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Accelerated Aging in Combined Stress Environments

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Abstract

Accelerated aging can be useful in estimating the lifetime of a component of interest. If under ambient conditions a single environmental variable is the predominant cause of the aging process, accelerated aging is often accomplished by raising the level of this variable above its ambient value. The relationship between the mean time to failure and the value of the accelerated environmental variable is extrapolated to ambient conditions in order to estimate the ambient lifetime of the component. Often, however, the ambient deterioration of a component is due to a combination of two or more environmental stresses. Synergism is sometimes important in such cases so that the deteriorating effects of the various environments are not additive. Because of possible complications caused by synergistic effects, no general method currently exists for carrying out accelerated aging in combined environments. The present paper proposes a general phenomenological model potentially applicable to combined environment situations. The model is applied to literature data on the thermoradiation sterilization of Bacillus subtilis var niger for which significant synergistic effects were found for combined thermal and radiation environments. The proposed model does an excellent job in predicting the experimental data.

Introduction

In many instances it becomes necessary to use some form of accelerated aging (Winter, et. al., 1964) in order to estimate the lifetime of a component under ambient or use conditions. The most common method of accelerated aging is referred to as the over-stress technique; it involves increasing an environmental variable (eg. temperature) above its ambient value in order to accelerate the aging process. In order to be valid, the environmental variable chosen must be the one that governs the degradation processes leading to component failure under ambient conditions. This paper will be concerned with the most common type of over-stress testing, the use of constant stress conditions. The goal of this technique is to determine a functional relationship between the accelerating environmental variable and some measure of degradation such as the average failure time.

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The derived functional relationship is then extrapolated to the ambient environmental stress condition in order to estimate failure times under use conditions.

The above discussion concerned the acceleration of aging caused by raising a single environmental stress above its ambient value. Often the deterioration of a component under ambient conditions is due to a combination of two or more types of environmental stresses. The degrading effects of the various environments may be additive or synergistic. There is at present no general method of accelerated aging which can be used when significant synergistic effects exist. The purpose of the present paper is to introduce a simple model which may allow combined environment accelerated aging to be carried out in such cases. The model depends on the use of constant over-stress experiments, so a brief review of the fundamentals of the constant over-stress technique will be given in the next section. The postulated model for combined environment accelerated aging will then be described. The final section of the paper will use literature data to test the postulated model.

Constant Over-Stress Technique of Accelerated Aging

Let Greek letters α, β,.... represent different types of stress environments (eg. α = temperature, β = radiation). Specific levels of stress will be denoted by subscripts. For instance α_i might correspond to a temperature stress of 400°K. A hazard rate $H(\alpha_i,t)$ is defined as the rate at which components fail under the stress α_i. With $g(\alpha_i,t)$ representing the number of good components vs time under the constant stress α_i

$$H(\alpha_i,t) = \frac{-dg(\alpha_i,t)}{dt} \Big/ g(\alpha_i,t) \qquad (1)$$

Integrating for time zero to time t

$$\frac{g(\alpha_i,t)}{g(0)} = \exp\left[-\int_0^t H(\alpha_i,t)dt\right] = G(\alpha_i,t) \qquad (2)$$

where $g(0)$ represents the number of good components at time zero and $G(\alpha_i,t)$ represents the fraction of good components remaining after time t. If $G(\alpha_i,t)$ and $G(\alpha_j,t)$ represent the fractions of good components remaining vs time in two constant stress environments, α_i and α_j respectively, then the relationship between $G(\alpha_i,t)$ and $G(\alpha_j,t)$ can be written

$$G(\alpha_i,t) = G\left(\alpha_j,\ a_{ji}(t)\right) \qquad (3)$$

where $a_{ji}(t)$ is called the time transformation function. Particularly simple cases occur when the time transformation function is equal to a constant A_{ji} times time, i.e.

