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A METHOD OF ANALYZING RADIOACTIVE DECAY CURVES

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A METHOD OF ANALYZING RADIOACTIVE DECAY CURVES

A method of analyzing radioactive decay curves (or curves of the same functional form, such as absorption curves) is outlined in this paper. Although a graphical method and the method of least squares can be applied, it seemed desirable to look for another method. The graphical method, though simplest to execute, is not an objective method, nor does it furnish an estimate of the errors in the computed parameters. The method of least squares, though objective, is laborious and requires a knowledge of the decay constants, since these are not in linear form for least squaring. Another criticism is that it does not yield a simple formula for estimating errors. The proposed method is somewhat less objective than the method of least squares, but is simpler to apply, yields the decay parameters, and permits a more satisfactory estimate of errors.

The experimentally determined decay curve, $A(t)$, is considered to represent the sum of a number of activities, $A_i e^{-\lambda_i t}$, at any time, t. That is,

$$A(t) = \sum_i A_i e^{-\lambda_i t} \tag{1}$$

where A_i and λ_i are respectively the activity at time zero and the decay constant for species "i".

It is assumed that $A(t)$ may be represented within experimental error by $e^{f(t)}$ where $f(t)$ is a simple polynomial in t. Otherwise stated, $f(t)$ is fitted to $\ln A(t)$. The curve fitting can, with a little experience, be done quite rapidly by trial and error methods, or the polynomial can be least squared to $\ln A(t)$. It will be assumed, for purposes of discussion, that $f(t)$ is obtained by a least squaring procedure. It is proper to least square $\ln A(t)$ rather than some other function of $A(t)$ if the probable relative experimental error in $A(t)$ is the same over the experimental range of time. This is only approximately true, but usually more nearly correct than assuming constant probability of absolute error.

Having obtained f(t), one may write,

$$\sum_i A_i e^{-\lambda_i t} = e^{f(t)} \tag{2}$$

Equation (2) is differentiated (i-1) times to yield a total of i equations. These are solved for the individual A_i in terms of the λ's and derivatives of f.

For a two component system,

$$A_1 = \frac{1}{\lambda_2 - \lambda_1}\left[f' + \lambda_2\right] e^{\lambda_1 t} e^{f(t)} \tag{3}$$

For a three component system,

$$A_1 = \frac{1}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}\left[\lambda_2\lambda_3 + (\lambda_2 + \lambda_3) f' + f'^2 + f''\right] e^{\lambda_1 t} e^{f(t)} \tag{3'}$$

Systems containing more than three activities over most of the experimental range are not often dealt with because the analysis becomes so poor. Formulas will not be given for such systems, but the extension is obvious.

Equations (3) and (3') allow the computation of A_i at any value of t. However, computations at different values of t should not be weighted equally. The weighting factor for each A_i is ascertained by requiring it to be a function which will cause the average relative difference between $e^{f(t)}$ and $\sum_i \bar{A}_i e^{-\lambda_i t}$ to be zero. The A_i which are computed with this weighting factor are denoted by $\bar{A}_i$. One requires:

$$\int_0^{t_f} \sum \bar{A}_i \frac{e^{-\lambda_i t}}{e^{f(t)}} dt - \int_0^{t_f} dt = 0 \tag{4}$$

Representing A_i computed from (3) and (3') at time t by $A_i(t)$, and the weighting factor by $g_i(t)$,

$$\bar{A}_i \int_0^{t_f} g_i(t)\, dt = \int_0^{t_f} A_i(t)\, g_i(t)\, dt \tag{5}$$

Hence,

(6) $$\int_0^{t_f} \sum_i \bar{A}_i\, g_i(t)\, dt = \int_0^{t_f} \sum_i A_i(t)\, g_i(t)\, dt$$

From the method of deriving $A_i(t)$,

(7) $$\sum A_i(t) \frac{e^{-\lambda_i t}}{e^{f(t)}} = 1$$

Therefore, if $g_i(t)$ is given by

(8) $$g_i(t) = \frac{e^{-\lambda_i t}}{e^{f(t)}}$$

Then combining (6), (7) and (8) it is found that (4) is satisfied.

The averaging factor for a given species is simply proportional to the fraction of the total activity at any time which is due to the activity of the given species at the same time.

