.

## APPENDIX A

### ABSOLUTE REACTION RATE THEORY

#### A.1 Historical Developments

Wilhelmy, in 1850, was the first to correctly formulate the kinetic law of a first order chemical reaction. He studied the acid-catalyzed hydrolysis of sucrose using a polarimeter and observed that the concentration,  $c$ , of sucrose decreases exponentially with time:

$$\frac{dc}{dt} = -k_1 c$$

or

$$\log c = -k_1 t + \text{constant}$$

or

$$c = c_0 e^{-k_1 t} \quad (23)$$

where  $c_0$  is the initial concentration of sucrose at time  $t = 0$ , and  $k_1$  is the "specific rate" or "rate constant" for the reaction. The expression rate constant, however, is misleading since at a minimum  $k$  is a function of temperature and pressure.

The next important step in the development of modern reaction kinetics was the proposal by Guldberg and Waage of a Principle of Mass Action in reaction rates and chemical equilibria. In a series of papers between 1864 and 1879 they described and explained the effect of changing concentrations on the rates of simple reactions in which the exponents of the

concentration terms in the rate expression are the stoichiometric coefficients of the reactants: (e.g., the reversible combination of an alcohol with acetic acid to form an ester and water). The concept of Mass Action is not as generally applicable to reaction rates as it is to equilibria, since many reactions involve more than one discrete step and a simple one-to-one correspondence between stoichiometric coefficients and exponents in the differential equation for the rate of the overall reaction does not exist.

Van't Hoff, in 1877, independently enunciated the Principle of Mass Action and applied it to heterogeneous systems. He further proposed that an equilibrium theory can be used to calculate the flow rate from one state into another and provided a thermodynamic description of the temperature dependence of the chemical equilibrium constant (1884). At equilibrium the net rate of reaction is zero; that is, the forward and reverse rates of reaction are zero. For products (a) and (b) and reactants (c) and (d)

$$(a)(b) k_f = (c)(d) k_b$$

or

$$\frac{(c)(d)}{(a)(b)} = K_c = \frac{k_f}{k_b} \quad (24)$$

where  $k_f$  is the specific rate of the forward reaction and  $k_b$  is the specific rate of the reverse reaction;  $K_c$  is the concentration equilibrium constant. The Van't Hoff equation for the temperature dependence of the equilibrium constant may be written as

$$\frac{d \log K_c}{dT} = \frac{\Delta E}{RT^2} \quad (25)$$

where the increase of energy,  $\Delta E$ , is equal to the heat of reaction at constant volume. It follows from (24) and (25) that

$$\frac{d \log k_f}{dT} - \frac{d \log k_b}{dT} = \frac{\Delta E}{RT^2} \quad (26)$$

Van't Hoff suggested that (26) could be written as two equations

$$\frac{d \log k_f}{dT} = \frac{E}{RT^2} + A$$

and

$$\frac{d \log k_b}{dT} = \frac{E'}{RT^2} + A \quad (27)$$

where  $\Delta E = E - E'$  and  $A$  is a constant.

The final impetus for development of modern kinetic theory came from Arrhenius who, in 1889, concluded that in a reacting system there is an equilibrium between ordinary molecules and "active" molecules, and that only molecules in an "activated state" are energetic enough to undergo reaction. He had observed that the temperature dependence of the inversion of sucrose is too great to be explained either by an increase in kinetic energy of all molecules or by an increased dissociation of the acid catalyst. Arrhenius therefore suggested that van't Hoff's equations (27) be written in the form

$$\frac{d \log k}{dT} = \frac{E_A}{RT^2} \quad (28)$$

or in integrated form, assuming that  $E_A$  is a constant,

$$\log k = - \frac{E_A}{RT} + \text{constant}$$

or

$$k = A e^{-\frac{\Delta E_A}{RT}} \quad (29)$$

where  $\Delta E_A$  is the empirical apparent activation energy and is the difference between the average energy of active molecules and the average energy of all molecules. The integrated form of the Arrhenius equation (29), is only valid if these two average energies have the same temperature dependence.

Many subsequent developments in the early 1900's led to the theory of absolute reaction rates which established a theoretical basis for the analysis of the rate of change of atomic interactions and, therefore, chemical reactions including description of many of the basic processes of bond breakage and formation, diffusion, plastic deformation, viscous flow, and failure and fracture of materials. More general discussions of the development and application of Absolute Reaction Rate Theory than that presented here may be found in Glasstone, Laidler and Eyring (1941), and Krausz and Eyring (1975).

Scheffer and Kohnstamm (1911) introduced the idea of an activation entropy such that

$$\Delta E_A = \Delta H - T\Delta S$$

and considered that molecules go from the reactant to the product state in the "forward" direction and that products go from the product to the reactant state in the "backward" direction. Accordingly,

$$k_f = A_f \exp\left(\frac{\Delta S}{k}\right) \exp\left(\frac{-\Delta H_f}{kT}\right)$$

and

$$k_b = A_b \exp\left(\frac{\Delta S_b}{k}\right) \exp\left(-\frac{\Delta H_b}{kT}\right)$$

where  $\Delta H$  and  $\Delta S$  are the heat and entropy of the reaction at equilibrium. Macroscopic equilibrium is observed when the forward and backward rates are equal.

Marcellin (1915) recognized that, in statistical mechanics terminology, the rate of reaction is controlled by the passage of reacting systems from the part of phase space corresponding to the reactants to the part that corresponds to the products. London (1928) next proposed an approximate quantum mechanical method for calculating the potential energy surface for the simplest types of bi-molecular reactions. Eyring and Polanyi (1931 a,b) developed London's method further into a semi-empirical method which at last permitted application of statistical mechanics to reaction kinetics in an unambiguous fashion.