$$a_{ji}(t) = A_{ji}t \tag{4}$$

In such constant acceleration cases, A_{ji} is called the acceleration factor from environment a_j to environment a_i. Many phenomena can lead to non-constant acceleration situations. Examples are (a) when two reactions with different dependence on accelerating stress level are important to the degradation and (b) when the range of accelerating stress levels encompasses some transition (eg. glass) of a material. In the present paper we ignore such complications and restrict ourselves to constant acceleration situations. If constant acceleration holds for an a type stress, the dependence of the acceleration factor A_{ji} on the levels of stress will define the acceleration function $A_a(a)$. One of the goals of accelerated aging is to determine the functional form of $A_a(a)$ and use the derived functional form to extrapolate to the use stress level.

When the hazard rate $H(a_i,t)$ is equal to a constant $k_a(a_i)$, the common case of first order behavior occurs. In this case

$$G(a_i,t) = \exp\left(-k_a(a_i)t\right) \tag{5}$$

and $k_a(a_i)$ is the first order rate constant. The value of this rate constant will completely describe the time dependence of the fraction of good components.

Proposed Model for Combined Environment Accelerated Aging

One of the difficulties encountered in accelerated aging is trying to account for the combined effects of more than one type of environmental stress, where the potential for synergism exists. The basis for the present model is similar to that used in the recently introduced Equalized Aging Process (EAP) of Paloniemi (1976). In the EAP method, which is relevant to thermal aging, an attempt is made to accelerate equally all important thermal reactions through control of the reacting gaseous atmosphere. The present aging model likewise attempts to accelerate by an equal amount all reactions, including synergistic reactions, pertinent to the combined environment degradation.

We begin by assuming that knowledge of the appropriate single environment acceleration functions exists. In other words, if one is interested in simulating the ambient aging in a combined environment encompassing two types of stresses, a and β, it is assumed that the acceleration functions appropriate to aging in the single environments, $A_a(a)$ and $A_\beta(\beta)$ respectively, have been determined. If the use stress level for the a type stress is denoted by a_u and one would like to simulate a time t_u in this environment by carrying out an over-stress experiment for a time t_a, then knowledge of $A_a(a)$ allows one to determine the accelerated over-stress condition a_a such that

$$G(a_a, t_a) = G(a_u, t_u) \tag{6}$$

Similarly, knowledge of $A_\beta(\beta)$ allows one to determine β_a such that

$$G(\beta_a, t_a) = G(\beta_u, t_u) \tag{7}$$

In the combined stress environment, denoted by a plus β, we define $G(a,\beta,t)$ as the fraction of good components remaining after time t. We then define the synergism for a combined environment experiment by writing

$$G(a, \beta, t) = G(a, t)\, G(\beta, t)\, G_s(a, \beta, t) \tag{8}$$

In other words $G(a, \beta, t)$ is written as the product of the single environment G's times a synergistic term $G_s(a, \beta, t)$. From accelerating aging tests one would like to be able to predict $G(a_u, \beta_u, t_u)$, the fraction of good components remaining in the use environment after the use lifetime. From Eq. (8)

$$G(a_u, \beta_u, t_u) = G(a_u, t_u)\, G(\beta_u, t_u)\, G_s(a_u, \beta_u, t_u) \tag{9}$$

The proposed approach envisions a series of experiments, each lasting a different time t_a, and having over-stress conditions a_a and β_a chosen such that Eqs. (6) and (7) are satisfied for a given t_a. A set of accelerating parameters (t_a, a_a, β_a) derived in this manner will be called a matched set to the use conditions (t_u, a_u, β_u). A matched set implies an equal acceleration of the single environment reactions with respect to the use environment. Thus the primary (initial) reactions governed by the stress environments a_a and β_a will occur in the same ratio as in the ambient environment but on a compressed time scale. If the synergism is due to secondary reactions (reactions dependent upon one or more of the primary reaction products) and the primary reactions are the rate determining steps, it is reasonable to postulate that the synergistic reactions in the accelerated experiments will be the same as in the use conditions except that they will occur in a time scale compressed by a factor equal to the compression of the single environment time scale. This implies that