The $\bar{A}_i$ parameters are computed from

(9) $$\bar{A}_1 \int_0^{t_f} \frac{e^{-\lambda_1 t}}{e^{f(t)}}\, dt = \frac{1}{\lambda_2 - \lambda_1} \int_0^{t_f} [f' + \lambda_2]\, dt$$

(9') $$\bar{A}_1 \int_0^{t_f} \frac{e^{-\lambda_1 t}}{e^{f(t)}}\, dt = \frac{1}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \int_0^{t_f} [\lambda_2\lambda_3 + (\lambda_2 + \lambda_3) f' + f'^2 + f'']\, dt$$

for two and three component systems respectively.

The latter are equivalent to

(10) $$\bar{A}_1 \int_0^{t_f} \frac{e^{-\lambda_1 t}}{A(t)}\, dt = \frac{1}{\lambda_2 - \lambda_1} \left[\lambda_2 t_f + f(t_f) - f(0)\right]$$

(10') $$\bar{A}_1 \int_0^{t_f} \frac{e^{-\lambda_1 t}}{A(t)}\, dt = \frac{1}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \left[\lambda_2\lambda_3 t_f - (\lambda_2 + \lambda_3)(f(t_f) - f(0)) + f'(t_f) - f'(0) + \int_0^{t_f} f'^2\, dt\right]$$

The integrals $\int_0^{t_f} \frac{e^{-\lambda t}}{e^{f(t)}}\, dt$ must be evaluated graphically, but since they are required to the accuracy with which $\bar{A}_i$ may be computed, they are easily evaluated. One may replace $e^{f(t)}$ by the original data, $A(t)$.

To compute the $\bar{A}_i$ parameters, it is necessary to know the number of components in the system and the values of the decay constants.

The basis of the determination of the latter follows.

If $e^{f(t)}$ exactly represents a function $\sum A_i e^{-\lambda_i t}$, A_i may be exactly computed at any value of t from equations (3) and (3') providing the correct λ_i's are chosen. If the choice of the λ_i's is not correct, (3) and (3') give each A_i as a function of t. The correct choice is made when each A_i from (3) and (3') is a constant, that is when $\frac{dA_i}{dt}$ is zero over the experimental time interval.

For a two component system,

(11) $$\frac{dA_1}{dt} = e^{\lambda_1 t} e^{f(t)} \left[\lambda_2\lambda_1 + (\lambda_2+\lambda_1) f' + f'' + f'^2\right]\left[\frac{1}{\lambda_2-\lambda_1}\right]$$

Values of λ_1 and λ_2 are selected so as to best require $\frac{dA_1}{dt}$ to be zero over the experimental range of time. As before, a weighting factor $\frac{e^{-\lambda_1 t}}{e^{f(t)}}$ is used. If λ_1 and λ_2 are chosen correctly,

$$\lambda_2\lambda_1 + (\lambda_2+\lambda_1) f' + f'' + f'^2 = 0$$

the identical condition would have been obtained if A_2 were required constant. Values of ($\lambda_2\lambda_1$) and ($\lambda_1 + \lambda_2$) are obtained by a least squaring process. The time axis is imagined to be divided into equal infinitesimal regions . Corresponding to each interval is a value of f', f'' and f'^2. Using this infinite sot of observational equations in the least squ ring formula, one obtains:

(12) $$\begin{cases} \lambda_2\lambda_1 \dfrac{\sum \delta t}{\delta t} + (\lambda_2+\lambda_1)\dfrac{\sum f_i' \delta t}{\delta t} = -\dfrac{\sum f_i'' \delta t}{\delta t} - \dfrac{\sum f'^2 \delta t}{\delta t} \\ \lambda_2\lambda_1 \dfrac{\sum f_i' \delta t}{\delta t} + (\lambda_2+\lambda_1)\dfrac{\sum f_i'^2 \delta t}{\delta t} = -\dfrac{\sum f_i' f_i'' \delta t}{\delta t} - \dfrac{\sum f_i'^3 \delta t}{\delta t} \end{cases}$$

