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PREDICTING LIFE EXPECTANCY AND SIMULATING
AGE OF COMPLEX EQUIPMENT USING
ACCELERATED AGING TECHNIQUES

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PREDICTING LIFE EXPECTANCY AND SIMULATING AGE
OF COMPLEX EQUIPMENT USING
ACCELERATED AGING TECHNIQUES*

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ABSTRACT

This document outlines some of the types of experiments which can be used to improve reliability, simulate age, and predict life expectancy of complex equipment. Brief discussion is given of failure mode tests and compatibility tests, which often give useful qualitative aging information. A detailed discussion is presented on accelerated aging methods, emphasizing an approach based on kinetic rate expressions. This kinetic approach offers a convenient framework for describing the importance of competing reaction pathways, transitions in a material, diffusion effects, and sorption effects. It is concluded that, when properly conceived and carried out, accelerated aging studies of materials and simple components offer the best opportunity for making quantitative age simulations and lifetime predictions of equipment.

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I. INTRODUCTION

During the storage and use of a piece of equipment, the materials and components contained in the equipment will be subjected to various combinations of environmental stresses. These stresses can cause adverse changes to occur, leading to equipment failure. The degradation and performance of the equipment can always be measured in real time by duplicating its expected environments. Many applications, however, require reliable performance for long periods of time. In such cases, the generation of real time data is impractical, so that age simulations or predictions of life expectancy must be based on experiments completed in a time short compared to the expected life. The purpose of this report is to outline the types of experiments needed to achieve such objectives and to indicate some potential pitfalls and misconceptions possible in the analyses of the requisite experimental data.

Section II describes a general approach which can be useful for improving design, simulating age, and predicting lifetimes of equipment. The emphasis here is on three important types of experiments: failure mode tests, compatibility tests, and accelerated aging tests. The first two give useful qualitative information, whereas quantitative predictions normally involve the interpretation of accelerated aging data. For this reason, Section III is devoted to a detailed description of accelerated aging techniques.

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II. GENERAL APPROACH

Depending on the application of a piece of equipment, the relative severity of its storage and use environments can vary greatly. The particular goals of an aging program will reflect the intended application. Suppose, for instance, that a piece of electrical equipment is electrically energized for a significant percentage of its lifetime and certain of its components are thermally stressed when energized. If those thermal stresses lead to the deterioration and eventual failure of some component, then the use conditions would be much more important to the aging than the storage conditions. A goal of an aging program for this equipment might be to predict its lifetime by simulating the in-use thermal stresses on the thermally sensitive component.

A different case involves a piece of equipment for which the use environment is equal to or less severe than the storage environment. For instance, a switch may be called upon to operate one time after being stored for many years in a hostile environment. The goal of an aging program for this switch would be to predict its lifetime through the simulation of the hostile storage stresses.

A more complicated situation occurs when both the storage and use environments can contribute to deterioration. An example involves long-term storage under hostile conditions followed by one-time operation under even more severe conditions. For instance, safety-related equipment in a nuclear power plant may age for up to 40 years under combined environments which can include radiation,

thermal, and humidity conditions. In a severe accident, this safety equipment may have to operate for significant periods of time under much more severe environmental conditions. In such cases, instead of predicting equipment lifetimes, the goal of an aging program would be to simulate a certain age of the equipment (e.g. to produce a 40-year old piece of equipment). This age-simulated equipment can then be tested under the severe environmental conditions representative of the postulated accident to determine whether aging affects its performance.

Although the three cases described above are representative of many aging situations, other complicated combinations of storage and use conditions exist. For instance, if hostile storage and use environments alternate many times during the equipment's lifetime, age simulations can become exceedingly difficult.

It is apparent that one goal of an aging program is either to predict the lifetime of a piece of equipment or to simulate a certain age of the equipment. Another important and related goal is increasing equipment reliability through changes in components and designs. To achieve such objectives requires a well-conceived experimental program; the purpose of this section is to outline the steps of a typical approach.

Design of Equipment

During equipment lifetime, its components and materials will see different combinations of environmental stresses. The stresses can be constant, periodic and/or intermittent; some common examples

include temperature, humidity, radiation, voltage, vibration, and pollutant gases (from external sources or generated internally). In the design of equipment, the choice of each component (or material) attempts to take into account the environmental stresses expected for that component and its known responses to these stresses based on past experience. In many instances, however, little reliable aging data exists for the component or material of interest. Even when aging data is available, it often applies to a single stress alone, thus limiting its utility in the presence of other environmental stresses. In addition, the degradation parameters followed in any prior studies may not be appropriate for the particular application. Finally, depending on the source of the data and on the care taken in its generation, the reliability of any previous aging studies may be suspect. It should be clear from the above that, during the design stage of equipment, reliable and extensive aging data in various environments can be an invaluable aid in choosing components and materials.

Compatibility Tests

As noted above, the choice of materials and components should be based on known responses to the expected environmental stresses. Occasionally, however, a potentially damaging stress is overlooked. For instance, a gaseous byproduct from one material may degrade a second material. Screening for such interaction effects is normally accomplished using compatibility tests. These tests involve putting a number of materials to-gether in a chamber in approximately the configuration that they

will have in the equipment, and then storing the chamber at as high a temperature as possible without causing some obvious problem. By monitoring the degradation of each material in the group and comparing the results with its degradation behavior alone, interactions can be observed; compatibility tests are thus an excellent source of qualitative information. A number of problems, however, preclude the use of these tests for making quantitative lifetime predictions. The most important problem comes from the uncertainty in estimating an acceleration factor; this uncertainty is due to the generally differing accelerations of the degradations of the various materials contained in the test. Another problem stems from the difficulty in deciding on the volumetric ratios and relative positions for the materials in the test. For these reasons, aging predictions or simulations should not be derived from compatibility studies.

Failure Mode Tests

Failure mode tests are designed to identify the weak links or the mechanisms by which equipment fails. This is accomplished by exposing the equipment to environments that have higher than use stress levels both singly and, where appropriate, in combination. For every failure that occurs, a failure mode can be determined. This information is often of immediate use for indicating where a change in material, components, or design may lead to enhanced reliability. Such changes, however, are not always possible, either because of expense (time or money) or because clearly superior replacement components do not exist. Each

failure mode discovered under the high stress conditions must
then be investigated more thoroughly and more quantitatively to
assess its importance under use conditions. This normally
involves the use of accelerated aging techniques.

Accelerated Aging Studies

The most reasonable approach to predicting equipment lifetime
and/or simulating equipment age involves accelerated aging tech-
niques. For each observed or suspected failure mode these tech-
niques attempt to determine, rationalize, and then extrapolate
to use conditions the functional relationship between the appro-
priate accelerating environmental stresses and the time to failure
(or to a certain amount of degradation). Although such techniques
can sometimes be accomplished on the equipment itself, it is usually
more appropriate to carry out a separate accelerated aging
study on each suspicious material or component (those implicated
by a failure mode and those suspected of possible degradation).
One reason is that a complex piece of equipment may have numerous
failure modes, each of which either is degraded by a different
environmental stress or has a different functional dependence
or the same environmental stress. In addition, for expensive
equipment, the large number of units necessary for extensive
whole equipment accelerated aging studies can be prohibitively
costly. If the equipment is large, the volume of environmental
aging chambers required can also cause problems. On the other
hand, accelerated aging studies on simple components or materials

usually offer the advantage of greater ease in controlling the
environmental variables and in accurately monitoring degradation
variables. Such studies also increase the feasibility of follow-
ing the damage through periodic destructive testing.

In planning accelerated aging tests, the results from failure
mode and compatibility tests are invaluable aids. The failure mode
tests indicate components and materials which limit the equipment's
lifetime and implicate the environments responsible for each failure
mode. In addition, they often suggest appropriate degradation para-
meters to monitor during the more extensive component and material
accelerated aging studies. The choice of these parameters is
crucial, since they must be closely correlated to the actual failure
modes in order to successfully predict equipment lifetimes. The
results from the compatibility tests can also be useful by pointing
out additional stress environments to utilize in the accelerated
aging studies. If, for instance, a compatibility test indicates
that a byproduct gas given off by a second material hastens the
degradation of the material or component of interest, this
byproduct should be one of the environmental stresses (e.g.
temperature, byproduct concentration) considered in the accelerated
aging studies.

Life Tests

Life tests are long-term failure measurements made under use
conditions. These tests are obviously reliable if time is available
to perform them. Unfortunately, the use conditions for equipment
and components may change as a design evolves or as requirements

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for the equipment are modified. In addition, a large number of units must be tested at each anticipated use condition in order to obtain statistically significant data. For these reasons, life tests can be very inefficient and expensive. Perhaps the best use of life tests is as a means of checking the predictions of accelerated aging tests.

Summary

In summary, three types of experiments are useful for optimizing equipment reliability and for predicting or simulating equipment degradation. Failure mode tests indicate: a) design flaws in the equipment, b) the materials, components, and environments important to each type of failure, and c) appropriate degradation parameters for monitoring the adverse changes. Accelerated aging studies of the implicated components and materials are useful for following their deterioration; by choice of an appropriate damage parameter, one attempts to correlate the deterioration to the equipment failures found in failure mode tests. Group material aging tests (or compatibility studies) show whether the aging of a specified material is affected by the aging of other materials in the group and thus indicate additional environmental stresses which should be included in the accelerated aging studies. Of the three tests, only accelerated aging tests lead to the possibility of quantitative prediction capabilities. For this reason, the remainder of this paper will be concerned with the use and interpretation of accelerated aging.