$$G_s(a_a, \beta_a, t_a) = G_s(a_u, \beta_u, t_u) \tag{10}$$

Equations (6), (7), (9) and (10) lead to

$$G(a_a, \beta_a, t_a) = G(a_u, \beta_u, t_u) \tag{11}$$

Therefore the fraction of good components remaining after the use conditions can be predicted from the matched set accelerated experiment. The correctness of the model can be tested by carrying out experiments using different matched sets of accelerating parameters. If the values of $G(a_a, \beta_a, t_a)$ are identical for all matched set experiments, good evidence for the validity of the model would exist. In the next section we will describe data on one system which appears to conform to the proposed model.

Experimental Confirmation of Proposed Model

An extensive study was conducted on the thermoradiation sterilization of Bacillus subtilis var niger by a group at Sandia Laboratories (Reynolds, 1969; Dugan, 1971; Sivinski and Reynolds, 1972; Reynolds and Brannen, 1972). Experiments were run under dry heat environments as well

as under gamma radiation (Cobalt -60) conditions, both at room temperature and at a number of elevated temperatures. To compare the sterilization effectiveness of the various environments, the fraction or number of survivors in a given environment was monitored versus time. Typical results for two thermoradiation runs (Reynolds and Brannen, 1972) are shown in Fig. 1, where the log of the fraction surviving is plotted

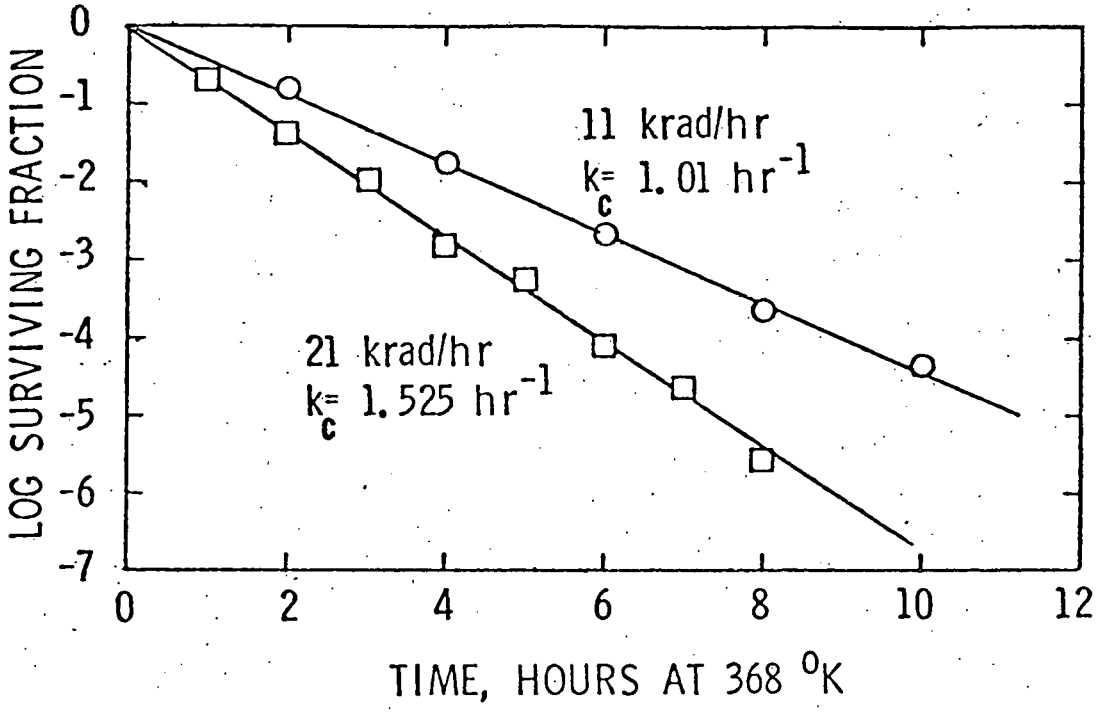

Figure 1: Typical Thermoradiation Sterilization Data for Bacillus subtilus var niger

