STUDY OF SPACE BATTERY ACCELERATED TESTING TECHNIQUES

PHASE II REPORT

IDEAL APPROACHES TOWARDS ACCELERATED TESTS AND ANALYSIS OF DATA

August, 1969

Contract No.: NAS 5-11594

Prepared by

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Goddard Space Flight Center
Greenbelt, Maryland

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October 13, 1969

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland 20771

Attention Mr. E. F. Colston (Code 716.2)

Gentlemen:

"Study of Space Battery Accelerated Testing Techniques"
Contract NAS 5-11594

Enclosed is a copy of the Phase II report, "Ideal Approaches Towards Accelerated Tests and Analysis of Data", prepared under Contract Number NAS 5-11594. As given on the official distribution list, two copies and one reproducible copy are being forwarded to the Scientific and Technical Information Center. Other copies are being distributed according to the contract requirements.

Yours truly,

J McCallum

John McCallum
Project Manager

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Enc.

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FOREWORD

This report describes work performed at Battelle Memorial Institute, Columbus Laboratories, 505 King Avenue, Columbus, Ohio, 43201, under Contract NAS 5-11594.

The authors wish to thank Mr. E. F. Colston, NASA Goddard Space Flight Center, for his review of this report and Dr. Troy H. Tidwell, Battelle-Columbus, for his assistance with developing the stress-strain relationships and associated concepts.

This report was submitted by the authors in July, 1969. Publication of this report does not constitute approval of the report's findings or conclusions by the National Aeronautics and Space Administration. It is published only for the exchange and stimulation of ideas.

ABSTRACT

The object of this research program is to develop testing procedures to accelerate the aging of electrochemical cells and batteries so that the equivalent of years of data may be acquired in significantly less time to enable a valid prediction of cell life. The program is divided into three phases. The first phase is a literature review. The second phase entails the recommendation of idealized accelerated testing techniques. A third phase will give recommendations for the implementation of a practical program.

In this second phase, empirical, statistical, and physical concepts are applied to the design of an ideal accelerated test. Approximately 300 cells would be required for a test that involves five levels of each of three stresses (gradients of temperature, voltage, and pressure). The data would be analyzed in terms of a proposed measure of quality which is numerically the inverse of observed changes in a cell within a given duty cycle. Empirical methods of analysis, such as the Automatic Interaction Detector Program, are proposed to search for precursors of failure; statistical methods, such as response surfaces, are proposed for assessing statistical validity and predicting parametric failures during the test; and physical methods based on stress-strain laws are proposed for obtaining an understanding of the physical mechanisms associated with the degradation of cells with time. Six kinds of stresses are identified in the development of the physical approach to accelerated testing: (1) pressure gradients, (2) voltage gradients, (3) temperature gradients, (4) concentration gradients, (5) velocity gradients (vibrations), and (6) frequency gradients (electromagnetic absorption). Each stress has associated with it a corresponding flux that is identified as a rate of strain. Static strains are also identified for the first four stresses itemized above. For the physical tests, qualities are measured at the same times in each cycle. An extrapolation of quality changes at high stress levels over a relatively few cycles is recommended to predict life at normal (the user's) stress level.

LIST OF SYMBOLS

Symbol	Description	Units
a	Area	cm^2
d	Differential operator	--
f	Frequency	sec^{-1}
g	Grams	g
h	Height; Planck's Constant	cm; erg·sec·photon^{-1}
i_c	Charging current	amp
i_d	Discharging current	amp
k_n	Proportionality coefficient in nth equation	--
l	Length	cm
m	Mass	g
n	Hourly rate of charge or discharge	hr
q	Heat	cal
r	Radius of capillary or sphere	cm
t	Time	sec
t'	Charge or discharge time	hr
v	Velocity	cm·sec^{-1}
x	Distance perpendicular to flux	cm
x_1	Coded duration of charge	day
x_2	Coded charging rate	ma
x_3	Coded temperature	F
y	Ampere-hour efficiency	%
A	Amount factor of energy	--
AH	Manufacturer's rated ampere-hour capacity	amp·hr
C	Concentration; charging current	moles·cm^{-3}; ma
C'	Heat content	cal·deg^{-1}
D	Diffusion coefficient; charging duration	cm^2·sec^{-1}; day
E	Emf or voltage	volt
E_c	Charge voltage	volt
E_d	Discharge voltage	volt
F	Force	dyne
F'	Faraday's constant	amp-hr·equiv.$^{-1}$
G	Gravitational acceleration	cm·sec^{-2}
H	Magnetic field intensity	dyne·pole^{-1}
I	Intensity factor of energy	--
L	Illumination	no. of photons or erg·sec
M	No. of moles or molecules; matrix	--
M^n	Manufacturer, n	--
O	Osmotic pressure	dyne·cm^{-2}
P	Pressure	dyne·cm^{-2}
P_n	Polynomial of nth degree	--
Q	Electrical charge: quality	coulomb; --
Q_o	Minimum acceptable quality	--
Q_s	Quality of cell or battery for stress, s	--
R	Gas constant	1.987 cal·deg^{-1}·mole^{-1}
T	Temperature	C, F or K
V	Volume	cm^3
V_m	Molar volume	cm^3
α	Magnetization	pole·cm
γ	Surface tension	dyne·cm^{-1}
∂	Partial differential operator	--
η	Viscosity	poise·(dyne·sec)·$^{-1}$ cm^{-2}
ρ	Density	g·cm^3
τ_n	Time constant in equation n	sec

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OBJECTIVES

The primary objective of the research described in this report consists of the development of an ideal accelerated test program for space batteries. To accomplish this objective, a variety of tasks have been pursued. These tasks include: (1) the identification of relevant electrochemical variables for describing cell quality; (2) the descriptions of empirical, statistical, and physical methods for predicting the degradation of quality over time; (3) the identification of required characteristics for ideal hardware and software for data acquisition and monitoring; and (4) the determination of the roles of destructive and nondestructive testing in the context of accelerated testing.

SUMMARY

The relevant electrochemical variables for describing cell quality are found to include intensity factors (temperature, pressure, voltage, and force) and their associated amount factors (heat, volume, charge, and displacement). The degradation of cell quality is expected to be expressible in terms of gradients in the intensity factors and fluxes of the associated amount factors (flow of amount per unit area per unit time).

Empirical methods of data analysis form a potentially powerful approach to the analysis of accelerated test data. The "tree" structure generated by an existing computer program, termed an Automatic Interaction Detector, serves as a good example of a useful empirical method. This method is illustrated using some failure data obtained from the Crane tests.

A general "response surface" method appears to be ideally suited for statistical analysis of accelerated test data. The method is illustrated in this report using published cell data. In general, it appears that this method is capable of making a transition between the pattern-detection capabilities of the empirical method and equations based on concepts identified by the physical approach to accelerated testing.

The physical methods found to be most suitable for accelerated testing are methods based on stress-strain models in a more general form: intensity gradient-flux density models. The physical concepts associated with these models are described in this report.

As would be expected, the ideal hardware would permit maximum flexibility in data acquisition, handling, and reporting. In addition, the computer system would allow some on-line monitoring, including the accumulation of counts and the generation of relative frequencies for empirical surveillance. Off-line storage of data would be suitable for statistical and physical analysis.

It is recommended that a blend of destructive and nondestructive tests be performed. However, the destructive tests are not associated with "over-stressing", but with a periodic destructive examination to determine the state of quality of good cells that exists after the elapse of a specified number of cycles at a specified level of stress. This procedure would allow the early detection of probable causes of failure.

AN EMPIRICAL APPROACH TO THE ANALYSIS OF ACCELERATED-TEST DATA

by

Ralph E. Thomas and John H. Waite

INTRODUCTION

Previous reports(1, 2)* have indicated some of the differences among the empirical, statistical, and physical approaches to the analysis of accelerated test data. In the empirical approach, the data may be regarded as containing unknown relationships embedded in noise. The analysis of the data consists of a search for structure. Moreover, the search is carried out with minimal assumptions regarding the kinds of structure that may be present. By applying a wide variety of "code-cracking" techniques, the data are processed in a way that will reveal "interesting" structure. The exact sequence of analysis is not predetermined. Instead, the kind of analysis that is made at each stage depends on what kind of structure has been extracted prior to that stage. Because "smoothing" may suppress "interesting" structure, the empirical analyst tends to smooth as little as possible. After "interesting" structures are identified in the data, statistical methods are then applied to assess the "persistency" of the structure in the noise background. The persistent structures are then recommended to the statistician or physicist for further study.

Because most data-processing methods involve a considerable amount of smoothing, few techniques are available for empirical analysis. The methods of nonparametric statistics and certain classification techniques, such as AID (Automatic Interaction Detector), offer some acceptable methods.

An Empirical Analysis Is Data Dependent

The exact sequence for using empirical methods need not be specified in advance. In general, whenever an "interesting" aspect of the data has been exposed, the empirical analyst attempts to exploit this aspect further by whatever methods seem appropriate. This means that the resulting analysis is sequential and "data dependent". Rarely would the same sequence of methods be applied to different sets of data.

Search for Association

The empirical analyst searches for relations by purely numerical methods. Typically, these methods involve processing the data using a blend of procedures based on a variety of classifications, histograms, marginal distributions, rank correlations, and combinatorial structures. The associations need not be "explained"; they are simply "exhibited". The explanations of the detected associations are left to the physical chemist.

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*References are given on page 102.

The Smoothing of Data

Because the smoothing, or averaging, of data loses information, the empirical analyst usually begins by processing the data in its raw form. For this reason, he usually detects errors, inconsistencies, and suspicious "outliers". After removing identified discrepencies, he is then able to search for more subtle features of the data. Only when these features persist with operating time is the analyst ready to average the data and claim that some structure has been detected.

On-Line Data Analysis

One of the important functions of empirical analysis arises in the monitoring of data as it is generated. Again, those methods that are suitable for detecting errors and outliers serve as good tools for maintaining a high level of quality of data. By on-line monitoring of the data, suspicious behavior among the measured values may be identified quickly and corrective measures may be taken if appropriate. Such monitoring usually does not require a knowledge of the physics of the cell or even of statistical quality control. Monitoring merely requires a well-planned supervision of the generated numbers. The characterizations of typical data behavior can be established by empirical methods during early portions of the experiments. These characterizations then may serve as quality-control criteria to be used as monitoring procedures during the remainder of the experiment. As discussed later, early changes in the data so generated are to be used empirically for the prediction of failures.

AN EMPIRICAL PHILOSOPHY FOR ACCELERATED LIFE TESTS

The preceding considerations may be combined to form a general empirical philosophy for the conduct of accelerated life tests. The following discussion is aimed at exhibiting the important features of this point of view. To begin the exposition, the assumptions associated with accelerated testing are restated:(2)

(1) The "quality" of a cell varies over time and, after the elapse of a sufficiently long time, the quality degrades.

(2) The time rate of degradation of quality depends on the "level of stress" experienced by the cell during its operating life.

(3) Higher degradation rates occur at higher stress levels.

(4) Accelerated life tests are run in order to establish acceleration factors that permit degradation rates at low stress levels to be predicted by using degradation rates obtained at higher stress levels.

As noted earlier, the empirical analyst prefers some on-line monitoring of the quality of the data. In this way, concern with spurious results is alleviated. Secondly, the on-line monitoring can be computer based so that concurrent numerical analysis is possible. This means that distributions, histograms, and associations can be generated in a sequential way and used both to monitor the quality of the data and to study possibly persistent structures found to occur in the data. Gradual changes in the persistent structures may permit the prediction of future behavior. In accelerated test applications, the aim is to predict the failure of a cell before the failure has actually occurred. This is the most convincing kind of prediction, because it is not subject to the "hindsight" criticism that may be associated with postexperimental analysis of the data.

An additional assumption may be made that makes the empirical approach still more specific. The measured values of variables associated with a group of nominally identical cells operated at the same stress level are expected to show some "typical" behavior. Cells having measured values of particular variables or combinations of variables that deviate from the typical behavior may be said to occupy a "tail" of the distribution of behavior. One of the objectives of the on-line empirical approach is to identify "typical" behavior and "tails". Those cells associated with a tail then are put under "suspicion". Such cells are expected either to be poor cells and fail early or to be exceptionally good cells and fail late. In either case, these cells warrant more detailed surveillance. If possible, the rate of data taking should be increased for the cells in the tails at the expense, perhaps, of taking fewer measurements on the cells associated with typical behavior. The increased monitoring rate may provide for the early establishment of trends, and this, in turn, would be expected to permit predictions of future behavior to be made more quickly.

Suppose that tails have been identified and are closely monitored over time but that no failures have occurred and no failures have yet been predicted. If a failure of a cell occurs under these conditions, it is clear that all of the cells in that same tail should be predicted to be "early failures". This can be done even if sufficient data have not been obtained to predict the times to failure. Moreover, if a cell fails that was associated with typical behavior, a reassessment of the conditions defining the tails may be appropriate. In summary, an empirical on-line monitoring of accelerated life tests may be structured to

(1) Establish and maintain a high level of quality for the data

(2) Identify persistent typical behavior and persistent tail behavior

(3) Increase the monitoring rate for cells showing persistent tail behavior

(4) Establish trends associated with gradual changes over time, with special emphasis on the tail cells

(5) Predict cell failures in persistent tails, based either on extrapolated trends for the tail or on the actual occurrence of a cell failure in the tail.

In the context of an ideal accelerated test, a minimum of at least five stress levels should be used for reasons explained in the Statistical Approach section of this report.

The empirical monitoring of the generated data then would be carried out at each level of stress. This procedure would permit the early study of possible relationships among behavior tails within stress levels and between stress levels. As a result, early predictions may be provided for the behavior at a lower stress level using the observed behavior at a higher stress level. One method for accomplishing early predictions involves "parametric" failures. This approach is described later in a section concerned with destructive and nondestructive testing.

APPLICATION OF THE AID PROGRAM TO CRANE DATA

As an example of an empirical analysis, the Automatic Interaction Detector (AID) computer program is applied to failure data obtained at the Quality Evaluation Laboratory, Crane, Indiana. The data are documented in a report by Waite and Epstein.(3)

Table 1 shows a listing of the 21 failure characteristics generated by Waite and Epstein for the Crane data. The characteristics were not chosen for the purposes of making an AID analysis. In fact, as discussed in Reference (1), the Waite-Epstein classification contains both failure modes and failure determinants and, consequently, the list is not well suited to either empirical or theoretical analysis. Nevertheless, an empirical study can be made to determine whether any of these failure characteristics are highly associated. The data serve primarily as a basis for illustrating the empirical approach.

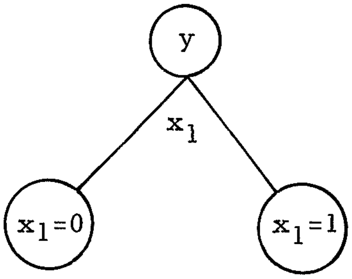
Description of the AID Program

The AID program is a computer program for identifying which independent variables are the best predictors of a given dependent variable. In an accelerated test application, recommended variables would be voltage quality, temperature quality, or pressure quality(2), as described in the Physical Approach section of this report. The independent variables consist of any measured values that are possible predictors of quality.

The AID program begins by determining how well each independent variable can predict high or low values of the dependent variable. If one of the independent variables is found to be perfectly associated with the dependent variable, then the data set is "split" using this independent variable. In the simplest case, suppose that the dependent variable can take only the values of 0 and 1. Further, suppose that there is an independent variable, say x_1, that also takes on values of 0 and 1 and that $y = 1$ whenever $x_1 = 0$ and $y = 0$ whenever $x_1 = 1$. In this case, x_1 is a perfect predictor of y. That is, given that $x_1 = 0$, y is always found to be 1, and given that $x_1 = 1$, y is always found to be 0. The AID program would identify x_1 as a good predictor of y and would split the entire set of data into two groups. In the first group, all the data for which $x_1 = 0$ would be included; in the second group, all the data for which $x_1 = 1$ would be included. Thus, the initial data (in one group) is split into two groups. It is convenient to represent such a split by a "tree" as follows:

TABLE 1. SUMMARY OF THE FAILURE CHARACTERISTICS FOR NICKEL-CADMIUM CELLS OBSERVED IN THE Q.E.L. CRANE TEST PROGRAM AS DOCUMENTED BY WAITE AND EPSTEIN(3)

(A)	Low voltage on charge
(B)	Low voltage on discharge
(C)	Separator: deteriorated, dissolved, burned, pinpoint penetration, short
(D)	Plate material shorted through separator
(E)	Separator impregnated with negative plate material
(F)	Migration of positive and/or negative plate material
(G)	Extraneous material between plates
(H)	Deposit on positive and/or negative terminals
(I)	Blistering on positive plate(s)
(J)	Plate(s) stuck to case
(K)	Excess scoring of case
(L)	Convex side(s): high pressure, bulge
(M)	Concave side(s): short(s) due to internal shift
(N)	Broken seal(s): ceramic, glass
(O)	Ceramic short
(P)	Electrolyte leak: weight loss, separator dry, electrolyte shorted-out cell
(Q)	Tab(s): burned, broken, welds weak
(R)	Third electrode shorted to plate
(S)	Cell blew up
(T)	Circuit, short, open
(U)	High voltage on charge



If perfect predictors cannot be found, the AID program simply identifies whatever predictor is "best" and splits the data using the best predictor. In quantitative terms, the best predictor is that independent variable which maximizes an F-ratio. In intuitive terms, the F-ratio is the ratio of the statistical variability of y that is accounted for by the variability of x_1 to the variability of y that is not accounted for by the variability of x_1. If all the variability is accounted for, the F-ratio is infinite; if none is accounted for, the F-ratio is zero. Thus, the AID program simply computes the F-ratios associated with each independent variable and splits the data using the variable that yields the maximum F-ratio.

Many other features associated with the AID program are given in Reference (4). The above description is generally all that is needed to explain the following illustrative examples.

Examples of AID Applications to Crane Data

Figure 1 shows a portion of one of the trees that results when the AID program is applied to the Crane data. This particular tree is obtained when Failure Characteristic (B), low voltage on discharge, from Table 1 is used as a dependent variable and the other variables in Table 1 are used as predictors of (B). In the node at the top of the figure, the ratio 280/377 appears. This ratio shows that Failure Characteristic (B) occurs 280 times in a total of 377 cases of cell failure.

It is seen that the variable that is most strongly associated with (B) is (T), short or open circuit, as shown by the symbol (T) in Figure 1. The F-ratio associated for this split is 52.96 and is shown beneath the symbol (T). The split shows that the initial 377 cases are divided into 275 cases and 102 cases, corresponding to the denominators of the fractions shown in the left and right nodes, respectively. For convenience, the absence of a failure characteristic is associated with the left branch of the split and the presence is associated with the right branch. Thus, the two nodes obtained with the first split give the following information:

(1) Out of 275 cases in which (T) was absent (no open or short circuits), 230 of these had low voltage on discharge.

(2) Out of 102 cases in which (T) was present (a short or open circuit observed), a total of 50 showed low voltage on discharge.

The AID program then examines these two groups and determines which variables are the best predictors for these groups. For example, the right node, formed by the

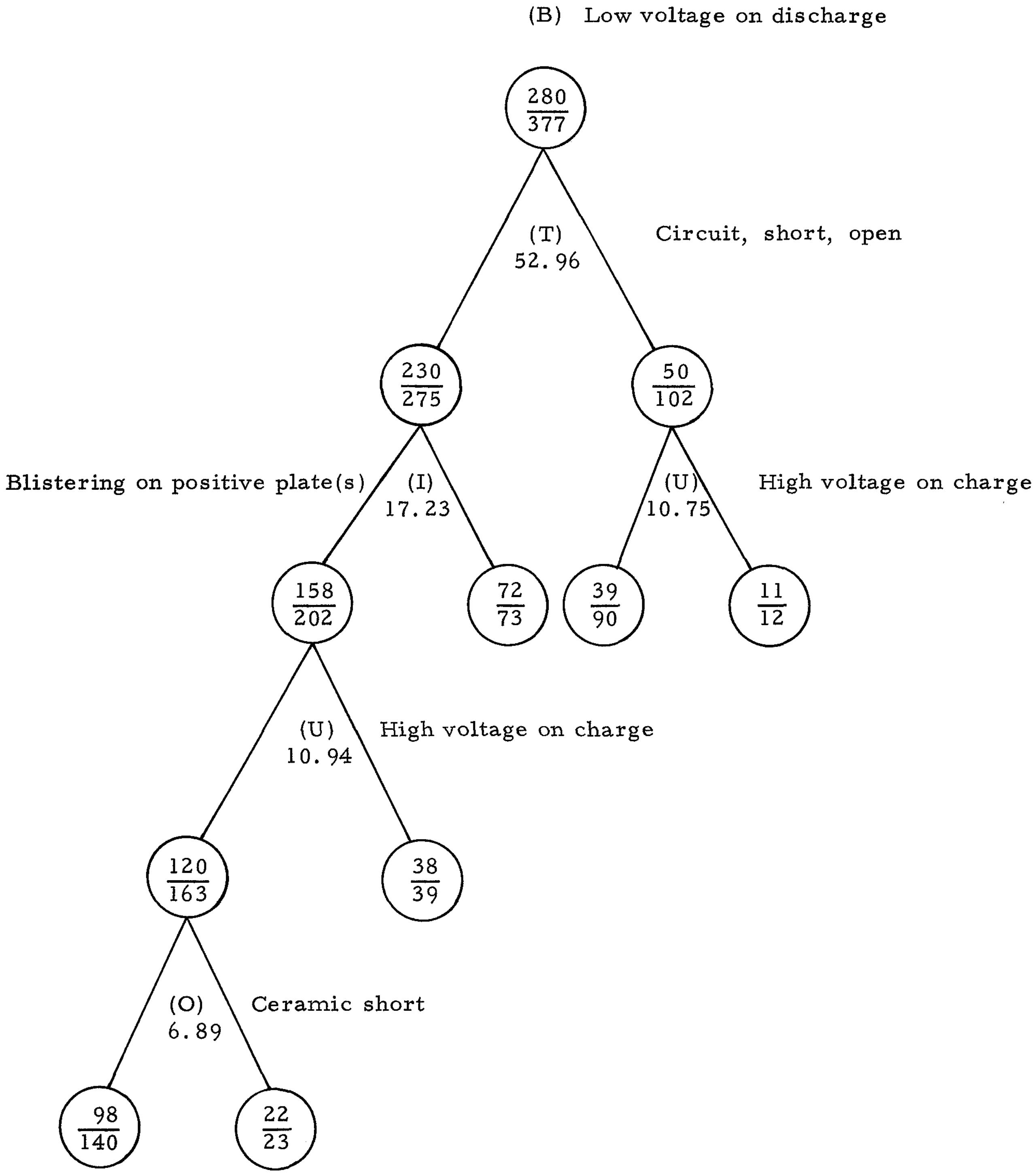


FIGURE 1. AID TREE, WITH F-RATIO, FOR PREDICTING LOW VOLTAGE ON DISCHARGE

split on (T), was split further on the basis of variable (U), high voltage on charge. The split on (U) gives the following information:

(1) There were 90 cells in which (T) was present and (U) was absent (that is, an open or short was present and a high voltage on charge was absent). Of these 90 cells, 39 showed low voltage on discharge.

(2) There were 12 cells in which (T) and (U) were both present (that is, either an open or short was present and a high voltage on charge was present). Of these 12 cells, 11 showed low voltage on discharge.

Figure 1 also shows additional branches of the tree that were obtained when splits were made using (I), blistering on positive plates, and (O), ceramic short. In summary, this tree shows that the failure characteristics that serve as the best predictors of (B) are the variables (T), (I), (U), and (O). None of the other variables from Table 1 appear in Figure 1 because their F-ratios were lower.

As this example shows, the AID tree yields a set of conditional predictors. The conditions are associated with the nodes traversed by a path from the top of the tree to a terminal group. Although the tree generated in this example shows that (T) is the best predictor of (B), it does not follow that (B) is the best predictor for (T). That is, a predictive relation may not be symmetric. It is shown in the next section how the AID program can be used to detect symmetric associations among variables.

An Empirical Search for Association

The AID program may be used to make an empirical search for association among variables. To exemplify one approach, the following steps were carried out:

(1) The AID program was run to predict the presence of (A), low voltage on charge, from Table 1. A large tree involving 125 groups was obtained. An examination of F-ratios showed that the following variables yielded statistically significant splits: BEILOTUCHP.

(2) A modified version of the AID program was run to obtain the variables least important as predictors of the presence of (A). In this case, large F-ratios were obtained at the end of the branches, and the following variables were found to yield significant splits: BEILOTUND.

(3) The seven variables common to Steps (1) and (2) namely, BEILOTU, were then run with each variable in this group serving, in turn, as the dependent variable and the remaining variables in this group serving as the independent variable.

(4) The following matrix then was obtained by identifying the best predictor for each variable.

Predictors

Variable to be predicted

$$\begin{array}{c|ccccccc|}
 & B & E & I & L & O & T & U \\
\hline
B & & & & & & X & \\
E & & & & X & & & \\
I & & & & & X & & \\
L & & & X & & & & \\
O & & & & & & X & \\
T & X & & & & & & \\
U & X & & & & & & \\
\hline
\end{array}$$

The X in the first row of the matrix shows that the best predictor of (B) in row 1 is the variable (T) in column 6, and we write B → T, which is read "(B) is predicted by (T)". In row 6, it is seen that the best predictor of (T) is (B) so that T → B. Thus, (B) and (T) are mutual predictors, and we write B → T → B. In a similar way, the second row shows that E → L; the fourth row shows that L → I, etc., and it is found that,

$$E \rightarrow L \rightarrow I \rightarrow O \rightarrow (T \rightarrow B \rightarrow T) \quad .$$

The last three letters are enclosed by parentheses to indicate that the predictors of (E) are now "trapped" to the letters (B) and (T). By continuing in this manner, the following summary is obtained for the variables associated with the seven rows:

(1) $(B \rightarrow T \rightarrow B)$

(2) $E \rightarrow L \rightarrow I \rightarrow O \rightarrow (T \rightarrow B \rightarrow T)$

(3) $I \rightarrow O \rightarrow (T \rightarrow B \rightarrow T)$

(4) $L \rightarrow I \rightarrow O \rightarrow (T \rightarrow B \rightarrow T)$

(5) $O \rightarrow (T \rightarrow B \rightarrow T)$

(6) $(T \rightarrow B \rightarrow T)$

(7) $U \rightarrow (B \rightarrow T \rightarrow B)$

These results show that, no matter what variable is to be predicted, the resulting sequence of best-predictor variables always terminates with the associated variables (B) and (T). A similar analysis may be based on the second-best predictors, and the results show that the set (I), (E), and (O) are associated variables. Together, these analyses suggest that low voltage on discharge (B) and short or open circuits (T) is the best set of associated predictors for the entire set of failure characteristics. After the effects of these variables are taken into account, the next best set of associated predictors consists of blistering on positive plates (I), separator impregnated with negative plate material (E), and ceramic shorts (O).

It should be reemphasized that these findings are given merely to exemplify one recent computer-based method of deducing empirical associations. Several other methods are available, including an extension of the trigram method.(3) Having detected associations by any of these methods, it remains for the statistician to assess the statistical significance of the association and it remains for the physical chemist to assess the physical meaning of these associations.

Summary of AID Trees

The seven AID trees used in the search for association are described in more detail in this section. Only the statistically significant portion of each tree is presented. A few observations then are made concerning some characteristics of each tree. In general, the terminal nodes are examined to determine which nodes are associated with high or low ratios.