III. ACCELERATED AGING STUDIES

General Approach

As indicated above, the most reasonable approach for predict-
ing or simulating equipment lifetimes involves accelerated aging
studies on the materials and components linked with possible
failures of the equipment. A combination of past experience,
failure mode tests and compatibility tests is used to identify
a) the materials and components suspected of possible degradation
during the equipment's lifetime and b) the environmental stresses
which cause the degradation. Each implicated component or material
is then aged in its appropriate accelerated stress environment;
the aging is monitored with a damage parameter or test chosen to
correlate with a known or possible failure mode. By determining
the functional relationship between the measured damage and the
accelerating stresses, rationalizing this relationship in terms
of the processes leading to damage, and extrapolating this rela-
tionship to the ambient conditions, predictions and simulations
of lifetimes become possible.

This section describes in some detail how accelerated
aging studies are accomplished by outlining the assumptions and
methodologies normally used. In addition, a number of complica-
tions and potential pitfalls of accelerated aging data are
described. Since it is common to have a single environmental
stress dominate a given failure mode, the present discussion
will be concentrated on aging in single stress environments.

The general case where two or more environmental stresses con-
tribute to the aging of a material is much more complex;[1] such
complications go beyond the intended scope of this paper.

We begin by assuming that we have identified, 1) a component
or material suspected of significant aging in a piece of equipment,
2) the stress environment implicated in its aging, and 3) an appro-
priate damage parameter, D, which monitors a property correlated to
its expected or observed failure mode.

Since it is the easiest and most common accelerated aging
method, we will restrict our discussion to the constant overstress
technique. In this technique, the stress variable of interest is
raised above its ambient value to a constant level, S, and the aging
is followed by monitoring the changes in the damage parameter, D.
In general, the time dependence of D cannot be expected to have a
simple functional form (e.g. first order decay); often, however, D
will be a smooth monotonically decreasing function of time as shown
in Fig. 1. The goal of accelerated aging is to accelerate all
important aging processes equally through an increase in the stress
level. If experiments are carried out at two different stress
levels and all the aging processes in the higher level experiment
are accelerated by the same factor, a_S, with respect to those in
the lower stress experiment, then the degradation of the physical
parameter, D, used to monitor the aging would also be expected to
accelerate by the same factor, a_S. This implies that for the same
amount of degradation the decay times in the lower stress exper-
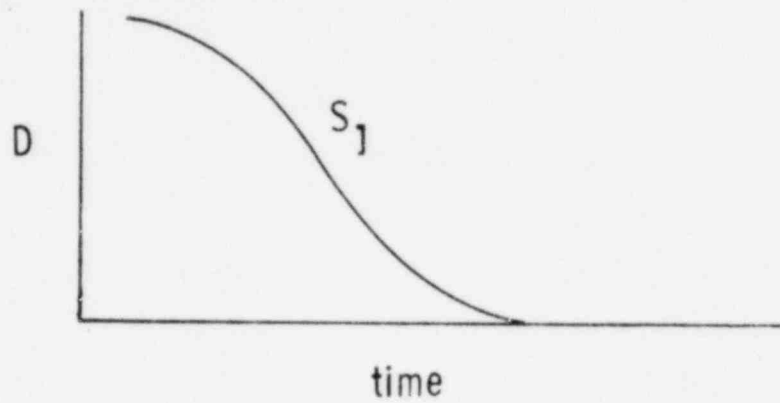iment would be a_S times longer than those of the higher stress

Figure 1.   Constant over-stress technique of accelerated aging.
Damage parameter, D, is followed vs. time at a constant stress
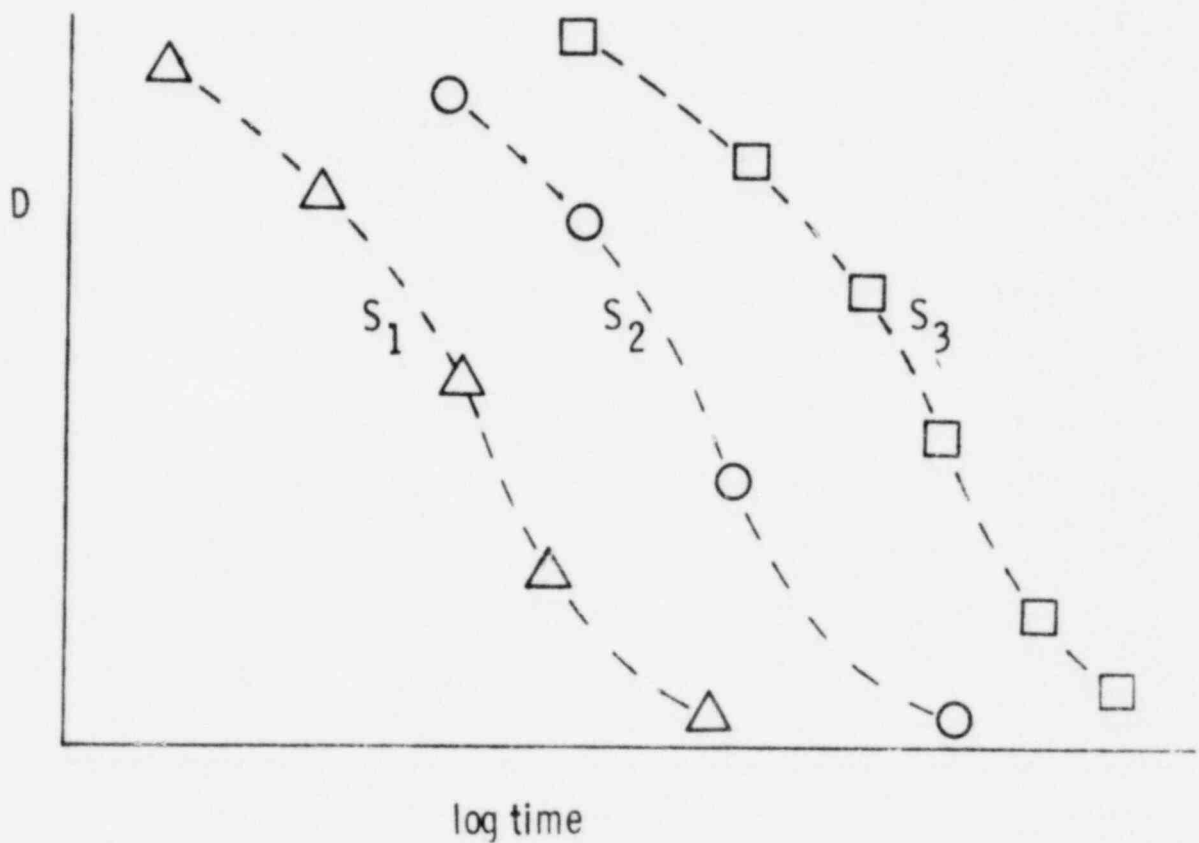level, S_1.

Figure 2.   Hypothetical accelerated aging data, where the damage
parameter, D, is followed vs. time at 3 different stress levels,
S_1, S_2, and S_3.

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experiment. Thus, as shown in Fig. 2 for three idealized experiments run at the three stress levels S_1, S_2, and S_3, the experimental decay curves would have the same shape when plotted versus log time. In other words, if constant acceleration is achieved, the decay curves at various stress levels will be superimposable by horizontal shifts on the log time axis. A convenient way to check for superposition is to first choose one of the experiments as a reference experiment (S_{ref}). Then for each experiment at a different stress level, S, one determines the constant multiplicative factor, a_S, which when multiplied by the experimental times corresponding to the stress level, S, gives products which are in best overall agreement with the times of the reference experiment. a_S is often referred to as the shift factor. When data is plotted vs. log t, the shift procedure corresponds to adding log a_S to the log t values representing a given stress experiment. As an example of such a procedure, Fig. 3 shows the result of shifting the data of Fig. 2; in this instance excellent superposition is indicated.

Whenever superposition is not found, the experimental conditions did not result in a constant acceleration of the processes underlying the chosen degradation variable. In such cases, any extrapolated predictions would be difficult and highly speculative. Being able to test for superposition underlines one advantage of experiments which follow the time evolution of damage. If only one data point (e.g., the failure time) is obtained for each experimental stress condition, superposition, and hence constant acceleration, cannot be verified.
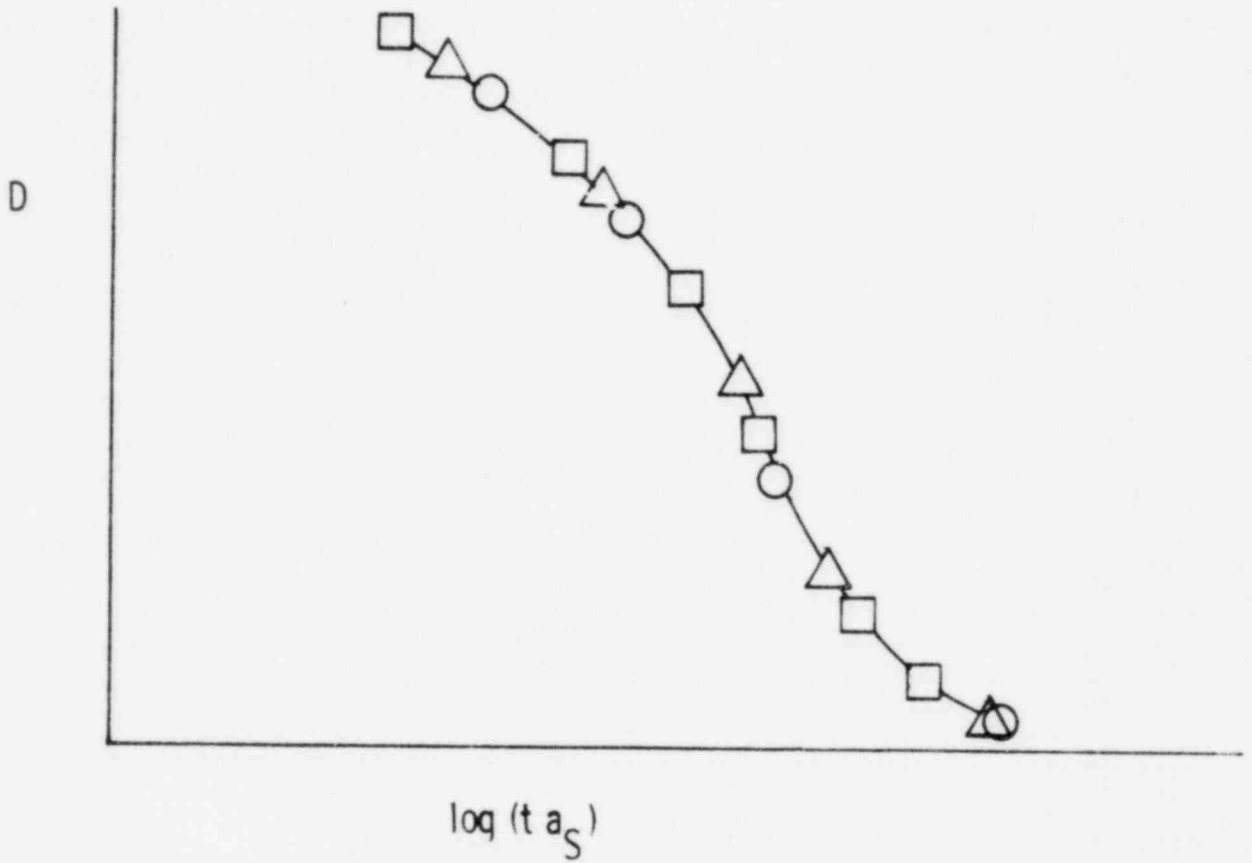
Figure 3. The data of Fig. 2 after time-stress superposition. a_S is the shift factor.