or

(13) $$\begin{cases} \lambda_2\lambda_1 \int_0^{t_f} dt + (\lambda_2+\lambda_1)\int_0^{t_f} f' dt = -\int_0^{t_f} f'' dt - \int_0^{t_f} f'^2 dt \\ \lambda_2\lambda_1 \int_0^{t_f} f' dt + (\lambda_2+\lambda_1)\int_0^{t_f} f'^2 dt = -\int_0^{t_f} f'' f' dt - \int_0^{t_f} f'^3 dt \end{cases}$$

or

(14) $$\begin{aligned} &\lambda_2\lambda_1 t_f + (\lambda_2+\lambda_1)(f(t_f) - f(0)) = -(f'(t_f) - f'(0)) - \int_0^{t_f} f'^2 dt \\ &\lambda_2\lambda_1 (f(t_f) - f(0)) + (\lambda_2+\lambda_1)\int_0^{t_f} f'^2 dt = -\tfrac{1}{2}(f'^2(t_f) - f'^2(0)) - \int_0^{t_f} f'^3 dt \end{aligned}$$

The unevaluated integrals are integrals of polynomials and may be easily evaluated. Having evaluated $\lambda_1\lambda_2$ and $(\lambda_1 + \lambda_2)$, λ_1 and λ_2 are evaluated as the roots of the quadratic:

$$\lambda^2 - (\lambda_1 + \lambda_2)\lambda + \lambda_1\lambda_2 = 0 \tag{15}$$

For a three component system, one obtains the following in a similar fashion:

(13')
$$\lambda_1\lambda_2\lambda_3\int_0^{t_f} dt + (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)\int f' dt + (\lambda_1 + \lambda_2 + \lambda_3)\int (f'' + f'^2)dt = -\int (f''' - 3f'f'' - f'^3)dt$$
$$\lambda_1\lambda_2\lambda_3\int f' dt + (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)\int f'^2 dt + (\lambda_1 + \lambda_2 + \lambda_3)\int f'(f'' + f'^2)dt = -\int f'(f''' - 3f'f'' - f'^3)dt$$
$$\lambda_1\lambda_2\lambda_3\int (f'' + f'^2)dt + (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)\int f'(f'' + f'^2)dt + (\lambda_1 + \lambda_2 + \lambda_3)\int (f'' + f'^2)^2 dt = -\int (f'' + f'^2)(f''' - 3f'f'' - f'^3)dt$$

The three λ's are evaluated from the roots of the cubic

$$\lambda^3 - (\lambda_1 + \lambda_2 + \lambda_3)\lambda^2 + (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)\lambda - \lambda_1\lambda_2\lambda_3$$

The integrals appearing in (13') are simply integrals of polynomials.

If one or more λ_i values are known in advance, the computations are greatly simplified as each known λ_i value can replace an equation in (13) or (13').

Although it was previously stated that this method permits a more satisfactory discussion of errors than the method of least squaring, the discussion is not complete. An inherent weakness of this method is that derivatives of an empirical function, f(t), are required. In many-component systems, a complete discussion of errors requires an estimate of the errors appearing in higher derivatives of f(t) which is not easily possible.

The errors in $\bar{A}_1$ are considered to arise from two independent sources, the uncertainty in the decay constant values and errors in f(t) arising from counting errors. The former type will be referred to as "λ error", while the latter will be called "statistical error". Expressions for the "λ error" can be obtained for systems of any number of components when this method is used (and also when the method of least squaring is used) simply by differentiating the equations used to obtain $\bar{A}_1$ with respect to the λ_i. The method here suggested, however, gives rise to very much simpler expressions.

A much less satisfactory discussion for "statistical error" is possible for two and three component systems and practically nothing for more complex systems.

In a two component system, $\bar{A}_1$ is given by,

$$\bar{A}_1 (\lambda_2 - \lambda_1) \int \frac{e^{-\lambda_1 t}}{A} dt = f(t_f) - f(o) + \lambda_2 t_f$$