Figure 2 shows the AID tree obtained for predicting the presence of failure characteristic (B), low voltage on discharge, for the Crane data on 377 failed cells. Figure 2 is the same as Figure 1, except that the percentages corresponding to the ratios are also given but the F-ratios for splits are not given. In each node, the upper number gives the percentage of the cells that show low voltage on discharge and the lower numbers give the ratio of the number of cells that show low voltage on discharge to the total number of cells in the group. The top of the tree shows, for example, that B was present in approximately 74 percent of the 377 cells. The total number of cells having (B) present is shown by the numerator as 280. The best variable for predicting the presence or absence of (B) is seen to be (T), short or open circuit. Among the 275 cells for which (T) is absent, 230 of these, or 84 percent, have (B) present, as shown by the left node of the split on (T). The right node shows that, when (T) is present, 49 percent of the cells have low voltage on discharge. The next split on Failure Characteristic (I), blistering on positive plates, shows that, if (I) is present (right node) and (T) is absent, then the observed frequency is 99 percent and the cell will have low voltage on discharge. Similarly, the next split on Failure Characteristic (U), high voltage on charge, shows that, if (U) is present, (I) is absent, and (T) is absent, then 97 percent of the 39 cells in this classification have low voltage on discharge. Finally, the split on failure characteristic (O), ceramic short, shows that, if (O) is present, (U) is absent, (I) is absent, and (T) is absent, then 96 percent of the 23 cells in this classification have low voltage on discharge.

It may be noted that the "terminal" nodes of the tree are composed of five groups having 98, 22, 38, 72, and 50 cells with low voltage on discharge. The total of these numbers is 280, as shown in the initial node. Thus, the tree classifies the 280 cells having low-discharge voltages into five groups of cells. Three of these groups show high frequencies for the presence of (B), namely, 96, 97, and 99 percent, and these three groups account for a total of 22 + 38 + 72 = 132 cells out of the 280 cells in the initial group having (B) present. This shows that low voltage on discharge can be correctly predicted with an observed frequency in excess of 95 percent for 47 percent of the cells having a low voltage on discharge.

Figure 3 shows the AID tree obtained for predicting the presence of failure characteristic (E), separator impregnated with negative plate material. This figure shows that 40 cells out of the total of 377 showed this characteristic. Further, if (L) is present (high pressure, bulge, convex sides), then only 6 of 121 cells have the separator impregnated with negative plate material. If, in addition, (O), ceramic short is present, then only 44 cells are involved, and only two of these had the separator impregnated with negative material. Thus, for this AID tree it is seen that, if

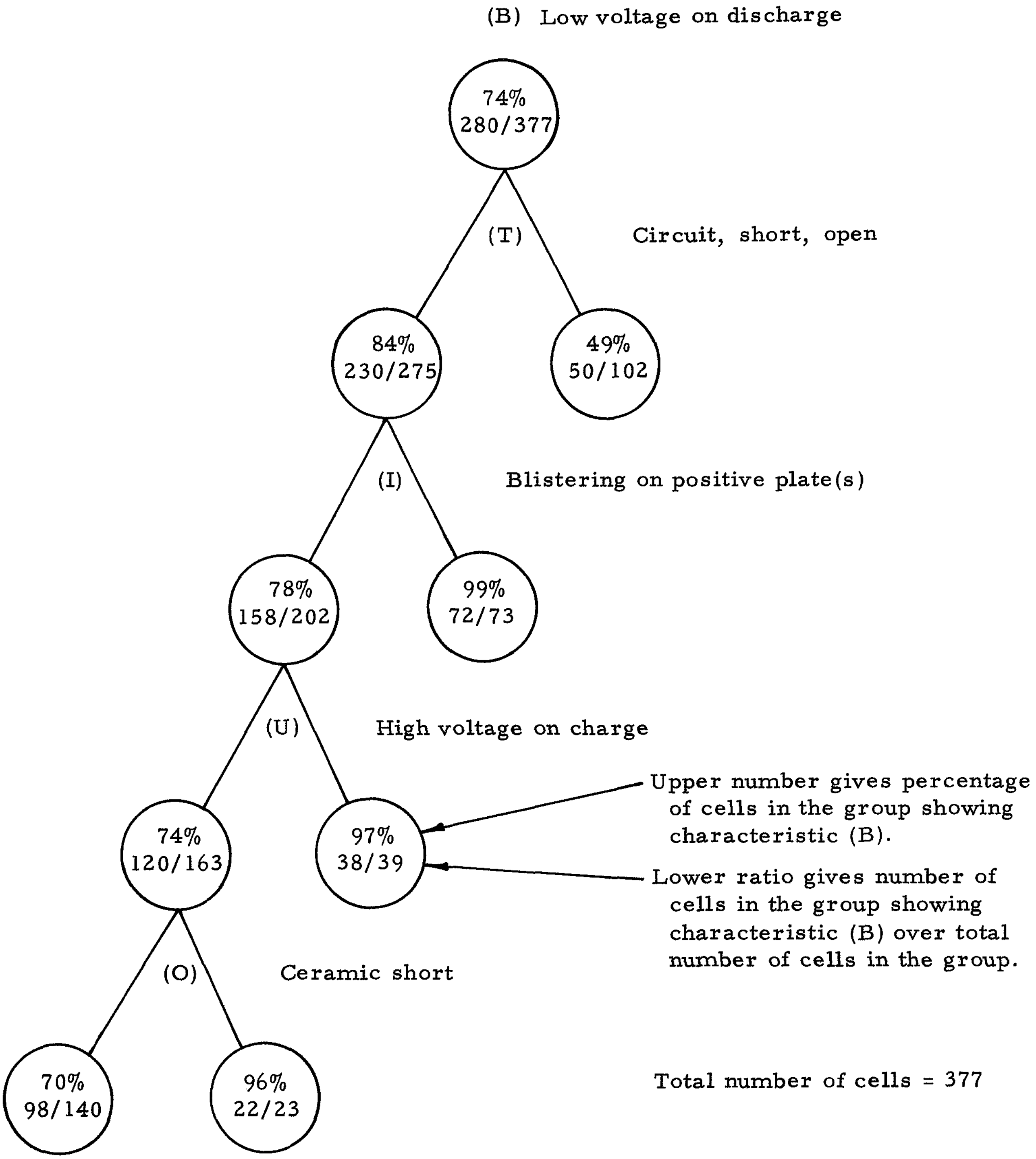


FIGURE 2. AID TREE FOR PREDICTING LOW VOLTAGE ON DISCHARGE

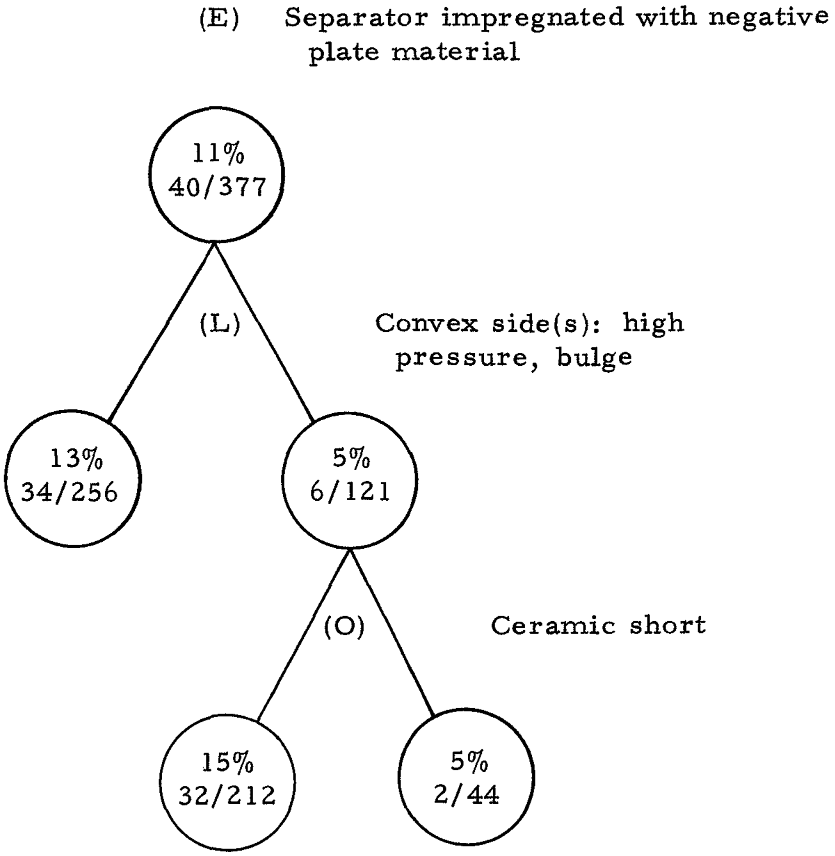


FIGURE 3. AID TREE FOR PREDICTING SEPARATOR IMPREGNATED WITH NEGATIVE PLATE MATERIAL

high pressure, bulge, or convex sides are present, it would be predicted that the cell would not have separators impregnated with negative plate material.

Figure 4 shows the AID tree for predicting failure characteristic (I), blistering on positive plates. Two nodes are of special interest in this tree. The first of these occurs at the bottom of the tree and corresponds to the left node of the split using (T), circuit short or open. This group of 35 cells may be characterized as follows:

(T) absent (no open or short circuit)

(B) absent (no low voltage on discharge)

(L) absent (no high pressure, bulge, or convex sides)

(O) absent (no ceramic shorts).

Among these 35 cells, not one occurred which showed blistering on the positive plates.

The split on (E), separator impregnated with negative plate material, shows that five cells had the following characteristics:

(E) present (separator was impregnated with negative plate material)

(O) present (ceramic short).

Every one of the five cells having (E) and (O) present also showed blistering on positive plates.

Figure 5 shows the AID tree for predicting high pressure, bulge, or convex sides. The most extreme frequency is associated with 12 cells characterized as follows:

(U) present (high voltage on charge)

(T) present (circuit short or open)

(E) absent (separator not impregnated with negative plate material)

(I) absent (no blistering on positive plates).

Among these 12 cells, there was no cell that showed high pressure, bulge, or convex sides.

Figure 6 shows the AID tree for predicting ceramic shorts. One terminal node with low percentage involves 21 cells having the following characteristics:

(E) present (separator impregnated with negative plate material)

(B) present (low voltage on discharge)

(I) absent (no blistering on positive plates)

(T) absent (no short or open circuit).

Among these 21 cells, there was no cell having a ceramic short. Other terminal nodes with low percentages are seen to include those given by (B) absent, (I) absent, and (T) absent, and by (E) absent, (U) present, (I) present, and (T) absent.

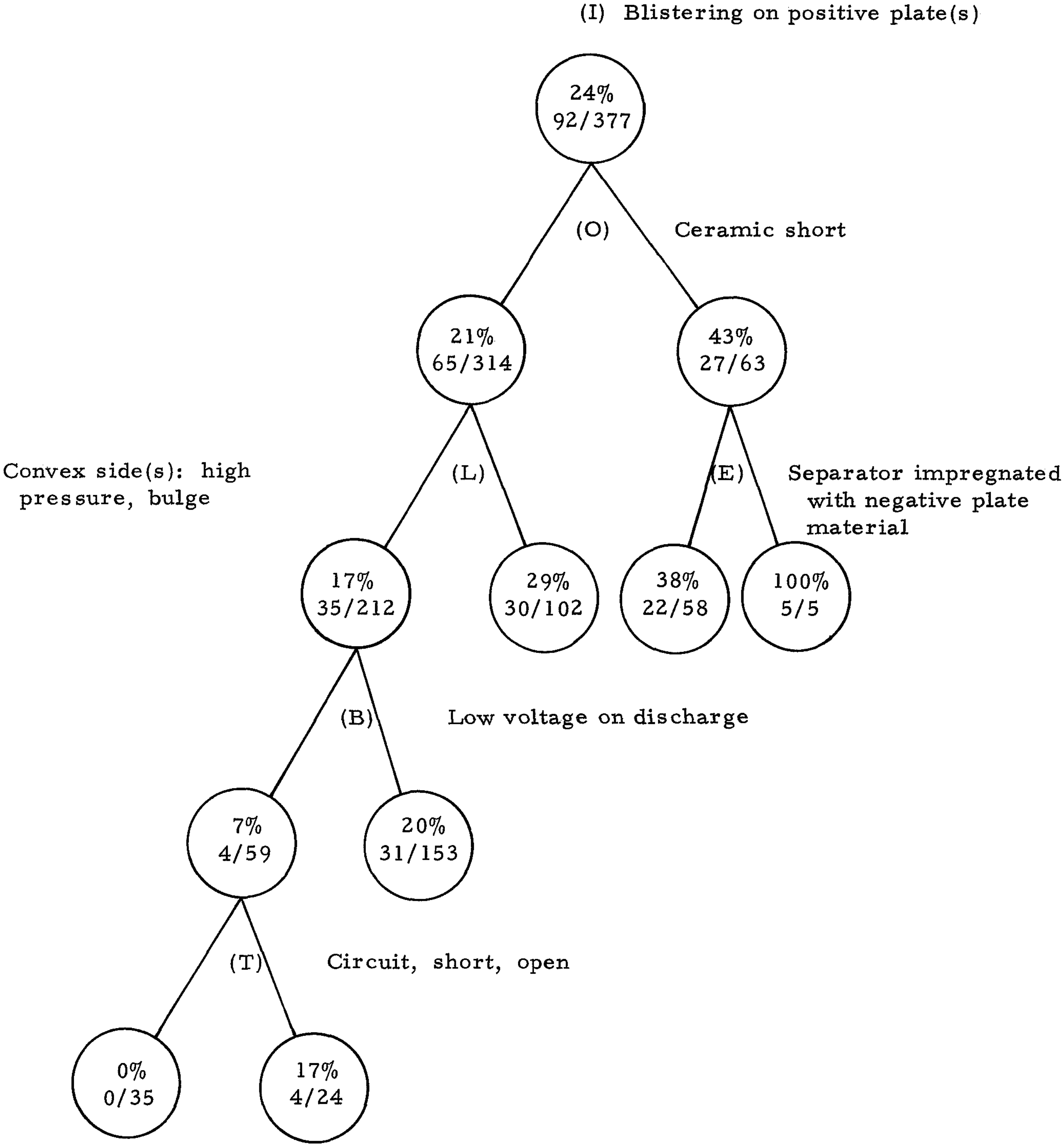


FIGURE 4. AID TREE FOR PREDICTING BLISTERING ON POSITIVE PLATES

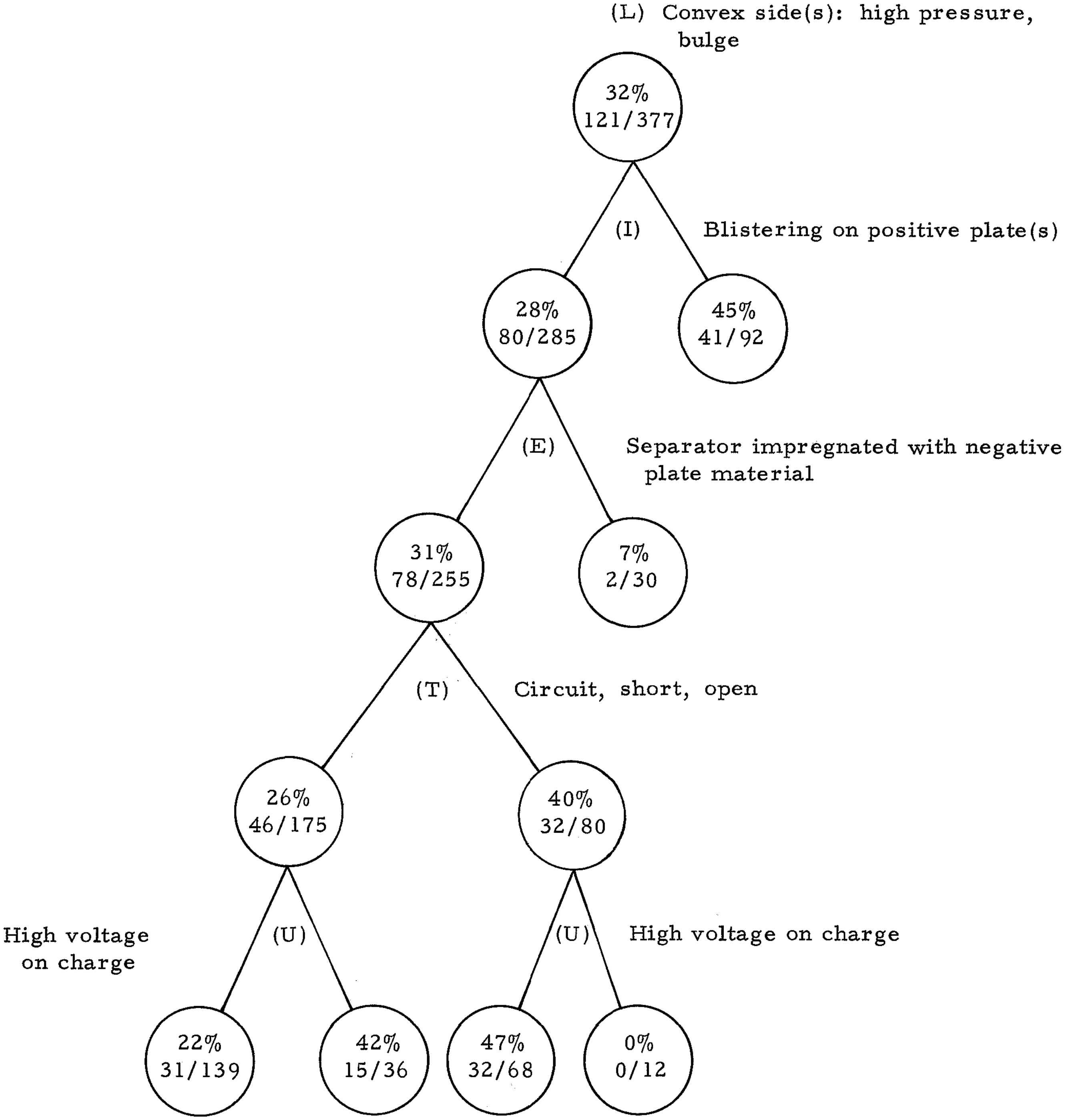


FIGURE 5. AID TREE FOR PREDICTING HIGH PRESSURE, BULGE, OR CONVEX SIDES

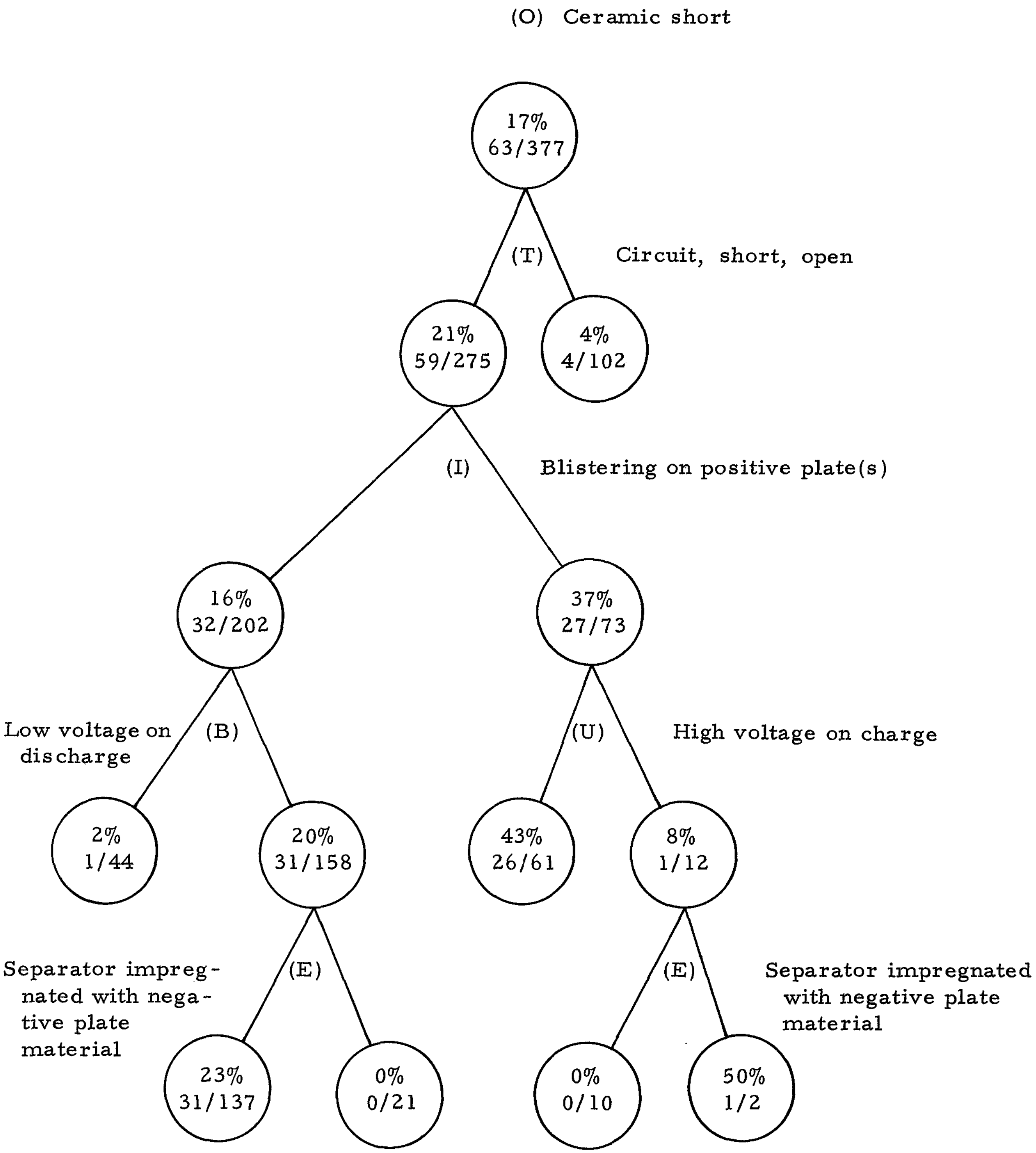


FIGURE 6. AID TREE FOR PREDICTING CERAMIC SHORTS

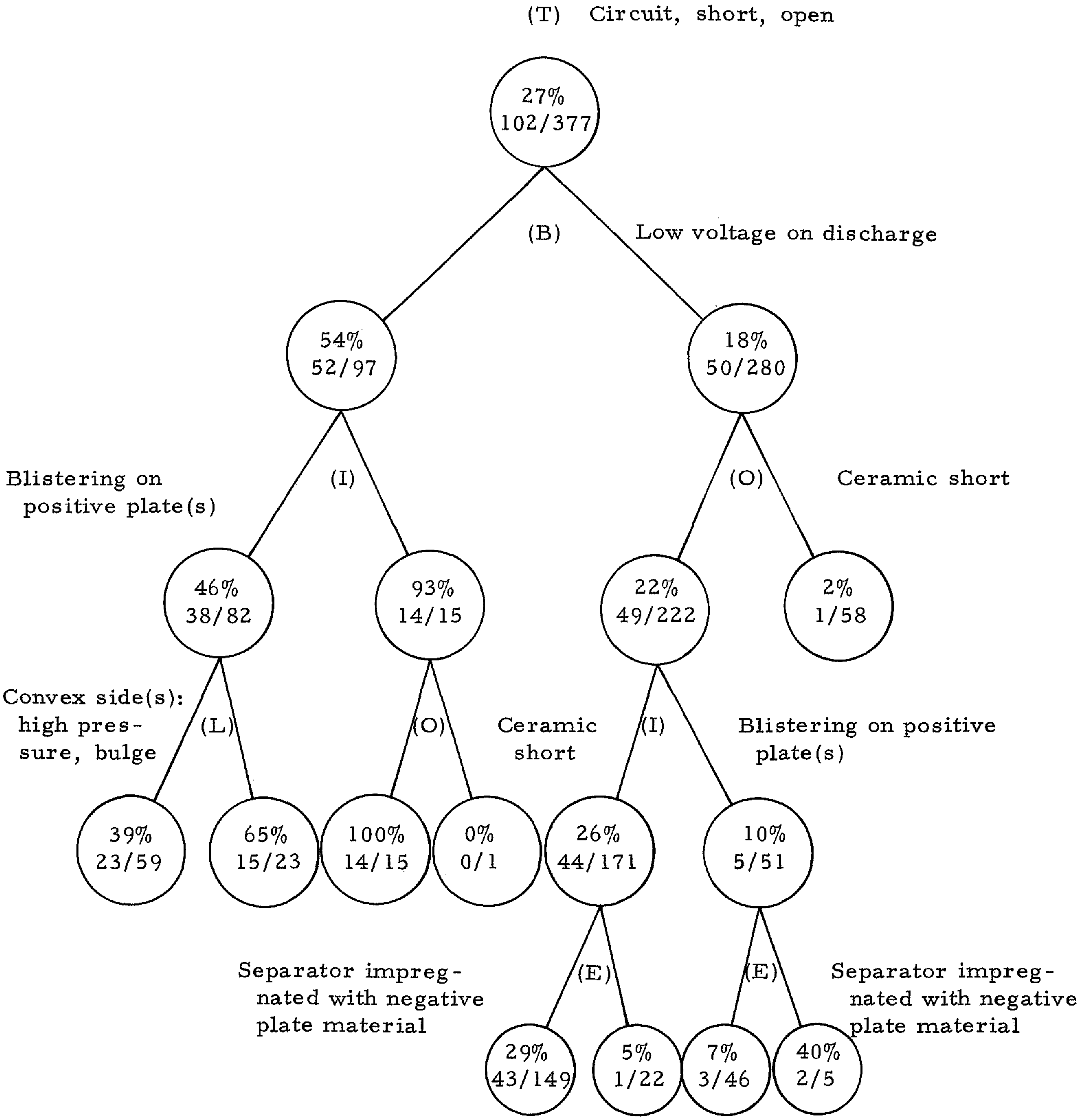


FIGURE 7. AID TREE FOR PREDICTING SHORT OR OPEN CIRCUITS

Figure 7 shows the AID tree for predicting short or open circuits. The tree shows one perfect split on characteristic (O), ceramic short, into 100 and 0 (zero) percentage nodes. After splitting on (B), (I), and (O), a set of 14 cells is defined by the following characteristics:

(O) absent (no ceramic short)

(I) present (blistering on positive plates)

(B) absent (no low voltage on discharge).

For these 14 cells, every one showed an open or short circuit. The other group formed by this split consisted of a single cell which showed a ceramic short, blistering on the positive plates, and no low voltage on discharge.

Figure 8 shows the AID tree for predicting high voltage on charge. Only one failure characteristic yielded a split having a statistically significant F-ratio. This characteristic is low voltage on discharge. The tree shows that only 2 percent of the cells that had high voltage on charge also had low voltage on discharge.

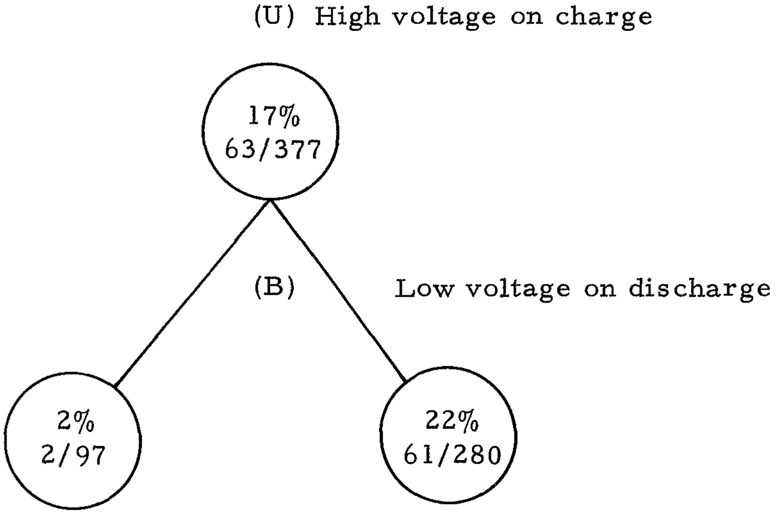


FIGURE 8. AID TREE FOR PREDICTING HIGH VOLTAGE ON CHARGE

In summary, it should be noted that the classifications yielded by the AID trees are generated by a computer. No "understanding" of the nature of the variables is required. It should not be surprising if some of the classifications have an evident physical meaning. It would be hoped that the classifications yielded by the computer program would suggest additional classifications that may be overlooked because of the large number of possible combinations of the variables. A simple calculation shows that, for the 21 variables listed in Table 1, a total of over 2 million distinct combinations of failure characteristics is possible. A large portion of these combinations is actually evaluated by the computer program. This is one of the remarkable characteristics of computer-based empirical methods such as AID.