If superposition is verified, the next step is to determine the functional relationship between a_S and the environmental stress level, S, and then rationalize the relationship in terms of the processing leading to damage. Certain functional relationships are found to be commonly applicable to specified types of environmental stresses. For example, when S refers to the radiation dose rate, R, the shift factor is often found to be proportional to the dose rate,[2] i.e.

$$a_R \propto R \tag{1}$$

This relationship is easily rationalized as the expected relationship when the damage simply depends on the integrated radiation dose. When voltage stresses are used, such as in the aging of capacitors, the shift factor is often[3] proportional to the voltage, V, raised to an exponent, n

$$a_V \propto V^n , \tag{2}$$

although no satisfactory explanation for Eq. (2) has been derived. The most common stress used in accelerated aging is temperature, T. The shift factor for thermal stresses is often related to a so-called Arrhenius term[3]

$$a_T \propto \exp\left(-E_a/RT\right) \tag{3}$$

where R is the gas constant and E_a is the Arrhenius activation energy. Arrhenius behavior can be verified by plotting $\ln a_T$ vs. T^{-1} as shown in Fig. 4 for the four temperatures, T_1, T_2, T_3,
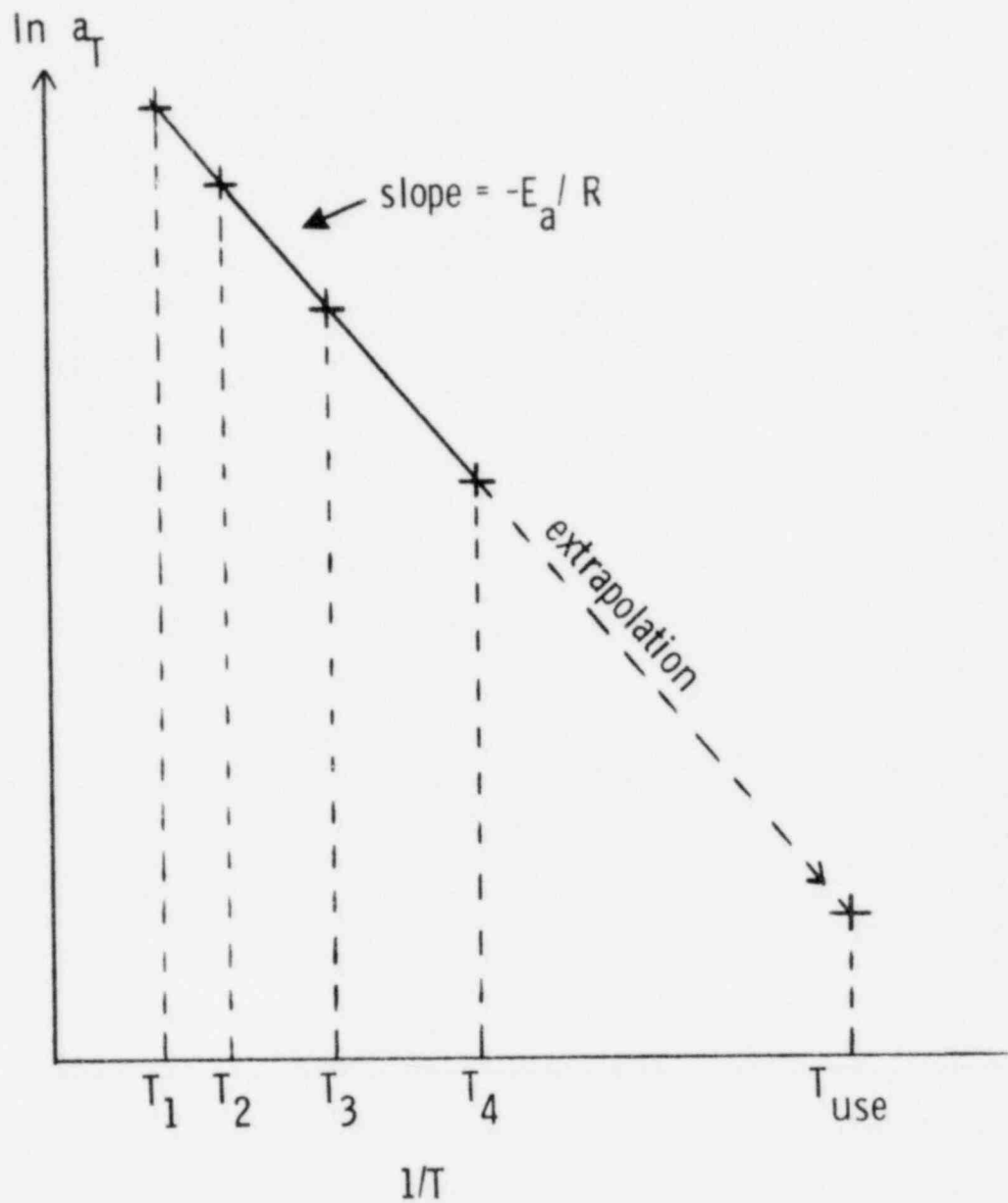
Figure 4. Arrhenius plot of ln of the thermal shift factor, a_T, vs. inverse temperature ($°K^{-1}$) for the 4 temperatures, T_1, T_2, T_3, and T_4. The resulting straight line behavior is extrapolated to the use temperature, T_{use}.

and T_4. If a straight line results, Arrhenius behavior is indicated. The slope of the line is $-E_a/R$. Arrhenius behavior is usually rationalized as coming from the chemical reactions underlying the degradation, since the rate constants for most chemical reactions are found to have an Arrhenius dependence on temperature.

If the functional relationship between a_S and S can be determined, then extrapolation of the relationship to the ambient stress level is possible. An example is shown in Fig. 4 where the Arrhenius line is extrapolated to the use temperature. The resulting predicted value of ln a_T at the use temperature can then be used with the accelerated results, such as those shown in Fig. 3, to make predictions of the changes in the physical parameter vs. time under use temperature conditions.

Thermal Aging

The previous section described accelerated aging principles which, in general, can be applied to any type of environmental stress. Since a large percentage of accelerated aging studies involve thermal environments, this section will concentrate on a detailed discussion of thermal aging. In particular, thermal aging will be analyzed in terms of the underlying chemical reactions leading to degradation, and the discussion will indicate reasons for the often observed Arrhenius behavior. Finally, a number of the potential complications which can occur in thermal aging will be highlighted together with prescriptions for ameliorating their effects.

Kinetic Treatment of Aging - Material aging processes are generally caused by changes in chemical species making up the material. These changes are mostly due to chemical reactions, but can also come from physical processes such as the slow evaporation of a volatile component. Ideally, the changes in a material can be followed by following the concentrations of the various chemical constituents in the material. For example, one could follow the concentrations of chemical cross-links, fillers, important chemical groups being destroyed or formed, etc. In practice, however, this is extremely difficult for complex materials such as a filled polymer. Instead, it is more convenient to monitor a macroscopic parameter, D, known to be related to the damage. This damage parameter, which is often a mechanical or electrical variable, is assumed to be some function of the concentrations of the various constituents contained in the material, i.e.,

$$D = f(C_A, C_B, C_C, \cdot \cdot \cdot) \tag{4}$$

where $C_A, C_B, C_C, \cdot \cdot \cdot$ denote the concentrations of the A,B,C, . . . species, respectively. If, after the ambient lifetime, a certain set of constituent concentrations (and, hence, a certain value of D) exists, then successful accelerated aging can be achieved by duplicating the final values of all the concentrations (and, hence, D) in a shorter period of time by using a higher than ambient temperature.

To discuss this approach in more detail, it is convenient to use a standard kinetic theory treatment[4] in which the rate of

change of the various concentrations is given in terms of rate expressions

$$\frac{dC_A}{dt} = k_1(T) \, C_A^a \, C_B^b \, C_C^c \ldots + k_2(T) \, C_A^d \, C_B^e \ldots + \ldots \qquad \qquad (5)$$

$$\frac{dC_B}{dt} = k_3(T) \, C_A^g \, C_B^h \ldots + \ldots \qquad \qquad (6)$$

$$\vdots$$

In other words the instantaneous rate of change of the concentration of A is given by the sum of a number of terms each representing a particular reaction pathway leading to changes in the concentration of A. For each term the rate is usually found to be proportional to the product of the concentrations of various reactant and product species (A, B, C, ...) raised to certain powers. The proportionality constants, for example $k_1(T)$, are referred to as the reaction rate constants; since they are normally temperature dependent, they are written explicitly as functions of the temperature, T. Similar rate expressions will, in general, hold for the B, C ... species as shown.