## A.2 Application of Absolute Reaction Rate Theory to Solids

Many time-dependent physical processes in materials can be characterized by an initial configuration, which by a continuous change of configuration space coordinates move into a final configuration. The potential energy surface in configuration space involves as many dimensions as are required to define a configuration plus one more for the energy.

On the potential energy surface stable molecules are in valleys and two valleys are connected by a pass that leads through a saddle point

which is referred to as the "transition" or "activated" state and which represents the highest point of the most favorable reaction path on the potential energy barrier separating two stable configurations. The configuration corresponding to the transition or activated state is called the transition or activated complex and the path which the systems follow is called the activation path. The distance traveled along the activation path is taken to be the reaction coordinate.

The activated state is, by definition, always a saddle point with positive curvature in all degrees of freedom except the one that corresponds to the crossing of the potential energy barrier for which it is negative. Therefore, an activated complex has all of the properties of a stable complex with the usual thermodynamic properties except that the normal vibrational mode along the direction of the reaction coordinate is unstable. That is, the normal vibration frequency is imaginary. If the curvature of the potential energy barrier in the neighborhood of the activated state is small, then the degree of freedom in the reaction coordinate may be treated statistically as a translational degree of freedom.

A fundamental postulate of the theory of absolute reaction rates is that equilibrium always exists between the initial and activated states. This assumption implies that the reaction does not appreciably disturb the equilibrium concentration of the activated complexes. It is further assumed that the activated complexes decompose at a definite rate. The specific rate of a reaction can then be determined by calculating the concentration of activated complexes and their rate of passage over the potential energy barrier using the methods of statistical mechanics.

A transmission coefficient,  $\kappa$ , is normally introduced to represent the probability of a mass point, corresponding to the system in configuration

space, upon reaching the activated state crossing over into the product state. This coefficient, which represents reflection about and tunneling through the energy barrier may be neglected in most processes in polymeric solids without appreciable error since the molecular masses considered are much greater than an electron mass, temperatures are much above absolute zero, and energy barriers are wide and flat near the top.

The potential energy change along the reaction coordinate for an elementary reaction is shown in Figure 3. The zero energy state is taken as the ground state of the reactants, and  $E_f^\ddagger$  is the activation energy in the forward direction at absolute zero.

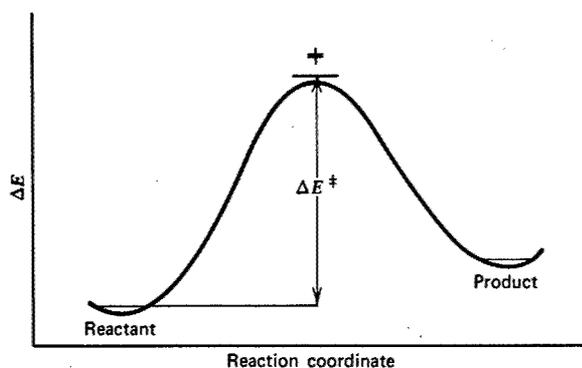


FIGURE 3. SCHEMATIC OF POTENTIAL ENERGY BARRIER (AFTER GLASSTONE, LAIDLER AND EYRING, 1941).

The activated state is reached when a complex is at the top of the energy barrier and lies within an activation "box" of arbitrary length,  $\delta$ , as shown in Figure 3. The rate at which the reaction occurs is given by the concentration of activated complexes,  $C^\ddagger$ , per unit volume lying within the activation length  $\delta$ , multiplied by the frequency at which the activated complexes pass through  $\delta$ .

Assuming that there is an equilibrium distribution of velocities in the activated state, the average velocity,  $\bar{V}_f$ , of the complexes translational motion along the metastable degree of vibrational freedom in the forward direction is given by

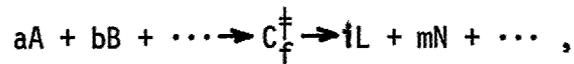
$$\bar{V}_f = \left( \frac{kT}{2\pi m^\ddagger} \right)^{\frac{1}{2}} \quad (30)$$

where  $m^\ddagger$  is the mass of the activated complex,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The ratio  $\bar{V}_f/\delta$  represents the time or frequency at which the activated complexes travel the distance  $\delta$ . Thus, the rate of the forward reaction over a single potential energy barrier is given by

$$\begin{aligned} (\text{Rate})_{\text{forward}} &= \kappa_f C_f V_f^\ddagger \\ &= \kappa_i \frac{C_f^\ddagger}{\delta} \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}}, \end{aligned} \quad (31)$$

where the transmission coefficient,  $\kappa$ , has been introduced to represent the probability of a mass point, corresponding to the system in configuration space, upon reaching the activated state, continuing into the product state. This coefficient is ordinarily used to correct the theoretical rate of passage over the energy barrier and lack of equilibrium, both of which tend to decrease  $\kappa$ ; or barrier leakage (i.e., tunneling), which tends to increase  $\kappa$ .  $\kappa$  may be neglected for most processes in solids without appreciable error since the molecular masses considered are much greater than an electron mass, temperatures are much above absolute zero, and the energy barriers are wide and flat near the top.