The Search for Embedded Statistical Designs

An empirical analysis of data aims to detect structure in the data. The preceding examples show how the AID program gives rise to tree structures. It is sometimes possible to find standard statistical designs embedded in empirically detected structures. Such statistical designs include both factorial and hierarchial designs. Consider, for example, the AID tree shown in Figure 5 for predicting high pressure, bulge, and convex sides. The subtree associated with the variables (T) and (U) can be analyzed as a 2 x 2 factorial experiment. This results from the fact that (T) occurs at two levels (present or absent) and (U) occurs at two levels for each level of (T). This symmetrical kind of split does not usually occur. For example, in the left branch of Figure 7, variable (L) is used to split the low level of (I) and a different variable, (O), is used to split the high level of (I).

The search for such embedded designs is desirable because, when such designs are found, it then is possible to assess the statistical significance of the structure using standard statistical methods. In Figure 5, for example, suppose that the number of cells having high pressures, bulges, or convex sides are analyzed using Yates' method.$^{(5)}$ The data for this analysis may be obtained directly from the four bottom nodes in the AID tree:

(T, U)	N	(1)	(2)	Main Effects, Interactions
(0, 0)	31	15 + 31 = 46	32 + 46 = 78	78/4 = 19.5
(0, 1)	15	0 + 32 = 32	-32 - 16 = -48	-48/2 = -24
(1, 0)	32	15 - 31 = -16	32 - 46 = -14	-14/2 = -7
(1, 1)	0	0 - 32 = -32	-32 + 16 = -16	-16/2 = -8

The coordinates in the left-hand column show the combinations of levels associated with (T) and (U). The coordinates (0, 0), for example, indicate that both (T) and (U) are absent; (0, 1) indicates that (T) is absent and (U) is present, etc. The column labeled N gives the number of cells found to be associated with the corresponding treatment combination. Columns labeled (1) and (2) show the additions and subtractions made using the numbers in the preceding column to obtain the main effects and interactions given in the last column. In brief, the interpretation of the last column is as follows:

(1) The first entry simply shows that the average number of cells involved in the four treatment combinations is 19.5.

(2) The second entry shows that the main effect of U is equal to -24. This means that the average number of cells showing high pressure, bulge, or convex sides is decreased by 24 when high voltage on charge is present relative to those cells in which high voltage on charge is absent.

(3) The third entry shows that the main effect of (T) is equal to -7. This means that the average number of cells showing high pressure, bulge, or convex sides is decreased by 7 when short or open circuits are present relative to those cells when short or open circuits are absent.

(4) The fourth entry shows that the interaction between (T) and (U) is equal to -8. Because this interaction is not 0 (zero), it means that the effect of (U) depends on whether or not (T) is present and vice versa. That is, the effect of open or short circuits on the number of cells showing high pressure, bulges, or convex sides depends on whether high voltage on charge is present or absent.

This example serves to suggest the manner in which embedded statistical designs can be identified and analyzed in a standard statistical manner.

Assessing the Statistical Significance of the AID Tree

Because of the sequential manner in which the AID tree is developed, a theory does not exist on how to obtain an overall, or global, assessment of the statistical significance of a particular AID tree. As examples, statisticians would like to know - if a similar set of cells were tested and analyzed using the AID program, would the same tree structure be obtained? Would the same sequence of variables be identified as good predictors?

A statistical assessment of each individual split in an AID tree can be made using an analysis of variance. This analysis yields an F-ratio whose statistical significance can be judged. The entire tree then represents a set of F-ratios with one F-ratio for each split. However, an accepted method for combining the various "local" F-ratios to form a single "global" F-ratio is not available. As an approximation to obtaining a statistically significant AID tree, it is possible to apply an analysis of variance to each split in the AID tree and retain the split in subtrees only if the F-ratio is statistically significant. This procedure was followed in obtaining the preceding examples of AID trees.

At a global level, an approximate statistical assessment can be made in terms of the terminal nodes of a particular AID tree. For example, consider the AID tree for predicting high pressure, bulge, or convex sides in Figure 5. A standard analysis-of-variance table for the terminal nodes for this tree is shown as follows:

ANALYSIS OF VARIANCE

Source	Sum of Squared Deviations	Degrees of Freedom	Mean Square	F-Ratio
Between terminal nodes	7.78	5	1.556	7.78
Within terminal nodes	74.38	371	0.200	--
Total	82.16	376	--	--

The F-ratio of 7.78 is statistically significant at the 5 percent level of significance. Thus, the AID tree associated with this analysis would be expected to be obtained again if a similar set of data were analyzed.

Analytic Formulations

Because of the importance of tree structures in empirical analyses, it becomes desirable to express a tree in algebraic form so that the equation of the tree then may be examined for algebraic structure. This analysis, in turn, may aid in understanding the physical mechanisms involved in the tree structure.

To show that such a procedure is possible, the following equation may be verified for the percentages given in the terminal nodes of the AID tree for predicting high pressure, bulge, or convex sides:

$$P = (22)\,(1-U)\,(1-T)\,(1-E)\,(1-I)/2^4 + (42)\,(1+U)\,(1-T)\,(1-E)\,(1-I)/2^4$$

$$+ (47)\,(1-U)\,(1+T)\,(1-E)\,(1-I)/2^4 + (7)\,(1+E)\,(1-I)/2^2 + (45)\,(1+I)/2 \quad ,$$

where P denotes the percentage of the cells showing high pressure, bulge, or convex sides in each terminal node. The variables (U), (T), (E), and (I) are set equal to 1 or -1, accordingly, as the associated failure characteristic is present or absent. For example, if (U), (T), (E), and (I) are all absent, then $U = T = + = I = -1$ and all terms except the first are equal to 0 (zero), so that

$$P = (22)\,(2)\,(2)\,(2)\,(2)/2^4 = 22 \quad ,$$

as shown in the lower left-hand node in Figure 5. The remaining percentages in Figure 5 may be calculated similarly from the above equation. The percentages are seen to occur as coefficients in the algebraic formulation.

This example shows that the AID tree can be mathematically represented in a form analogous to regression equations. However, in contrast to regression, the assumptions associated with an AID tree are minimal. Moreover, the algebraic structure is more suitable for physical interpretation than is the diagrammatic structure associated with an AID tree.

SUMMARY OF EMPIRICAL APPROACH

The preceding examples show that empirical methods are capable of extracting a considerable amount of data structure with the single prior assumption that the data can be identified. The generality of the AID-tree structure is particularly attractive as an empirical tool to be used in the analysis of accelerated-test data. Considerable information may be obtained from direct examination of such trees to determine the relative importance of predictive variables and the effects of various conditions along different branches of the tree. Still more information may be obtained by making computations related to statistical reliability estimates, F-ratios, and embedded statistical designs. The algebraic expression of the tree gives still further insight into the mathematical relations among the variables. All of these observations show that empirical methods form a potentially powerful approach to data monitoring and analysis. The difficulties associated with the empirical approach stem largely from a lack of computer software.

Table 2 gives a summary of the data requirements for the empirical approach to the accelerated testing of rechargeable cells. The table shows that the empirical approach requires full identification of the cells to be put on test, together with all data obtained from preliminary examinations, acceptance tests, and/or screening tests. Such data may be found to be highly correlated with observed cell behavior during the accelerated test. To provide adequate data for an empirical analysis, it is recommended that cell-voltage measurements be taken every 2 minutes within each charge/discharge cycle, with an additional requirement that at least 12 cell-voltage measurements be obtained in each cycle.

TABLE 2. DATA REQUIREMENTS FOR AN EMPIRICAL APPROACH TO AN IDEAL ACCELERATED TESTING PROGRAM FOR RECHARGEABLE CELLS

Data Requirements	Use of the Data
Full identification of cells to be put on test, including manufacturer type, size, lot number, plate formation data, previous history, etc.	This requirement may permit the association of the pretest experience with observed behavior of the cell during the test.
Preliminary examination data, including results of acceptance testing, screening tests, tear-down tests, etc.	To permit the possible association of the initial condition of the cell with observed behavior of the cell during the test.
Twelve cell-voltage measurements should be taken within each charge/discharge cycle, or measurements should be taken at 2-minute intervals, whichever yields more data.	Empirical methods such as the AID program described in this report would be applied to analyze the data and relate degradation of quality to stress level, initial condition, and pretest experience of the cell.

Because of the extensive data-analysis requirements of the empirical approach, an off-line computer system is required. In addition, some on-line computer capability is required for minimal processing, including the "tagging" of certain output data for more efficient off-line data processing. In an ideal test program, an on-line computer capability of 16,000 words is recommended.

A STATISTICAL APPROACH TO THE ANALYSIS OF ACCELERATED-TEST DATA

by

Ralph E. Thomas

INTRODUCTION

A response-surface analysis is developed in this section as a method that exemplifies a statistical approach to the analysis of accelerated-test data. The response surface was selected because it appears to be well suited making a transition between an empirical approach and a statistical approach. In the empirical approach, the response surface is fitted exactly to the observed data so that no "smoothing" or averaging of data is involved. Typically, the statistician objects to the exact fitting of a response surface, because the surface in such a case is fitted to the combined signal and noise components of the data. The statistician prefers to assess the magnitude of the noise component of the data and then fit a smoothed response surface. In this case, the surface does not, in general, pass through the data points. Instead, the surface forces "near" the data points with a miss distance that is associated with the noise component or experimental error. To illustrate the selected method, the following paragraphs give an example in which both an exact fit (empirical) and a smoothed fit (statistical) are given for the same set of data. In addition, the coefficients attained by this approach may be plotted as functions of time. The resulting response surface then "moves" and allows predictions to be made of future positions of the surface. In turn, these predictions can be interpreted in terms of predicted future behavior of the cells on test. For these reasons, the selected approach is called a "dynamic response surface" approach to the analysis of accelerated-test data. The principal characteristics of this approach are summarized next.

A DYNAMIC-RESPONSE SURFACE APPROACH FOR THE ANALYSIS OF ACCELERATED-TEST DATA

In this section of the report, a response-surface approach is described that has the following properties:

(1) Measurements of cell quality are expressed as surface functions of the remaining variables at given instants of time.

(2) These surface functions may be constructed so that the resulting equations fit the measured values exactly, with the result that empirical analysis is not hampered by smoothing of the data.

(3) The same approach may be used to smooth the data and obtain results that are consistent with current statistical methods of analysis.

(4) The coefficients of the fitted equations may be studied to determine their behavior over time and thereby aid in predictions of future cell characteristics.

(5) The magnitudes of the coefficients, their associated time rates of change, and their relationships to various subsets of the variables may suggest physical mechanisms that are associated with degradations over time of the quality surface.

In brief, the technical approach involves the fitting of orthogonal polynomials to the data. Such an approach is described in References (6), (7), and (8). In order to extend the customary approach to the context of accelerated testing, the mathematical method is described below. For purposes of exposition, data published by Albrecht(9) are used as a basis for developing the method. The extensions of the method to the case of measurement tables at successive times then are described briefly.

Albrecht's Data: A Statistical Description

Table 3 shows a portion of Albrecht's data. The table gives the values of amp-hr efficiency, in percent, for various "treatment combinations" of temperature (room or -20 F), charging rate (7 or 14 ma), charge duration (3, 7, or 10 days), and manufacturer (coded as 2, 3, or 5). The reader is referred to Albrecht's paper for a thorough discussion of these results. In the present development, these data are simply used as a convenient basis for illustrating the response-surface method of approach to data analysis.

TABLE 3. AVERAGE AMPERE-HOUR EFFICIENCY OF NICKEL-CADMIUM BATTERIES(a)

Manufacturer:		2 (-1)(b)				3 (0)				5 (1)			
Temperature:		-20 F (-1)		RT (1)		-20 F (-1)		RT (1)		-20 F (-1)		RT (1)	
Current, ma:		7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)
Charging	3 (-1)	95.9	97.6	67.8	81.4	98.0	93.3	113.3	84.9	99.4	116.0	43.4	76.1
Duration,	7 (0)	96.5	96.6	77.8	77.9	96.7	98.4	87.3	91.2	100.0	88.3	85.0	84.8
days:	10 (1)	102.4	98.9	76.5	67.5	104.7	100.4	75.1	76.9	83.9	90.7	68.6	71.7

(a) Data obtained from Tables IV and V of Albrecht, F., Reference (9).

(b) Numbers in parentheses denote coded values.

In standard statistical terminology, Table 3 shows results for an experiment involving four "factors". The temperature factor has two "levels" corresponding to -20 F and room temperature; the charge-duration factor has three levels corresponding to 3, 7, and 10 days; the charging rate has two levels corresponding to 7 or 14 ma of current and manufacturer has three levels corresponding to respective supplier. Statistically, these data represent the results of a 3x2x2x3 factorial experiment having 36 "treatment combinations", as shown by the 36 numbers given in Table 3. The objective of the following paragraphs consists of fitting a particular five-dimensional response surface to these data.

A Local Response Curve

Consider the results associated with Manufacturer 2, a temperature of -20 F, and a charging current of 7 ma. The amp-hr efficiencies are given by 95.9, 96.5, and 102.4 percent and correspond to charge durations of 3, 7, and 10 days, respectively. For simplicity, the charge durations are coded as -1, 0, 1, as shown by the numbers in parentheses in Table 3. This coding requires that the three charge durations be equally spaced, so that the coding strictly requires a charging duration of 6.5 days instead of 7 days. This discrepancy is not important, however, for the development of the following procedure.

The response surface will be developed in several steps. In the first step, a quadratic equation is fitted to the results shown below:

Charge Duration, days	Coded Value	Amp-Hr Efficiency, percent
3	-1	95.9
7	0	96.5
10	1	102.4

Three columns are appended to these results as follows:

Charge Duration, days	Coded Charge Duration, x_1	Amp-hr Efficiency, y	$P_0(x_1)$ 1	$P_1(x_1)$ x_1	$P_2(x_1)$ $3x_1^2-2$
3	-1	95.9	1	-1	1
7	0	96.5	1	0	-2
10	1	102.4	1	1	1

The three columns on the right give the values of the three polynomials $P_0(x_1) = 1$, $P_1(x_1) = x_1$, and $P_2(x_1) = 3x_1^2-2$ at the coded values of x. For example, the numbers in the last column are obtained by evaluating $P_2(x_1) = 3x_1^2-2$ at x_1 values of -1, 0, and 1. It is also seen that these columns are mutually orthogonal. For example, the last two columns show that (-1) (1) + (0) (-2) + (1) (1) = 0. A similar result holds for any pair of the last three columns. As shown later, this orthogonality property is of special importance in statistical analysis of the data.

By means of the four columns on the right of the preceding tabulation, the following determinant is then formed and set equal to zero:

$$\begin{array}{|cccc|} y & 1 & x_1 & (3x_1^2-2) \\ \hline 95.9 & 1 & -1 & 1 \\ 96.5 & 1 & 0 & -2 \\ 102.4 & 1 & 1 & 1 \end{array} = 0.$$

An expansion of this determinant gives a quadratic equation that is desired for relating amp-hr efficiency, y, to duration of charge, x_1. The expansion yields

$$6y - 589.6 - 19.5x_1 - 5.3(3x_1^2-2) = 0$$

so that

$$y(x_1) = 98.27 + 3.25x_1 + 0.88(3x_1^2-2)$$

is the desired equation. Substitution of $x_1 = -1, 0, 1$ into this equation yields $y(-1) = 95.9$, $y(0) = 96.5$, and $y(1) = 102.4$, so that the equation gives an exact fit to the original data points.

Interpretation of the Coefficients

The coefficients of the quadratic equation obtained above may be interpreted as follows:

(1) The constant term, 98.27, is the average amp-hr efficiency over all three temperatures; i.e., $98.27 = (95.9 + 96.5 + 102.4)/3$.

(2) The change in amp-hr efficiency between charging durations of 7 days and 3 days is given as $96.5 - 95.9 = 0.6$. Similarly, the change in amp-hr efficiency between the charging durations of 7 days and 10 days is given as $102.4 - 96.5 = 5.9$. The average of these two changes is given as $(0.6 + 5.9)/2 = 3.25$. This is seen to be the coefficient of x in the fitted equation. For this reason, the coefficient may be associated with the average "linear effect" of charging duration on amp-hr efficiency.

(3) The coefficient of the x-squared term, 0.88, may be associated with the "quadratic effect" of charging time on amp-hr efficiency.

These meanings of the coefficients will be retained in the extended surface-fitting procedures that follow.

An application of the same procedure to the second column of Table 3 yields a second response curve that relates amp-hr efficiency to charging duration for the same Manufacturer 2 at -20 F with a charging current of 14 ma. The determinant is easily written down by inspection:

$$\begin{array}{cccc} \underline{y} & \underline{1} & \underline{x_1} & \underline{(3x_1^2-2)} \\ \end{array}$$
$$\left|\begin{array}{cccc} 97.6 & 1 & -1 & 1 \\ 96.6 & 1 & 0 & -2 \\ 98.9 & 1 & 1 & 1 \end{array}\right| = 0.$$

An expansion of this determinant yields the following equation:

$$y(x_1) = 97.70 + 0.65x_1 + 0.55(3x_1^2-2) \quad .$$

This equation gives a second relation between amp-hr efficiency and charging duration. The relation differs from that obtained previously by the fact that the associated data were taken at a charging rate of 14 instead of 7 ma. The differences in the corresponding coefficients of the two equations thus may be associated with the difference in charging current. To obtain a quantitative expression that brings charging current into the equation, it is necessary to combine these two response curves into a response surface. This is done in the next section. First, note that each of these equations simply replaces three measured values with three coefficients. In the above example, the measured amp-hr efficiencies, 97.6, 96.6, and 98.9, are replaced by the coefficients 97.7, 0.65, and 0.55. The value of these replacements lies in the fact that the coefficients have physical interpretations given by the average amp-hr efficiency, the linear effect of charging duration of amp-hr efficiency, and the nonlinear (quadratic) effect of charging duration on amp-hr efficiency. Because the fit is exact, no information is lost in transforming the measured values into the coefficients. Because no "smoothing" takes place, an empirical analysis is not hindered. On the other hand, if smoothing is desired, it is easily accomplished as shown in a later section.

Table 4 shows a listing of the coefficients obtained for each column of data appearing in Table 3. The first three columns of Table 4 give the coded values that correspond to those given in parentheses in Table 3. Columns 4, 5, and 6 give the coefficients A, B, and C of a response equation,

$$y(x_1) = A + Bx_1 + C(3x_1^2 - 2) \quad ,$$

for each of the 12 rows. In the next section, these equations will be further combined to represent the effects of charging current, temperature, and manufacturer.

Extending Response Curves to Response Surfaces

For the first two columns of Table 3, the following equations have been obtained:

$$y(x_1) = 98.27 + 3.25x_1 + 0.88(3x_1^2 - 2)$$

and

$$y(x_1) = 97.70 + 0.65x_1 + 0.55(3x_1^2 - 2) \quad .$$

These two equations give exact fits to Albrecht's data for Manufacturer 2 and a temperature of -20 F. The first equation relates amp-hr efficiency to charging duration at 7 ma; the second equation relates amp-hr efficiency to charging duration at 14 ma. These two equations now will be combined into a single equation that expresses amp-hr efficiency, y, as a function of both charging duration, x_1, and charging rate, x_2.

To begin, note that the matrix of coefficients appended to the data to obtain the above equations is given by

$$M_3 = \begin{array}{c} \\ \\ \\ \end{array}\begin{array}{ccc} \underline{P_0(x)} & \underline{P_1(x)} & \underline{P_2(x)} \\ \end{array}$$

$$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix}$$

where $P_0(x) = 1$, $P_1(x) = x$, and $P_2(x) = 3x^2-2$. This matrix of coefficients is a standard matrix and may be used for any factor that has three levels. In the previous cases, for example, charging duration had three levels with coded values of -1, 0, 1 corresponding to 3, 7, and 10 days. Because the order of the matrix must equal the number of levels of the factor being analyzed, it is necessary to have a 2x2 matrix for a factor with two levels, a 3x3 matrix for a factor with three levels, etc.

Table 5 shows the basic matrices for the orthogonal polynomials used in this development for factors having two through five levels. More extensive tables of such matrices may be found in several references.(10, 11)

As shown in Table 5, the matrix associated with a factor having two levels is given by

$$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$$

Because the charging current has two levels, 7 and 14 ma, this matrix is to be associated with the analysis of charging current. In order to generate an equation that accounts for both charging duration and charging current, it is necessary to combine the M_2 and M_3 matrix. Symbolically, the matrix, M, may be written as follows:

$$M = \begin{bmatrix} M_3 & -M_3 \\ M_3 & M_3 \end{bmatrix} ,$$

so that it has M_3 matrices as its elements and, further, that these M_3 matrices are multiplied by the corresponding elements of the M_2 matrix. Substitution of the numerical values yields

$$M = \left[\begin{array}{ccc:ccc} 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 0 & -2 & -1 & 0 & 2 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ \hdashline 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 0 & -2 & 1 & 0 & -2 \\ 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right] ,$$

TABLE 4. SUMMARY OF COEFFICIENTS FOR RESPONSE CURVES BASED ON CHARGING DURATION(a)

Experimental Conditions					
Mftr	Temp	ma	Average(b)	Linear Effect of Charging Duration(c)	Quadratic Effect of Charging Duration(d)
-1	-1	-1	98.27	3.25	0.88
-1	-1	1	97.70	0.65	0.55
-1	1	-1	74.03	4.35	-1.88
-1	1	1	75.60	-6.95	-1.15
0	-1	-1	99.80	3.35	1.55
0	-1	1	97.37	3.55	-0.52
0	1	-1	91.90	-19.10	2.30
0	1	1	84.33	-4.00	-3.43
1	-1	-1	94.43	-7.75	-2.78
1	-1	1	98.33	-12.65	5.02
1	1	-1	65.67	12.60	-9.67
1	1	1	77.53	-2.20	-3.63

(a) Based on data of Reference (9).
(b) Constant term in response equation.
(c) Coefficient of x_1 in response equation.
(d) Coefficient of $(3x_1^2 - 2)$ in response equation.

TABLE 5. BASIC MATRICES FOR GENERATION OF RESPONSE SURFACES

Number of Levels of a Specified Factor	Basic Matrix
2	$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$
3	$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix}$
4	$M_4 = \begin{bmatrix} 1 & -3 & 1 & -1 \\ 1 & -1 & -1 & 3 \\ 1 & 1 & -1 & -3 \\ 1 & 3 & 1 & 1 \end{bmatrix}$
5	$M_5 = \begin{bmatrix} 1 & -2 & 2 & -1 & 1 \\ 1 & -1 & -1 & 2 & -4 \\ 1 & 0 & -2 & 0 & 6 \\ 1 & 1 & -1 & -2 & -4 \\ 1 & 2 & 2 & 1 & 1 \end{bmatrix}$

and the determinant that yields the desired equation is the following:

$$
\begin{array}{c|cccccccc|l}
(x_2, x_1) & y(x_1, x_2) & 1 & x_1 & (3x_1^2-2) & x_2 & x_1x_2 & (3x_1^2-2)x_2 & \\
\hline
(-1,-1) & 95.9 & 1 & -1 & 1 & -1 & 1 & -1 & \\
(-1,0) & 96.5 & 1 & 0 & -2 & -1 & 0 & 2 & \\
(-1,1) & 102.4 & 1 & 1 & 1 & -1 & -1 & -1 & \\
(1,-1) & 97.6 & 1 & -1 & 1 & 1 & -1 & 1 & = 0. \\
(1,0) & 96.6 & 1 & 0 & -2 & 1 & 0 & -2 & \\
(1,1) & 98.9 & 1 & 1 & 1 & 1 & 1 & 1 &
\end{array}
$$

It is noted that charging rate x_2 has been coded so that $x_2 = -1$ when the charging rate is 7 ma and $x_2 = 1$ when the charging rate is 14 ma. The coded values corresponding to the treatment combinations are shown in the column at the left of the determinant. These correspond to the coded values shown in parentheses in Table 3. If the determinant is expanded using the elements of the first row, a polynomial of the following form will be obtained:

$$y(x_1, x_2) = A + Bx_1 + C(3x_1^2-2) + Dx_2 + Ex_1x_2 + F(3x_1^2-2)x_2$$

where A, B, C, D, E, and F are coefficients.

For Albrecht's data, the expansion of the above determinant yields

$$y(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2-2) - 0.28x_2 - 1.30x_1x_2 - 0.17(3x_1^2-2)x_2.$$

This equation gives the amp-hr efficiency $y(x_1, x_2)$ as a function of the coded values of charging duration x_1 and charging current x_2. Geometrically, the equation represents a response surface in three dimensions.

The interpretation of the coefficients obtained for this response surface is analogous to that given above for the previous response curves:

Coefficient	Interpretation
A	Average amp-hr efficiency
B	Linear effect of charging duration on amp-hr efficiency
C	Quadratic effect of charging duration on amp-hr efficiency
D	Linear effect of charging current on amp-hr efficiency
E	Linear-by-linear interaction between charging duration and charging current
F	Quadratic-by-linear interaction between charging duration and charging current.

More detailed assessments of the above kinds of coefficients may be found in statistical references.(12, 13, 14) For the present, it is sufficient to note that the procedure described gives an exact fit to the data. Thus, for example, if the preceding equation is evaluated at the point corresponding to a charging duration of 3 days and a charging current of 14 ma, then $x_1 = -1$, $x_2 = 1$, and the amp-hr efficiency is found to be given by $y(-1, 1) = 97.6$, as desired.

It should be emphasized that this calculation is made with the coded values shown in parentheses in Table 3. These coded values represent the coordinates of a point below the response surface. This kind of coding greatly simplifies the calculations. In the coding used in these examples, the lowest level of a factor is coded as -1 and the highest level is coded as +1. In this way, all points between -1 and 1 represent conditions within the range of the experimental conditions. The coded values of any condition within the extremes is obtainable by linear interpolation. For example, the coded value, x, corresponding to a specified level, z, of a factor that varies between z_{min} and z_{max}, is given by

$$x = -1 + 2\left(\frac{z - z_{min}}{z_{max} - z_{min}}\right) .$$

It is seen that, when $z = z_{min}$, coded value x is equal to -1 and, when $z = z_{max}$, the coded value is equal to +1. In the above example, the minimum and maximum values of charging duration are given by 3 and 10 days, respectively, so that

$$x_1 = -1 + 2\left(\frac{z_1 - 3}{10 - 3}\right) = (2z_1 - 13)/7 .$$

Similarly, the maximum and minimum values of charging current are 7 and 14 ma, so that

$$x_2 = -1 + 2\left(\frac{z_2 - 7}{14 - 7}\right) = (2z_2 - 21)/7 .$$

With these expressions, the coded values corresponding to 4 days and 12 ma are given by

$$x_1 = (8 - 13)/7 = -5/7$$

and

$$x_2 = (24 - 21)/7 = 3/7 .$$

An interpolated value for the amp-hr efficiency then may be obtained for these conditions by substitution in the response-surface equation:

$$\begin{aligned} y(-5/7,\ 3/7) &= 97.98 + 1.95(-5/7) + 0.72(3(-5.7)^2-2) \\ &- 0.28(3/7) - 1.30(-5/7)\,(3/7) \\ &- 0.17(3(5/7)^2-2)\,(3/7) = 96.56 . \end{aligned}$$

Similar interpolations may be made for other conditions of interest.