It is clear from Eqs. (4)-(6) that the kinetics underlying degradation can be quite complex. In many cases, however, the degradation is dominated by the changes of a single species, whose concentration is controlled by one reaction pathway of molecularity 2 or less. Eqs. (4)-(6) would then simplify to expressions such as

$$D = f(C_A) \qquad \qquad (7)$$

$$\frac{dC_A}{dt} = k_1(T) \, C_A^a \, C_B^b \qquad \qquad (8)$$

For convenience, we will use these expressions as a basis for much of the discussion that follows. Although more complicated expressions will often be appropriate, in many of these cases the general conclusions which will be derived using Eqs. (7) and (8) as bases are still valid.

Suppose that the concentration of the B component in Eq. (8) remains constant during the time when the material degrades. This occurs, for example, a) if the degradation is very sensitive to a small amount of reaction in which very little of the B component is used up, or b) if the B component is in such abundance that its concentration changes are small for large changes in the concentration of A, or c) if B represents a dissolved gaseous reactant (e.g. oxygen or water vapor) which is replenished from the atmosphere much faster than it is used up during the reaction. Whenever B is a constant, it can be included in the rate constant by defining a new rate constant $k_1' = k_1 C_B^b$. This leads to

$$\frac{dC_A}{dt} = k_1'(T) \; C_A^a \tag{9}$$

which can be rearranged and integrated from time 0 to time t to give

$$F(C_A) = \int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^a} = k_1'(T) \; t \tag{10}$$

where $F(C_A)$ is defined as shown and C_{A_0} is the concentration of A at time 0. Eq. (10), indicates that if the proper function of

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C_A is plotted vs. time at temperature T, a straight line of slope $k_1^!(T)$ will result. To relate this to aging predictions, we first recall that successful accelerated aging requires a verification that different accelerated stress (temperature) levels have damage parameter D vs. time curves which are superposable through the use of multiplicative shift factors, a_T (Fig. 3). The manner in which the shift factor a_T was defined implies that for a constant value of D

$$a_T \, t = \text{a constant} \tag{11}$$

Since $D = f(C_A)$, a given constant value of D corresponds to a given concentration of A. But from Eq. (10), for a constant value of C_A

$$k_1^!(T) \, t = \text{a constant} \tag{12}$$

Therefore, a_T must have the same dependence on temperature as $k_1^!(T)$ which means that the temperature dependence of the damage parameter comes from the temperature dependence of the reactions underlying it. The results of numerous studies indicate that a majority of reaction rate constants have an Arrhenius dependence on temperature, i.e.,

$$k \propto \exp \, (-E_a/RT) \tag{13}$$

where E_a, R, and T have the same meaning as before (Eq. 3). Some theoretical reasons exist for such a relationship[4] based, for instance, on results from absolute reaction rate theory worked out

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by Eyring and others.[5] The above discussion, therefore, allows one to rationalize Arrhenius behavior for the degradation of a macroscopic damage parameter. It is also obvious that complete knowledge of the details of the chemical kinetics is not necessary for successful accelerated aging to be carried out. The kinetics have been discussed to: a) indicate the microscopic processes underlying the accelerated aging procedures and b) offer some theoretical justification for expecting Arrhenius behavior for a macroscopic damage variable. The kinetic formalism also offers a convenient framework for discussing some of the many complications which can lead to non-Arrhenius behavior and, therefore, predictive difficulties. A number of these complications are discussed below.

Aging Complications Caused When More Than One Reaction is Important to the Degradation - The discussion in the previous section was based on the situation where one reaction dominates the deterioration of a material, as described by Eqs. (7) and (8). In certain cases, however, a number of time dependent species will be important in determining the value of the degradation parameter and/or a number of pathways (reactions) will be significant in changing the concentration of an important species. In these situations, described by Eqs. (4)-(6), two or more rate constants will be important to the degradation. Unless the important rate constants fortuitously have the same temperature dependence, raising the temperature causes unequal acceleration of the various pathways. This inequality greatly complicates lifetime predictions and age

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simulations because it is generally impossible to exactly super-
pose accelerated data when all the underlying reactions are not
equally accelerated. However, given the experimental uncertainties
associated with most aging data and the possibility that the degra-
dation may be relatively insensitive to subtle changes in the
relative concentration of various species, "successful" super-
position may still be possible even when the important underlying
reactions are not equally accelerated. In fact, in certain cases,
exact superposition would be predicted even for unequal acceler-
ation of the underlying reactions. As an example, suppose

$$\frac{dC_A}{dt} = k_1(T) \ C_A + k_2(T) \ C_A \tag{14}$$

i.e., two reaction pathways occur, both of which are pseudo first
order with respect to A. The overall degradation will remain
first order in A regardless of the temperature; thus superposition
will occur. On the other hand, the temperature dependence of
the experimental shift factors, a_T, will not be Arrhenius unless
the activation energies for both reactions happen to be identical.
Assume, for instance, that

$$k_1(T) \propto \exp(-E_{a1}/RT) \tag{15}$$

$$k_2(T) \propto \exp(-E_{a2}/RT) \tag{16}$$

and $E_{a1} > E_{a2}$. In the temperature range where the reactions are of
comparable importance, hypothetical plots of $\ln a_T$ vs. $(T)^{-1}$ are

shown by the solid curve in Fig. 5. At the higher temperatures where the process with the higher activation energy dominates the degradation, this curve approaches linear behavior with a slope given by E_{a1}/R. Similarly, a straight line of slope E_{a2}/R will occur at the lower temperatures where the process of activation energy E_{a2} is dominant. In other words, the elevated temperature experiments will activate reactions which would not be significant under the ambient temperature conditions. If this higher temperature data (straight line) is extrapolated to the ambient temperature as shown in the figure, overly optimistic projections of usable life results. In analyzing aging data, one should, therefore, be aware that non-Arrhenius behavior and/or non-superimposable data are two indications that more than one reaction may be important to the degradation process. This discussion underscores the importance of minimizing extrapolation distances by carrying out accelerated experiments at the lowest temperatures that will provide reasonable acceleration. The larger the extrapolation to ambient conditions, the greater will be the danger of having the dominant reaction mechanism change.

A final note of caution about changes in degradation mechanisms concerns cases where the temperature range of interest encompasses a transition of a material (e.g. a crystalline melting point or glass transition temperature of a polymer). It should be anticipated that the dominant reactions above and below a transition might
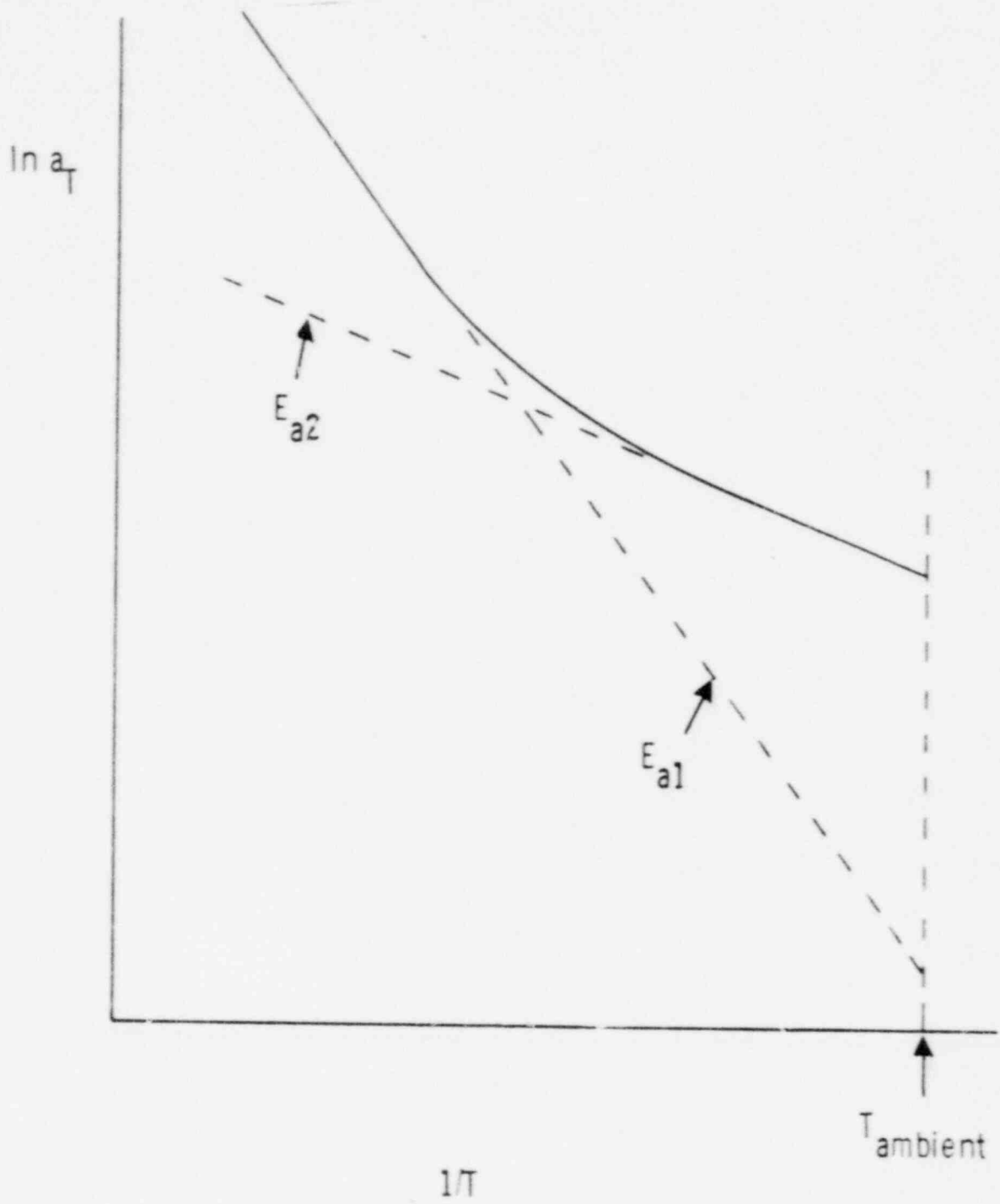
Figure 5. Hypothetical Arrhenius plots (ln of the thermal shift factor vs. inverse temperature) in temperature region where 2 reactions with different activation energies, E_{a1}, and E_{a2}, are important to changes in the degradation parameter.

be quite different so one must be extremely cautious before extra-
polating through a transition point.