Assuming that the reactants are in equilibrium with the activated complexes, that is for a reaction of the form



equilibrium statistics may be used to relate the concentration of reactants to the concentration of activated complexes. In particular, according to Boltzmann statistics, the concentration in the activated state  $C_f^\ddagger$  for reactions in the forward direction and in equilibrium with the reactants is

$$C_f^\ddagger = \frac{(Q_f^\ddagger)_{\text{TOTAL}}}{Q_A Q_B \dots} C_A C_B \dots \quad (32)$$

where  $(Q_f^\ddagger)_{\text{TOTAL}}$  represents the complete partition function for the activated complexes in the forward direction, and  $Q_A Q_B \dots$  represents the partition function of the system in the initial state. The use of classical statistics is valid provided that the products of the reaction exert no catalytic or inhibitory effects on the reaction. This is the usual situation for deformation, failure and fracture of solids since there is no interaction between activated complexes because they are spatially separated in the solid and do not increase in concentration. Consequently, the rate of the forward reaction is independent of the reverse or backward reaction, and activated complexes would still move in the forward direction even if the products of the reaction did not form.

Using (32) equation (31) may be written as

$$(\text{Rate})_{\text{forward}} = \kappa_f \frac{kT}{h} \frac{Q_f^\ddagger}{Q_f} \exp\left(\frac{-\Delta E_f^\ddagger}{kT}\right) C_A C_B \dots \quad (33)$$

where  $h$  is Planck's constant and  $Q^\ddagger$  is the partition function taken with respect to the ground level of the activated state and with the partition function for the translational degree of freedom

$$\frac{(2\pi m^\ddagger kT)^{\frac{3}{2}}}{h} \delta$$

for a mass  $m^\ddagger$  in a box of length  $\delta$  extracted from the total partition function,  $(Q^\ddagger)_{\text{TOTAL}}$ . In (33)  $Q_f = Q_A Q_B \dots$  and the activation energy  $\Delta E_f^\ddagger$ , is the energy difference between the reactant and activated complexes at absolute zero.

It is customary in the study of rate processes to define a rate constant,  $k$ , such that

$$(\text{Rate})_{\text{forward}} = k_f C_A C_B \dots \quad (34)$$

Thus, from (33) the specific rate constant for a reaction proceeding in the forward direction is

$$k_f = \kappa_f \frac{kT}{h} \frac{Q^\ddagger}{Q_f} \exp\left(\frac{-\Delta E_f^\ddagger}{kT}\right) \quad (35)$$

Similar developments can be made for reactions going from products to reactants in the backward or reverse direction,



so that

$$(\text{Rate})_{\text{backward}} = k_b C_L C_M \dots \quad (36)$$

where

$$k_b = \kappa_b \frac{kT}{h} \frac{Q^\ddagger}{Q_b} \exp\left(\frac{-\Delta E_b}{kT}\right) \quad (37)$$

and  $Q_b = Q_L Q_M \dots$

The net rate of reaction from (34) and (36) is

$$\text{Rate} = k_f C_A C_B \dots - k_b C_L C_M \dots \quad (38)$$

At equilibrium,  $C_f^\ddagger = C_b^\ddagger$ ; that is, the same number of activated complexes are crossing the energy barrier in each direction. It follows from (32) that

$$\frac{C_A C_B \dots}{Q_A Q_B \dots} = \frac{C_L C_M \dots}{Q_L Q_M \dots} \equiv \frac{C}{Q} \quad (39)$$

and from (35), (37) and (38) that the net rate of reaction is

$$\text{Rate} = kC = (k_f - k_b) C \quad (40)$$

where

$$\begin{aligned} k \equiv k_f - k_b &= \frac{kT}{h} \frac{Q^\ddagger}{Q} \left( \kappa_f \exp\left(\frac{-\Delta E_f^\ddagger}{kT}\right) - \kappa_b \exp\left(\frac{-E_b^\ddagger}{kT}\right) \right) \\ &= \kappa \frac{kT}{h} \frac{Q^\ddagger}{Q} \left( e^{-\frac{\Delta E_f^\ddagger}{kT}} - e^{-\frac{\Delta E_b^\ddagger}{kT}} \right), \end{aligned} \quad (41)$$

since  $\kappa_f = \kappa_b = \kappa \doteq 1$  for most processes in solids as noted previously.

If, on the other hand,  $k_f = k_b = k$ , which is often the case, then from (38)

$$\text{Rate} = k(C_A C_B \dots - C_L C_M \dots) \quad (42)$$

and

$$k = \kappa \frac{kT}{h} \frac{Q^\ddagger}{Q} e^{-\frac{\Delta E^\ddagger}{kT}} \quad (43)$$

The previous equations, in particular (35), (37) and (43), can also be expressed in terms of thermodynamic quantities. The particular choice of the length,  $\delta$ , of the potential box at the top of the energy barrier was immaterial in the previous developments since it drops out of the final expressions. If, on the other hand, the activated complex is a normal molecule with a stiff translational vibration, or if the value of the activated length,  $\delta$ , is chosen so as to make the translational partition function unity, i.e.,

$$\delta = \frac{h}{(2\pi m^\ddagger kT)^{\frac{1}{2}}}$$

then the total partition function has the value  $Q^\ddagger$  that appears in the previous equations, (33) through (41). In this case, the terms

$$\frac{Q_f}{Q_A Q_B \dots} \exp\left(\frac{-E_f^\ddagger}{kT}\right)$$

and

$$\frac{Q_b^\ddagger}{Q_L Q_M \dots} \exp\left(\frac{-\Delta W_b^\ddagger}{kT}\right)$$