Extending the Response Surface to Higher Dimensions

As shown by the preceding development, three dimensions are required to represent data involving two factors (one dimension for each factor and one dimension for the dependent variable). In general, a space of (n + 1) dimensions is required for n factors. Thus, for all of the data shown in Table 3, a five-dimensional space is required. The algebraic development of the required response surface is simple and merely requires a continuation of the approach developed thus far. For example, to represent the data shown in Table 3, an orthogonal matrix of order 36 must be generated, because there are 36 numbers to be represented. The first factor is charge duration x_1 and, because this factor has three levels, the associated basic matrix is given by

$$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} .$$

The second factor is charging current x_2 at two levels, with an associated basic matrix given by

$$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} ,$$

the third factor is temperature x_3 at two levels, with a basic matrix given by

$$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} ,$$

and the fourth factor is manufacturer x_4 at three levels, with a basic matrix given by

$$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} .$$

These matrices are sequentially combined as follows. As before, a new matrix is formed from M_1 and M_2 to obtain an intermediate matrix, M**:

$$M^{**} = \begin{bmatrix} (1)M_3 & (-1)M_3 \\ (1)M_3 & (1)M_3 \end{bmatrix} .$$

In the same manner, the next matrix, M***, is expressed in terms of M** as follows:

$$M^{***} = \begin{bmatrix} (1)M^{**} & (-1)M^{**} \\ (1)M^{**} & (1)M^{**} \end{bmatrix} ,$$

and the final matrix is given by

$$M^{****} = \begin{bmatrix} (1)M^{***} & (-1)M^{***} & (1)M^{***} \\ (1)M^{***} & (0)M^{***} & (-2)M^{***} \\ (1)M^{***} & (1)M^{***} & (1)M^{***} \end{bmatrix} .$$

It is seen that the procedure may be described as follows: Suppose that a matrix, M, has been generated for the first n factors. Suppose that the next factor to be included in the representation has k levels, with a basic matrix denoted by M_k. Then, the next matrix required to represent the (n + 1) factor is obtained from M_k by replacing each element of M_k with the product of the matrix M and the original element of M_k.

In the present example, it is found that

$$M^{*}=M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} ,$$

so that, as before,

$$M^{**} = \left[\begin{array}{ccc|ccc} 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 0 & -2 & -1 & 0 & 2 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ \hline 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 0 & -2 & 1 & 0 & -2 \\ 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right]$$

and

$$M^{***} = \left[\begin{array}{cccccc|cccccc} 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 \\ 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 & 1 & 0 & -2 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 1 & 0 & -2 & 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 \\ 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 \\ \hline 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 0 & -2 & -1 & 0 & 2 & 1 & 0 & -2 & -1 & 0 & 2 \\ 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right] .$$

The matrix M*** is capable of generating an equation that accounts for the dependence of amp-hr efficiency on charging duration, charging current, and temperature. A separate equation is generated for each manufacturer. These three equations may then be combined by means of M****. However, because the arguments are analogous for an any of these representations, it is more convenient to consider M*** in more detail and simply present the results obtained for M****.

The determinantal equation that arises from M*** for Manufacturer 2 is given below:

$$\begin{array}{|ccccccccccccc|}
\underline{y} & \underline{1} & \underline{x_1} & \underline{(3x_1^2-2)} & \underline{x_2} & \underline{x_1x_2} & \underline{(3x_1^2-2)x_2} & \underline{x_3} & \underline{x_1x_3} & \underline{(3x_1^2-2)x_3} & \underline{x_2x_3} & \underline{x_1x_2x_3} & \underline{(3x_1^2-2)x_2x_3} \\
95.9 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 \\
96.5 & 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 & 1 & 0 & -2 \\
102.4 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 \\
97.6 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\
96.6 & 1 & 0 & -2 & 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 \\
98.9 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 \\
67.8 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
77.8 & 1 & 0 & -2 & -1 & 0 & 2 & 1 & 0 & -2 & -1 & 0 & 2 \\
76.5 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 \\
81.4 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 \\
77.9 & 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 \\
67.5 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1
\end{array} = 0.$$

The expansion of this expression yields the following equation:

$$\begin{aligned}
y(x_1, x_2, x_3) = 93.35 &- 4.05x_1 - 0.025(3x_1^2-2) - 2.50x_2 \\
&+ 3.825x_1x_2 - 1.95(3x_1^2-2)x_2 - 5.23x_3 - 7.50x_1x_3 \\
&- 5.42(3x_1^2-2)x_3 - 1.283x_2x_3 + 3.725x_1x_2x_3 \\
&- 0.917(3x_1^2-2)x_2x_3 \quad .
\end{aligned}$$

A similar equation may be obtained for the other two manufacturers.

Table 6 shows a listing of terms of the five-dimensional response surface that represents all of the data given in Table 3. Column 1 gives the conventional statistical labels associated with the various terms of the polynomial expansion. The second column gives the algebraic form of the terms appearing in the response equation, and the last column gives the computed coefficients of these terms. The computations were made with a FORTRAN program written to compute the response coefficients for as many as five factors with as many as five levels per factor.

TABLE 6. SUMMARY OF COEFFICIENTS FOR RESPONSE SURFACE BASED ON CHARGING DURATION, CHARGING CURRENT, TEMPERATURE, AND MANUFACTURER[(a)]

Effects and Interactions	Term	Coefficient
Average	1	87.91
Linear effects		
Charging duration, D	x_1	-2.08
Charging current, C	x_2	0.56
Temperature, T	x_3	-9.74
Manufacturer, M	x_4	-1.20
Linear-by-linear interactions		
DxC	x_1x_2	-1.53
DxT	x_1x_3	-0.48
DxM	x_1x_4	-1.41
CxT	x_2x_3	0.41
CxM	x_2x_4	1.85
TxM	x_3x_4	-0.40
Linear-by-linear-by-linear interactions		
DxCxT	$x_1x_2x_3$	-0.31
DxCxM	$x_1x_2x_4$	-0.73
DxTxM	$x_1x_3x_4$	4.66
CxTxM	$x_2x_3x_4$	0.73
Quadratic effects		
D^2	$(3x_1^2-2)$	-1.06
M^2	$(3x_4^2-2)$	-2.72
Quadratic-by-linear interactions		
D^2xC	$(3x_1^2-2)x_2$	0.54
D^2xT	$(3x_1^2-2)x_3$	-1.85
D^2xM	$(3x_1^2-2)x_4$	-1.18
DxM^2	$x_1(3x_4^2-2)$	0.99
CxM^2	$x_2(3x_4^2-2)$	1.53
TxM^2	$x_3(3x_4^2-2)$	-2.25
Quadratic-by-quadratic interaction		
D^2xM^2	$(3x_1^2-2)(3x_4^2-2)$	-0.52

TABLE 6. (Continued)

Effects and Interactions	Term	Coefficient
Linear-by-linear-by-quadratic interactions		
$DxCxM^2$	$x_1x_2(3x_4^2-2)$	-2.68
$DxTxM^2$	$x_1x_3(3x_4^2-2)$	3.51
$CxTxM^2$	$x_2x_3(3x_4^2-2)$	0.85
D^2xCxT	$(3x_1^2-2)x_2x_3$	-0.36
D^2xCxM	$(3x_1^2-2)x_2x_4$	1.68
D^2xTxM	$(3x_1^2-2)x_3x_4$	-1.38
Linear-by-linear-by-linear-by-linear interaction		
DxCxTxM	$x_1x_2x_3x_4$	-0.15
Linear-by-linear-by-linear-by-quadratic interactions		
$D^2xCxTxM$	$(3x_1^2-2)x_2x_3x_4$	-0.35
$DxCxTxM^2$	$x_1x_2x_3(3x_4^2-2)$	-2.02
Quadratic-by-quadratic-by-linear interactions		
D^2xCxM^2	$(3x_1^2-2)x_2(3x_4^2-2)$	1.24
D^2xTxM^2	$(3x_1^2-2)x_3(3x_4^2-2)$	-0.65
Quadratic-by-quadratic-by-linear-by-linear interaction		
$D^2xCxTxM^2$	$(3x_1^2-2)x_2x_3(3x_4^2-2)$	0.28

(a) Based on data of Reference (9).

Exploration of the Response Surface

Once a set of data has been represented by a response surface, a wide variety of questions can be answered by examining properties of the surface. The meaning of the answers will depend on the meaning of the data. For Albrecht's data, for example, it may be meaningful to interpolate within the range of the experimental conditions for charging duration, charging current, and temperature, because these variables are continuous. However, interpolation between manufacturers is not meaningful, because manufacturer is a discrete (nominal) variable. In general, interpolation of a given variable is expected to be meaningful if the variable is continuous; it is not expected to be meaningful if the variable is discrete.

Most properties of surfaces can be extracted from their equations by locating maxima and minima, finding directional derivatives, gradients, radii of curvature, tangent planes, etc. These properties may all be determined if the surface is represented by an equation that can be differentiated. The response surface generated by orthogonal polynomials allows easy differentiation, so that surface properties are easily deduced. Because such mathematical investigations are standard calculus procedures, they are not examined in any greater detail in this report. However, in order to emphasize the practical results obtainable from these surface properties, it is noted that questions of the following kinds could be examined for Albrecht's data:

(1) Within the range of the experiment, what conditions would be expected to yield the maximum amp-hr efficiency for the cells obtained from Manufacturer 3?

(2) What combinations of charging durations and charging rates would be expected to yield an amp-hr efficiency of 98 percent for the cells obtained from Manufacturer 2?

(3) Given operating conditions at a charging duration of 7 days, a charging current of 10 ma, and a temperature of 32 F for the cells of Manufacturer 5, what combined change in temperature and charging rate would be expected to yield the maximum increase in amp-hr efficiency?

Most of these questions require interpolation within the experimental points. It should be emphasized that it is <u>not</u> asserted that either interpolations or extrapolations would yield "good" results. In general, the validity of each case would require special examination. For the proposed application, the primary virtue of the fitted response surface does not lie in obtaining answers to these kinds of questions. Instead, the virtue lies in the fact that the coefficients of these polynomials yield a perfect fit at the data points, so that no interesting structure is lost by smoothing. Moreover, as indicated above, the coefficients have physically meaningful interpretations. Further, as outlined in the next section, the behavior of the coefficients may be monitored over time to obtain time rates of change of the surface properties. These changes may be useful indicators of the underlying changes in physical processes over time. Consequently, these changes would be expected to be useful in establishing degradation rates as functions of stress in accelerated tests.

Representation of Quality as a Dynamic-Response Surface

The previous section has shown how a response surface may be fitted to a set of data involving several factors and several levels for each factor. To apply this approach to an ideal accelerated test, it is proposed that the dependent variables be "quality", as defined in previous reports.(1, 2) Thus, a response surface would be generated to represent the quality of the cells on test at various time intervals. In symbolic terms, let $Q(x_1, \ldots, x_n;t)$ denote the quality response surface at time t. This symbolism shows that the quality is assumed to be expressible in terms of n factors $x_1, \ldots, x_n$. The number of levels for each factor is not shown by the symbol. The use of orthogonal polynomials will yield a polynomial surface. In contrast to the case exemplified with Albrecht's data, the coefficients are regarded as time dependent. By computing the coefficients periodically and making plots of their values as a function of time, it would be possible to monitor the dynamic structure of the quality surface over time. More specifically, it is proposed that extrapolations be made of these coefficient trajectories in order to estimate their magnitudes at future measurement times. In this way, a predicted response surface would be generated prior to taking the measurements. By comparing the predicted response surface with the actual response surface, considerable experience would be gained that would aid in obtaining answers to the following kinds of questions:

(1) How far into the future can reasonably good forecasts of the quality response surface be made?

(2) Are data being taken too frequently or too infrequently for forecasting purposes?

(3) Is the degradation of quality occurring more rapidly under certain conditions? (Should data be taken more frequently under these conditions?)

Graphical Interpretations

As outlined in previous reports, it is assumed that quality degrades over time and that the rate of degradation of quality is increased by increasing the stress. Clearly, satisfactory definitions for quality and stress are needed in order to use this conceptual framework. It appears that useful definitions of quality are available. However, the problem of obtaining useful definitions of stress is much greater and is discussed in the physical approach to accelerated testing included in this report.

An empirical approach toward defining stress consists of fitting a dynamic response surface to the accelerated-test data and then determining, for example, which portions of the surface are decreasing most rapidly over time. Presumably, the treatment combinations under these portions of the surface provide the most stress.

Figure 9 shows a sketch of these ideas in the form of a dynamic response surface. The vertical axis represents the measured quality. The (x_1, x_n)-plane represents the n-dimensional space associated with the n factors. The two surfaces denote the response surfaces at two successive times. The upper surface shows a gradient vector that is a linear combination of the n factors that can be associated with the greatest expected increase of quality obtainable by choosing appropriate linear combinations of the factors. In general, this space derivative exists at each point of a given response surface and is obtained by partial differentiation of the quality response surface with respect to $x_1, \ldots, x_n$. The lower surface represents a quality response surface at a later time. The figure suggests a larger decrease of quality for the left portion of the surface. This is suggested by the vector labeled $\frac{dQ}{dt}$. The magnitude of this vector involves the time rates of change of the coefficients of the polynomials used to represent the response surface. The figure also shows a contour labeled "Failure level". This boundary is associated with those conditions that give a minimal acceptable value of quality Q_0. The boundary results from a cross section of the lower response surface obtained with a plane parallel to the (x_1, x_n)-space. The equation of this boundary is obtained by setting $Q = Q_0$ in the response-surface equation.

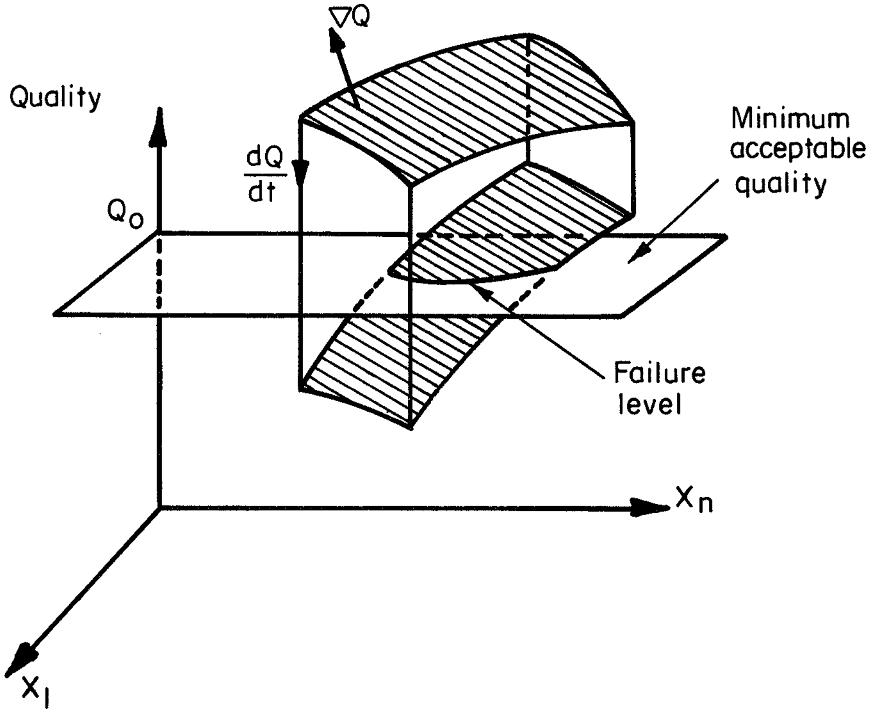


FIGURE 9. DYNAMIC RESPONSE SURFACE SHOWING THE DEGRADATION OF QUALITY

Figure 10 shows the kinds of plots that may be used to monitor the coefficients of the fitted response surface. The dashed lines and the triangular symbols represent predicted future values of the coefficients. Substitution of these predicted values into the response-surface equation will yield a predicted response surface. The six plots are hypothetical and are expressed in terms of average quality, together with the various linear and quadratic effects that would arise from three levels of charging duration

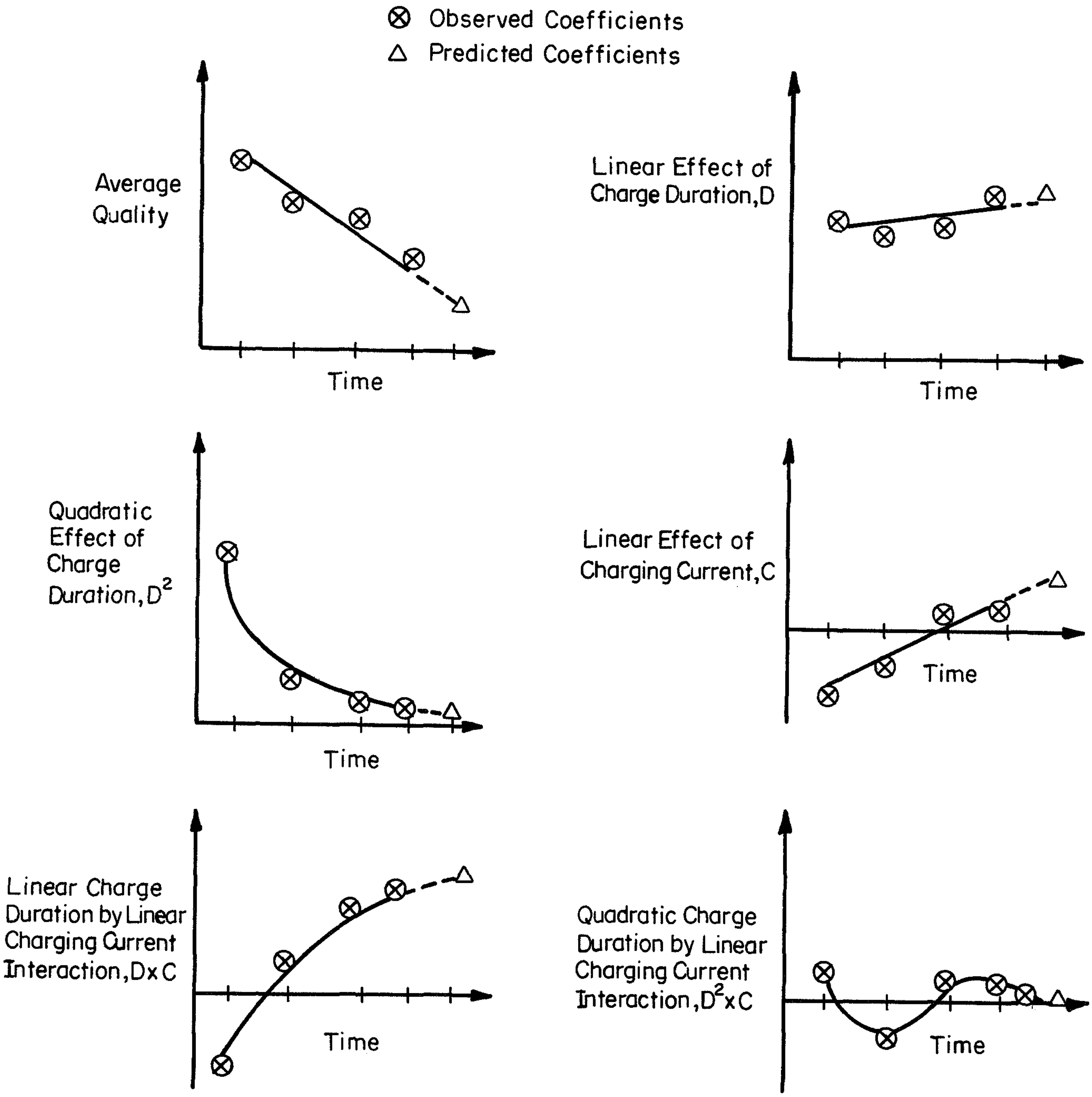


FIGURE 10. HYPOTHETICAL PLOTS ILLUSTRATING THE PREDICTION OF THE RESPONSE-SURFACE COEFFICIENTS AS A FUNCTION OF TEST TIME

and two levels of charging current. A total of 36 plots would be required to forecast the response surface for the kind of data presented in Table 3. Various methods are available for fitting and extrapolating such curves with computer software. Such methods will not be considered in more detail in this report.

Statistical Smoothing of the Response Surface

The previous arguments focus attention on the fact that the response surfaces fit the data exactly at each data point. Statistical considerations generally involve the assumption that each data point consists of two components, a "signal" and a "noise". In general, the purpose of statistical methods is to identify and assess the magnitudes of these two components. By fitting a response surface so that it passes exactly through the data points, the surface has been fitted to the noise component as well as to the signal component. If the data are quite noisy, the usefulness of the response surface becomes questionable. Ideally, the statistician would smooth out the noise component and fit a response surface to the remaining signal component.

In many instances, the identification of the noise contribution at each data point is difficult if not impossible. Consequently, several procedures have evolved which are assumed to be useful. One of these methods involves fitting a response surface exactly, as described earlier, and then omitting the higher degree terms from the polynomial equation. For example, if only the first-degree terms are retained, then the resulting response surface is the customary hyperplane of linear regression analysis. On the other hand, if some of the coefficients of higher degree terms are large, it would be expected that these terms should be retained in the smoothed response surface because the dropping of these terms would be likely to produce large discrepancies between the data points and the response surface. A standard statistical method exists for determining which terms of the exact response surface should be retained. The method is illustrated below with a portion of Albrecht's data.

As shown earlier, the data of the first two columns of Table 3 are fitted exactly by the following response surface:

$$\begin{aligned} y(x_1, x_2) &= 97.98 + 1.95x_1 + 0.72(3x_1^2-2) - 0.28x_2 \\ &\quad - 1.30\, x_1x_2 - 0.17(3x_1^2-2)x_2 \end{aligned}$$

where x_1 denotes the coded value of charge duration, and x_2 denotes the coded value of charging current. As a consequence of the orthogonality of the fitted polynomials, it may be shown that the total variance among the y-values can be partitioned into six components. Each term in the response equation accounts for one of these components. In general terms, the total scatter of the data is measured in terms of the variance. This scatter then is partitioned into six components. The statistical problem consists of determining which of those six components are "noise" and which are "signal".

The portion of the total scatter that is associated with each term is easily obtained from the determinantal equation used to compute the response surface. As shown earlier, the following determinant may be written for the present example:

$$\begin{array}{|ccccccc|}
\underline{y(x_1, x_2)} & \underline{1} & \underline{x_1} & \underline{(3x_1^2-2)} & \underline{x_2} & \underline{x_1 x_2} & \underline{(3x_1^2-2)x_2} \\
95.9 & 1 & -1 & 1 & -1 & 1 & -1 \\
96.5 & 1 & 0 & -2 & -1 & 0 & 2 \\
102.4 & 1 & 1 & 1 & -1 & -1 & -1 \\
97.6 & 1 & -1 & 1 & 1 & -1 & 1 \\
96.6 & 1 & 0 & -2 & 1 & 0 & -2 \\
98.9 & 1 & 1 & 1 & 1 & 1 & 1
\end{array} = 0 \; .$$

The component of variance associated with the $1.95x_1$ term of the response-surface equation given above is computed as follows:

$$SSD = (1.95) \left[(95.9)(-1) + (102.4)(1) + (97.6)(-1) + (98.9)(1) \right]$$

where the bracketed factor is obtained by taking the scalar product of Column 1 and Column 3 of the above determinant. The symbol SSD denotes the sum of squared deviations for x_1. Thus, it is found that $SSD_{x_1} = (1.95)(7.8) = 15.21$. In a similar way, the sum of squares associated with the $0.72(3x_1^2-2)$-term is found from Columns 1 and 4 to be given by $SSD\,(3x_1^2-2) = (0.72)(8.6) = 6.192$. Continuing in this manner and summarizing the results, the following analysis-of-variance tabulation is yielded:

Source of Variance	Sum of Squared Deviations, SSD	Degrees of Freedom, df
Linear effect of charging duration, D	15.210	1
Quadratic effect of charging duration, D^2	6.192	1
Linear effect of charging current, C	0.476	1
Linear-by-linear interaction, DxC	6.760	1
Quadratic-by-linear interaction, D^2xC	0.340	1
Total	28.978	5

It is noted that the sum of squares of the deviations associated with the constant (average) of the response equation is not shown because the tabulation is intended to partition the variations about this average value. The third column gives the degrees of freedom. In general, there is one degree of freedom associated with each coefficient of the response equation. The five degrees of freedom in the above tabulation plus a degree of freedom for the constant term gives six degrees of freedom corresponding to the six data points fitted by the response surface.

In order to assess the statistical significance of the magnitudes of the SSD's, a measure of the magnitude of the "noise" is needed. If the six data points are averages, then the scatter within these averages is often used as a measure of the "noise". For example, if each of six data points is based on an average of five cells and the SSD associated with these averages is equal to 12.00, then the statistical analysis would take the following form:

Source of Variance	SSD	df	Mean Square	F-Ratio
Linear effect of charging duration, D	15.210	1	15.210	30.42
Quadratic effect of charging duration, D^2	6.192	1	6.192	12.38
Linear effect of charging current, C	0.476	1	0.476	0.95
Linear-by-linear interaction, DxC	6.760	1	6.760	13.52
Quadratic-by-linear interaction, D^2xC	0.340	1	0.340	0.68
Experimental error	12.000	24	0.500	--
Total	40.978	29		

The 24 degrees of freedom associated with the experimental error is obtained from the product of the number of means times four degrees of freedom per mean. The mean-square column is obtained by dividing the SSD's by the corresponding degrees of freedom. The F-ratios are formed by dividing each of the mean squares by mean square for experimental error.

If it is assumed that the deviations about the means are normally distributed, then the mean squares have χ^2-distributions, and the F-ratios have F-distributions.(15) Large F-ratios then indicate a large "signal" relative to the "noise" measured as the experimental error. In customary analyses, a large F-ratio is often taken to be a value that exceeds the "noise" level by an amount so large that the probability that it is not associated with a signal is less than 0.05. In these terms, the threshold F-ratio for the above tabulation is found to be 4.26, corresponding to the 95 percent fractile of the F-distribution with one and 24 degrees of freedom. Those F-ratios larger than 4.26 then are declared to be statistically significant. In the above tabulation the linear effect of charging duration, the quadratic effect of charging duration, and charging current are statistically significant. The linear effect of charging current and the quadratic-by-linear interaction, D^2xC, are not statistically significant.

Because the effects associated with the x_2 term and the $(3x_1^2-2)x_2$ term of the response surface are not statistically significant, these terms would be dropped from the response-surface equation. Thus, for the above example, the smoothed response surface has the following equation:

$$\hat{y}(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2-2) - 1.30x_1x_2 \quad .$$

The surface represented by this equation will not pass through the data points exactly because, presumably, the noise has been smoothed out. The following tabulation shows a comparison of the actual points and the values given by the smoothed response surface:

Data Point, (x_2, x_1)	Actual Value, $y(x_1, x_2)$	Smooth Value, $\hat{y}(x_1, x_2)$	Difference, $(\hat{y}-y)$	$(\hat{y}-y)^2$
(-1, -1)	95.9	95.45	-0.45	0.2025
(-1, 0)	96.5	96.54	0.04	0.0016
(-1, 1)	102.4	101.95	-0.45	0.2025
(1, -1)	97.6	98.05	0.45	0.2025
(1, 0)	96.6	96.54	-0.06	0.0036
(1, 1)	98.9	99.35	0.45	0.2025
			Total	0.8152

The last column shows the square of the differences between the actual amp-hr efficiencies and the smoothed values. The sum of the squared differences is equal to 0.8152. Within rounding errors, this sum is equal to the sum of the SSD's associated with the deleted terms. That is, the SSD for charging current in the above analysis-of-variance tabulation is seen to be 0.476, and the SSD for D^2xC is seen to be 0.340. The sum of these SSD's is 0.816, which is approximately equal to 0.8152. Thus, the sum of the squares of the differences between the actual and smoothed data give the same measure of the "noise" that was associated with noise in the analysis-of-variance tabulation.