Aging Complications Caused by Diffusion Effects - Earlier, using
Eqs. (7)-(9), we discussed the case where only one reaction is
important to a material's degradation. Implicit in the transfor-
mation from Eq. (8) to Eq. (9) was the assumption that the con-
centration of B was constant and could, therefore, be included in
the rate constant. This occurs whenever B is in large excess or,
if B comes from a medium surrounding the material (e.g., $B = O_2$
or H_2O), whenever diffusion effects are unimportant.

As an aid in discussing these effects, suppose Eq. 8 represents
an oxidation reaction ($B = O_2$) occurring in a polymer sheet of
thickness ℓ. If oxygen is replenished from the surrounding air
atmosphere by diffusion into the polymer with a diffussion constant
D_S, then the oxygen concentration in the sheet will be described by

$$\frac{\partial C_{O_2}}{\partial t} = D_s \frac{\partial^2 C_{O_2}}{\partial x^2} - k C_A^a C_{O_2}^b \qquad (17)$$

where $x = 0$ at the center of the sheet and $x = \pm \ell/2$ at the edges.
Eq. (17) shows that at equilibrium, the concentration of O_2 at a
given location is a balance between the rate of O_2 replenishment
from diffusion effects and the rate of O_2 consumption through reaction.
If replenishment is not fast enough to keep the O_2 concentration in
the center of the sheet at its equilibrium sorption value, then the
O_2 concentration will depend on time until equilibrium is reached,

after which it will be spatially dependent (lower oxygen concentrations towards center of sample). Because of these so-called diffusion effects, the degradation rate will depend on spatial position in the sample and, therefore, on sample thickness. A degradation rate which depends on sample thickness is in fact one of the best methods by which diffusion effects are recognized. Another clue to important diffusion effects comes from temperature dependent studies. For most gases of interest, the activation energy for D_S in polymers is around 10 kcal/mole,[6] whereas the activation energy for thermal oxidative degradation is typically much larger, ranging around 20-30 kcal/mole. Therefore, as diffusion effects become important, raising the temperature normally increases their importance, until eventually the Arrhenius activation energy approaches 10 kcal/mole. Diffusion effects are therefore indicated by a low activation energy or by an activation energy which decreases as the temperature is raised, as shown in Fig. 6. Comparing Figs. 5 and 6, it is apparent that diffusion effects can cause difficulties similar to those caused by having two reactions important to the degradation. Again, one way of minimizing the chance for such an effect to occur is to minimize the aging temperatures used. Diffusion effects can also be minimized by reducing the thickness of the samples being aged until the degradation no longer depends on the sample thickness.

One final note of caution is necessary. In certain cases, diffusion limited degradation will occur under use conditions,
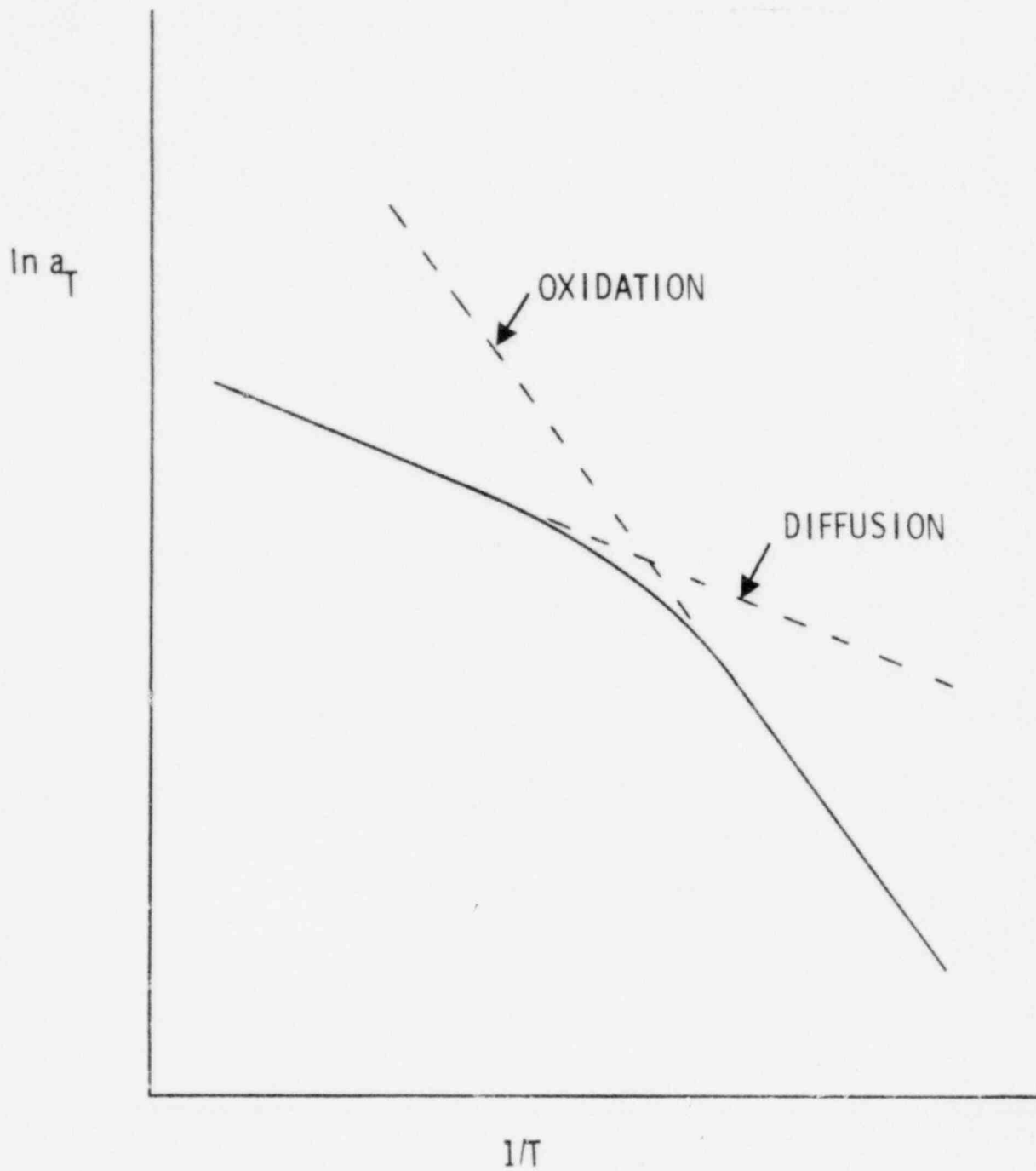
Figure 6.   Hypothetical Arrhenius plot for an oxidation degradation process which becomes diffusion controlled at higher temperatures.

for instance when an important gaseous or liquid reactant sur-
rounds a thick glassy material. In such cases, extreme caution
must be used when attempting to accelerate the degradation.

Aging Complications Caused by Sorption Effects - In the previous
section we showed that even when a single reaction of molecularity
two dominates degradation, it is advantageous to keep the concen-
tration of one component (e.g. C_B) constant during aging. This
allows C_B to be included in the reaction rate constant as discussed
for Eqs. (8) and (9). When B is a gaseous reactant such as oxygen
(O_2) or water vapor (H_2O) which must diffuse into the degrading
material, this entails going to a low enough temperature or thin
enough sample so that the reaction is not diffusion limited. When
diffusion effects are absent, C_B will be time independent and equal
to its equilibrium value determined by the sorption characteristics
of B in the material of interest. However, in general, equili-
brium sorption concentrations are temperature dependent, which
means that the rate expression of Eq. (8) becomes

$$\frac{dC_A}{dt} = k_1(T) \; C_A^a \; C_B(T)^b \tag{18}$$

In other words, the temperature dependence of the degradation comes
from a combination of the temperature dependence of the kinetic rate
constant, k_1, and the temperature dependence of C_B. There are some
subtle and very interesting complications caused by this sorption
effect and these will be discussed in detail in this section.

It is convenient to describe sorption in terms of isotherms,
which give the relationship at constant temperature between the

equilibrium concentration of penetrant in a material, C_B, and the partial vapor pressure, P_B, of gas surrounding the material. The relationship is written

$$C_B = \sigma (P_B) P_B \tag{19}$$

where σ is the solubility coefficient, which, in general, depends on P_B. When σ is independent of P_B, linear or so-called ideal sorption behavior results.

$$C_B = \sigma P_B \tag{20}$$

This equation is Henry's Law, and this behavior is found for most permanent gases such as O_2 sorbed by polymers at pressures less than approximately two atmospheres. Non-ideal behavior where σ depends on P_B usually occurs for condensable fluids like H_2O. These two cases turn out to have quite different implications for accelerated aging studies and will, therefore, be discussed separately.