must be interpreted as the equilibrium constants for the activated and initial states, and the final and activated states, respectively, with all molecules treated as being normal. Denoting these equilibrium constants by  $K_f^\ddagger$  and  $K_b^\ddagger$ , respectively, (35) reduces to

$$k_f = \kappa_f \frac{kT}{h} K_f^\ddagger \quad (44)$$

(37) reduces to

$$k_b = \kappa_b \frac{kT}{h} K_b^\ddagger \quad (45)$$

and reduces to

$$k = \kappa \frac{kT}{h} K^\ddagger \quad (46)$$

The equilibrium constants,  $K^\ddagger$ , may be expressed in terms of the Gibb's free energy of the process,  $\Delta G$ , by means of thermodynamic equations of the form

$$-\Delta G^\ddagger = kT \log K^\ddagger \quad (47)$$

Therefore, (44) - (46) become

$$k_f = \kappa_f \frac{kT}{h} \exp\left(\frac{-\Delta G_f^\ddagger}{kT}\right) \quad (48)$$

$$k_b = \kappa_b \frac{kT}{h} \exp\left(\frac{-\Delta G_b^\ddagger}{kT}\right) \quad (49)$$

and

$$k = \kappa \frac{kT}{h} \exp\left(\frac{-\Delta G}{kT}\right) \quad (50)$$

If  $G^\ddagger$  is replaced by its equivalent

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (51)$$

where  $\Delta H^\ddagger$  is the heat or enthalpy of activation and  $\Delta S^\ddagger$  is the entropy of activation, then the reaction rates are expressed as

$$k_f = \kappa_f \frac{kT}{h} \exp\left(\frac{\Delta S_f^\ddagger}{k}\right) \exp\left(\frac{-\Delta H_f^\ddagger}{kT}\right) \quad (52)$$

$$k_b = \kappa_b \frac{kT}{h} \exp\left(\frac{\Delta S_b^\ddagger}{k}\right) \exp\left(\frac{-\Delta H_b^\ddagger}{kT}\right) \quad (53)$$

and

$$k = \kappa \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{k}\right) \exp\left(\frac{-\Delta H^\ddagger}{kT}\right) \quad (54)$$

The similarity between the equations of absolute reaction rate theory developed in this section and the Arrhenius expression (29), and the linear temperature dependence of the pre-exponential multiplier in the Arrhenius equation are immediately evident.

### A.3 Activation in the Presence of an Applied Stress

An external constraint, such as an applied force or stress, a concentration gradient, an electrical potential, etc., distorts the potential energy surface in relation to the work performed in moving from the equilibrium state to the activated state. If the work of the external constraints, which may act individually or collectively, is denoted by  $W$ , then the height of the potential energy barrier is decreased by an amount  $W_f$  for systems moving in the forward direction and increased by an amount  $W_b$  for systems moving in the backward direction, as illustrated in Figure 4 for an applied stress.

The corresponding rate constants are given by

$$k_f = \kappa_f \frac{kT}{h} \frac{Q^\ddagger}{Q_f} \exp\left(\frac{-\Delta E_f^\ddagger - W_f}{kT}\right) = k_f^\ddagger e^{W_f/kT} \quad (55)$$