Interpretation of the Response Surface

The preceding development has shown how measured data can be represented by a response surface. For simplicity of exposition, the response surface has been generated as a linear combination of orthogonal polynomials. Such a representation appears "artificial" and, in general, would not be expected to yield equations that may be recognized as equations of physical processes. The variables of most physical equations can be represented as dimensionless variables, with functional relations involving exponential powers and products occurring more frequently than linear combinations. Linear combinations appear to arise most frequently in Taylor's-series approximations to the true functional relation. However, when the true functional relation is not known, the derivatives required for a Taylor's-series expansion cannot be taken. In such a case, it may be asked whether it is possible to estimate the derivatives from data and then attempt to deduce the functional relation that would give rise to the empirically derived Taylor's series. It is shown next that such an approach is convenient when the data are represented as a response surface of the form developed earlier.

Consider the following response surface derived for the first two columns of Table 3:

$$y(x_1,x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2-2) - 0.28x_2$$
$$- 1.30x_1x_2 - 0.17(3x_1^2-2)x_2 \quad .$$

The following tabulation gives a list of the non-zero partial derivatives of this response surface:

$$\frac{\partial y}{\partial x_1} = 1.95 + 4.32x_1 - 1.30x_2 - 1.02x_1x_2$$

$$\frac{\partial y}{\partial x_2} = -0.28 - 1.30x_1 - 0.17(3x_1^2-2)$$

$$\frac{\partial^2 y}{\partial x_1^2} = 4.32 - 1.02x_2$$

$$\frac{\partial^2 y}{\partial x_1 \partial x_2} = -1.30 - 1.02x_1$$

$$\frac{\partial^3 y}{\partial x_1^2 \partial x_2} = -1.02 \quad .$$

These derivatives are next evaluated at the point $(\bar{x}_1, \bar{x}_2)$, where $\bar{x}_1$ and $\bar{x}_2$ denote the mean values of x_1 and x_2, respectively. Because x_1 has been coded to have values -1, 0, 1, the mean value is seen to be equal to 0. Similarly, because x_2 = -1, 1, the mean value of x_2 is equal to 0. Thus, the evaluation of the partial of y with respect to x_1 at $(\bar{x}_1, \bar{x}_2)$ is given by

$$\left(\frac{\partial y}{\partial x_1}\right)\Bigg|_{(\bar{x}_1,\bar{x}_2)} = \left(\frac{\partial y}{\partial \bar{x}_1}\right) = 1.95 \quad .$$

Similarly, the remaining partial derivatives evaluated at $(\bar{x}_1, \bar{x}_2)$ are obtained from the preceding expressions.

Next, suppose that the true, but unknown, functional equation for the response surface has a Taylor's-series expansion about the point (x_1, x_2), and let

$$f(x_1,x_2) = f(\bar{x}_1,\bar{x}_2) + \frac{\partial f}{\partial \bar{x}_1}(x_1-\bar{x}_1) + \frac{\partial f}{\partial \bar{x}_2}(x_2-\bar{x}_2)$$

$$+ \frac{1}{2}\left[\frac{\partial^2 f}{\partial x_1^2}(x_1-\bar{x}_1)^2 + 2\frac{\partial^2 f}{\partial \bar{x}_1 \partial \bar{x}_2}(x_1-\bar{x}_1)(x_2-\bar{x}_2) + \frac{\partial^2 f}{\partial \bar{x}_2^2}(x_2-\bar{x}_2)^2\right]$$

$$+ \frac{1}{6}\left[\frac{\partial^3 f}{\partial \bar{x}_1^3}(x_1-\bar{x}_1)^3 + 3\frac{\partial^3 f}{\partial \bar{x}_1^2 \partial \bar{x}_2}(x_1-\bar{x}_1)^2(x_2-\bar{x}_2)\right.$$

$$\left. + 3\frac{\partial^3 f}{\partial \bar{x}_1 \partial \bar{x}_2^2}(x_1-\bar{x}_1)(x_2-\bar{x}_2)^2 + \frac{\partial^3 f}{\partial \bar{x}_2^3}(x_2-\bar{x}_2)^3\right] .$$

denote such an expansion through third partial derivatives. If this function is to represent the same data that were fitted by means of the orthogonal polynomials, then it seems reasonable to set $\bar{x}_1 = \bar{x}_2 = 0$ and equate the values of the partial derivatives. These substitutions yield the following expression for $f(x_1, x_2)$:

$$f(x_1,x_2) = f(0,\ 0) + \left(\frac{\partial y}{\partial \bar{x}_1}\right)x_1 + \left(\frac{\partial y}{\partial \bar{x}_2}\right)x_2 + \frac{1}{2}\left(\frac{\partial^2 y}{\partial \bar{x}_1^2}\right)x_1^2$$

$$+ \frac{\partial^2 y}{\partial \bar{x}_1 \partial \bar{x}_2}x_1x_2 + \frac{1}{2}\left(\frac{\partial^2 y}{\partial \bar{x}_2^2}\right)x_2^2 + \frac{1}{2}\left(\frac{\partial^3 y}{\partial \bar{x}_1^2 \partial \bar{x}_2}\right)x_1^2 x_2 .$$

The substitution of the computed numerical values for the partial derivatives yields:

$$f(x_1,x_2) = f(0,\ 0) + 1.95x_1 + 0.06x_2 + \frac{1}{2}(4.32)x_1^2$$

$$- 1.30x_1x_2 + \frac{1}{2}(-1.02)x_1^2x_2$$

or, equivalently,

$$f(x_1,x_2) = f(0,\ 0) + 1.95x_1 + 0.06x_2 + 0.72(3x_1^2) - 1.30x_1x_2 - 0.51x_1^2x_2$$

and, finally,

$$f(x_1,x_2) = [f(0,0) + 1.44] + 1.95x_1 - 0.28x_2 + 0.72(3x_1^2-2)$$

$$- 1.30x_1x_2 - 0.17(3x_1^2-2)x_2 \quad .$$

The equating of constant terms yields

$$f(0,0) + 1.44 = 97.98 \quad ,$$

so that $f(0,0) = 95.54$. It may be noted that $f(0,0)$ denotes the function evaluated at the average values of x_1 and x_2. For nonlinear functions, this average may not be equal to the average value of the function. That is,

$$f(E\{x_1\}, E\{x_2\}) \neq E\{f(x_1,x_2)\} \quad ,$$

and this accounts for the fact that $f(0,0)$ does not equal 97.98 in this example.

The result of these substitutions is a Taylor's-series expansion that has been generated by the data. Except for the constant term, the expansion agrees identically with that obtained by the polynomial expansion. The final step would consist of attempting to deduce a functional form of f which would give rise to the computed Taylor's-series expansion. This approach makes it clear that every effort should be made to eliminate the noise from the response surface by statistical smoothing before attempting to deduce the functional form of f.

Determining the Dynamics of the Response Surface

The preceding developments have been concerned with the mathematical interpretation of a response surface at a given time. It is proposed, however, that the response surface can be computed at successive measurement times, so that "motion" of the surface can be studied. It has already been noted that an empirical method for studying the motion is obtained by plotting the computed values of the coefficients at successive times. Extrapolations of these plots will yield predicted response surfaces that subsequently may be compared with observed response surfaces. By varying the time horizon of the prediction, some feedback may be obtained that will yield desired changes in measurement times to give improved predictions over the longest possible time intervals. As described, this empirical plotting procedure does not directly yield equations of motion for the response surface. Because the motion of the response surface over time is expected to result from degradations of physical components, it is expected that the surface will move in accord with time dependencies associated with physical processes of certain components. Time dependencies of physical processes typically are represented mathematically by differential equations. In general, then, it would be desirable to obtain a differential equation that describes the motion of the response surface. Some methods for accomplishing this are summarized below.

In the physical approach to the analysis of accelerated-test data, the assumption of a rate-process equation, the Arrhenius model or the Eyring model(2), for example, may give a sufficiently valid correlation, with the observed results that the general problems of fitting differential equations to data may not arise. However, if these correlations are not acceptable, some fitting method is required. One approach would consist of deducing differential equations that give rise to the observed trajectories generated by the coefficients of the response surface. Because the differential equations would not be uniquely defined by a discrete set of observed values, this approach would generate a class of differential equations. It is hoped that some member of the class would be identifiable as an appropriate relation for some suggested physical-degradation mechanism. Although the deduction of differential equations from observed trajectories generated by the coefficients is conceptually clear, it is obvious that considerable difficulty would probably be encountered in associating the equations with physical processes. The difficulty arises not from the methods of analysis but from the fact that the physical mechanisms, their interactions, and their time rates would need to be deduced from noisy data that likely contains measurements of some irrelevant variables and does not contain measurements of some relevant variables. It is for these reasons that a mathematical response-surface approach appears to be highly attractive as a general method of approach to accelerated testing.

DATA REQUIREMENTS OF THE STATISTICAL APPROACH

It has been noted above that statistical methods typically are based on averages. In general, averages are preferred over single observations because averages are more "stable" than the observations of which they are composed. That is, the standard deviation of an average is smaller than that of a single observation by a factor $1/\sqrt{n}$, where n denotes the number of observations in the average. In the context of an accelerated-test program for batteries, this means that the statistical approach would require a "matched" set of cells to be tested at each stress level, so that appropriate averages may be taken over the cells in each matched set. Because of the cost of spacecraft cells, it is desirable that a minimum number of matched cells be used at each stress level. For statistical stability, it is recommended that averages be based on observations obtained from five matched cells. The standard deviations of such averages then would be less than half that associated with single observations. Moreover, by the central-limit theorem, averages of five observations would be expected to be normally distributed, approximately, even though the individual observations of which they are composed may not be normally distributed.

A somewhat different argument may be made to determine the minimum number of stress levels to be recommended for an accelerated test. The argument begins by noting that the stress levels are to be chosen over a specific range of stress levels. The lowest stress level should correspond to the intended-use condition for the cells. The highest stress level should be the highest possible level consistent with the requirement that the dominant degradation mechanism is not changed. That is, stress levels that are too severe will yield failed cells in short time intervals, but the failures will occur for reasons that are not valid at the stress level associated with the intended-use condition.

It is often difficult to predict the maximum stress level that can be used without changing the dominant degradation mechanism. Consequently, a "guess" has to be made and then the data must be analyzed to determine whether the guess was satisfactory. In the simplest approach, the data obtained from each stress level may be examined to determine if a change in degradation mechanism is evident. This examination sometimes may be done by plotting the degradation rate as a function of a suitable measure of stress level. Linear plots sometimes may provide evidence that no change in mechanism has occurred; nonlinear plots suggest a change in mechanism. Consequently, it appears that a minimum of five stress levels are required to show the presence of two mechanisms. The lowest two stresses would be associated with the mechanism at use conditions; the highest two stress levels would be associated with a possibly different degradation mechanism at the high-stress level; and the intermediate-stress level would be associated with the transition between the two degradation mechanisms.

In brief, five stress levels are required to detect a change in the dominant degradation mechanism if such a change occurs. Thus, a minimum of five matched cells should be tested at each of five stress levels varying between the intended-use condition and the maximum-stress level believed to be consistent with the requirement that the dominant degradation mechanism remains unchanged.

Additional considerations indicate that it is appropriate to test more than five matched cells at each stress level in an ideal accelerated test. In particular, as shown in a later section on destructive and nondestructive testing, a total of 15 matched cells is recommended for testing at each stress level. This is done in order to provide for a periodic random selection and destructive examination of a cell at each stress level. This examination would be carried out a total of five times during the test program and the recommended number of cells would be increased from five to ten for each stress level. An additional increase of five cells at each stress level also is recommended in the ideal program to provide cells for special-purpose tests, transient tests, and for unforeseen experimental contingencies (accidental destruction of a cell, etc.).

SUMMARY OF STATISTICAL APPROACH

The developments of this section show that a statistical response surface provides a good basis for the analysis of accelerated-test data. Such an analysis can be accomplished off-line by a computer. Moreover, both an exact fit (empirical) and a smoothed fit (statistical) can be generated easily from the same data. Thus, the method provides a good tool for making the transition between an empirical and statistical analysis. The time dependence of the response surface can be obtained by plotting the coefficients of the response surface against time. This procedure will permit predictions to be made of future positions of the response surface which, in turn, may be interpreted as predictions of future behavior of the cells on test.

Statistical arguments also show that a minimum of five matched cells should be tested at each of five stress levels. Ten additional cells at each of the five stress levels are recommended in order to provide for periodic destructive examination of operational cells and to provide some additional cells for special-purpose tests, transient tests, and for unforeseen experimental contingencies.

Table 7 shows a summary of the data requirements for a statistical approach to an ideal accelerated-test program. In addition to the 15 cells for each stress level, the table shows that voltage measurements should be taken 12 times within each charge/discharge cycle.

TABLE 7. DATA REQUIREMENTS FOR A STATISTICAL APPROACH TO AN IDEAL ACCELERATED-TESTING PROGRAM FOR RECHARGEABLE CELLS

Requirement	Purpose of Requirement
At least 15 matched cells for each stress level, with removal of 2 randomly selected cells at 5 equally spaced times during the expected duration of the test.	With this procedure, 5 cells would be expected to complete the entire test; of the 2 randomly selected cells, one would be subjected to a tear-down test (a) and the other would be available for special-purpose tests, transient tests, or experimental contingencies.
Voltage measurements should be taken at 12 time intervals within each charge-discharge cycle.	An average-voltage curve with its standard deviation would be computed for each set of matched cells. The data would be analyzed off-line, using statistical methods such as the response-surface technique described in this report.

(a) The purpose of the tear-down test is discussed in the section of this report on Destructive and Nondestructive Testing.

A PHYSICAL APPROACH TO ACCELERATED TESTING

by

John McCallum and Eric W. Brooman

INTRODUCTION

The empirical and statistical approaches to the accelerated testing of cells and batteries are "content independent". That is, interpretation is based upon the data obtained, with no reference to the physics of the actual processes occurring inside the devices. To all intents and purposes, the empiricist and statistician see a cell or battery as just a "black box" from which issue the data they need for their analysis. On the other hand, by definition, the physical approach is content dependent. An ideal application of the physical approach to accelerated testing and analysis of the data can be made only if the processes occurring within the cells are known or can be represented by mathematical relationships that have physical significance.

Various physical approaches to accelerated testing are summarized in an U. S. Air Force report.(2) They involve the use of (1) an Arrhenius model, (2) an Eyring model, (3) stress-strain models, (4) dimensional analysis, and (5) the theory of models. Various arguments are developed regarding these approaches, but readers of this report should recognize that none of these approaches have widespread acceptance in battery technology. Moreover, the physical principles for choosing experiments are less developed than are the statistical and empirical techniques for working with the data after the experiments have been performed. Therefore, this part of the report describes the positive results from an extensive mental exercise to develop an ideal physical approach to accelerated testing.

Stress-strain models are developed in detail. Each new consequence of the development is checked for consistency with known and accepted physical laws and principles. When consistency is seen, the development is carried further. Inconsistencies were avoided by using existing knowledge to guide the development. With this style of reporting, readers may see some voids and problems in the development, but they should see nothing wrong in it. Alternative approaches were considered. These alternatives subsequently are named in the form of questions with abbreviated answers. The reason for this format is to emphasize as broad a theoretical basis as possible for an ideal physical accelerated test and only to mention the less desirable approaches.

The ideal physical accelerated test can be described in terms of the following general assumptions(2):

(1) Each cell has a quality that may be derived from physical measurements.

(2) This quality varies with time (or cycle number) and degrades after a sufficiently long time (or number of cycles).

(3) Higher degradation rates of quality occur at higher levels of stress.

(4) The rate of degradation eventually will lead to failure by the degradation of quality to an unacceptable level.

(5) The physical mechanisms contributing to the degradation of quality do not change in relative dominance during the test.

For assumptions (1) and (2), the general definition of the quality of a cell at a particular time within a charge-discharge cycle was previously given as

$$\text{Quality} = Q_s = 1/\Delta s \cdot n \tag{1}$$

where Q_s was to be calculated from an observed change of stress, Δs, at an hourly rate of charge or discharge, n. Stress was said to be associated with "the intensity factor of a form of energy" for assumption (3). From these premises, qualities then are to be computed as a function of changes in the operating stresses at different time intervals or after a specified number of cycles in order to obtain the time rate or cycle rate of degradation of each quality. Using the quality observed in the initial cycle and a time rate of degradation of quality, extrapolation from early measurements to predict the time to failure for any predefined low-quality value leads to the desired physical-accelerated-test method.

The third assumption itemized above requires that the degradation rate of quality can be accelerated with higher levels of stress. This assumption is crucial to the whole development of an ideal physical accelerated test, because it demands some rigor for the meaning of "stress". Therefore, succeeding parts of this report will develop the subject of stresses, with the following results:

(a) The five general assumptions above are retained.

(b) The above definition of stress for assumption (3) is changed from meaning an intensity factor in the previous report to mean an intensity gradient in the present report.

(c) The symbolism and description of Equation (1) is changed to

$$\text{Quality} = Q_I = 1/\Delta I \cdot n \tag{1a}$$

where Q_I is to be calculated from observed changes of intensity factors, ΔI, at an hourly rate of charge or discharge, n, so that the original intent of quality measurements with Equation (1) is retained in Equation (1a).

(d) Measurements of both initial qualities and the time rate of degradation of qualities are necessary for an accelerated life test.

THE SELECTION OF STRESSES

In the previous report to the U. S. Air Force(2), McCallum proposed that all forms of storable energy can be described in terms of an Intensity Factor and an Amount Factor. Three requirements are given for these factors:

First of all, the mathematical product of the intensity factor times the amount factor must yield the dimension of work or energy.

Second, intensity factors must be consistent with the Principle of Higher Intensity, which states:

> "When two reservoirs of the same form of energy are allowed to interact with one another, energy always flows from the reservoir having the higher intensity factor."

The Second Law of Thermodynamics is a special case of the above principle as applied to heat energy. When two reservoirs of heat are allowed to interact, then heat will always flow from the reservoir having the higher intensity factor (temperature).

Third, amount factors of energy must be consistent with the Principle of Conservation of Amounts, which states for a closed system:

> "When two or more reservoirs of the same form of energy are allowed to interact with one another, the sum of the amount factors remains constant."

Faraday's Laws of Electrolysis are special cases of the principle of conservation of amounts.

Table 8 lists twelve common forms of energy and their suggested intensity and amount factors. For each horizontal row, the intensity factor, Column 2, and amount factor, Column 3, satisfy the three requirements just listed. Thus, the two factors for each row are multiplied together to give the units of work in Column 4. Each intensity factor satisfies the principle of higher intensity. Each amount factor satisfies the principle of conservation of amounts. It is axiomatic for this development of a physical accelerated test that any form of energy can be factored so as to be consistent with the listing in Table 8. Subsequently, the intensity factors are related to stress for increasing degradation rates. The intensity factors are also used for measurement of qualities with Equation (1a).

To illustrate further the way in which intensity factors may be selected, consider mechanical (kinetic) energy in Item (6) of Table 8. Readers of this report will know from elementary mechanics that kinetic energy is given by $1/2\ mv^2$. To factor this work function into its intensity and amount factors, one has the following choices:

(a) amount = m and intensity = v^2

(b) amount = mv and intensity = v

(c) amount = v and intensity = mv or

(d) amount = v^2 and intensity = m.

All four choices satisfy the first criterion that amount times intensity gives work. Amount factors (a) and (b) both satisfy the principle of conservation of amounts. Amount factors (c) and (d) do not satisfy the principle of conservation of amounts and therefore make (c) and (d) invalid choices for amount factors. Similarly, both choices (a) and (b) satisfy the principle of higher intensities, whereas (c) and (d) do not. Therefore, both

TABLE 8. INTENSITY AND AMOUNT FACTORS OF VARIOUS FORMS OF ENERGY

Energy Form	Intensity Factor	Amount Factor	Work $[ml^2t^{-2}]$
1. Mechanical (one degree of freedom)	Force, F dyne, $[mlt^{-2}]$	Distance, x cm, $[\ell]$	F.x dyne cm
2. Mechanical (two degrees of freedom)	Surface tension, γ dyne cm^{-1}, $[mt^{-2}]$	Area, a cm^2, $[\ell^2]$	γ.a dyne cm
3. Mechanical (three degrees of freedom)	Pressure, P dyne cm^{-2}, $[ml^{-1}t^{-2}]$	Volume, V cm^3, $[\ell^3]$	P.V dyne cm
4. Acoustical (sound)	Sound pressure, p dyne cm^{-2}$[ml^{-1}t^{-2}]$	Volume displacement V, cm^3$[\ell^3]$	p.V dyne cm
5. Mechanical (rotational)	Torque, T´ dyne cm, $[ml^2t^{-2}]$	Angular displacement, φ, radians	T´.φ dyne cm
6. Mechanical (kinetic)	Velocity, v cm second^{-1}, $[lt^{-1}]$	Momentum, mv/2 gm cm sec^{-1} or dyne second, $[ml^2t^{-1}]$	$1/2.m.v^2$ dyne cm
7. Gravitational (potential)	Height, hG cm^2 sec^{-2} $[l^2t^{-2}]$	Mass, m dyne sec^2 cm^{-1}$[m]$	mGh dyne cm
8. Electrical	Voltage, E volt, $[(\epsilon^{-1}mlt^{-2})^{1/2}]$	Charge, Q coulomb, $[(\epsilon ml^3t^{-2})^{1/2}]$	E.Q volt coulomb
9. Thermal	Temperature, T degree, $[\theta]$	Heat capacity, C´ calorie degree^{-1}, $[ml^2t^{-2}\theta^{-1}]$	T.C´ calorie
10. Chemical	Osmotic pressure, O dyne cm^{-2}, $[ml^{-1}t^{-2}]$	Molar volume, V_m cm^3, $[\ell^3]$	O.V_m dyne cm
11. Light	Frequency, f second^{-1}, $[t^{-1}]$	Illumination, L photons, or erg-second $[ml^2t^{-1}]$	f.L dyne cm
12. Magnetic	Magnetic potential, H dyne cm pole^{-1} $[m^{1/2}l^{1/2}t^{-1}\mu^{-1/2}]$	Magnetic pole, α pole $[m^{1/2}l^{3/2}t^{-1}\mu^{1/2}]$	H.α dyne cm

choices (a) and (b) are valid for listing in Table 8. Actually, only choice (b) is listed because that choice subsequently leads to a variety of consistent results in Table 9, whereas choice (a) leads to unrecognizable relationships.

Some of the other energy forms in Table 8 are less or more complicated than that just described in energy Type 6, mechanical (kinetic) energy. However, the points to be emphasized are these:

(a) All forms of energy can be factored into intensity and amount factors.

(b) Stresses for accelerated tests are to be associated with intensity gradients by means of equations yet to be derived.

(c) Changes in each intensity factor in Table 8 could be used in Equation (1a) for definition of qualities if there are practical reasons to do so.

STRESS-STRAIN RELATIONSHIPS

Generalized Stress, Strain, and Rate of Strain

In previous work on failure mechanisms and accelerated testing(2), stress-strain models are proposed as one way of describing a variety of accelerated tests. The models are based on generalized concepts of stress and strain, such as those applied to metallurgical processes like elasticity and creep. From standard reference texts(16), generalized stress and strain are defined in such a way that the product of stress times strain gives units of work per unit length, area, or volume for one-dimensional, two-dimensional, and three-dimensional geometry, respectively. For three-dimensional geometry, then:

$$\text{Stress x strain} = \text{work/cm}^3 \qquad (2)$$

and

$$\text{Stress x rate of strain} = \text{work/cm}^3 \cdot \text{sec} = \text{power/cm}^3 \ , \qquad (3)$$

when volumes are measured in cm^3.

With Equations (2) and (3), the previous report(2) suggested how the definitions of quality in Equation (1) might describe a stress-rate-of-strain relationship for an electrochemical cell. The earlier work then suggested that the amount factors in energy Types 1, 3, 8, and 9 of Table 8 could be related quantitatively to the hourly rate of discharge in Equation (1). Thereby, the four stresses related to (1) force, (2) pressure, (3) voltage, and (4) temperature could be described by a stress-strain relationship analogously with Hooke's Law, namely:

$$\text{Stress is proportional to strain} \qquad (4)$$

or by a stress-rate-of-strain relationship analogously with Newton's Law of Viscous Flow, namely, Stress is proportional to rate of strain . (5)

Also, the previous work[2] suggests that stresses can be created internally or externally relative to the spacecraft cell. These four stresses, controlled four ways, theoretically give 16 methods for constructing accelerated tests. Hypothetically, up to 16 factorial combinations might exist if all the 16 methods were independent of one another.

As part of the present project to devise the ideal accelerated test, the above-mentioned concepts will be extended, modified, and tested in connection with the energy forms in Table 8. Equations (2), (3), (4), and (5) will be maintained. In Table 8, sound energy, 4, rotational energy, 5, potential energy, 7, and magnetic energy, 12, will be dropped from further consideration because they are thought to be of little practical significance for the testing of cells. The intensity and amount factors in Table 8 will be retained, with the exception of chemical energy, 10, and thermal energy, 9. The intensity factor for chemical energy is changed from pressure to concentration because the two units are related through Van't Hoff's relationship.[17] The amount factor for chemical energy is changed from molar volume to number of moles and the amount factor for thermal energy is changed from heat content (calories per degree) to heat, calories, for reasons that will be explained in the paragraphs to follow.

Generalized Fluxes

While putting Table 8 together, consideration was given to Fick's Laws of Diffusion and what possible connection there might be between the amount and intensity factors in Table 8 and the variables in Fick's laws. Fick's First Law of Diffusion reads:

$$\text{Flux} = D \cdot dC/dx \tag{6}$$

where D is called a diffusion constant, C is a concentration, moles/cm^3, and x is a distance perpendicular to the flux. The flux is measured in moles per cm^2 per second. Fick's Second Law reads:

$$dC/dt = D \cdot d(\text{Flux})/dx = D \cdot d^2C/dx^2 \tag{7}$$

where t is time, with the other symbols already described. While pondering Equations (6) and (7), it was recognized that concentration, C, is proportional to osmotic pressure so that either concentration, C, or osmotic pressure, O, could be placed in the intensity-factor column of Table 8 for energy type 6. Moreover, moles (or molecules) are directly convertible to a volume through the molecular volume data from conventional handbooks and may, therefore, be placed in the amount-factor column of Table 8 at Type 6. A consequence of these substitutions is that their product then yields osmotic chemical work, as in the work column of Table 8.