against time in the environment. The decays can be approximated as first order; the combined environment rate constants k_c for first order behavior are shown in the figure. Similar first order behavior was found for all other experimental conditions. Eqs. (5) and (8) with α and β representing temperature, T, and radiation dose rate, R, can then be used to show that $G_s(T, R, t)$ must also be described by a first order rate constant $k_s(T, R)$. Thus in the present case, Eq. (8) can be rewritten in terms of rate constant as follows

$$k_c(T, R) = k_T(T) + k_R(R) + k_s(T, R) \qquad (12)$$

To test the model for combined environment accelerated aging, we must first determine the single environment acceleration functions appropriate to temperature and radiation, $A_T(T)$ and $A_R(R)$, respectively. $A_T(T)$ can be obtained from the thermal data. In Fig. 2 the log of the thermal rate constant is plotted versus inverse temperature and it is clear that the thermal data can be approximated as Arrhenius with an activation energy of 35 Kcal/mole.

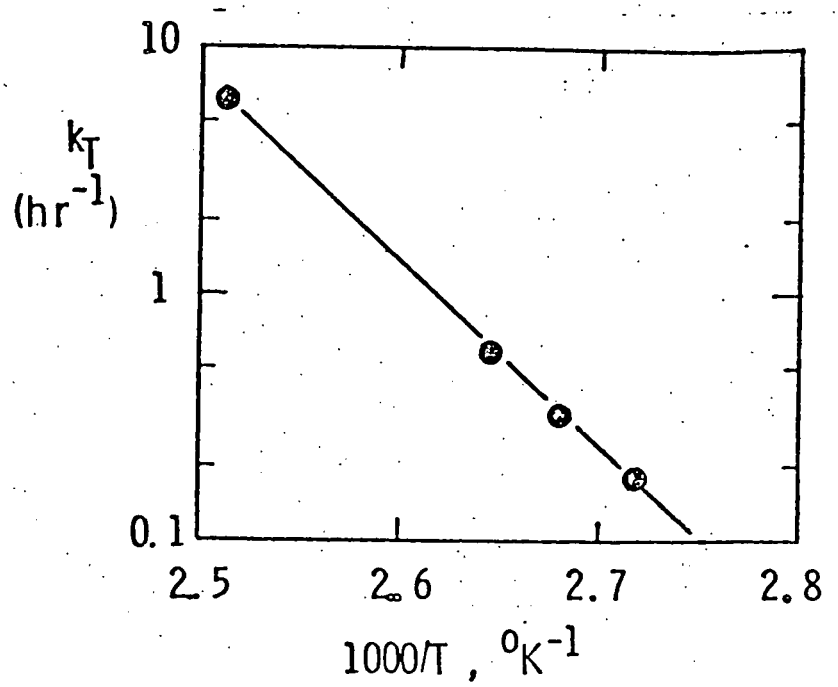

Figure 2: Arrhenius Plot of Thermal Rate Constants

Therefore

$$A_T(T) \propto \exp\left(\frac{-35 \text{ Kcal/mole}}{R_g T}\right) \tag{13}$$

In order to obtain $A_R(R)$, experiments at various radiation dose rates must be run at a low enough temperature such that the $k_T(T)$ term and the $k_S(T,R)$ term in Eq. (12) are insignificant compared to the $k_R(R)$ term. At room temperature for Bacillus subtilus var niger this condition is not satisfied since small contributions from the $k_S(T,R)$ term still exist. Fortunately, it has been concluded from numerous studies on the radiation sensitivity of viruses, bacteria, and cells of mammalian and plant systems (Dugan and Trujillo, 1971) that