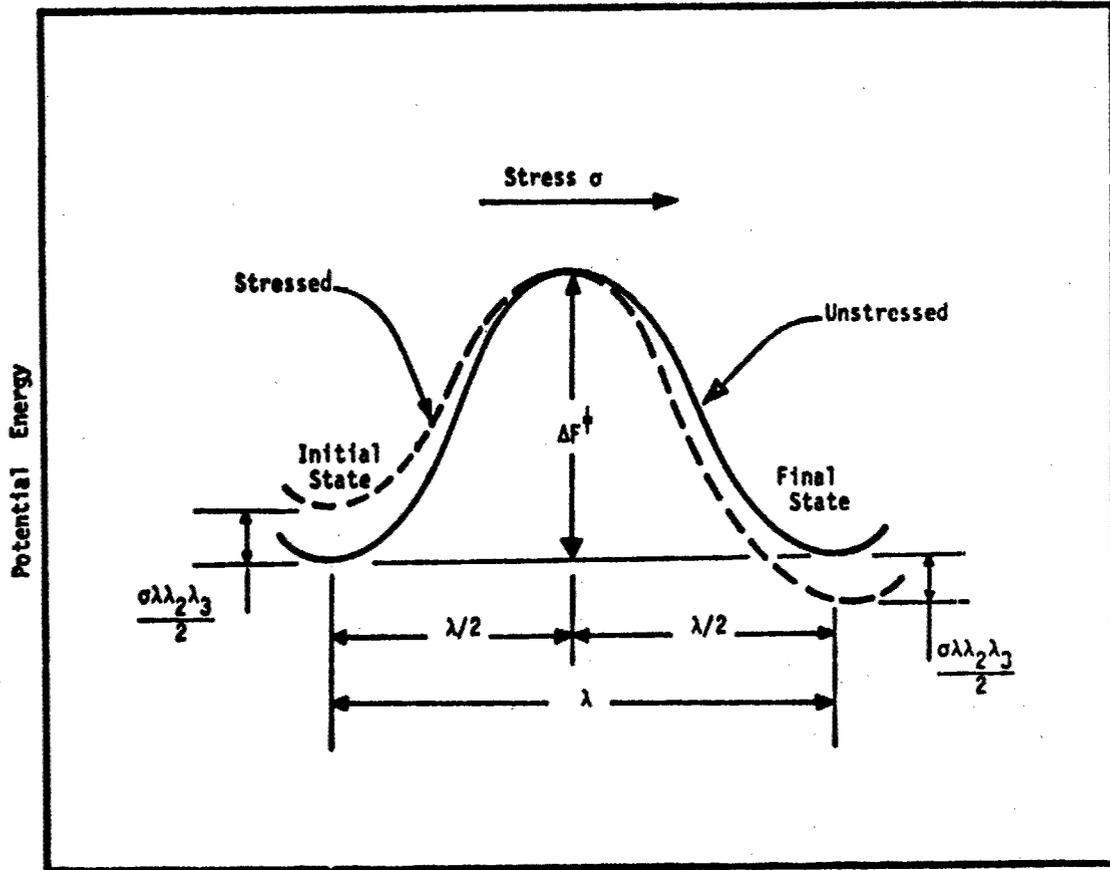


FIGURE 4. EFFECT OF APPLIED STRESS ON ACTIVATION ENERGY BARRIER

and

$$k_b = \kappa_b \frac{kT}{h} \frac{Q^\ddagger}{Q_f} \exp\left(\frac{-\Delta E_b^\ddagger - W_b}{kT}\right) = k_b^\ddagger e^{W_b/kT} \quad (56)$$

If the potential energy barrier is symmetrical, as illustrated in Figure 4, with  $k_f^\ddagger = k_b^\ddagger = k^\ddagger$  and  $W_f = W_b$ , then from (55) and (56) the net rate of flow is given by

$$k = k_f - k_b = k^\ddagger \left( e^{+\frac{W}{kT}} - e^{-\frac{W}{kT}} \right) = 2k^\ddagger \sinh \frac{W}{kT} \quad (57)$$

For many processes of flow and fracture the backward reactions do not occur, or occur at such a slow rate that the term  $e^{-W/kT}$  can be neglected so that

$$k = 2k^\ddagger e^{\frac{W}{kT}} = 2\kappa \frac{kT}{h} \frac{Q^\ddagger}{Q} e^{\frac{-\Delta E^\ddagger}{kT}} e^{\frac{W}{kT}} \quad (58)$$

If the external work,  $W$ , is small compared to  $kT$ , (57) may be linearized to give

$$k = 2k^\ddagger \frac{W}{kT} \quad (59)$$

Equations (55) through (59) may also be expressed in terms of the Gibb's free energy using (47) and (51):

$$\frac{Q^\ddagger}{Q} = \exp\left(\frac{-\Delta E^\ddagger}{kT}\right) = \left(\frac{-\Delta G^\ddagger}{kT}\right) \quad (60)$$

and

$$k^\ddagger = \kappa \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{kT}} = \kappa \frac{kT}{h} e^{\frac{-\Delta S^\ddagger}{k}} e^{\frac{-\Delta H^\ddagger}{kT}} \quad (61)$$

If the free energy,  $\Delta G^\ddagger$  is associated with a molal quantity of reactant complexes, rather than a single group of molecules forming one reactant complex, then noting

$$\Delta G_m^\ddagger = N_a \Delta G^\ddagger$$

and

$$R = N_a k$$

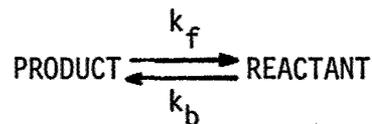
where  $N_a$  is Avogadro's number, (61) becomes

$$k^\ddagger = \kappa \frac{kT}{h} e^{\frac{-G_m^\ddagger}{RT}} \quad (62)$$

where the subscript m indicates that the free energy is measured per unit mole.

#### A.4 Activation Over A System of Energy Barriers

Many chemical reactions and deformation and failure processes are often more complicated than the simple type of reaction discussed in previous sections,



and intermediate products and reactants may form before the final state is reached. In general, it is necessary to analyze each step of a reaction and by appropriately combining individual rate constants  $k_i$ , derive an overall rate constant  $k$  for the reaction. In deformation and fracture processes it is often necessary for the reaction to occur over a system of energy barriers before fracture occurs or any appreciable contribution is made to the flow process. The potential energy barriers may form either a parallel system (Figure 5), a consecutive system (Figure 6), or a combination of these two (Figure 7).

If the deformation is controlled by several independent mechanisms, these form a system of parallel energy barriers and the flow over each energy barrier is independent of the flow over any of the others. A consecutive system of energy barriers is encountered when the deformation