A much more significant consequence of this interchange of units follows from the above line of reasoning in that Fick's Laws may then be generalized for all forms of energy in terms of intensity and amount factors, thus:

$$\text{Flux} = \text{amount/cm}^2 \cdot \text{sec} = \frac{1}{a} \cdot \frac{\partial A}{\partial t} = k_8 \cdot \partial I/\partial x \; . \tag{8}$$

TABLE 9. GENERALIZED STRESS-STRAIN AND STRESS-RATE-OF-STRAIN RELATIONSHIPS

Energy Form	Energy Source	Intensity Factor, I	Amount Factor, A	Flux Generality $\frac{1}{a}\frac{\partial A}{t} = k_8 \cdot \frac{\partial I}{\partial x}$	Conservation Generality $\frac{\partial I}{\partial t} = k_{17} \cdot \frac{\partial^2 I}{\partial x^2}$	Stress/Strain Generality $\frac{\partial I}{\partial x} = k_{27} \cdot \frac{A}{a}$	Impulse/Amount Generality $\Delta I = k_{33} \cdot \frac{\partial A}{\partial t}$	Impulse/Rate Generality $\Delta I = k_{44} \cdot \frac{\partial^2 A}{\partial t^2}$
1. Mechanical (one degree of freedom)	Motion	Force, F	Distance, x	Not appropriate	Not appropriate	Not appropriate	$\Delta F = k_{34} \cdot \frac{\partial x}{\partial t}$ (Newton's 1st Law, Stoke's Law)	$\Delta F = k_{46} \cdot \frac{\partial^2 x}{\partial t^2}$ (Newton's 2nd Law)
2. Mechanical (two degrees of freedom)	Liquids	Surface tension, γ	Area, a	Not appropriate	Not appropriate	Not appropriate	$\Delta \gamma = k_{36} \cdot \frac{\partial a}{\partial t}$	$\Delta \gamma = k_{44} \cdot \frac{\partial^2 a}{\partial t^2}$
3. Mechanical (three degrees of freedom)	Liquids or gases	Pressure, P	Volume, V	$\frac{1}{a} \cdot \frac{\partial V}{\partial t} = k_{11} \cdot \frac{\partial P}{\partial x}$ (Poiseuille's Law)	$\frac{\partial P}{\partial t} = k_{18} \cdot \frac{\partial^2 P}{\partial x^2}$	$\frac{\partial P}{\partial x} = k_{29} \cdot \frac{V}{a}$ (Sound energy)	$\Delta P = k_{37} \cdot \frac{\partial V}{\partial t}$ (Poiseuille's Law)	$\Delta P = k_{44} \cdot \frac{\partial^2 V}{\partial t^2}$
4. Electrical	Electricity	Voltage, E	Charge, Q	$\frac{1}{a} \cdot \frac{\partial Q}{\partial t} = k_{14} \cdot \frac{\partial E}{\partial x}$ (Ohm's Law)	$\frac{\partial E}{\partial t} = k_{19} \cdot \frac{\partial^2 E}{\partial x^2}$ (Ohm's Law)	$\frac{\partial E}{\partial x} = k_{28} \cdot \frac{Q}{a}$ (Capacitance relationship)	$\Delta E = k_{38} \cdot \frac{\partial Q}{\partial t}$ (Ohm's Law)	$\Delta E = k_{47} \cdot \frac{\partial^2 Q}{\partial t^2}$ (Inductance relationship)
5. Thermal	Heat	Temperature, T	Heat, q (calories)	$\frac{1}{a} \cdot \frac{\partial q}{\partial t} = k_{15} \cdot \frac{\partial T}{\partial x}$ (Fourier's Law)	$\frac{\partial T}{\partial t} = k_{20} \cdot \frac{\partial^2 T}{\partial x^2}$ (Fourier's Law)	$\frac{\partial T}{\partial x} = k_{27} \cdot \frac{q}{a}$	$\Delta T = k_{39} \cdot \frac{\partial q}{\partial t}$ (Fourier's Law)	$\Delta T = k_{44} \cdot \frac{\partial^2 q}{\partial t^2}$
6. Chemical	Chemical species in solution	Concentration, C	Moles, M	$\frac{1}{a} \cdot \frac{\partial M}{\partial t} = k_{16} \cdot \frac{\partial C}{\partial x}$ (Fick's 1st Law)	$\frac{\partial C}{\partial t} = k_{21} \cdot \frac{\partial^2 C}{\partial x^2}$ (Fick's 2nd Law)	$\frac{\partial C}{\partial x} = k_{30} \cdot \frac{M}{a}$	$\Delta C = k_{40} \cdot \frac{\partial M}{\partial t}$ (Mass Action Law)	$\Delta C = k_{44} \cdot \frac{\partial^2 M}{\partial t^2}$
7. Kinetic	Motion	Velocity, v	Momentum, mv	$\frac{1}{a} \cdot \frac{\partial (mv)}{\partial t} = k_{22} \cdot \frac{\partial v}{\partial x}$ (Bernoulli's Theorem)	$\frac{\partial v}{\partial t} = k_{24} \cdot \frac{\partial^2 v}{\partial x^2}$	$\frac{\partial v}{\partial x} = k_{27} \cdot \frac{mv}{a}$	$\Delta v = k_{41} \cdot \frac{\partial (mv)}{\partial t}$ (Newton's 1st Law, Stoke's Law)	$\Delta v = k_{44} \cdot \frac{\partial^2 (mv)}{\partial t^2}$ (Hooke's Law)
8. Light	Radiation	Frequency, f	Illumination, L (no. of photons)	$\frac{1}{a} \cdot \frac{\partial L}{\partial t} = k_{25} \cdot \frac{\partial f}{\partial x}$ (The Rad)	$\frac{\partial L}{\partial t} = k_{17} \cdot \frac{\partial^2 L}{\partial x^2}$	$\frac{\partial f}{\partial x} = k_{27} \cdot \frac{L}{a}$	$\Delta f = k_{42} \cdot \frac{\partial L}{\partial t}$ (Planck's Law)	Not appropriate

Equation (8) will be called the Flux Generality, where a is the area in cm^2. It is read in words as follows: "the change in amount per unit area per unit time is proportional to the intensity gradient".

This flux generality obviously is limited to three-dimensional space because the intensity gradient must be perpendicular to the area. Even so, the application of the flux generality to the other energy forms in Table 8 offers an excellent opportunity to see whether the intensity and amount factors are chosen properly.

More importantly for the subject of accelerated tests is the fact that Equation (8) leads to a generalized stress, rate-of-strain relationship given by Equation (3), when strain is equated to amount/cm^2 and stress is equated to the intensity gradient. Then, fluxes are equivalent to a rate of strain. Therefore,

$$\text{Stress} \cdot \text{rate of strain} \equiv (\text{intensity gradient}) \cdot (\text{flux}) = \left(\frac{\partial I}{\partial x}\right) \cdot \left(\frac{1}{a} \cdot \frac{\partial A}{\partial t}\right) \cdot \equiv \text{power/cm}^3 \ . \tag{9}$$

Moreover,

$$\text{Stress} \cdot \text{strain} = (\text{intensity gradient}) \cdot (\text{amount/area}) = \text{work/cm}^3 \ . \tag{10}$$

It follows from Equations (9) and (10) that different stress levels in an accelerated test are to be associated with values of an intensity gradient. These stress levels in turn are to be associated with strains and rates of strain through the above interpretation of Equation (8), wherein the intensity gradient is a vector orthogonal to the two area dimensions.

The paragraphs to follow develop the above relationships for the various kinds of energy applicable to spacecraft batteries. The intent is to build a logical and valid basis for ideal physical accelerated life tests.

In Table 9, Columns 1, 3, and 4 have been repeated from Table 8, with the changes in energy Types 5 and 6 previously mentioned. Column 2 has been added to Table 9 to emphasize that neither the amount nor the intensity factors are, by themselves, energy forms. For example, in Type 3 of Table 9, mechanical energy is obtained by the product of pressure times volume, but the amount column is not an amount of mechanical energy but is an amount of liquid or gas or some other tangible material associated with the performance of mechanical work.

Substitution of the amount and intensity factors from Columns 3 and 4 into the flux generality of Equation (8) leads to the following relationships:

3. Mechanical: the flux of volume per unit area per unit time is proportional to the pressure gradient. Equation (8) then becomes,

$$\partial V/a \cdot \partial t = k_{11} \cdot \partial P/\partial x \ . \tag{11}$$

Equation (11) is a statement of Poiseuille's Law for liquid flow through capillary tubes of radius r:

$$\partial V/\pi r^2 \cdot \partial t = (r^2/8\eta) \cdot \partial P/\partial x \ , \tag{12}$$

where η is the liquid's viscosity and $(r^2/8\eta)$ is equivalent to k_{11} in Equation (11).

Moreover, since the change of volume on the left-hand side of Equation (11) is equal to cross-sectional area times change of distance, the areas cancel out and Equation (11) can be written as

$$\partial x/\partial t = k_{13} \cdot \partial P/\partial x \,. \tag{13}$$

Equation (13) is read as "velocity is proportional to the pressure gradient". This latter statement is an empirical law used by meterologists(18) noting that wind velocities are proportional to pressure gradients. Here, however, an empirical or experimental law has been derived from abstract principles of amounts and intensities having no limitations to the subject matter being considered. This agreement between predictions from starting principles about amounts and intensities with the observations from published knowledge is taken as evidence that the starting principles are correct. For an ideal physical test, then, one possible stress is a pressure gradient associated with a flux, as, for example, in gas movements between plates.

In a like manner, the validity of the flux generality can be tested by substitution of the other factors from Columns 3 and 4 of Table 9 into Equation (8), as follows:

4. Electrical: the number of coulombs, Q, per unit area per unit time is proportional to the voltage gradient,

$$\partial Q/a \cdot \partial t = k_{14} \cdot \partial E/\partial x \,. \tag{14}$$

The left-hand side of Equation (14) has the dimensions of current density and the proportionality constant has a dimension of conductivity with units of $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. Equation (14) is, therefore, a form of Ohm's Law. It was derived from principles having nothing to do with electricity. Such a derivation is strong support for Equation (8), because Ohm's Law is based on experimental observations and has not been derived heretofore from independent concepts. From the viewpoint of a physical accelerated test, the electrical stress associated with Equation (14) is the voltage gradient.

5. Thermal: the calories, q, per unit area per unit time are proportional to the temperature gradient,

$$\partial q/a \cdot \partial t = k_{15} \cdot \partial T/\partial x \,. \tag{15}$$

This substitution of the intensity and amount factor from Columns 3 and 4 of Table 9 leads to Biot-Fourier's Law of Heat Conduction. The amount factor for heat in Table 9 has been listed as calories, whereas calories per degree was listed in Table 8. This change of units was done, first, so that energy form 5 in Table 9 might be made consistent with other information in the table. The amount factor thereby is made consistent with the principle of conservation of amounts, but the product of intensity, Column 3, times the amount factor, Column 4, no longer leads to the proper dimension for thermal work.

With the recognition of a fundamental problem in the science of heat, it seems advisable to pass on to the relevancy of heat and temperature to accelerated tests. Temperature is often suggested as a stress factor for accelerated life tests, and its positions in Tables 8 and 9 are consistent with that general presumption. The main significance of Equation (15) is that it leads to the inference that a heat flux will have associated with it a temperature gradient and, therefore, a corresponding stress level for accelerating the degradation of battery qualities. Also, the derivation of the time-honored heat equation (Equation 15) from the consideration of nonthermal relationships provides additional confirmation for the validity of Equation (8).

6. Chemical: the moles, M, per unit area per unit time are proportional to the concentration gradient,

$$\partial M/a \cdot \partial t = k_{16} \cdot \partial C/\partial x \; . \tag{16}$$

This substitution of the intensity and amount factors from Columns 3 and 4 of Table 9 into Equation (8) was the origin of Equation (8), as previously described. Equation (8) is repeated above as Equation (16) in this development. The proportionality constant, k_{16}, is the well-known diffusion constant, D. One important consequence of Equations (8) or (16) and (9) is that a concentration gradient in a battery is predicted to be a stress.

Another important consequence derived from Equation (16) is the "Conservation Generality" in Column 6 of Table 9:

$$\partial I/\partial t = k_{17} \cdot \partial^2 I/\partial x^2 \; . \tag{17}$$

Equation (17) is read, "the time rate of change of intensity is proportional to the second derivative of intensity with respect to distance". Equation (17) may be recognized as Fick's Second Law of Diffusion, previously given as Equation (7). The second derivative in Equation (17) will be recognized as the change of flux with respect to distance.

Just as the proportionality constant, D, in Equation (6) is identical with the constant, D, in Equation (7), it follows that k_{16} is identical with k_{17} for chemical-energy factors. The importance of Equation (17) in connection with accelerated tests is that it provides physical and mathematical relationships for the determination of the proportionality constants in stress, rate-of-strain equations through the observation of transient phenomena.

Thus, for the ideal test involving a pressure gradient as a stress level, a series of measurements of a time rate of pressure change could provide an additional tool for measuring the rate at which the stress, rate-of-strain coefficient is changing:

$$\partial P/\partial t = k_{18} \cdot \partial^2 P/\partial x^2 = k_{11} \cdot \partial^2 P/\partial x^2 \quad , \tag{18}$$

where $k_{18} = k_{11}$ and the volume flux of Equation (18) is nonuniform in direction x. Similarly, for the electrical, thermal, and chemical energies in column 6, a measure of the change of intensity with time could be used as a measure of changing fluxes and stress levels, as follows:

$$\text{Electrical:} \quad \partial E/\partial t = k_{19} \cdot \partial^2 E/\partial x^2 = k_{14} \cdot \partial^2 E/\partial x^2 \tag{19}$$

$$\text{Thermal:} \quad \partial T/\partial t = k_{20} \cdot \partial^2 T/\partial x^2 = k_{15} \cdot \partial^2 T/\partial x^2 \tag{20}$$

$$\text{Chemical:} \quad \partial C/\partial t = k_{21} \cdot \partial^2 C/\partial t^2 = D \cdot \partial^2 C/\partial x^2 \tag{21}$$

Returning to the flux generality in Column 5 of Table 9:

7. Kinetic: the change of momentum, mw, per unit area per unit time is proportional to the velocity gradient,

$$\partial(mv)/a \cdot \partial t = k_{22} \cdot \partial v/\partial x \tag{22}$$

Since, by Newton's Second Law of Motion, the change of momentum with respect to time is equivalent to force, the left-hand side of Equation (22) has units of dynes/cm^2, which is pressure. Therefore,

$$P = k_{23} \cdot \partial v/\partial x \quad ; \tag{23}$$

Equation (23) is an inversion of Equation (12), which is

$$v = k_{12} \cdot \partial P/\partial x \tag{12}$$

Equation (12) is an accepted relationship in the science of meteorology.(18) Equation (23) is a special case of Bernoulli's Theorem of Liquid Flow at constant potential energy. Equation (23) also relates pressure with a momentum flux. It suggests that the gas pressure in a closed container is proportional to the velocity gradient of the centers of mass of the molecules strinking the container walls. This suggestion is believed to be a new concept in the kinetic theory of gases that could account for different behavior for gases having different elastic constants. Equation (23) also suggests that the pressure on a satellite during its reentry is proportional to its velocity gradient. Similarly, Equation (23) suggests that the pressure exerted on a battery case is proportional to the velocity gradient of the battery during a vibration test. Therefore, a stress factor for a vibration test is, by inference, the velocity gradient. The velocity is the product of amplitude times frequency of vibration. The distance over which the velocity changes direction must be known in order to calculate the velocity gradient. Moreover, by analogy with the other energy forms in Table 9, the conservation generality of Column 6 is expected to apply so that

$$\frac{\partial v}{\partial t} = k_{24} \cdot \frac{\partial^2 v}{\partial x^2} \tag{24}$$

All of the above suggestions appear to be amenable to experimental validation. If future work were to validate the suggestions, those results would provide strong support for Equation (8) and the concepts being developed in this section of this report.

8. Light: the number of photons, L, per unit area per unit time, is proportional to the frequency gradient,

$$\partial L/a \cdot \partial t = k_{25} \cdot \partial f/\partial x \tag{25}$$

If each photon in Equation (25) is multiplied by Planck's constant, the left-hand side of the equation then assumes the dimension of an action flux:

$$\frac{\text{erg} \cdot \text{sec}}{\text{cm}^2 \cdot \text{sec}} = k_{26} \cdot \partial f/\partial x = \text{ergs/cm}^2 \tag{26}$$

Equation (26) is a relationship new to the writers of this report. It suggests that an appropriate definition of light intensity should show a proportionality to a frequency gradient. The equation also suggests that radiation damage should be directly proportional to a frequency gradient during absorption. The concept of a frequency gradient has been evoked elsewhere.(19) The concept brings to mind a possibly new explanation for the "red-shift" phenomenon in astronomy.

Ideally, at least, light energy or some other form of radiation would be one of the sources for accelerating degradation of quality. A frequency gradient would be the stress factor. A photon flux would be the rate of strain. The product of the stress times rate of strain then is closely related to the radiological unit for absorption rates as recently described in Henley and Johnson(20):

> "Many units have been devised to characterize the absorption of ionizing radiation. In recent years, however, there has been a general acceptance of the recommendations of the ICRU that the use of certain units be restricted as follows: 1 rad = 100 ergs/g = 6.24×10^{13} ev/g – the absorbed dose rate is the quotient of the rad divided by a unit of time, e.g., rad/sec."

These definitions are quoted to suggest that if the rad were defined officially in terms of ergs/cm^3 rather than ergs/g (the two definitions differ only by the density of the absorbing material), then absorption phenomena would be consistent with the flux generality and all the energy forms in Table 9.

Summary of Stress, Rate-of-Strain Relationships

Stress factors that have been suggested for the ideal physical accelerated test are summarized in Table 10. They are derived from the flux generality of Equation (8):

$$\text{Amount/cm}^2 \cdot \text{sec} = \frac{1}{a} \cdot \partial\,(\text{amount})/\partial t = k_8 \cdot \partial\,(\text{intensity})/\partial x \qquad (8)$$

TABLE 10. SUMMARY OF STRESSES AND STRAINS FOR RECHARGEABLE CELLS FROM RATE-OF-STRAIN RELATIONSHIPS

Stress	Associated Strain	Rate-of-Strain Equation
Pressure gradient	Volume flowing per unit area	(10)
Voltage gradient	Coulombs per unit area	(14)
Temperature gradient	Calories flowing per unit area	(15)
Concentration gradient	Moles flowing per unit area	(16)
Velocity gradient	Change of momentum per unit area	(22)
Frequency gradient	Photons absorbed or emitted per unit area	(25)

The ideal accelerated test will separate, combine, and control the various physical stresses in Table 10 so as to accelerate and retain the dominant failure mechanisms during a shortened test time.

Generalized Strains

Equations (3), (5), and (8) through (26) have shown a large variety of rate-of-strain relationships. All of them would be used in the ideal physical accelerated test to accelerate the rate of degradation of quality. The derivation of accepted physical laws and well-known relationships in Columns 5 and 6 of Table 9 give strong credence to the physical approach being proposed. However, simultaneous attempts to derive a similar generalized stress-strain relationship (Equation 4) have been less certain. It is true that Table 10 lists six kinds of strain with seven different units. But all the strains in Table 10 satisfy a rate-of-strain proportionality to stress called for in Equation (5). Some of them, however, also satisfy the strain proportionality to stress called for in Equation (4) for three-dimensional geometry:

$$\partial I/\partial x = k_{27} \cdot A/a \qquad (27)$$

The three-dimensional stress-strain values at the top of Table 10 substituted into Equation (27) lead to the relationship that the pressure gradient between stored liquids is proportional to the volumes of liquid stored per unit area between the reservoirs:

$$\partial P/\partial x = k_{28} \cdot V/a \quad . \qquad (28)$$

Of course, Equation (28) applies only to cubical containers in which the three spatial dimensions are orthogonal, as described previously for Equation (10).

The electrical stress and strain leads to

$$\partial E/\partial x = k_{29} \cdot Q/a \quad , \qquad (29)$$

which is the standard capacitance equation(21) for parallel-plate condensers.

With further use of Equation (27), a chemical stress could also be expected:

$$\partial C/\partial x = k_{30} \cdot M/a \quad . \qquad (30)$$

An example of Equation (30) is osmosis after equilibrium when M/a is the moles per unit area of membrane and $\partial C/\partial x$ is the concentration gradient across the membrane of thickness, ∂x.

Thermal energy, 5, kinetic energy, 7, and light energy, 8, are not usually thought of as being stored in a static condition. If they were so stored, thermal, kinetic, and light forms of energy would have stress/strain relationships as follows:

Thermal energy: "the temperature gradient is proportional to calories per unit area"

Kinetic energy: "the velocity gradient is proportional to impulse per unit area"

Light energy: "the frequency gradient is proportional to the action per unit area".

Each of these stress-strain relationships would be recognized and utilized in the development of an ideal accelerated test.

It follows that the ratio of coefficients k_{27}/k_8 has the dimension of time. This ratio of coefficients is analogous with "RC" time constants in electrical circuity and with the "elastic/viscous flow" coefficients of spring and dash-pot circuits.(2) Similar time constants will exist for any physical system having simultaneous flux, as described by Equation (8), and storage, as described by Equation (27), of the same form of energy:

$$k_{27}/k_8 = \tau_{31} \tag{31}$$

The existence of Equation (31) also suggests the use of transient measurements as a means of determining the coefficients associated with stress-strain and stress, rate-of-strain equations.

The stress-strain relationship of Equation (27) shows one of the reasons why the definition of battery quality in Equation (1a) must specify a time of charge and discharge within each cycle. Thus, the definition

$$Q_I = 1/\Delta I \cdot n \tag{1a}$$

leads to a quality measurement that depends on the time of charge or discharge, t'. Also, the amount and intensity factors in Equation (27) depend on t'. Therefore, quality could also be defined in terms of charge and discharge times.

$$Q_I' = Q_I \cdot t' = t'/\Delta I \cdot n \tag{32}$$

Since stresses in Table 10 have been identified as intensity gradients and the strains as amounts/cm^2, the degradation of voltage quality given by Equation (32) would be accelerated by the stress given by Equation (29). The specific use of Equations (28) and (30) to accelerate the quality described by Equation (32) requires a quantitative relationship between coulombs charged or discharged with volume (Equation 28) and with moles (Equation 30). Both quantitative relationships exist in Faraday's Laws of Electrolysis.

Readers should note that the qualities of Equation (1a) and (32) are not the same as the stresses in Table 10, because qualities have been defined in terms of intensity factors in Column 3 of Table 9, whereas stresses have been defined in terms of intensity gradients in Columns 5 and 7 in Table 9. Thus, qualities will be measured in terms of pressures, voltages, temperatures, and so forth, whereas stresses will be used (whether measured or not) as pressure gradients, voltage gradients, temperature gradients, and so forth. This situation is exacly analogous with the difference between resistances and resistivities or between flows (amount per unit time) and fluxes (amount per unit time per unit area). The differences between intensity factors and intensity gradients should become even more apparent with the following developments.

The Impulse/Amount Generality

The impulse/amount generality in column 8 of Table 9 is also based on the intensity and amount factors in columns 3 and 4 of Table 9 and states, simply:

The change of intensity, ΔI, is proportional to the time rate of change of the amount, $\partial A/\partial t$:

$$\Delta I = k_{33} \cdot \partial A/\partial t \quad . \tag{33}$$

Equation (33) is called the "Impulse/Amount Generality" because its coefficient, k_{33}, has the dimension of impulse per unit of amount. It differs from the flux generality of Equation (8) in that geometric, orthogonal dimensions are not used.

Substituting next the intensity and amount factors of columns 3 and 4 of Table 9 into Equation (33), the following are obtained:

1. Mechanical: Force is proportional to velocity,

$$\Delta F = k_{34} \cdot \partial x/\partial t \quad . \tag{34}$$

Equation (34) is a relationship used to derive Stoke's Law of Viscous Flow for falling bodies:

$$F = 6\pi\, \eta \cdot r \cdot v \quad , \tag{35}$$

where η is the viscosity of the fluid through which the sphere, of radius r, is falling at a velocity $v = dx/dt$. Then, $k_{34} = 6\pi\, \eta\, r$. The proportionality constant, k_{34}, is frequently called the "moving friction" coefficient. Equation (34) is an empirical law based on many experimental observations. Its derivation from abstract principles is not normally found in the literature. However, a statistical derivation is possible.(22)

2. Surface: a change of surface tension is proportional to the time, rate of change of area,

$$\Delta \gamma = k_{36} \cdot \partial a/\partial t \quad . \tag{36}$$

This quantitative dependence of surface tension on changing areas has not been found in the literature. However, all textbooks on physical chemistry report that surface-tension measurements require slow measurements approaching steady-state conditions in order to achieve reproducible and reliable tension data.

3. Mechanical: a change of pressure is proportional to the volume flow rate,

$$\Delta P = k_{37} \cdot \partial v / \partial t \quad . \tag{37}$$

Equation (37) is a special case of Poiseuille's Law for Fluid Flow, previously given in this report as Equation (12), when path length and cross-sectional area are constant. For example, the volume rate of water flowing from a water faucet is proportional to the pressure drop within the faucet.

4. Electrical: a change of voltage is proportional to the coulombs per second.

$$\Delta E = k_{38} \cdot \partial Q / \partial t \quad . \tag{38}$$

Equation (38) is a statement of Ohm's Law of Electrical Conductance, in which k_{38} is the circuit resistance. Ohm's Law is also an empirical law based on experimental observations which, prior to this report, has not been derived from abstract principles having nothing to do with electricity. Its derivation from Equation (33) lends credibility to the principles involved.

5. Thermal: the temperature drop is proportional to the rate of flow of calories,

$$\Delta T = k_{39} \cdot \partial Q / \partial t \tag{39}$$

Equation (39) is Fourier's Law for Heat Conduction.

6. Chemical: the concentration change is proportional to the moles per second increasing or decreasing,

$$\Delta C = k_{40} \cdot \partial M / \partial t \tag{40}$$

Equation (40) leads to a form of the Mass-Action Law of Equilibrium when applied to both reactants and products.

7. Kinetic: the change of velocity is proportional to the time rate of change of momentum

$$\Delta V = k_{41} \cdot \partial (mv) / \partial t \tag{41}$$

Equation (41) is same as Equation (34), because $\partial(mv)/\partial t = \Delta F$. Therefore, the same relationship for two forms of mechanical energy, 1 and 7, was derived from the same generality of Equation (33). This agreement supports the validity of Equation (33) as well as the factors chosen for Columns 3 and 4 in Table 9.

8. Light: the frequency change is proportional to the rate of loss of photons,

$$\Delta f = k_{42} \cdot \partial L / \partial t \tag{42}$$

When the number of photons, L, is multiplied by Planck's constant, Equation (42) becomes

$$\Delta f = k_{43} \cdot \Delta \text{ergs} \tag{43}$$

Equation (43) is Planck's Law for light energy, in which k_{43} is the reciprocal of Planck's constant. This derivation of Planck's Law from the impulse/amount generality is the main reason why the intensity and amount factors for light have been retained in Table 9 as further evidence for a valid classification of dimensions.

The Impulse/Rate Generality

The Impulse/Rate Generality is also based on the intensity and amount factors in Columns 3 and 4 of Table 9 and states, simply:

> The change of intensity, ΔI, is proportional to the second derivative of amount with respect to time, $\partial^2 A/\partial t^2$:

$$\Delta I = k_{44} \cdot \partial^2 A/\partial t^2 \tag{44}$$

Equation (44) is called the "Impulse/Rate Generality" because its coefficient, k_{44}, has the dimension of impulse divided by the time rate of change of amount. Therefore, the ratio of k_{44} to k_{33} has the dimension of time:

$$k_{44}/k_{33} = \tau_{45} \quad . \tag{45}$$

This ratio in Equation (45) will provide a characteristic time constant, τ_{45}, that is analogous with the time constant for an inductive/resistive electrical circuit.

Substituting the intensity and amount factors of Columns 3 and 4 from Table 9 into Equation (44) leads to the following relationships:

> 1. Mechanical: the change of force is proportional to the second derivative of distance with respect to time,

$$\Delta F = k_{46} \cdot \partial^2 x/\partial t^2 \tag{46}$$

This is Newton's Second Law of Motion, "Force is proportional to acceleration", wherein the constant k_{46} is mass. Such a derivation of Newton's Second Law from abstract principle is strong confirmation of the validity of the abstract principles upon which the derivation is based.

> 4. Electrical: the change of voltage is proportional to the second derivative of coulombs with respect to time,

$$\Delta E = k_{47} \cdot \partial^2 Q/\partial t^2 \tag{47}$$

Equation (47) is the accepted law of electromagnetic induction in which k_{47} is the self-inductance coefficient.

Similar relationships have been deduced from the impulse/rate generality of Equation (44) and are tabulated in Column 9 of Table 9. After making these considerations, a total relationship between certain intensities and their corresponding amount factors in Columns 3 and 4 of Table 9 was noted:

$$I = k_{48}A + k'_{48}\partial A/\partial t + k''_{48}\partial^2 A/\partial t^2 \quad . \tag{48}$$

Examples of Equation (48) are the equation of motion of a damped, simple harmonic oscillator(23), or the equation for the total voltage drop in a simple electrical circuit containing a capacitance, a resistance, and a self-inductance.(21) In the latter example, the coefficients k_{48}, k'_{48}, and k''_{48} can be identified in physical terms as the reciprocal capacitance, the resistance, and the self-inductance, respectively. Also, $k'_{48} = k_{33}$ and $k''_{48} = k_{44}$, by analogy.