$$k_R(R) = CR \tag{14}$$

i.e., a linear relationship exists between the radiation rate constant and the radiation dose rate, R. For Bacillus subtilis var niger, it has been estimated (Dugan and Trujillo, 1971) that $C = 0.0234 \text{ Krad}^{-1}$. For our purposes the exact value of C is immaterial since we are interested only in the radiation acceleration function $A_R(R)$, which is proportional to R, i.e.,

$$A_R(R) \propto R \tag{15}$$

With the above estimates of the single environment acceleration functions, $A_T(T)$ and $A_R(R)$, a test of the model proposed for combined environments could be carried out if synergism was important and if a number of experiments conducted under "matched set" combined environment conditions

had been performed. Since "matched set" conditions were not utilized in the above experiments, a slightly different approach will be used to test the model. In this approach, data obtained at 368°K and various radiation dose rates will be transformed, assuming the correctness of the model, to obtain predicted data versus radiation dose rate at other temperatures. The predicted results will then be compared to actual experimental data.

The solid line in Fig. 3 plots the experimental rate constant $k_c(368, R)$ versus radiation dose rate R using the 368°K experimental data.

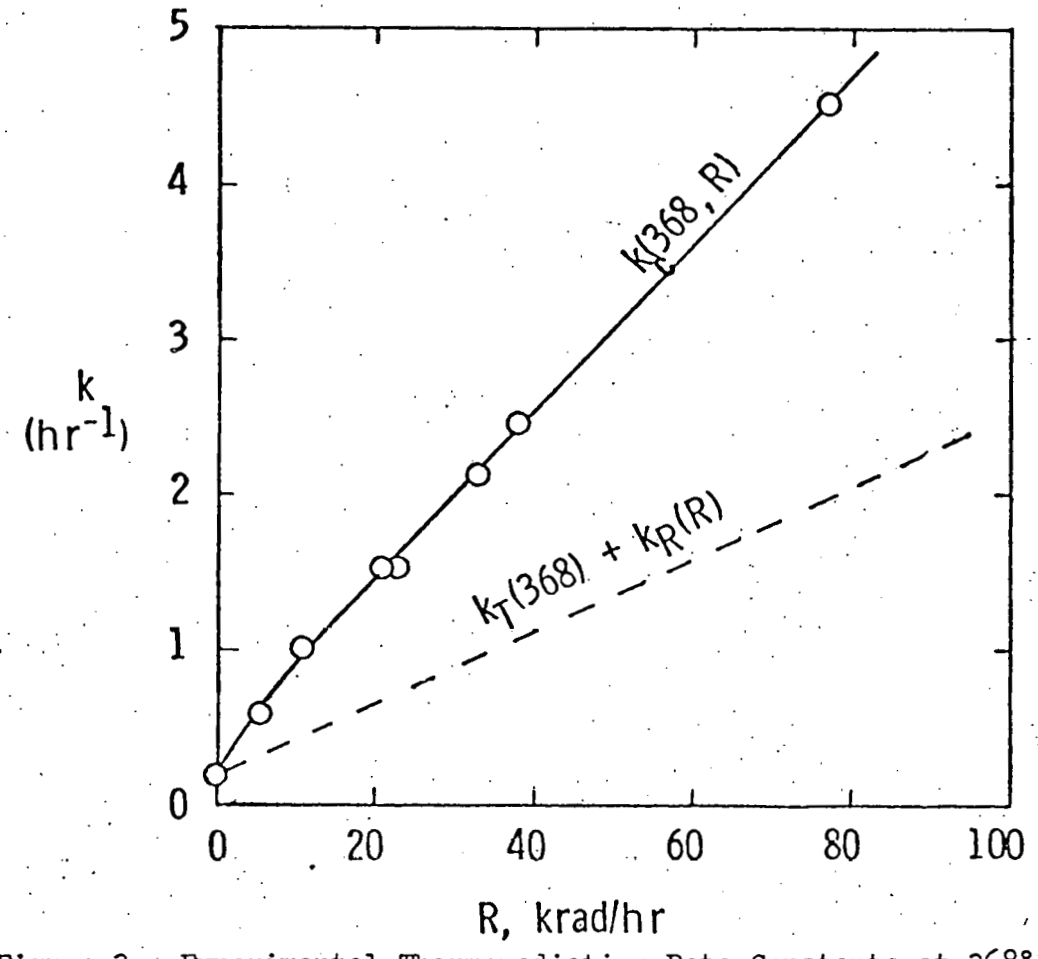

Figure 3: Experimental Thermoradiation Rate Constants at 368°K Compared to the Sum of the Single Environment Rate Constants