the bulk of the error in A_1 results from the absolute error in $f(t_f)$ and $f(o)$ rather than in the integral. It is assumed that each experimentally determined value of f has the same probability of absolute error, namely $\mathcal{E}_o$. The values of $f(t_f)$ and $f(o)$, which result from the least squared polynomial have less error than $\mathcal{E}_o$, the probable relative error of a single measurement of A(t). The actual value, $\bar{\mathcal{E}}_o$, depends upon how many measurements are made per unit of time and upon $f'(t)$ at t_f and zero time. The probable error in the right hand side of the above equation will be taken as $\bar{\mathcal{E}}_o$ where $\bar{\mathcal{E}}_o < \mathcal{E}_o$. Although the resulting expression for the relative error in $\bar{A}_1$ is somewhat indefinite due to the uncertainty in $\bar{\mathcal{E}}_o$, its general form is instructive and also it may, in many cases, be shown to be less than the error one gets due to the "λ error". The "statistical error" in $\bar{A}_1$ is:

$$(16) \quad \frac{d\bar{A}_1}{\bar{A}_1} = \frac{\bar{\mathcal{E}}_o}{(\lambda_2 - \lambda_1) \int \frac{A_1 e^{-\lambda_1 t}}{A} dt} = \frac{\bar{\mathcal{E}}_o}{\ln \frac{e^{(\lambda_2 - \lambda_1) t_f} + A_2/A_1}{1 + A_2/A_1}}$$

This should be compared with the "λ error" expression:

$$(17) \quad \frac{d\bar{A}_1}{\bar{A}_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1} \frac{d\lambda_1}{\lambda_1} \left[1 + \frac{\int_0^{t_f} \frac{t(\lambda_2 - \lambda_1) e^{-\lambda_1 t}}{A} dt}{\int \frac{e^{-\lambda_1 t}}{A} dt} \right] + \frac{\lambda_2}{\lambda_1 \lambda_2} \frac{d\lambda_2}{\lambda_2} \frac{\ln \frac{e^{(\lambda_1 - \lambda_2) t_f} + A_1/A_2}{1 + A_1/A_2}}{\ln \frac{e^{(\lambda_2 - \lambda_1) t_f} + A_2/A_1}{1 + A_2/A_1}}$$

Figure 1 gives values of $\frac{1}{\bar{\varepsilon}_0}\frac{d\bar{A}_1}{\bar{A}_1}$ corresponding to the "statistical error" for values of $\bar{A}_2/\bar{A}_1$ and $|\lambda_2-\lambda_1|t_f$. The $|\lambda_2-\lambda_1|t_f$ axis is converted to a t_f axis by multiplying the coordinate values by $\frac{1}{|\lambda_2-\lambda_1|}$. Figures 2 and 3 similarly give the relative errors in $\bar{A}_1$ corresponding to the relative errors in λ_1 and in λ_2. In this case, however, the errors depend upon the ratio of decay constants in addition to the difference. The curves in Figures 2 and 3 represent constant values of $\frac{d\bar{A}_1}{\bar{A}_1}\times\frac{\lambda_2-\lambda_1}{\lambda_1}\times\frac{\lambda_1}{d\lambda_1}$ and $\frac{d\bar{A}_1}{\bar{A}_1}\times\frac{\lambda_2-\lambda_1}{\lambda_2}\times\frac{\lambda_2}{d\lambda_2}$. The curves in Figures 2 and 3 also represent constant values of $\frac{d\bar{A}_1}{\bar{A}_1}$ which are obtained by multiplying the values given on the curves by $\frac{\lambda_1}{\lambda_2-\lambda_1}\times\frac{d\lambda_1}{\lambda_1}$ and $\frac{\lambda_2}{\lambda_2-\lambda_1}\times\frac{d\lambda_2}{\lambda_2}$, respectively.

In a three component system, a crude estimate of the "statistical error" may be made by assuming that f is related to the exact value of ln A, f^*, by

$$f = f^* - \bar{\varepsilon}_0 + \frac{2\bar{\varepsilon}_0}{t_f}t$$

The expression for $\frac{d\bar{A}_1}{\bar{A}_1}$ due to the "statistical error" becomes

$$(18)\quad \frac{d\bar{A}_1}{\bar{A}_1} = \frac{2\bar{\varepsilon}_0}{\lambda_1 t_f}\left[\frac{\lambda_1}{\lambda_1-\lambda_3}+\frac{\lambda_1}{\lambda_1-\lambda_2}\right] + \frac{2\bar{\varepsilon}_0}{\lambda_1 t_f}\cdot\frac{\lambda_1(\lambda_2-\lambda_3)}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)}\left[\frac{\bar{A}_2}{\bar{A}_1}\frac{\int\frac{e^{-\lambda_2 t}}{A}dt}{\int\frac{e^{-\lambda_1 t}}{A}dt} - \frac{\bar{A}_3}{\bar{A}_1}\frac{\int\frac{e^{-\lambda_3 t}}{A}dt}{\int\frac{e^{-\lambda_1 t}}{A}dt}\right.$$