In Equation (48), the first term, with k_{48}, will have values other than zero for steady-state conditions of stored energy, as in an electrical capacitor as well as for dynamic forms of the energy. Conversely, the second and third terms of Equation (48) will have non-zero values only for dynamic conditions, as when electrical current flows. The first and second terms in Equation (48) will have non-zero values whether the amount rate is steady state or changing, whereas the third term, with k''_{48}, will have values other than zero only when the amount rate is changing. These distinctions between the various terms of Equation (48) could be used to distinguish between the various kinds of stresses contributing to the total stress on a battery because of the different ways that intensity factors can be changed.

Interaction of Stresses

With eight forms of energy having the numerous relationships indicated in Table 9, the need to consider how to use, or to avoid using, the various combinations in the ideal accelerated life test is apparent. Thus, Table 10 was followed by the conclusion:

> "The ideal accelerated test will separate, combine, and control the various physical stresses in Table 10 so as to accelerate and retain the dominant failure mechanisms during a shortened test time".

The paragraphs to follow are aimed at answering how to separate, combine, and control the various physical stresses.

The major tools for handling the various interactions of energy are the conservation laws. The First Law of Thermodynamics is the most all inclusive:

> "Energy can neither be created nor destroyed; when one form of energy disappears another form of energy always appears in equivalent quantity."(24)

This law is important for applying Table 9 to cells or batteries, because it requires quantitative accounting for all the energy. For example, as chemical energy, 6, is converted into electrical energy, 4, there will be some changes in thermal energy, 5, mechanical energy, 1, surface energy, 2, volume expansion energy, 3, and kinetic energy, 7. With all events, the total energy within a sealed cell does not disappear. This energy is either converted to one form from another form of energy within the cell or the energy passes out of or into the sealed cell to or from the environment. For a closed system, in the thermodynamic sense of including the cell or battery and its environment, the total energy will be conserved:

Total energy = sum of energies for all processes (49)

Therefore, if the proportions of various energies as a function of strain and of rate-of-strain are known, then the various physical stresses can be deduced from their corresponding relationships in Table 9. For example, if 20 watt-hours of electrical energy are taken from a sealed cell, there will be X_1 watt-hours of heat generated plus X_2 watt-hours of mechanical work plus X_3 watt-hours of chemical work at some given rate, η_1. At a different rate, η_2, and for the same electrical output of 20 watt-hours, the proportions of X_1, X_2, and X_3 may be different, but the total energy must remain constant so that energy is neither created nor destroyed. Equation (49) must be satisfied.

Another conservation tool for separating, combining, and controlling physical stresses may be deduced from the principle of conservation of amounts. In stating this principle prior to Table 8 of this report, emphasis was given to the interaction between two reservoirs of the same energy form:

> "When two or more reservoirs of the same form of energy are allowed to interact with one another, the sum of the amount factors remain constant."

Faraday's Laws of Electrolysis are cited as well-known examples of the principle of conservation of amounts. However, the developers of an ideal physical accelerated test should recognize that the principle of conservation of amounts can be applied to conversions of energy forms. For energy conversions, this principle is applied to conserve amounts, while at the same time, the concept of efficiency may be introduced. Thus, for example, with Faraday's Laws of Electrolysis, every coulomb (the amount factor) shows up as electrons, ions, molecules, or free radicals and not one net electron is created or destroyed. However, in a nickel-cadmium cell, a loss of electron at the positive electrode may oxidize nickel hydroxide during charging or may cause the evolution of oxygen gas. The efficiency of either oxidation process could lie between 0 (zero) and 100 percent, inclusive; but the total balance of electrons, without exception, is always 100 percent. Similarly, every photon either exists or is annihilated by reaction according to Einstein's Law of Photoelectricity. Every molecule in solution either passes through a membrane by osmotic pressure or it does not pass through. There is no uncertainty about such events, and amount factors in a closed system remain constant:

The sum of amount factors entering = the sum of amount factors stored and leaving. (50)

A consequence of Equation (50) and the Principle of Conservation of Amounts is that the fluxes of Equation (8) must also be conserved:

The sum of fluxes entering = the sum of fluxes leaving and interacting. (50a)

For example, the flux of photons entering is equal numerically to the flux of photons transmitted plus the flux of amount factors created by the absorption of photons.

This conservation of amounts and fluxes means all the energy forms in Table 9 can be separated, combined, or controlled in a quantitative fashion, and Equations (50) and (50a) must be satisfied as well as Equation (49). Once amounts and appropriate geometries have been determined, the generalities of columns 5, 6, 7, 8, and 9 in Table 9 give a relationship to intensities and stresses and, through Equations (1a) or (32), to cell or battery qualities thereby. The ideal accelerated life test then will measure (a) initial qualities and (b) time rate or cycle rate of quality degradation at high stress levels. Then, extrapolations to normal or operational stress levels will allow predictions of times to cell failures under normal operating conditions. Moreover, because the qualities and stresses will have been based on quantitative work, stress/strain, and stress/rate-of-strain relationships, the failure mechanisms will have a physical meaning.

BATTERY FAILURES AND FAILURE MECHANISMS

Failure Definition

Failures for sealed spacecraft cells or batteries are defined in the previous work for the U. S. Air Force(2), in essence: a cell or battery has failed when it is unable to deliver on discharge or accept on charge a predetermined current for a specified length of time within a certain voltage tolerance set by the user.

In order to develop failure-analysis procedures, it is found necessary to define failure modes, failure determinants, and failure mechanisms. These definitions are repeated below because the ideal physical accelerated life test will shorten the time to failure without changing the failure mode, the failure determinant, or the failure mechanism. Thus, these modes, determinants, and, especially, their mechanisms should be properly identified.

Failure ≡ volts, amperes, and/or time out of tolerance

Failure mode ≡ failure dimension(s) that went out of tolerance

Failure determinant ≡ cause of failure mode = cause or result of an electrical fault at a particular component

Failure mechanism ≡ cause(s) of failure determinant.

For example, the voltage may fall below an acceptable level on charge (mode) because of an electrical short between the electrodes (determinant) caused by the migration and reprecipitation of negative electrode material in the separator (mechanism). Overall, a loss in voltage quality is observed.

With reference to Equation (1a), the above definition of failure could be related through voltage or hourly rate to battery electrical quality. That is, a battery will have failed when its electrical quality, from Equation (1a), has become unacceptable to the user. The other definitions of quality to be associated with the stresses in Column 5 of Table 9 or Column 1 of Table 10 will not be used as a definition of failure here because the users of spacecraft batteries can be expected to accept any pressure, temperature, or concentration provided that electrical quality remains acceptable. From a physical point of view, therefore, the nonelectrical energy forms in Tables 8 and 9 are of interest for failure analysis and for accelerated testing only insofar as the nonelectrical processes can be related to electrical qualities.

Failure Determinants and Mechanisms

Spacecraft cells and batteries may be tested under three ideal electrical regimes:

(1) Constant voltage

(2) Constant current

(3) Constant power.

In any one practical application, however, not only may one or more of these regimes may be used, but also the regulation may be far from constant. In any test, the cycle period (time) will usually be fixed, so that, if a cell or battery does not perform satisfactorily for the whole duration of the cycle, the failure mode can be described in terms of either the voltage or the current, rather than time, going out of tolerance. In constant-power applications, the cycle period (time) is also usually fixed, so that, again, in Table 11, only the voltage and current tolerances have been given as the variables of interest in failure analyses. Table 11 also gives the total number of possible failure modes associated with these variables. These six modes are the first tool for classifying the failure analysis data in a search for failure determinants and mechanisms.

The next step toward describing failure mechanisms is to identify the various determinants associated with each failure mode. For controlled testing of cells or batteries with constant current or constant voltage, the determinants used to describe the $+E_c$ mode are the same as those for the $-i_c$ mode and, similarly, for the $-E_c$ and $+i_c$ the $-E_d$ and $+i_d$ modes. Many of the determinants to be listed in Table 12 can be related to, or observed, as internal-resistance changes. Observations associated with the $+E_c$ mode will usually show as excessive gas pressures, while for $-E_c$ and $-E_d$, a loss of capacity can be identified. With these simplifications in mind, it is possible to compile a list of failure determinants and mechanisms applicable to spacecraft cells and batteries which, interpreted properly, can be used to describe any failure mode.

Table 12 lists the suggested failure mechanisms for the determinants of the voltage or corresponding current failure modes, as deduced from information reported in the literature. Certain mechanisms, namely, 2(a), 6(b), 7(c), 8(b), and 9(c) are not

TABLE 11. LIST OF POSSIBLE FAILURE MODES FOR SEALED SPACECRAFT CELLS

Limiting or Test Application	Variable	Failure Mode	Description
Current	Voltage, E	$+E_c$	Too high voltage on charge
		$-E_c$	Too low voltage on charge
		$-E_d$	Too low voltage on discharge
Voltage	Current, i	$+i_c$	Too high current on charge
		$-i_c$	Too low current on charge
		$-i_d$	Too low current on discharge
Power	Voltage, E, and Current, i	$+i_c$, $-i_c$	Too high current or too low current on charge
		$+E_c$, $-E_c$	Too high voltage or too low voltage on charge
		$-i_d$, $-E_d$	Too low current or voltage on discharge

TABLE 12. LIST OF POSSIBLE FAILURE MECHANISMS ASSOCIATED WITH THE DETERMINANTS OF THE VOLTAGE OR CURRENT FAILURE MODE

Failure Mode	Failure Determinant	Suggested Failure Mechanisms
(1) $+E_c$ or $-i_c$	Temporary or permanent passivation of electrodes	(a) Carbonate film buildup on surface of electrode due to increased CO_2 in electrolyte
		(b) Changes in crystallinity and porosity with cycling
(2) $+E_c$ or $-i_c$	Improper balance of active materials	(a) Improper charge balancing of elements
(3) $+E_c$ or $-i_c$	Electrolyte loss, or composition change	(a) Loss from evaporation/spray due to faulty closures, including corrosion of the seals
		(b) Absorption of CO_2 from the air or from degradation of the separator: soluble electrode materials reacting to give insoluble product, surfactants, additives, etc.
(4) $+E_c$ or $-i_c$	Change in properties of separator	(a) Increased resistance due to change in composition, porosity, wettability, etc.
(5) $+E_c$ or $-i_c$	Corrosion of tabs, collectors, terminals	(a) Reduction in cross-sectional area leading to increased cell resistance
		(b) Deterioration of contacts, welds, grids, etc., leading to increased cell resistance
(6) $-E_c$ or $+i_c$	Short circuit between electrodes	(a) Migration of negative electrode material and redeposition in separators
		(b) Extraneous material between electrodes, due to poor quality control or nickel-sinter corrosion
		(c) Degradation of separator, including "burning" and the effects of sterilization
(7) $-E_c$ or $+i_c$	Short circuit between electrodes and case	(a) Breakdown of insulating properties of seals
		(b) Excessive migration of active electrode materials, shape change
		(c) Auxiliary electrode tab touching other electrodes – poor quality control

TABLE 12. (Continued)

Failure Mode	Failure Determinant	Suggested Failure Mechanisms
(8) $-E_d$ or $+i_d$	Short circuit between electrodes	(a) Migration of negative electrode material and redeposition in separators
		(b) Extraneous material between electrodes due to poor quality control or nickel-sinter corrosion
		(c) Degradation of separator, including "burning" and the effects of sterilization
(9) $-E_d$ or $+i_c$	Short circuit between electrodes and case	(a) Breakdown of insulating properties of seals
		(b) Excessive migration of active electrode materials
		(c) Auxiliary electrode tab touching other electrodes – poor quality control
(10) $-E_d$ or $+i_d$	Loss of electrode capacity	(a) Memory effects, temporary or permanent passivation, drying out of positive electrodes, all leading to inefficient charging
		(b) Change in balance of active materials in electrodes
		(c) Spontaneous decomposition of active materials
		(d) Reduction of charged materials by hydrogen evolved due to corrosion or by soluble organic materials in electrolyte or reduced active material

time dependent in the sense that they might be monitored during an accelerated test. For example, mechanisms such as 7(c) and 9(c) might result from poor quality control and need not be considered as part of an ideal accelerated life test. All the other mechanisms in Table 12 will change as some function of time and should, therefore, be related to stresses and strains in Table 9 for structuring an accelerated test. Note that, because of the definitions given for an ideal accelerated life test, the useful mechanisms for analysis of data, by necessity, are rate processes.

A review of the failure-analysis literature shows that the most frequently reported determinants or mechanisms for all common types of sealed cells are those listed in Table 13:

TABLE 13. FAILURE DETERMINANTS OR MECHANISMS IN ORDER OF THEIR PREVALENCE OF OCCURRENCE

(1) Internal shorts
(2) Seal or case leaks
(3) Loss of capacity
(4) Migration of active materials
(5) Separator degradation
(6) Excessive gas pressures
(7) Tab faults
(8) Carbonation of electrolyte
(9) Cell imbalance

These are listed in their approximate order of frequency of occurrence, and no effort is made to differentiate between failure determinants or mechanisms in making the tabulation. Some idea of the relative dominance of the failure determinants for nickel-cadmium batteries is given in Table 14, taken from Sparks.(25) The numbers given in Table 14 represent the failure rate x 10^{-9} per hour. It should be realized that Tables 13 and 14 are not totally unbiased for two reasons. First, only data reported in the available literature were used to compile the listings. Second, during life testing, and often during actual use, a temporary loss of capacity occurs. This loss is not reported because reconditioning of the cells (e.g., by capacity checks) erases the effect. Thus, the cell may eventually fail by internal shorting and be reported as such, even though reconditioning was necessary to restore the temporary loss of capacity.

TABLE 14. TYPICAL FAILURE OCCURRENCES FOR NICKEL-CADMIUM CELLS(25)

Failure "Determinant"	Years of Life						Notes
	1	2	3	4	5	6	
Plate-to-plate short	50	50	50	100	200	500	--
Terminal-to-case short	10	10	20	50	100	500	Single-seal design
Terminal-to-case short	3	4	6	8	12	17	Two-seal design
Seal, case leak	10	20	35	55	75	100	--
Cell Imbalance	10	20	50	100	500	1000	--

In terms of an ideal test, then, the important failure determinants to be considered are

(1) Plate-to-plate short circuits (Determinant 6 in Table 12)

(2) Plate-to-case shorts for one-seal design or case-to-terminal shorts for two-seal-closure designs (Determinant 7 in Table 12)

(3) Loss of plate capacity (Determinant 10 in Table 12).

The migration of active materials, Number 4 in Table 13, and separator degradation, Number 5 in Table 13, both are included in the three determinants listed above.

Excessive gas pressures, Number 6 in Table 13, which can cause cell bulging or rupture and, hence, electrolyte loss, are related to $+E_c$ and $-E_d$ and are influenced by such variables as ambient temperature, electrolyte level, and balance of active materials. If the cell voltage is adequately controlled and limited on charge or discharge, then the problem of gas evolution and accumulation will not arise when there is enough excess negative-electrode capacity.

AN IDEAL PHYSICAL APPROACH TO ACCELERATED TESTING

The physical approach to accelerated testing developed in this report has not been reduced to practice. It is a conceptually ideal approach to the measurement of cell or battery qualities and the time or cycle rate of change of those qualities as a function of various stresses at different levels of intensity. From the viewpoint of physical chemistry, therefore, the ideal test program for NASA would be based on some understanding of the mechanisms causing failures such that the stresses and strains in Table 10 would be related to each failure mechanism. The equations in Table 9 would show the relevant variables to be measured and how these variables were to be dealt with. Interrelations between different kinds of stresses would be deduced on the basis of the conservation laws. Initial qualities, Q_I of Equation (1a) or Q_I' of Equation (32), would be measured. Only two qualities are necessary: (1) voltage charge quality and (2) voltage discharge quality, because only electrical qualities are associated with battery failures. All stresses other than electrical would be related to the voltage qualities, Q_E. Then, the rate at which Q_E changes with number of cycles or time would be measured at high stress levels to allow an early prediction of failure at normal operating stress levels.

To illustrate how this ideal test might be reduced to practice, consider some of the failure determinants or mechanisms reported in the battery literature and listed in Table 12:

(1) Internal shorts - from Table 10, these should be related to

- (a) Concentration gradients
- (b) Temperature gradients
- (c) Voltage gradients

(2) Seal or case leaks - from Table 10, these should be related to

- (a) Pressure gradients
- (b) Temperature gradients
- (c) Velocity gradients (vibration)

(3) Loss of capacity - from Table 10, these should be related to

- (a) Concentration gradients
- (b) Voltage gradients
- (c) Temperature gradients.

In each example, temperature gradients appear to be a contributing factor to failure. Therefore, the relationships between temperature gradients and the other stresses appear to be one of the most important considerations for development of the future accelerated tests.

Another important stress appears to be a concentration gradient. Such a stress cannot be measured directly inside sealed cells. Therefore, future techniques must make use of other stresses and strains to control, to vary, and to measure, by inference, the concentration gradients.

ALTERNATIVE APPROACHES

The preceding paragraphs have developed a physical approach for a conceptual, ideal space-battery accelerated-test program for NASA and have listed relevant electrochemical cell variables, dependencies, and interrelations showing how they are to be dealt with, as called for in Phase II of the contractual Statement of Work. In arriving at the conceptual design, optimal approaches were also considered, as called for in the same Statement of Work. Alternative considerations are listed below in the form of questions as a record of work done for NASA. The answers are abbreviated to one or two sentences in most cases, so that major attention will be directed to the concepts selected earlier, with only minor attention given to concepts below which were abandoned or left in a state of fragmentary consideration.

Question 1. Why start with such a vague concept as quality?

Abbreviated Answer. We might talk about "states", "performances", or "properties" instead of "qualities", but these are semantic problems. The important point is that failures and accelerated life tests are to be based on a degradation of "quality" as interpreted by the users. A particular definition of quality, however, has been recommended because it has been mathematically associated with coefficients of stress/strain and stress/rate-of-strain equations, and can be given numerical values. For example, combining Equation (1a) with Equation (14) gives voltage quality, Q_E, in terms of the flux areas, a, the ampere-hour capacities, AH, and the distances over which voltage gradients occur, Δx:

$$Q_E = a \cdot k_{14}/\Delta x \cdot AH \tag{52}$$

Thus, when voltage qualities change with aging, it means the proportionality constants of Equations (14) and (52) may have changed. Of course, nonelectrical stresses may also change voltage quality, in accordance with relationships deduced in Table 9 and in Equation (48).

Question 2. Why is quality defined as a reciprocal relationship in Equations (1a) and (32)?

Abbreviated Answer. For psychological reasons, it was thought desirable to have higher quality associated with larger numerical values.

Question 3. Why not define qualities in terms of dimensionless numbers?

Abbreviated Answer. Dimensionless ratios generally have the advantage of expressing measurements relative to dimensions within the system being measured. However, any definition must be user oriented because battery quality is a subjective term whose meaning depends on the user's application. Thus, Equation (1a) requires that qualities be measured at the same time in each cycle for a given hourly rate of discharge. Then, the predicted life is relevant only to the chosen cycle times and cycle rates which, for practical reasons, should also be as close as possible to the desired user's rates and times. Conceptually, there is no such thing as an absolute and universal quality, because there is no such thing as an absolute and universal battery application. Certain requirements are necessary so far as an ideal accelerated life test is concerned:

(1) Quality must not mean life, because life is defined as time required for the quality to degrade to an unacceptable level.

(2) Quality must degrade with aging, and the rate of degradation of quality must increase with higher stress levels.

(3) Quality must be defined so that battery vendors cannot derive artificial quality ratings without commensurate benefits for the user's application.

(4) The user's definition of quality must be related to the user's definition of failure.

(5) Quality must be expressable with numerical values whose measurements can be quantitatively verified.

It is also desirable, but not necessary, that quality numbers should be convenient to say or to write, such as numbers between 0.1 and 100. It is possible to define qualities so that their numbers would fall between zero and unity, with a zero meaning zero quality and unity meaning perfect quality. It is also possible to devise quality standards. Users can and will define qualities any way they want to, but, for an accelerated life test, the above five requirements for quality must be satisfied. Equation (1a) is believed to fulfill the above requirements and has the added advantages of being related to physical processes and concepts.

Question 4. Qualities have been given a physical significance noted in the answer to Question 1, but where are the functions for showing how qualities should degrade with time?

Abbreviated Answer. If such functions were known, there would be no need for accelerated tests.

Question 5. Isn't there a better basis for selecting intensity and amount factors than the "principle of higher intensity" and the "principle of conservation of amounts"?

Abbreviated Answer. A great deal of thought has been given to intensive versus extensive variables, to tangible versus intangible parameters, to generalized forces and displacements, and to other concepts in an attempt to define the necessary and sufficient conditions for selecting intensity and amount factors. The two principles asked about, plus the principle that "any form of energy can be described as a product of amount and intensity factors", are all necessary conditions for selecting the factors. The amount and intensity factors should also satisfy the generality equations at the top of columns 5, 6, 7, 8, and 9 in Table 9. Both factors should be usable in appropriate applications of Equation (48). Moreover, the amount and intensity factors will be found to satisfy other general relationships, such as

$$\Delta I = k \Delta A \quad , \tag{53}$$

examples of which are rectilinear and rotational compliance as well as electrical and acoustical capacitance(32);

$$\text{kinetic energy} = (1/2) \cdot k_{54} \cdot (\partial A / \partial t)^2 \quad , \tag{54}$$

where k_{54} has common names such as mass, inductance, inertance, or moment of inertia;

$$\text{potential energy} = (1/2) A^2 / k_{55} \quad , \tag{55}$$

where k_{55} has common names such as compliance or capacitance; and

$$\text{dissipation} = k_{56}(\partial A/\partial t)^2 \quad , \tag{56}$$

where k_{56} will be a "resistance factor" for each energy form. Further work is needed to deduce and to demonstrate the usefulness and limitations of amount and intensity factors. Moreover, the amount and intensity factors should be related to Onsager's Reciprocity Relationships(33), to Lagrange's Equations(34), and to Hamilton's Equations(34), if possible. Then, the present physical approach to accelerated testing will have been tied in with a vast body of physical and mathematical knowledge.

Question 6. If qualities are observed to increase with time (or number of cycles), what happens to the accelerated life test that is based on an extrapolation of decreasing qualities?

Abbreviated Answer. Failures will not occur with either increasing or constant voltage quality. Therefore, the test must be continued for a sufficiently long time (or number of cycles) to observe consistent degradation of voltage quality.

Question 7. Do higher degradation rates of quality occur at higher levels of stress or at higher levels of work?

Abbreviated Answer. Every stress has an associated strain, the product of which is work per unit volume. Therefore, stress, strain, rate of strain, or work can be related to degradation rates, because they can all be related to one another. However, stress is used in Assumption 3 of the present development as a basis for an ideal physical accelerated test for these reasons:

(1) Stress, as used herein, is consistent with thermal, mechanical, and other accepted physical connotations of stress.

(2) The use of stress concepts in the present development have consistently led to useful predictions and results beyond those predictions resulting from work concepts.

Question 8. Why not describe degradation of quality in terms of entropy changes?

Abbreviated Answer. The physical approach developed in this report attempts to describe degradation of quality with conservation and vector concepts for which the concept of entropy is superfluous.

Question 9. Can transients be used to measure qualities and their degradation rates?

Abbreviated Answer. Yes, with appropriate future development of the concepts herein. The stress/strain and the stress/rate-of-strain relationships have characteristic time constants described with Equation (31). Also, Columns 6, 8, and 9 in Table 9, and the coefficients in Equation (48) involve time constants that could be used for transient measurements of qualities and their degradation rate.

Question 10. Is there not a more general and more useful definition of strain than "amount per unit area"?

Abbreviated Answer. In the context of Table 9, many instances in the literature could be cited which show

$$\partial I = k_{53} \cdot \partial A \quad , \tag{53}$$

$$\partial I = k_{57} \cdot \partial A/\mathrm{cm}^3, \text{ and} \tag{57}$$

$$\partial I = k_{58} \cdot \partial A/A \tag{58}$$

Equation (58) is believed to be a more general and, hence, a more useful definition of stress and strain than Equation (2). Thus,

$$\text{stress x strain} = \text{work}/\mathrm{cm}^3 \tag{2}$$

is a special case of the more general definition:

$$\text{stress x strain} = \text{work/amount} \tag{59}$$

Further work will be necessary to develop these important considerations.

SUMMARY OF PHYSICAL APPROACH

As shown in this section, an ideal physical approach to the accelerated testing of rechargeable cells requires an operational measure of the quality of a cell. It is recommended that the quality of a cell at a particular time within a charge-discharge cycle be defined as follows:

$$\text{Quality} = Q_I = \frac{1}{\Delta I \cdot n} \quad , \tag{1}$$

where Q_I is calculated from an observed intensity factor change, ΔI, at an hourly rate of charge or discharge, n.

It is further shown, using stress/rate-of-strain relations, that the stresses acting on a cell are related to intensity gradients that are associated with changes of voltage, temperature, pressure, and concentration over some finite distances within cells. The relevant distances within cells are either fixed or unmeasurable. Concentration gradients cannot be measured directly because the cells are sealed. Consequently, it is recommended that accelerated tests for cells should be set up and analyzed in terms of measurements of voltages, temperatures, and pressures. The initial qualities and their rates-of-degradation then would be used to predict time to failure for any given cell.

Table 15 shows the data requirements for a physical approach to an ideal accelerated test program for rechargeable cells. The voltage, temperature, and pressure measurements would be taken at the end of discharge and at the end of charge in each charge-discharge cycle. The voltage gradients would be varied two ways: by five levels of strain and by five levels of rate-of-strain. The computation of qualities with their time rates of change would be easily accomplished by an off-line computer.

A major accomplishment of the physical approach consists of the identification of stresses as intensity gradients. This single accomplishment allows a variety of complexities with spacecraft cells to be simply correlated with a vast body of accepted physical knowledge. A wide assortment of stresses and accelerated tests thereby are inferred. For example, it is seen from Table 12 that:

Pressure Gradients can be both static and dynamic. Static pressure gradients can exist across the cell case, between electrodes, or between pores of electrodes. Dynamic pressure gradients can be associated with fluxes of moving materials, either solid, liquid, or gaseous. The way in which individual cells are retained in a battery of cells could be an important variable in connection with cell life as effected by pressure gradients.

Voltage Gradients will vary with depth of discharge, amount of overcharge, and with rates of charge and discharge. Voltage gradients will depend also on cell and electrode dimensions, both areas and thicknesses. Thus, a cell designed for an initial high quality may not be well designed for long life. Voltage gradients may, or may not, have associated with them temperature gradients and concentration gradients, but if these additional gradients exist, there will be an increase in the rate of degradation of voltage qualities.

Temperature Gradients are always to be expected in operating spacecraft cells. If a test were to be designed so that absolutely uniform temperatures were to be retained throughout cells, there would be no temperature gradients and no temperature stress. Any effects of temperature would then be associated with the concentration gradients, the pressure gradients, or the voltage gradients brought about by the constant temperature level. Since uniform temperatures cannot be attained in actual tests, there will always be temperature gradients. These gradients should be directly proportional to the temperature differences in a cell, because the physical dimensions of cells change very little. Hence, the rate of temperature changes and the relationships in Columns 6, 8, and 9 of Table 11 could reveal degradation of cell qualities.

Concentration Gradients are never absent in sealed cells. Even in a completely discharged state, the negative electrodes are saturated with $Cd(OH)_2$ and the positive electrodes are saturated with $Ni(OH)_2$, which create concentration gradients. In the charged state, concentration gradients could be maximized. Soluble organics from the separator and other elements and compounds can provide concentration gradients which cannot be monitored but which can accelerate the degradation of quality.