This data was chosen because of its large range of radiation dose rates and its well behaved character. The solid line drawn through the data is used for the calculations. Also plotted in Fig. 3 is a dotted line which represents the sum of the single environment rate constants $k_T(368)$ and $k_R(R)$, where $k_R(R)$ is estimated using Eq. (14) with $C = 0.0234\ \text{Krad}^{-1}$. Comparing this plot to $k_c(368, R)$, it is apparent that synergistic effects are extremely important for the combined radiation plus temperature environment. Therefore this should be an appropriate system in which to test the proposed combined environment

model. If synergism didn't exist, testing of the model would not be meaningful.

By using the results for $k_c(368, R)$ and assuming that the proposed model is valid, we can construct predicted results at other temperature and radiation conditions. For instance to calculate the predicted rate constant at 363°K and 10 Krad/hr, $k_c(363, 10)$, we note that the single environment thermal results give

$$\frac{k_T(368)}{k_T(363)} = 1.93 \tag{16}$$

Using Eq. (15) the model therefore predicts that

$$k_c(368, 19.3) = 1.93\ k_c(363, 10) \tag{17}$$

From Fig. 4, $k_c(368, 19.3) = 1.42\ hr^{-1}$; Eq. (17) then predicts $k_c(363, 10) = 0.74\ hr^{-1}$. This compares with the experimental value of $0.78\ hr^{-1}$. Data calculated in the above manner were used to generate rate constant versus R curves at four temperatures, 363°K, 378°K, 393°K, and 398°K. The results are shown as solid curves in Fig. 4. The choice of temperatures was dictated by having experimental data at these temperatures; these experimental data (triangles, circles, hexagons and squares) are also plotted in Fig. 4. The results suggest that the proposed model does an excellent job in predicting the experimental results for the present system. This indicates that the model may be useful for combined environment accelerated aging.

It should be noted that equations similar to Eq. (12) and (14) were previously used to model this same data (Dugan, 1971; Dugan and Trujillo, 1971). In this earlier modelling the synergism was described semi-empirically by

$$k_s = (R)^{C_1/T}\, e^{C_2}\, e^{-C_3/R_g T} \tag{18}$$

where C_1, C_2, and C_3 are constants determined from the experimental data.