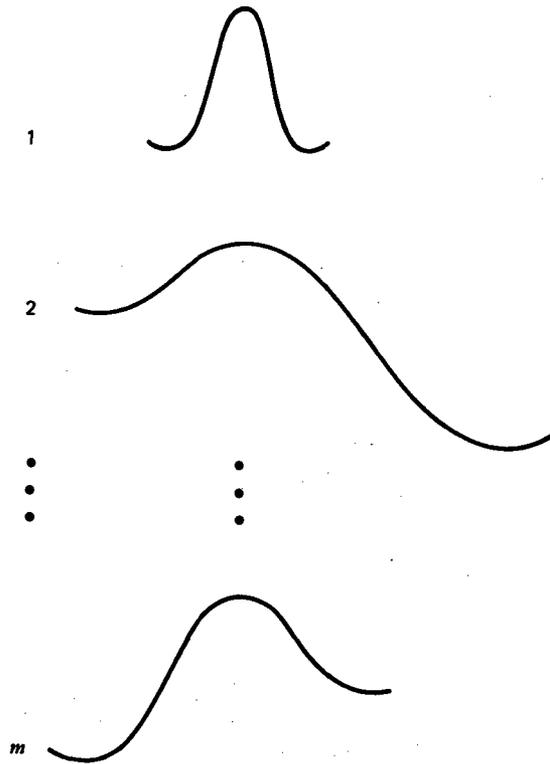


FIGURE 5. A PARALLEL SYSTEM OF  $m$  ENERGY BARRIERS

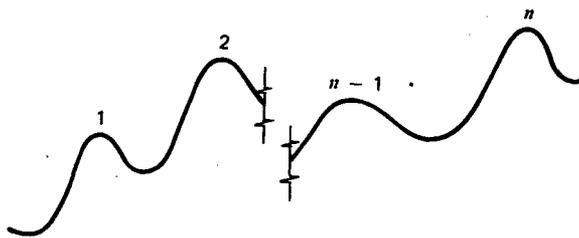


FIGURE 6. A CONSECUTIVE SYSTEM OF  $n$  ENERGY BARRIERS

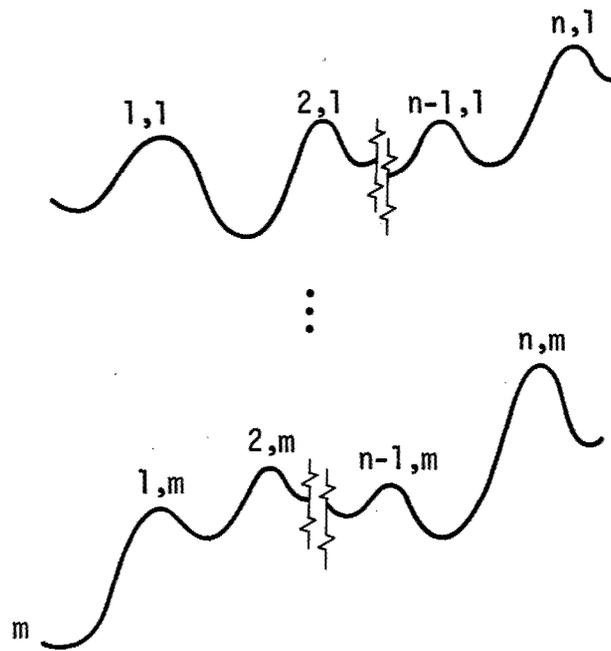


FIGURE 7. A COMBINED SYSTEM OF  $m$  PARALLEL ENERGY BARRIERS, EACH CONSISTING OF  $n$  CONSECUTIVE ENERGY BARRIERS IN SERIES

or failure process is such that a series of obstacles has to be overcome before a contribution is made to the overall flow. In this case, activation over an energy barrier occurs only after the previous energy barrier has been overcome.

The rate of flow over  $n$  consecutive energy barriers is given by

$$\text{Rate}_n = \left( \rho_1 - \rho_{n+1} \exp[(\Delta G)_1/kT] \right) \left( \sum_{i=1}^n \frac{1}{(k_i)} \right)^{-1} \quad (63)$$

where  $\rho_1$  represents the concentration of flow units held up by the first obstacle and  $\rho_{n+1}$  represents the concentration of flow units in the final

position that go backward over the  $n$ th barrier. The rate constant for the  $i$ th obstacle is given by

$$k_i = \kappa \frac{kT}{h} \frac{Q^\ddagger}{Q_i} \exp\left(\frac{-\Delta E_i}{kT}\right) = \kappa_i \frac{kT}{h} \exp\left(\frac{-\Delta G_i}{kT}\right) \quad (64)$$

where  $\Delta E_i$  is the apparent activation energy and is expressed as

$$\Delta E_{if} = \Delta E_{if}^\ddagger - W_{if}(\sigma)$$

for the forward activation and

$$\Delta E_{ib} = \Delta E_{ib}^\ddagger - W_{ib}(\sigma)$$

for the backward activation, and the work  $W$  is a function of the appropriate stress component. The subscript  $l$  indicates that the apparent free energy difference is taken with respect to the ground level of the  $\rho_l$  state.

When  $m$  processes are acting in parallel then the total rate of flow-unit activation is

$$\text{Rate}_m = \sum_{j=1}^m k_{jf} \rho_{j,\text{initial}} - \sum_{j=1}^m k_{jb} \rho_{j,\text{final}} \quad (65)$$

where  $\rho_{j,\text{initial}}$  is the concentration of flow units in front of the  $j$ th parallel energy barrier and in equilibrium with the activated complexes moving in the forward direction and  $\rho_{j,\text{final}}$  represents the concentration after the  $j$ th barrier and in equilibrium with the activated complexes moving in the backward direction.

For the general case of  $m$  systems of  $m$  barriers in parallel where each parallel branch has  $n$  barriers in series, the rate of flow over the system is obtained from combining (63) and (65).

$$\text{Rate}_{m,n} = \sum_{j=1}^m \left[ \frac{\rho_1 - \rho_{n+1} \exp[(\Delta G)_1/kT]}{\sum_{i=1}^n 1/(k_i)_1} \right] \quad (66)$$

where  $n$  depends on which branch is considered and

$$n = n(j), \rho_1 = \rho_1(j), \Delta G = \Delta G(j) \text{ and } k_i = k_i(j)$$

The subscript one again indicates that the activation free energies have to be related to the ground level of the initial state in each branch.

In transport processes over multiple activation barriers, each activation over an energy barrier system contributes a unit amount to the physical quantity that changes during the process. This physical quantity may be stress, strain, crack growth or some other transport related quantity. The total, macroscopic rate is the product of the unit amount of change of the physical quantity multiplied by the rate expressed by the appropriate form of (63), (65) or (66).