The expression for the "λ error", obtained by differentiating equation (9'), is

$$(19)\quad \frac{d\bar{A}_1}{\bar{A}_1} = \frac{\int\frac{\lambda_1 t e^{-\lambda_1 t}}{A}dt}{\int\frac{e^{-\lambda_1 t}}{A}dt}\frac{d\lambda_1}{\lambda_1} + \left[\frac{\lambda_1}{\lambda_1-\lambda_2}+\frac{\lambda_1}{\lambda_1-\lambda_3}\right]\frac{d\lambda_1}{\lambda_1}$$

$$+ \frac{\bar{A}_2}{\bar{A}_1}\frac{\lambda_2(\lambda_3-\lambda_2)}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)}\frac{\int\frac{e^{-\lambda_2 t}}{A}dt}{\int\frac{e^{-\lambda_1 t}}{A}dt}\frac{d\lambda_2}{\lambda_2}$$

$$+ \frac{\bar{A}_3}{\bar{A}_1}\frac{\lambda_3(\lambda_2-\lambda_3)}{(\lambda_1-\lambda_3)(\lambda_1-\lambda_2)}\frac{\int\frac{e^{-\lambda_3 t}}{A}dt}{\int\frac{e^{-\lambda_1 t}}{A}dt}\frac{d\lambda_3}{\lambda_3}$$

APPENDIX

The method of obtaining the λ_i's is simply to require the derivatives of A(t) to be related at all t consistent with the differential equation whose solution is A(t). Using operator notation, the differential equation for

$$A(t) = \sum_i A_i e^{-\lambda_i t}$$

is

$$\prod_i (D + \lambda_i) A(t) = 0$$

For i = 2,

$$A'' + (\lambda_1 + \lambda_2) A' + \lambda_1 \lambda_2 A = 0$$

For i = 3,

$$A''' + (\lambda_1 + \lambda_2 + \lambda_3) A'' + (\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3) A' + \lambda_1\lambda_2\lambda_3 A = 0$$

etc.

Since A is represented by $e^{f(t)}$, one requires

$$\prod_i (D + \lambda_i) e^{f(t)} = 0$$

or

$$e^{f(t)} \prod_i (D + \lambda_i + f'(t)) \cdot 1 = 0$$

or

$$\prod_i (D + \lambda_i + f'(t)) \cdot 1 = 0$$

For i = 2,

$$f'' + f'^2 + (\lambda_1 + \lambda_2) f' + \lambda_1 \lambda_2 = 0$$

This expression might just as well have been obtained by substituting $A = e^{f(t)}$ in the differential equation for A. One then selects the values of $(\lambda_1 + \lambda_2)$ and $\lambda_1\lambda_2$ (in the case i = 2) by the least squares method of fitting functions to functions previously explained. Therefore, one formally least squares

$$f'' + f'^2 + (\lambda_1 + \lambda_2) f' + \lambda_1 \lambda_2 = 0$$

with summations replaced by $\int_0^{t_f} (\ ) dt$, i.e.

$$\lambda_1\lambda_2 \int_0^{t_f} dt + (\lambda_1 + \lambda_2) \int f' dt = -\int f'' dt - \int f'^2 dt$$

$$\lambda_1\lambda_2 \int f' dt + (\lambda_1 + \lambda_2) \int f'^2 dt = -\int f'' f' dt - \int f'^3 dt$$

From the operator form of the differential equation it is seen that the method yields the coefficients of the expansion of $\prod_i (\lambda - \lambda_i)$. Therefore, one must finally obtain the roots of a polynomial of order i.