Permanent Gases - For permanent gases (e.g. O_2) dissolved in polymers at low pressures, solubilities are low (C < 0.2%), and Henry's Law (Eq. 20) applies.[6] The temperature dependence of the solubility coefficient is given by an Arrhenius-like expression.

$$\sigma = \sigma_O \exp(-\Delta H_S/RT) \tag{21}$$

where ΔH_S is the heat of solution. The absolute value of ΔH_S is

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typically small (less than a few kcal/mole) so that the equili-
brium solubility either increases or decreases slightly with
increasing temperature. Hypothetical isotherms for O_2 in a given
material at three temperatures $(T_3 > T_2 > T_1)$ are shown in Fig. 7
for the case of ΔH_S small and positive. Suppose O_2 is important
to the degradation of this material and the important kinetic
process is described by

$$\frac{dC_A}{dt} = k_1 \, (T) \, C_A^a \, C_{O_2}^b \qquad (22)$$

If one wanted to do aging experiments at the three temperatures T_1,
T_2, and T_3 and extrapolate the results to the ambient temperature,
T_{amb}, one approach would entail keeping C_{O_2} independent of temper-
ature and equal to its value under the ambient temperature condi-
tions. Fig. 8 shows sorption isotherms for the four temperatures
of interest. If a one atmosphere air environment is present under
ambient conditions, then the partial pressure of O_2 under ambient
conditions, P_{amb}, is approximately 0.2 atmosphere. This corresponds
to the ambient dissolved O_2 concentration, C_{amb}, as shown in Fig.
8. For the three accelerated experiments, knowledge of their iso-
therms allows us to choose appropriate O_2 partial pressures, given
by P_1, P_2, and P_3 so as to keep the dissolved O_2 concentration
constant as the temperature is changed. This will make the temper-
ature dependence of the degradation come solely from the temper-
ature dependence of the rate constant k_1. The measured activation
energy will, therefore, represent the activation energy for the
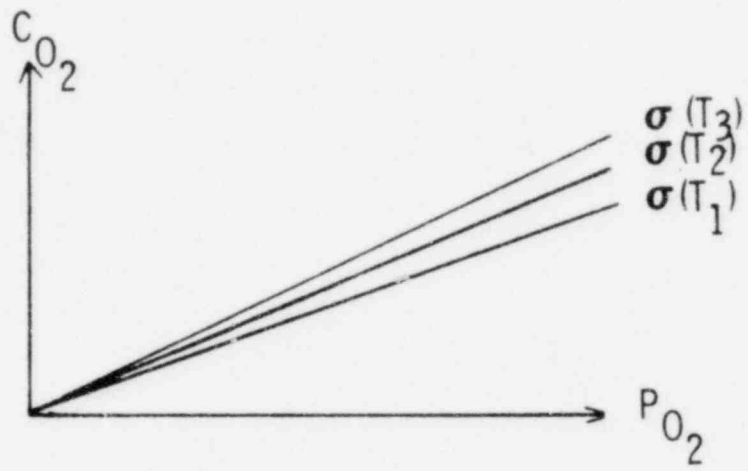thermo-oxidation degradation process.

Figure 7. Typical Henry's Law isotherms for oxygen at the 3 temperatures T_1, T_2, and T_3. The concentration of dissolved oxygen, c_{O_2}, is plotted vs. the oxygen partial pressure, P_{O_2}. The slopes of the lines give, σ, the solubility coefficient.
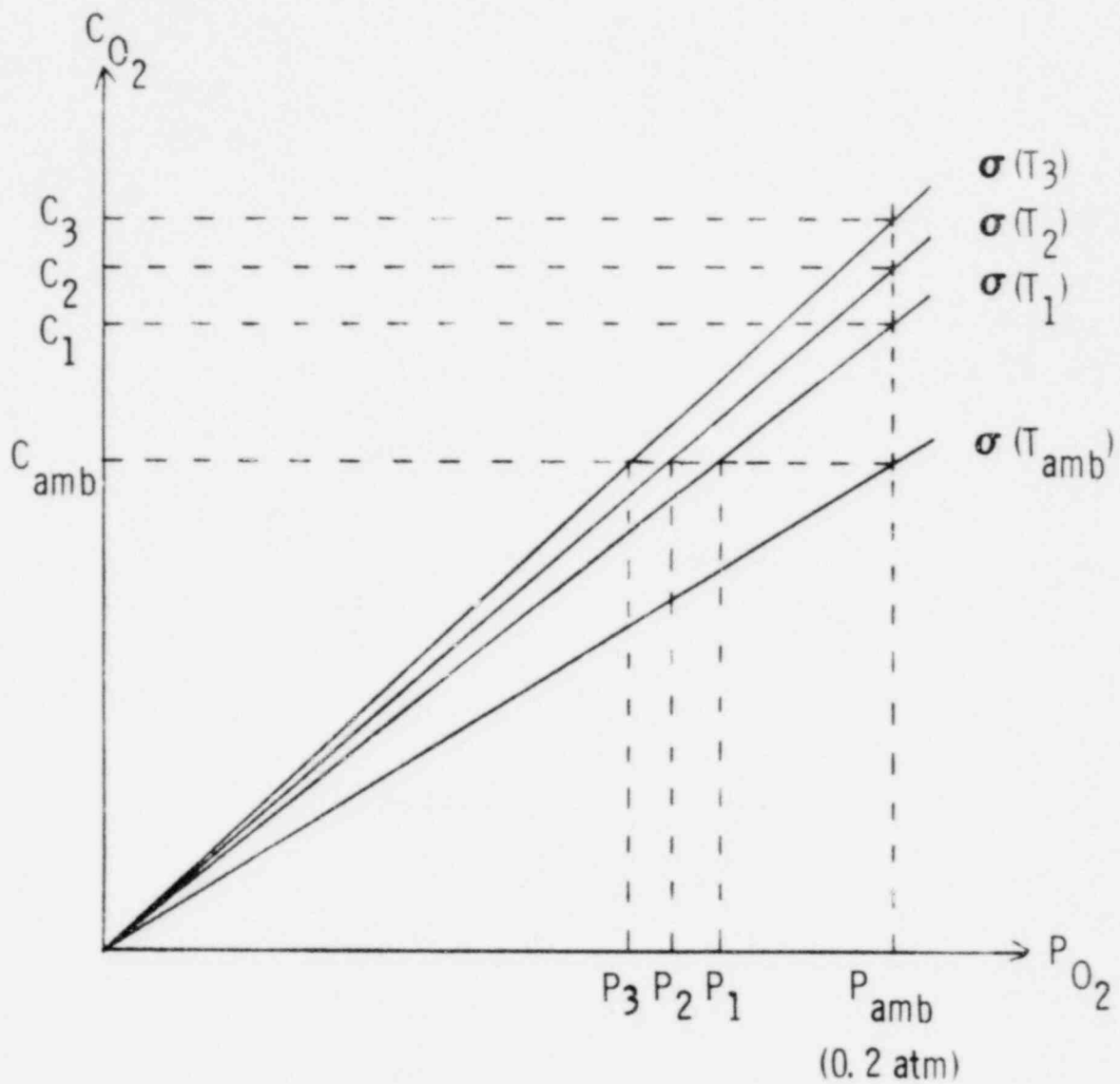
Figure 8. Typical Henry's Law isotherms for oxygen at the ambient (or use) temperature, T_{amb}, and at 3 accelerated temperatures, T_1, T_2, and T_3. The oxygen partial pressure under ambient conditions is P_{amb}, which corresponds to a dissolved oxygen concentration, C_{amb}. The accelerated experiments can either be carried out keeping C_{amb} constant (and, therefore, at P_1, P_2, and P_3) or keeping P_{amb} constant (and, therefore, at C_1, C_2, and C_3).

Unfortunately, carrying out experiments in the manner described above necessitates knowledge of the sorption isotherms under both accelerated and ambient conditions. Since such results are seldom available, the usual experimental procedure is to carry out the accelerated experiments using the gas concentration representative of the ambient conditions, i.e. P_{amb}. Under these conditions, Fig. 8 shows that the concentration of dissolved O_2 would correspond to C_1, C_2, and C_3 at the three accelerated temperatures. Therefore, the temperature dependence of Eq. (22) would include a contribution from the C_{O_2} term. We can combine C_{O_2} with the rate constant by defining an effective rate constant

$$k_{eff}(T) = k_1(T) \ [C_{O_2}(T)]^b \qquad (23)$$

Since

$$k_1(T) \propto \exp \ (-E_a/RT) \qquad (24)$$

and from Eqs. (20) and (21)

$$C_{O_2}(T) \propto \exp \ (-\Delta H_s/RT) \qquad (25)$$

we obtain

$$k_{eff}(T) \propto \exp[(-E_a - b\Delta H_s)/RT] \qquad (26)$$

In other words, experiments carried out at a constant P_{amb} will lead to degradation with an Arrhenius dependence on temperature. The experimentally measured activation energy will be E_{eff} which is given by

$$E_{eff} = E_a + b\Delta H_s \tag{27}$$

The true activation energy, E_a, for thermo-oxidative degradation is typically around 20 to 30 kcal/mole. Since the absolute value of ΔH_s is a few kcal/mole for permanent gases[6] and the absolute value of the exponent b is normally less than 2, the value of E_{eff} is similar to E_a.

The above discussion shows that, due to the Arrhenius dependence of sorption for permanent gases, accelerated aging predictions can usually be made by carrying out accelerated experiments under the atmospheric conditions representative of the ambient environment, even though temperature dependent sorption effects enter. In fact, it is often advantageous to carry out the experiments in this way since the data can be used to make predictions for different ambient temperatures as long as the ambient atmosphere remains constant (e.g. ambient air). In contrast, experiments carried out using the more rigorous technique of keeping C_{amb} constant cannot be directly used to make predictions at a different T_{amb}, since they are designed to simulate the ambient atmospheric conditions only at one specified ambient temperature.