#### A.5 Interpretation and Discussion of Activation Parameters

If the specific rate constant, as given by (64), for example, is multiplied by the contribution of each activation to the process and by the number of molecular segments or flow segments taking part in the process, then the macroscopic rate for the process is obtained in the form

$$\dot{M}_R = \dot{M}_R^o \frac{kT}{h} \exp\left(\frac{-\Delta G}{kT}\right) \quad (67)$$

where the "frequency factor",  $\dot{M}_R^o$ , an orientation factor correlating local rates with observed macroscopic rates. The Gibb's free energy  $\Delta G$  has been previously defined by

$$\Delta G = \Delta G^\ddagger - W(\sigma)$$

so that (67) may be written

$$\dot{M}_R = \dot{M}_R^o \frac{kT}{h} \exp\left(\frac{-\Delta G^\ddagger}{kT}\right) \exp\left(\frac{W(\sigma)}{kT}\right) \quad (68)$$

Equation (67) or (68) represents the macroscopic rate of a process moving in the forward direction. Considering processes which can also move in a backward direction leads to, as before, for a symmetrical energy barrier.

$$\dot{M}_R = 2\dot{M}_R^o \frac{kT}{h} \exp\left(\frac{-\Delta G^\ddagger}{kT}\right) \sinh\left(\frac{W(\sigma)}{kT}\right) \quad (69)$$

Equation (69) is the general form of the Eyring rate equation for deformation, flow and fracture of materials with  $\dot{M}_R$  and  $\dot{M}_R^o$  appropriately interpreted for the particular process being considered. For example, the constant strain rate or creep loading  $\dot{M}_R$  is interpreted as accumulated strain,  $\epsilon$ , and  $\dot{M}_R = \dot{\epsilon}$ ,  $\dot{M}_R^o = \dot{\epsilon}_o$ . For stress relaxation  $\dot{M}_R = \dot{\sigma}$ , and for failure or fracture by bond slippage or bond breakage,  $\dot{M}_R = -\frac{1}{N} \frac{dN}{dt}$ . In practice, (69) is used at low stress levels when contributions to backward reactions are not negligible and (68) is used at high stress levels where the backward reactions do not occur, or are negligible. This latter situation

corresponds to permanent irreversible changes in molecular structure, such as fracture, while the former corresponds to reversible molecular changes such as those associated with viscous flow of a fluid.

The external work,  $W(\sigma)$ , is defined in terms of the local stress, although, for simplicity, it is frequently assumed that the local internal stress distribution is identical to the external macroscopic stress distribution. The work  $W(\sigma)$  was originally developed and is still often written as the product of stress and an "activation volume",  $V^\ddagger$ , which was assumed independent of stress:

$$W(\sigma) = \sigma V^\ddagger \quad (70)$$

The assumed stress independence of  $V^\ddagger$  leads to a linear stress vs. log rate dependence at constant temperature and implies a linearly varying, i.e., triangular, potential energy barrier for the process [see, e.g., Pink (1977)]. It is also frequently assumed that the other parameters in the Eyring theory, i.e.,  $\dot{M}_R^\circ \frac{kT}{h}$  and  $\Delta G^\ddagger$  are also material constants, independent of stress, strain, rate, temperature, etc. For many materials under limited testing conditions and with particular test methods, these assumptions have yielded good agreement between theory and experiment. However, it has been suggested that the linear stress-log rate behavior is dependent upon the particular test method employed, and that deviations from this behavior may be accounted for by incorporating the appropriate temperature and stress dependency in the Eyring parameters; rather than introducing additional rate controlling mechanisms to account for observed discontinuities in a plot of stress versus log rate (Pink, 1977). For example, the activation volume,  $V^\ddagger$ , represents the "activation area" swept

out by the reacting complexes during the activation process, multiplied by the distance traveled along the reaction coordinate in going from either one equilibrium state to another or from the initial state to the activated state, and thus  $V^\ddagger$  should vary linearly with temperature and inversely with stress. This behavior has been observed for many metals and polymers [see, e.g., Kubat and Rigdahl (1976)] including epoxy resins [Theocarus (1962)]. Unaware of any stress dependence, Ree and Eyring (1955a,b), Kauzman (1941), Sherby and Dorn (1952), Graham, et al. (1969) and Robinson, et al. (1970) have observed the proper linear temperature dependence of the activation volume. Zhurkov (1965), interestingly enough, treated the activation volume as a constant independent of stress and temperature and claimed to explain the fracture behavior for 50 different materials including metals, alloys, non-metallic crystals and polymers.

Based on the above observations it has been suggested that the external work be formulated as an integral

$$W(\sigma) = \int_0^\sigma V^\ddagger(\sigma') d\sigma' \quad (71)$$

to account for the stress dependence of  $V^\ddagger$  [see, e.g., Pink (1977)]<sup>1</sup>.

Whether (70) or (71) is used to interpret the activation volume it may be defined as the derivative of the free energy  $\Delta G$ ,

$$V^\ddagger = - \left( \frac{\partial \Delta G}{\partial \sigma} \right)_{T,P,STRUCT} \quad (72)$$

---

<sup>1</sup>Prevorsek and Lyons (1964) have suggested the use of the strain energy density for an assumed linear elastic solid to represent the work, and Knauss (1963, 1965), DeVries, Roylance and Williams (1971), and Robinson (1973) have suggested the use of the free energy functional for a linear viscoelastic material.

where the subscripts T,P and STRUCT indicate that the derivative is evaluated at constant temperature, pressure and structure.