Acknowledgment

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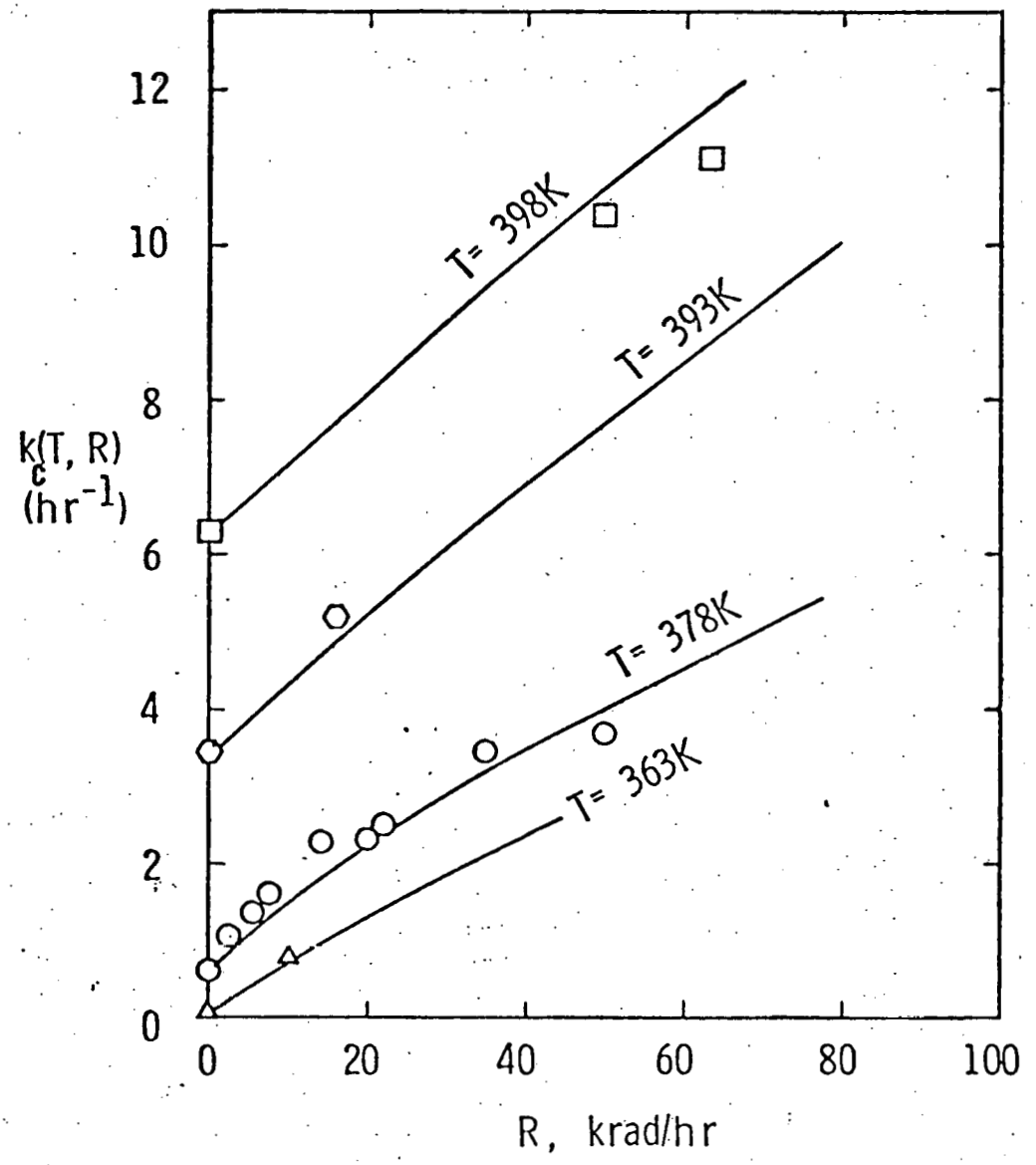

Figure 4: Thermoradiation Rate Constants Predicted from Model (solid curves) Compared to Experimental Rate Constants

References

1. Winter, B. B., Dennison, C. A., Hietula, H. J., and Green, F. W., "Accelerated Life Testing of Guidance Components," AD-448079 (1964).

2. Paloniemi, P., and Lindstrom, P., 1976 IEEE International Symposium on Electrical Insulation, Montreal, p. 28 (1976) and refs. therein.

3. Reynolds, M. C., "The Feasibility of Thermoradiation for Sterilization of Spacecraft - A Preliminary Report," Sandia Laboratories Research Report No. SC-RR-69-857, (1969).

4. Dugan, V. L., Space Life Sciences 2, 498 (1971).

5. Sivinski, H. D., and Reynolds, M. C., Life Sciences and Space Research X, Akademie-Verlag, Berlin (1972), 33.

6. Reynolds, M. C., and Brannen, J. P., in Radiation Preservation of Food (Proc. Symp. Bombay, 1972), IAEA, Vienna, (1972).

7. Dugan, V. L., and Trujillo, R. E., "Biological Inactivation by Thermoradiation," Sandia Laboratories Research Report No. SC-RR-71-0616, (1971).