Condensable Gases-- Sorption isotherms for condensable gases are typically more complex than for permanent gases.[6] For condensable

gases, the isothermal solubility coefficient, σ, is often depend-
ent on the partial pressure, P, so that C is not linear in P. In
addition, the solubility at constant P often decreases rapidly with
temperature. As an example, Fig. 9 shows a common type of behavior
found for water vapor sorption in polymers. At a given temperature,
linear behavior at the lower values of P changes into non-linear
behavior at higher values of P. As the temperature is increased,
the curves shift rapidly to the right. Such behavior can greatly
complicate accelerated aging predictions. Suppose for instance,
that water is important to the degradation of a material and that
the dominant kinetic process is given by a relationship similar
to Eq. (22)

$$\frac{dC_A}{dt} = k_2(T) \; C_A^d \; C_{H_2O}^e \tag{28}$$

If aging at the four temperatures shown in Fig. 9 were carried
out using an atmosphere of constant water vapor concentration,
P_{const}, then the equilibrium water concentration sorbed in the
polymer would be given by C_1, C_2, C_3, and C_4, as shown in the
figure. Analogous to Eq. (23), the temperature dependence of the
degradation would be given by a combination of the temperature
dependence of the rate constant k_2 and the temperature dependence
of the water sorption, i.e.

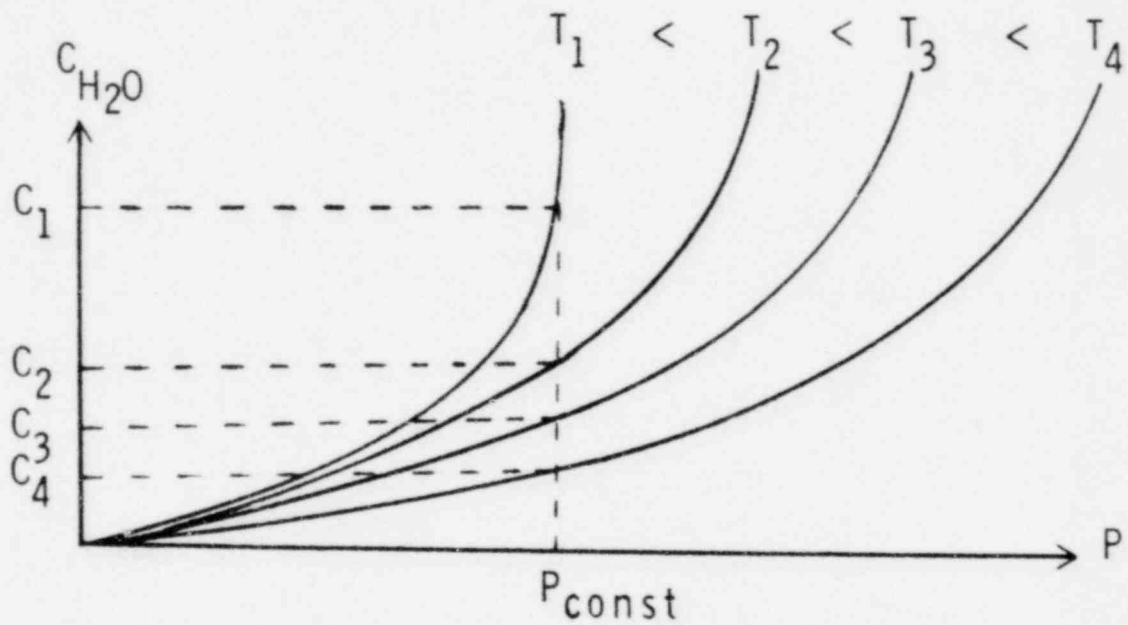$$k_{eff}(T) = k_2(T) \; [C_{H_2O}(T)]^e \tag{29}$$

Figure 9.   Typical isotherms for water vapor and other condensable
fluids.

In contrast to the situation for O_2 sorption, however, the non-linear complex isotherms for water sorption imply that, in general, $C_{H_2O}(T)$ will not have an Arrhenius dependence on temperature. This means that non-Arrhenius behavior will often be found for the macroscopic damage parameter, precluding extrapolation of the data. An example of this situation is shown in Fig. 10 using literature data on the reversion of a polyurethane potting compound in humidity environments.[7] The study followed changes in durometer hardness (the macroscopic damage parameter) of the material at various combinations of temperature and humidity. The reversion time was arbitrarily defined as the time required for the hardness to drop to 20. In Fig. 10, the log of the reversion time is plotted vs. inverse temperature for a constant water vapor concentration, P_{const}, of 4×10^{-3} moles/liter. The non-Arrhenius character of the data makes extrapolation difficult. In this instance, the non-Arrhenius effects are not due to a second reaction becoming important at lower temperatures but are a consequence of the sorption behavior of water.

Analogous to the situation discussed earlier for permanent gases, it would be possible to make predictions for materials reacting with condensable gases if the accelerated experiments could be carried out under conditions in which the temperature dependence of the concentration of the sorbed species was Arrhenius. Much data exist which indicate that at a given constant relative humidity (RH), the solubility coefficient, and hence C_{H_2O}, has a small dependence on temperature and is approximately Arrhenius, i.e.,
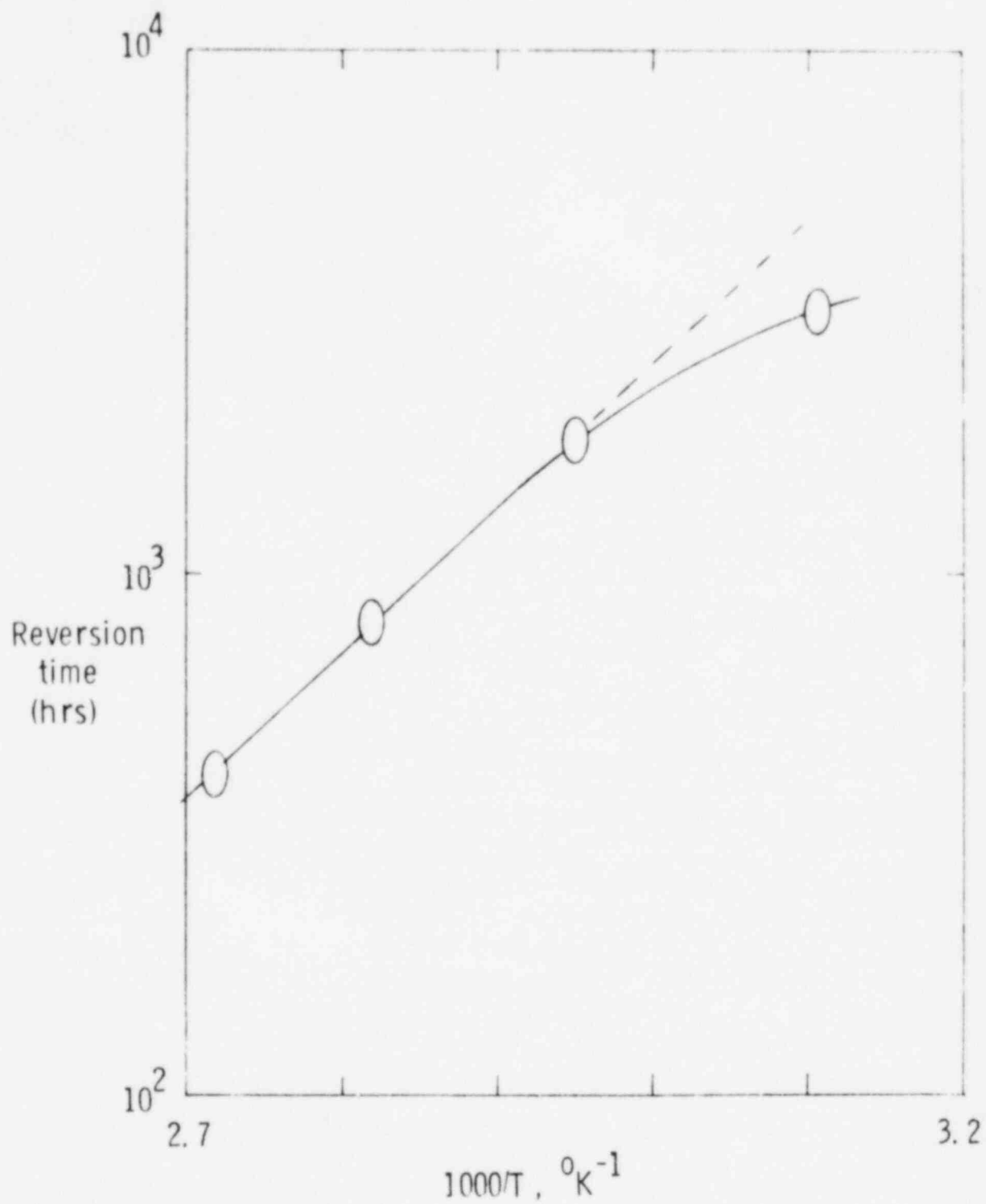
Figure 10. Log of the reversion time for a polyurethane potting compound plotted vs. inverse temperature for a constant water vapor concentration of 4×10^{-3} moles/liter. The data comes from reference 7.

$$\sigma(RH) = \sigma_o(RH) \; \exp(-E_c/RT) \tag{30}$$

E_c, the activation energy for the solubility coefficient at constant RH, is often found to depend only on the system studied, not on the particular value of the relative humidity. As evidence for this phenomenon, some representative literature sorption data are shown in Figs. 11[8] and 12[9], where equilibrium water sorption is plotted vs. RH at a number of temperatures. The data of Fig. 11 indicates that E_c is equal to zero for all values of RH; analysis of the data of Fig. 12 gives an E_c of +5.0 kcal/mole, also independent of RH. For water sorption in various materials, E_C usually ranges from 0 to 5 kcal/mole.