Neither the Gibbs free energy nor the activation volume can be determined directly by experimentation, and rigorous evaluation of activation energies and activation volumes is a formidable task, not yet amenable to solution. Thus, the usual procedure is to deduce "apparent" or "experimental" activation energies and volumes for the overall process or processes by curve-fitting observed macroscopic behavior to theoretical predictions. The experimental activation volume,  $V_e$ , may be determined from the relation

$$V_e = -kT \left( \frac{\partial \log \dot{M}_R / \dot{M}_R^\circ}{\partial \sigma} \right)_{T,P,STRUCT} \quad (73)$$

Alternatively,  $\Delta G$  may be written in terms of entropy and enthalpy,

$$\Delta G = \Delta H - T\Delta S$$

so that

$$\dot{M}_R = \dot{M}_R^\circ \frac{kT}{h} \exp\left(\frac{\Delta S}{k}\right) \exp\left(\frac{-\Delta H}{kT}\right) \quad (74)$$

with

$$\Delta H = \Delta H^\ddagger - W(\sigma) = \Delta H^\ddagger - \int_0^\sigma V^\ddagger(\sigma') d\sigma' \quad (75)$$

Thus, activation volume is determinable from the activation enthalpy which is experimentally measurable:

$$V_e = - \left( \frac{\partial \Delta H}{\partial \sigma} \right)_{T,P,STRUCT} \quad (76)$$

The experimental activation volume may also be written in the form [see, e.g., Krausz and Eyring (1975) or Pink (1977)],

$$V_e = \lambda_\sigma kT \quad (77)$$

where  $\lambda_\sigma$  is a rate sensitivity parameter, determinable experimentally from the relation

$$\lambda_{\sigma, \text{exp}} = \left( \frac{\Delta\sigma}{\log(\dot{M}_{R1}/\dot{M}_{R2}^{\circ})} \right)_{T, P, \text{STRUCT}} \quad (78)$$

where  $\Delta\sigma$  is the increase in stress when the macroscopic rate  $\dot{M}_R$  is increased from  $\dot{M}_{R1}$  to  $\dot{M}_{R2}$ . Equation (74) assumes that the pre-exponential multiplier  $M_R$  is not affected by rate changes although there are some indications that it is sensitive to structural changes which are rate sensitive [Krausz and Eyring (1975), Pink (1977)].

The previous discussion has been limited to the case where the pressure is constant; however, it is well known that the strength and deformation properties of polymers are pressure dependent. This pressure dependence may be incorporated in the free energy by writing

$$\begin{aligned} \Delta G^{\ddagger} &= \Delta G_1^{\ddagger} + \int_{P=1}^P \left( \frac{\partial \Delta G_1^{\ddagger}}{\partial P} \right) dP \\ &= \Delta G_1^{\ddagger} + \Delta V^{\ddagger} (P - P_1) \\ &= \Delta G_1^{\ddagger} + \Delta V^{\ddagger} P \end{aligned} \quad (79)$$

It then follows that

$$\Delta V_P^\ddagger = - \left( \frac{\partial \log \Delta G}{\partial P} \right)_{T, \sigma, \text{STRUCT}}$$

or by analogy with (73)

$$(\Delta V_P^\ddagger)_e = -kT \left( \frac{\partial \log \left( \frac{\dot{M}_R}{\dot{M}_R^0} \right)}{\partial P} \right)_{T, \sigma, \text{STRUCT}} \quad (80)$$

Alternatively, taking account of applied deviatoric,  $\tau$ , and hydrostatic stresses,

$$W(\tau, P) = \int_0^\tau V_{\tau}^\ddagger(\tau') d\tau' + \int_0^P V^\ddagger(P') dP' \quad (81)$$

so that a "pressure-activation" volumemay be determined, for example, by

$$(V_P)_e = \left( \frac{\partial \Delta H}{\partial P} \right)_{T, \tau, \text{STRUCT}} = -kT \left( \frac{\partial \log \left( \frac{\dot{M}_R}{\dot{M}_R^0} \right)}{\partial P} \right)_{T, \tau, \text{STRUCT}} \quad (82)$$

The pressure and deviatoric activation volumes are related by

$$V_P = V_{\tau} \left( \frac{\partial \tau}{\partial P} \right)_{T, \text{STRUCT}} \quad (83)$$

to allow for a dependence of shear stress on pressure.

The experimental activation energy is evaluated from an Arrhenius plot. If the applied work is independent of temperature change, then tests conducted at two different temperature yields, for example,

$$\frac{\dot{M}_{R1}}{\dot{M}_{R2}} = \frac{T_1}{T_2} \exp \left[ \frac{-\Delta G}{k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right] \quad (84)$$

Alternatively, writing

$$\sigma_a = \sigma_{\text{eff}} + \sigma_i(\text{local}) \quad (85)$$

where  $\sigma_a$  is the applied stress,  $\sigma_{\text{eff}}$  is the effective local stress and  $\sigma_i$  is the internal (temperature dependent) stress, then since

$$\left( \frac{\partial \Delta S}{\partial T} \right)_{\sigma_{\text{eff}}} = \frac{1}{T} \left( \frac{\partial \Delta H}{\partial T} \right)_{\sigma_{\text{eff}}} \quad (86)$$

it follows that the slope of the Arrhenius plot gives the experimental activation enthalpy,

$$\Delta H = \left[ \frac{\partial \log \left( \frac{\dot{M}_R}{\dot{M}_{RT}^0} \right)}{\partial (1/T)} \right]_{\sigma_a} \quad (87)$$

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