Drawing # 5838

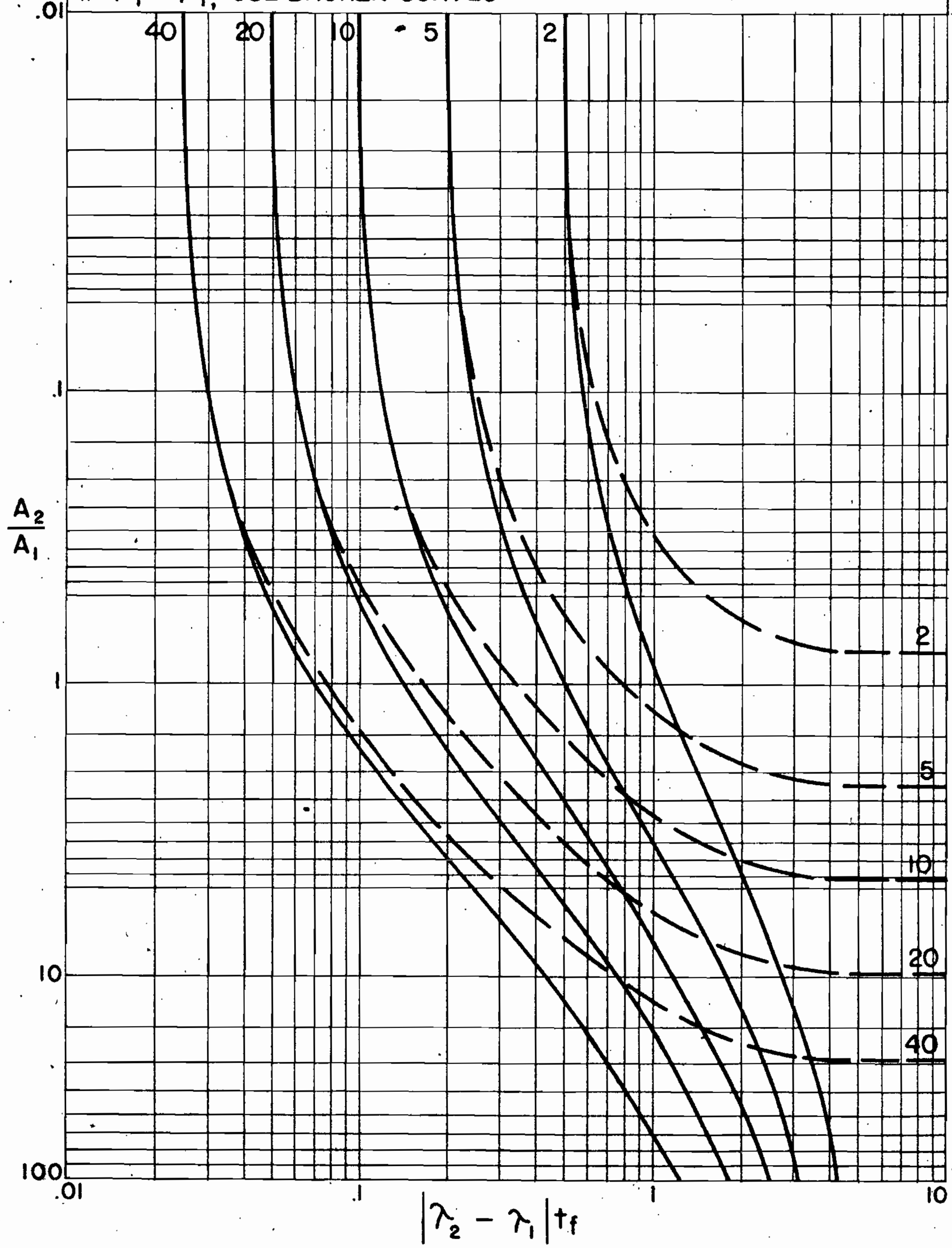
FIG. 1

"STATISTICAL ERROR"

EACH CURVE REPRESENTS A CONSTANT VALUE OF $\frac{1}{\varepsilon_0} \frac{dA_1}{A_1}$