The observation that C_{H_2O} approximates Arrhenius behavior at constant RH makes the analysis of condensable gas data at constant RH completely analogous to permanent gas data analysis at constant P_{amb}. The same reasoning that led to Eq. (27) indicates that degradation data analyzed under constant RH conditions should be Arrhenius with the experimentally measured effective activation energy given by

$$E_{eff} = E_a + e \; E_c \tag{31}$$

An instructive example of the above comes from a reanalysis at constant RH of the data from reference 7. This data gave non-Arrhenius behavior when analyzed at constant water vapor concentration, as shown in Fig. 10. The reanalysis is shown in Fig. 13, where the log of the reversion times are plotted vs. inverse temperature at four different relative humidities (25%, 50%, 75%,
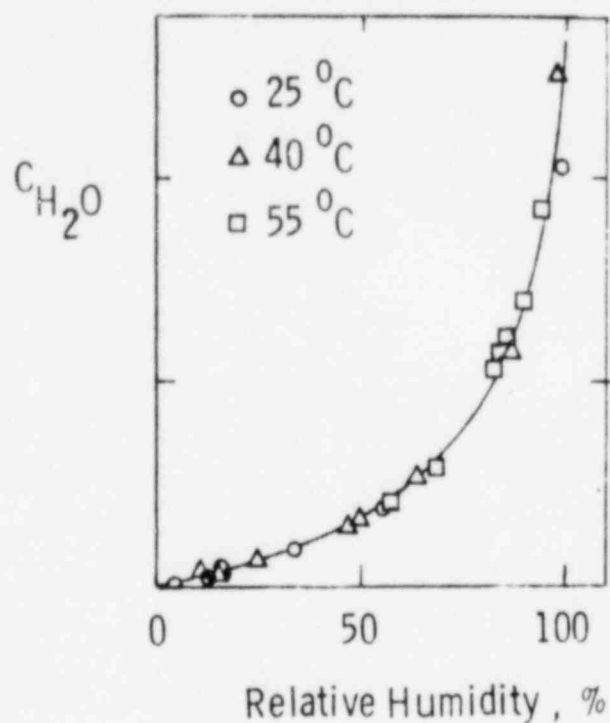
Figure 11. Sorption isotherms for water vapor in a polyurethane membrane, plotted vs. relative humidity. Data from reference 8.
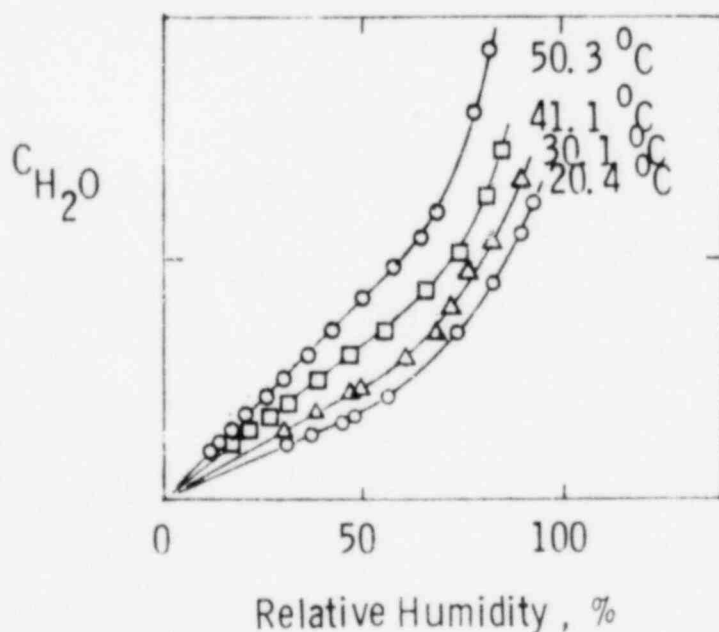

Figure 12. Sorption isotherms for water vapor in a silicone material, plotted vs. relative humidity. Data from reference 9.
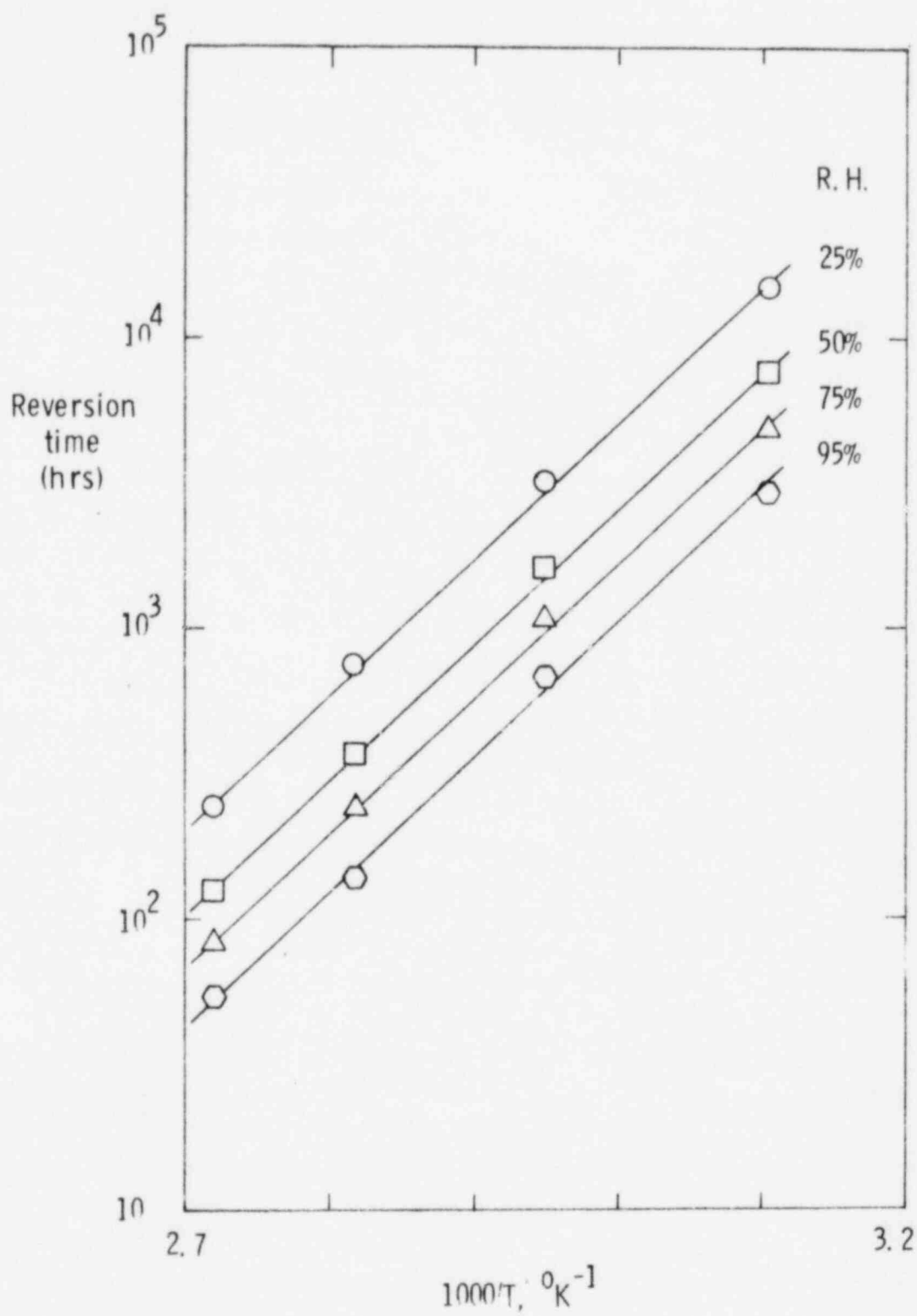
Figure 13. Arrhenius plot of the data from reference 7 analyzed at various constant relative humidities.

and 95%). This analysis gives the expected Arrhenius behavior with F_{eff} equal to 21 kcal/mole. Extrapolation of the data to other conditions is now possible. It is clear from Eq. (31) that in order to obtain the true E_a for hydrolysis, detailed kinetic experiments, as well as extensive sorption studies, must be carried out. To make aging predictions, however, these studies are often unnecessary.

Although the preceding discussion dealt primarily with humidity effects, similar sorption behavior is often found for other condensable fluids. Therefore, when a condensable vapor is important to the degradation of a material, accelerated aging studies should be done at constant relative pressure P/P_o of the condensable. Arrhenius behavior at constant relative pressure will likely result.

Finally, it should be pointed out that the quite different sorption behavior of non-condensable and condensable gases has extremely important consequences whenever a constant mixture of such gases is used in accelerated aging situations. Suppose a material is suspected of being susceptible to both hydrolysis and oxidation and one is attempting to screen for the dominant degradation mechanism by aging the material at various elevated temperatures surrounded by an atmosphere containing constant partial pressures of oxygen and water vapor. Because of the quite different sorption behaviors of oxygen and water, such experiments would typically accelerate the oxidative degradation to a much larger degree that the hydrolysis. The results could lead to the conclusion that hydrolysis is not important to the degradation

even in instances where hydrolysis dominates the degradation at ambient conditions.

IV. CONCLUSIONS

Accelerated aging techniques offer the best opportunity for predicting lifetimes or simulating age of complex equipment. Careful planning and analysis of data are required to maximize the reliability of any predictions made from such techniques. It is usually preferable at each elevated stress level to follow changes of variables (degradation parameters) with time rather than simply obtaining the failure times. The added information available allows a test of superposition, which, if verified, gives good evidence for constant acceleration of the significant degradation processes. Long term aging experiments are preferable to shorter term tests since the shorter extrapolations to use conditions needed for the former increase the accuracy of the extrapolations and reduce the chance for changes in the dominant degradation mechanism.

When temperature is used to accelerate the aging of a component, Arrhenius activation energies around 10 kcal/mole and/or deterioration which is thickness dependent are indicative of diffusion limited degradation. Diffusion effects can often be eliminated by using thinner samples and/or lower temperatures. Non-Arrhenius behavior can come from changes in the dominant reaction mechanism or from non-Arrhenius sorption behavior of a gaseous reactant. Arrhenius behavior is often recovered by aging at lower temperatures in the former case and by carrying out the aging experiments at constant relative pressure of gaseous reactant in the latter.

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