TABLE 15. DATA REQUIREMENTS FOR A PHYSICAL APPROACH TO AN IDEAL ACCELERATED TESTING PROGRAM FOR RECHARGEABLE CELLS

Data Requirements	Remarks
1. Cell weights and volumes	1. Qualities may be converted to equal weights or sizes for intercomparison of cells with units such as mho/cm^3 or mho/g.
2. Cell length, width, and height	2. Physical dimensions may be useful for estimating gradients.
3. Cell specific heats, (calories/degree/gram)	3. For physically meaningful units of temperature qualities, it may be desirable to convert Equation (1a) into units such as amperes/calorie.
4. Charge and discharge current	4. All tests will be made at constant current.
5. Environmental temperature	5. All temperature changes in a cell will be measured relative to constant environmental temperatures.
6. Cell ampere-hour capacities	6. Cells being placed on life tests should be matched on the basis of equal AH capacities.
7. Initial end-of-charge voltage	7a. Cells being placed on life tests should be matched on the basis of equal end-of-charge voltages.
	7b. Voltage changes, ΔV in Equation (1a), will then be measured relative to initial end-of-charge voltage.
8. End-of-charge and End-of-discharge voltages at (a) + terminal vs 3rd electrode and - terminal vs 3rd electrode, or (b) + and - terminals.	8. Calculation of cell voltage qualities, Equation (1a)
9. End-of-charge and End-of-discharge temperatures at (a) Positive terminals and (b) Center of active materials on outside of case	9a. Calculation of temperature qualities with units such as amperes/calorie
	9b. For diagnostic purposes during subsequent failure analyses.
10. End-of-charge and End-of-discharge pressures	10a. Calculation of pressure qualities with units such as amperes/liter-atmosphere
	10b. For diagnostic purposes during subsequent failure analyses
	10c. For safety purposes by avoiding explosions or bursting cells

Velocity Gradients can be associated with vibration tests. In general, a high-quality cell will show negligible electrical effects due to vibration. For spacecraft cells, vibration tests would be useful for acceptance specifications, but, once the cells are in space, the effects of vibration should be negligible.

Frequency Gradients in Table 12 refer to adsorption of electromagnetic radiation. If there is negligible adsorption, there will be negligible stress and, hence, negligible effect on cell life.

DESTRUCTIVE AND NONDESTRUCTIVE TESTING

by

Ralph E. Thomas

INTRODUCTION

In an ideal accelerated test for spacecraft batteries, a blend of nondestructive and destructive testing is advantageous. The previous portions of this report are concerned primarily with nondestructive tests. In this portion, some of the characteristics of destructive testing are considered. For an ideal test, it is argued that the degradation processes that lead to failure may be identified before failure occurs by making a destructive examination of cells that are operationally good. If these processes are identified, then the physical approach to accelerated testing can associate this information with physical stresses for making failure predictions for improving cell design to eliminate failures or for changing environmental conditions to reduce the operating stresses, etc. The following paragraphs describe destructive testing in more detail.

DESTRUCTIVE TESTING

Destructive tests can be included in an accelerated-test program in several different ways:

(1) A cell may be destroyed by operating the cell at high levels of stress.

(2) A cell may be removed from test and subjected to a destructive examination before failure.

(3) A cell may be examined after failure to determine the immediate cause of failure.

(4) A cell may be examined after failure to affirm that failure mechanisms were unchanged by the accelerated test conditions.

In the first case, the cell is considered to have ceased to function as a cell; it is removed from test; and an autopsy is performed to determine the failure determinants and/or mechanisms. In the second case, a cell that is operating satisfactorily is removed from test and is destructively examined in order to infer its operational "state" at the time it was removed from test. In the third and fourth cases, destructive tests are used as diagnostic tools to aid in the physical interpretation of the results from the accelerated-test program.

Destruction of a Cell on Test

The operational failure of a cell on test may result from intentional destruction or unintentional destruction. If the destruction is intentional, it usually means that high stress levels were deliberately chosen in order to determine the life of the cell under especially adverse conditions. In some accelerated tests, the stress levels are increased continuously over time until failure occurs. Such testing is not considered to be an ideal accelerated test because the cell may have failed for a different reason than that which would occur under normal stress levels. Nevertheless, in preliminary or exploratory experiments, useful information may sometimes be obtained by such deliberate destruction. Destruction is especially useful if the cell is subjected to a critical physical examination designed to indicate what degradation processes caused the failure to occur.

In other instances, a cell may cease to operate during a test even though the stress levels were not intended to exceed those maximum levels of stress that are consistent with normal failure processes. In these cases, a considerable amount of information may be obtained by a thorough autopsy of the cell. Causes of catastrophic failures might be revealed and, hence, remedial action could be taken by the manufacturer(s).

Failure-analysis procedures to perform "autopsies" have been outlined elsewhere for nickel-cadmium and silver-zinc cells.(30) Hence, these will not be discussed in further detail here. Work has also been performed on "tear-down" analyses of unused, nonfailed cells.(31) The purpose of these tests is to provide reference data with which the autopsy data may be compared in an effort to identify the degradation processes. Both of these procedures or analyses are applicable also to the parametric failures discussed next.

Parametric Failures

In an ideal accelerated test, at least five stress levels of increasing magnitude may be desirable for statistical reasons.(2) The least severe stress level would correspond to intended use conditions and the most severe stress level would be the maximum stress level that would not change the dominant failure mechanism(s) associated with the conditions of use. Under the above conditions, any failure that occurs is then relevant to the normal use condition. However, the penalties associated with this restriction are of two kinds: (1) the acceleration factor may be small and (2) no operational failures may occur within a reasonable period of time. In other words, to ensure the validity of the accelerated test, it may be that no operational failures are obtained.

In order to minimize the effect of this no-failure problem, an ideal accelerated test would include a set of "parametric" definitions of failure. That is, definitions of failure would be constructed so that, whenever a particular measurement or combination of measurements is "out of tolerance", then the cell would be judged to be a "parametric" failure even though the cell is operationally good.

It is recommended that a sequence of five such parametric definitions be set up that vary between the most stringent tolerances (Type 5) and normal operational tolerances (Type 1). Thus, a cell would be expected to show, first, a Type-5 failure, then a Type-4 failure, and so on until the cell fails operationally as a Type-1 failure. In general, a cell would only be removed from test when it becomes a Type-1 failure. The other parametric failures merely serve to trace the degradation of the cell quality over time. The parametric definitions allow predictions to be made regarding the time at which a cell would arrive at the Type-1 level and thereby give a prediction of the operational life of the cell. When several cells are used at each stress level, the predictions can be made statistically valid. Moreover, when several cells are used at each of several stress levels, statistical correlations may be obtained between the stress level and the predicted time to reach a Type-1 failure. This may be done even if Type-1 failures do not occur during the accelerated test, provided statistically established transitions have occurred among the more stringent parametric failure modes. In other words, the sequence of parametric failure modes serves as an aid for extrapolation to obtain the time to failure for each stress level. These extrapolated times then can be extrapolated over stress levels to obtain the extrapolated time to failure at the use-stress level.

Destruction of Operational Cells

As described above, a sequence of parametric failure modes may be used to monitor the transition of cells through successive parametric failure modes. This may be done at each stress level. The transitions would be expected to occur more rapidly at the higher stress level.

In some instances, it may be desirable to select a cell that had failed in a given parametric mode and to destructively examine the cell. This would be done in order to gain further understanding of the state of degradation, failure mechanisms, etc., that may be occurring in ways that are not detectable or identifiable by means of the nondestructive measurements that can be made during the previously described, ideal accelerated test. Consequently, it is recommended that a few operationally good cells be destructively examined during the course of an ideal accelerated test to assess the value of such examinations. Based on the results of such examinations, it may be appropriate to increase or decrease the frequency of such destructive examinations.

In summary, the destructive examination of operational cells after the elapse of various test times is recommended as a method of monitoring the degradation processes during the course of operational life. Because the cell is destroyed by the examination, the usefulness of the obtained information depends to a large extent on the similarities of the destroyed cell to the other operational cells in the same parametric failure mode at the same stress level. That is, to be most useful, it must be possible to infer that the same state of physical degradation holds for the remaining associated cells. In principle, this may be done by careful selection of the cells to be used at each stress condition. With these restrictions, the physical examinations may then yield information that is useful in establishing the relations between states of physical degradation and thus provide valuable information for an analysis of the type described under ideal physical accelerated tests.

GENERAL HARDWARE CONSIDERATIONS

by

Orval L. Linebrink and Ralph E. Thomas

INTRODUCTION

In specifying an experimental procedure in which batteries are to be subjected to accelerated tests and the results observed, the problem of the adequacy of available hardware arises. Such hardware may be best discussed in three general categories. The first category involves the supply and controls necessary to charge and discharge the cells under test. These considerations include the programming controls that automatically put the cells through a selected schedule of cycles with automatic changes within any cycle. The second category of hardware involves the measurement of all variables deemed significant. The measurements must be selected in such a fashion that any of the analyses previously described in this report can be performed. The third category is concerned with intrumentation required in order to store and analyze the data generated during the cycle tests. These three categories are discussed separately. It will become apparent that some type of computer will be necessary to satisfy these requirements.

TEST-CONTROL AND PROGRAMMING REQUIREMENTS

From the various concepts of the ideal accelerated tests previously presented, there exist some common requirements. All of these concepts are based upon some form of cycle operation of the cells at various levels of stresses. Adequate ranges for the charging and discharging rates must be provided to insure that the stress levels are not limited by the power supplies. In addition, power supplies must be sufficiently stable to establish and to maintain constant current or constant voltage modes of operation. Solid-state instrument technology incorporated in currently available power supplies is capable of excellent long-term use with adequate voltage and current ranges and controlled regulations to a few hundreths of a percent. Models specified in catalogs can be selected to meet anticipated demands for accelerated tests. However, the regulatory performance of these power supplies should be checked from time to time to ensure either constant current or constant voltage operation. The ripple content of the output should also be within the manufacturer's specifications as a check of hardware performance.

Programming of the cycling regime of the cells may be accomplished with commercial programmers. However, the compiling of an on-line programmer with feedback computer control of the program parameters may require some specialized electromechanical units to insure that the sequencing, synchronizing, and repeatibility of the programming units do not introduce variations in the data.

MEASURING AND RECORDING TEST VARIABLES

Ideal accelerated tests require recordings of the performance of individual cells and groups of cells. Stress levels and operating conditions must be defined in terms of practical measurable quantities. Some quantities, which themselves are not easily or accurately measured, may be inferred by measuring related phenomena and then calculating the desired quantities from known relationships. For example, the thermal-energy content of a cell may be obtained from measurements of temperatures, specific heats, and masses of the various components. The adequacy of a temperature-gradient measurement is limited by the difficulty of locating a temperature sensor in the proper place. If some of the stress levels or performance phenomena, however, cannot be measured or inferred with present techniques, then they become the subject for needed research.

The recording of battery-performance parameters for accelerated tests presents two demands that are opposite in nature. On the one hand, the changes which describe degradation in batteries over many cycles occur at a very slow rate. On the other hand, the changes in any one parameter, such as voltage, may show a rapid change during portions of an individual charge-discharge cycle. Hence, the recording demands vary from the need for a fast, continuous recording to those instances in which a single recording every few hours or every few days might be sufficient.

The accuracy of recorders, as well as most other instruments, is most often specified as a percentage of full scale. Hence, in the selection of recorders or other instruments, choice of a proper range for the instrument is even more important than the specified accuracy alone. For example, if it is desired to measure a voltage difference of 0.1 volt within an accuracy of 1 percent, then the measuring instrument must have a resolution of 0.001 volt. Assuming a cell voltage is 1.250 volts and the instrument chosen gives 4 digits, it is apparent that 1 digit in the fourth place represents 1 percent of the changes being observed. Since most digital meters have errors of some small percentage error, ±1 in the last place, a 5-place readout is needed to insure a 1 percent resolution of the changes in voltage. Instruments of the differential voltmeter type lessen this requirement for a 5-place readout. Differential voltmeters are designed to yield the difference between an unknown voltage and a stable reference voltage (0.1 percent is quite common). With such an instrument, a 1 percent recorder with a span of 0.1 volt can give results equal in accuracy to the 5-place instrument mentioned above.

The recording rate of the required data system should not yield voluminous redundant data when little or no change in the variables of interest are being observed. The frequency of measurement can be altered to insure efficient use of the equipment. Prior experience or good judgment can suggest the magnitude of changes in the variables which may be of interest to the analysis and subsequent predictions. These changes can be used with the on-line control/acquisition computer. In such a test, the data are continuously scanned, but only changes equal to or greater than those of interest are recorded.

AN IDEALIZED COMPUTER SYSTEM FOR DATA ANALYSIS

As indicated by the previous sections of this report, an ideal accelerated test for spacecraft cells would permit three kinds of data analysis: empirical, statistical, and physical. The empirical analysis is initiated on-line, serves as an initial filter for the detection of errors, makes tentative classifications of the raw data, and then generally processes the accumulated data by a sequence of procedures designed to exploit selected structures detected in the data. The statistical analyses are initiated after the collection of a batch of data and generally are based on the assessment of the statistical significance, precision, and confidence levels associated with various averages and correlations. Special emphasis is given to those quantities that indicate the possible persistence of time-based trends found to occur in the data. The physical analysis of data can be initiated on-line to compute initial qualities and to show their time rate of degradation.

Software for Empirical Analysis

The empirical approach requires an assortment of software packages that permit the generation of a wide variety of multivariate combinatorial classifications over time. New classifications must be generated, as warranted, by the data structures observed in prior classifications. The output format required for empirical analysis consists primarily of graphical displays of measured values, frequency histograms, and tables. In general, the data-processing requirements are mathematically primitive because classifications are emphasized. However, storage requirements are created by the large number of measurements that must be processed. Additional requirements are created by the desire for a completely flexible on-line interaction with the data acquisition, handling, and reporting system. It appears that some recently developed software may permit the interactive capabilities required by the empirical analyst.(28,29) However, the need for specific empirically oriented software for data analysis is acute. Considerable software development appears to be required in this area to obtain a wide variety of mutually compatible programs that may be implemented in any sequence found appropriate by on-line interaction with the raw data.

Software for Statistical Analysis

The ever increasing availability of statistical software suggests that standard programs are available from many sources for analysis of accelerated-test data. Some ad hoc programming may be required to obtain statistical assessments of unusual data structures detected by empirical methods. However, these needs can only be anticipated when all causes of unusual data structure are understood from a physical-process viewpoint.

In contrast to the on-line interactive requirements of the initial empirical analyses, the statistical programs generally suffice with batch modes of operation. Ideally, such batch analyses would be made during time that is available for use by the same computer system that is used for data acquisition.

Software for Physical Analysis

Software packages for analysis of accelerated-test data using the physical approach are virtually nonexistent. One NASA-developed program based on dimensional analysis may be particularly useful(30, 31), but standard programs based on the Arrhenius or Eyring models, for example, do not appear to exist. In general, it may be premature to develop such software for routine application until a better understanding is obtained of the physical mechanisms associated with degradation of cells over time. Once the physical mechanisms and their associated laws are extablished, little difficulty would be expected in computerizing the physical analysis of accelerated-test data.

An Ideal Computer System

The ideal computer system would consist of two computers. One computer would be used on-line and one would be used off-line.

Off-Line Computer Requirements

The off-line computer should be a general-purpose computer large enough to handle empirical programs such as AID and the less-demanding programs associated with the statistical and physical approaches.

On-Line Computer Requirements

The on-line computer should permit the acquisition of data from a set of approximately 300 cells per life test at a scanning rate of one complete scan every 2 minutes or 12 complete scans per charge-discharge cycle, whichever yields more data. In addition, this computer would monitor the data, generate alarms, made conversions of units, and identify and tag data for subsequent off-line analysis. It is estimated that a 16,000-word memory would be sufficient for the on-line computer.

Provisions should be made to minimize downtime for the on-line computer. The data-monitoring system should have an emergency power source so that information relevant to power or mechanical outages could be recorded and subsequent data analysis minimally degraded.

The software should permit user intervention for the purpose of making changes in frequency of measurement and error-detection thresholds. The acquisition of data should have highest priority and would permit some empirical data processing between acquisition functions.

CONCLUSIONS

The physical approach to an ideal accelerated test for rechargeable cells shows that the test should be based on establishing the relations between the degradation rate of the quality of a cell and the stress levels experienced by the cell during operation. It is necessary that quality be defined as a numerical measure of the "goodness" of a cell. Moreover, it is necessary that stress levels represent quantitative measures of the "severity" of the operating conditions. For the ideal accelerated test, the quality of a cell at a particular time within a charge-discharge cycle is defined by the following expression

$$\text{Quality} = Q_I = \frac{1}{\Delta I \cdot n} \quad ,$$

where Q_I is calculated from a measurable change in an intensity factor, I, at an hourly rate of charge or discharge, n. Intensity gradients are found to be associated with the operating stresses on a cell and are measured in terms of voltage, pressure, and temperature variables for practical applications, as shown by Table 16.

TABLE 16. SUMMARY OF IMPORTANT STRESSES AND ASSOCIATED STRAINS APPLICABLE TO RECHARGEABLE CELLS

Stress	Rate of Strain	Recommended Qualities
Pressure gradient	Volume flow per unit area	$Q_p = \frac{\text{amperes}}{\Delta P \cdot \text{AH} \cdot \text{liters/F}}$
Voltage gradient	Coulombs flow per unit area	$Q_E = \frac{\text{mho}}{\text{cm}^3}$, or $Q_E = \frac{\text{mho}}{\text{gram}}$
Temperature gradient	Calories flow per unit area	$Q_T = \frac{\text{amperes}}{\Delta T \cdot \text{AH} \cdot \text{g/AH} \cdot C_v}$
Concentration gradient	Moles flow per unit area	None
Velocity gradient	Change of momentum per unit area	None
Frequency gradient	Photons absorbed per unit area	None

Under these definitions of quality and stress, an ideal accelerated test then is structured in accord with the following assumptions:

(1) The quality of a cell varies over time and, after the elapse of a sufficiently long time, the quality will degrade.

(2) The time rate of degradation of quality depends on the stress level experienced by the cell during its operating life.

(3) Higher degradation rates occur at higher stress levels.

(4) Cell failure will eventually result from the degradation of quality to an unacceptable level.

(5) For a valid accelelerated test, the dominant failure mechanism does not change over the range of stress levels used in the test.

A further structuring of the conceptual basis is obtained by strict adherence to the proposed definitions of failure mode, failure determinant, and failure mechanisms. The definitions are given as follows:

Failure mode: The identification of one or more electrical measurements (current, voltage, power, or coulombs) that are found to be out of tolerance under specified operating conditions.

Failure determinant: The identification of the component associated with the failure mode and its condition.

Failure mechanism: The physical or chemical processes that are associated with the failure determinant.

Table 15 shows that measurements of voltages, temperatures, and pressures should be taken during an accelerated test. The measurements should be taken at the end of discharge and end of charge in each charge-discharge cycle as a minimum requirement. The degradation of voltage quality over a sequence of charge-discharge cycles then should be plotted as a function of voltage, temperature, and pressure levels. Equations are shown in Table 9 for relating stress with fluxes and strains. Current densities are shown to have more physical significance than currents, just as voltage gradients are more significant than voltages. Where relevant areas and distances cannot be measured. equations have been deduced for changing and controlling stresses by changing and controlling intensity and amount factors. As a result, the physical approach to accelerated testing developed in this report appears to be theoretically tractable and operationally practical.

As a result of the statistical approach to the ideal accelerated test, it is concluded that 15 electrically matched cells should be put on test at each stress level. Five times during the test, a random selection and destructive examination of one of these cells should be carried out to obtain detailed data on the physical state of the cells after the elapse of various operating times. These examinations will destroy five of each 15 cells during the test. The recommended test also allows up to five additional cells per stress

TABLE 15. DATA REQUIREMENTS FOR A PHYSICAL APPROACH TO AN IDEAL ACCELERATED TESTING PROGRAM FOR RECHARGEABLE CELLS

Data Requirements	Remarks
1. Cell weights and volumes	1. Qualities may be converted to equal weights or sizes for intercomparison of cells with units such as mho/cm^3 or mho/g.
2. Cell length, width, and height	2. Physical dimensions may be useful for estimating gradients.
3. Cell specific heats, (calories/degree/gram)	3. For physically meaningful units of temperature qualities, it may be desirable to convert Equation (1a) into units such as amperes/calorie.
4. Charge and discharge current	4. All tests will be made at constant current.
5. Environmental temperature	5. All temperature changes in a cell will be measured relative to constant environmental temperatures.
6. Cell ampere-hour capacities	6. Cells being placed on life tests should be matched on the basis of equal AH capacities.
7. Initial end-of-charge voltage	7a. Cells being placed on life tests should be matched on the basis of equal end-of-charge voltages.
	7b. Voltage changes, ΔV in Equation (1a), will then be measured relative to initial end-of-charge voltage.
8. End-of-charge and End-of-discharge voltages at (a) + terminal vs 3rd electrode and - terminal vs 3rd electrode, or (b) + and - terminals.	8. Calculation of cell voltage qualities, Equation (1a)
9. End-of-charge and End-of-discharge temperatures at (a) Positive terminals and (b) Center of active materials on outside of case	9a. Calculation of temperature qualities with units such as amperes/calorie
	9b. For diagnostic purposes during subsequent failure analyses.
10. End-of-charge and End-of-discharge pressures	10a. Calculation of pressure qualities with units such as amperes/liter-atmosphere
	10b. For diagnostic purposes during subsequent failure analyses
	10c. For safety purposes by avoiding explosions or bursting cells

level to be removed from the test to provide for special-purpose tests, transient tests, and for unforeseen experimental contingencies. Thus, the basic experimental plan cells for 15 cells at each stress level, with five of these cells actually expected to complete the test.

It is further concluded that five levels of stress should be used in the test designs, with temperature, voltage, and pressure taken as three stresses. The voltage stress is to be varied both by strain (depth of discharge and amount of overcharge) and by rate of strain (hourly rate of charge and discharge). Thus, the required number of cells is given by (15 cells/stress level) x (5 stress levels/stress) x (3 stresses) plus the additional cells required for the two ways of altering voltage stresses, making a total of 300 cells.

Table 7 shows a summary of the data requirements for the statistical approach. In addition to the 15 matched cells for each stress level, the table shows that voltage measurements should be taken at 12 time intervals within each charge-discharge cycle.

It is concluded that a response-surface method of data analysis should be used. The data should be analyzed off-line by a computer capable of performing standard statistical analyses. The time dependence of the response surface should be analyzed concurrently to permit predictions of future electrical behavior of the cells during the accelerated test. The predictions should be made of the cycle times required for the quality of the cells at each stress level to degrade to various intermediate levels of quality between the initial quality and the unacceptable quality level associated with failure. These intermediate (parametric) failures would serve as a basis for developing improved prediction methods of cell quality during the performance of the accelerated tests.

From the empirical approach to accelerated testing, it is concluded that full identification of the cells put on test is required. All data relating to manufacturer, type, size, lot number, plate-formation data, and previous history must be available. In addition, data resulting from preliminary examinations, acceptance testing, screening tests, tear-down tests, etc., are to be included in the data file. It is further concluded that measurements of cell voltage should be made every 2 minutes within each charge-discharge cycle, with an additional provision that at least 12 cell-voltage measurements be obtained in each cycle.

Table 2 shows a summary of the data requirements for the empirical approach. Because of the extensive combinatorial data-analysis requirements of the empirical approach, an off-line computer system is required. In addition, some on-line computer capability (approximately 16,000 words) is required for some minimal processing, including the "tagging" of certain output data for more efficient off-line data processing.

The empirical methods used to analyze the data should include programs, such as the AID program, as exemplified in this report.

With its emphasis on correlation and the search for patterns, the empirical approach ensures that no precursor of failure is overlooked. The statistical approach ensures the statistical validity and reproducibility of predicted cell performance. The physical approach provides for an understanding of the physical mechanisms associated with the degradation processes. In general, it is concluded that the ideal accelerated test for rechargeable cells should be based on the simultaneous use of the empirical, statistical, and physical approaches.

Table 7 shows a summary of the data requirements for a statistical approach to an ideal accelerated-test program. In addition to the 15 cells for each stress level, the table shows that voltage measurements should be taken 12 times within each charge/discharge cycle.

TABLE 7. DATA REQUIREMENTS FOR A STATISTICAL APPROACH TO AN IDEAL ACCELERATED-TESTING PROGRAM FOR RECHARGEABLE CELLS

Requirement	Purpose of Requirement
At least 15 matched cells for each stress level, with removal of 2 randomly selected cells at 5 equally spaced times during the expected duration of the test.	With this procedure, 5 cells would be expected to complete the entire test; of the 2 randomly selected cells, one would be subjected to a tear-down test (a) and the other would be available for special-purpose tests, transient tests, or experimental contingencies.
Voltage measurements should be taken at 12 time intervals within each charge-discharge cycle.	An average-voltage curve with its standard deviation would be computed for each set of matched cells. The data would be analyzed <u>off-line</u>, using statistical methods such as the response-surface technique described in this report.

(a) The purpose of the tear-down test is discussed in the section of this report on Destructive and Nondestructive Testing.

related to statistical reliability estimates, F-ratios, and embedded statistical designs. The algebraic expression of the tree gives still further insight into the mathematical relations among the variables. All of these observations show that empirical methods form a potentially powerful approach to data monitoring and analysis. The difficulties associated with the empirical approach stem largely from a lack of computer software.

Table 2 gives a summary of the data requirements for the empirical approach to the accelerated testing of rechargeable cells. The table shows that the empirical approach requires full identification of the cells to be put on test, together with all data obtained from preliminary examinations, acceptance tests, and/or screening tests. Such data may be found to be highly correlated with observed cell behavior during the accelerated test. To provide adequate data for an empirical analysis, it is recommended that cell-voltage measurements be taken every 2 minutes within each charge/discharge cycle, with an additional requirement that at least 12 cell-voltage measurements be obtained in each cycle.

TABLE 2. DATA REQUIREMENTS FOR AN EMPIRICAL APPROACH TO AN IDEAL ACCELERATED TESTING PROGRAM FOR RECHARGEABLE CELLS

Data Requirements	Use of the Data
Full identification of cells to be put on test, including manufacturer type, size, lot number, plate formation data, previous history, etc.	This requirement may permit the association of the pretest experience with observed behavior of the cell during the test.
Preliminary examination data, including results of acceptance testing, screening tests, tear-down tests, etc.	To permit the possible association of the initial condition of the cell with observed behavior of the cell during the test.
Twelve cell-voltage measurements should be taken within each charge/discharge cycle, or measurements should be taken at 2-minute intervals, whichever yields more data.	Empirical methods such as the AID program described in this report would be applied to analyze the data and relate degradation of quality to stress level, initial condition, and pretest experience of the cell.

Because of the extensive data-analysis requirements of the empirical approach, an off-line computer system is required. In addition, some on-line computer capability is required for minimal processing, including the "tagging" of certain output data for more efficient off-line data processing. In an ideal test program, an on-line computer capability of 16, 000 words is recommended.

FUTURE WORK

The work of the next phase of this contract will focus on the practical implementation of an accelerated life test for spacecraft cells. A statistically designed experiment will be developed and will include recommendations regarding the following:

(1) What measurements should be made?

(2) What calculations are to be made with the measurements?

(3) With what precision and frequency should measurements and calculations be made?

(4) What are the specific instrumentation and computer requirements?

(5) How are "stress" levels to be established, measured, and maintained over time?

(6) What data are to be recorded, monitored, and analyzed?

(7) What computer hardware and software systems are required?

(8) What environmental controls are required?

As a result of the next phase of research, a practical accelerated test capable of immediate implementation will be designed within reasonable economic constraints, the resulting test program will approach the ideal program to the maximum extent permitted by available hardware and software.

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The following bibliography of reports dealing with accelerated testing is a continuation of the bibliography given in the Phase I Report. The same classification used previously in the Phase I Report is maintained, namely:

(a) Quality, acceptance, and screening tests

(b) Life (operational) tests, including failure analysis

(c) Life (accelerated) tests

(d) Test instrumentation and implementation

(e) Data reduction and analysis

(f) Life (accelerated) tests for components other than batteries having some relevance to spacecraft battery testing

(g) Mathematical and statistical theories related to accelerated testing.

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