IF $\lambda_2 > \lambda_1$, USE SOLID CURVES

IF $\lambda_1 > \lambda_1$, USE BROKEN CURVES



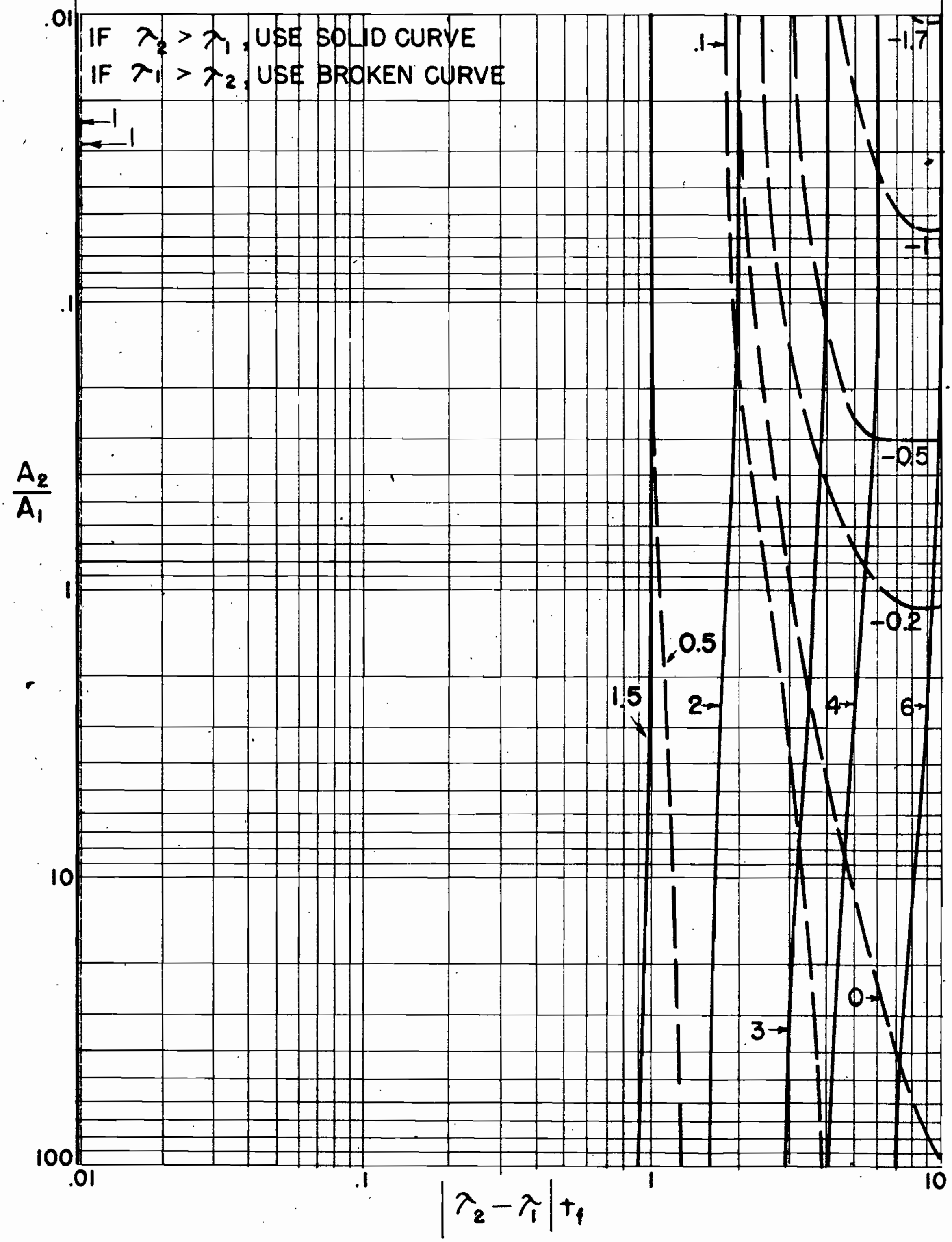
Drawing # 5839

FIG. 2

"λ_1 ERROR"

CURVES REPRESENT CONSTANT VALUES OF

$$\frac{dA_1}{A_1} \times \frac{\lambda_2 - \lambda_1}{\lambda_1} \times \frac{\lambda_1}{d\lambda_1}$$



Drawing # 5840

FIG. 3

"λ_2 ERROR"

CURVES REPRESENT CONSTANT VALUES OF

$$\left|\frac{\lambda_1 - \lambda_2}{\lambda_2}\right| \cdot \frac{\lambda_2}{d\lambda_2} \cdot \frac{dA_1}{A_1}$$