PROPAGATION OF ERRORS

An experiment has been performed; a variety of direct measurements have been made—weights, volumes, temperatures, measured electromotive forces, spectral absorbances, etc.,—and uncertainties in all of them have been estimated, either from statistical data obtained by repeated measurements or from judgment and experience. From the values obtained by direct measurement and with the aid of a phenomenological theory, a final numerical result is calculated. Let the desired numerical result be designated by $F$ and the directly measured quantities be designated by $x$, $y$, $z$, etc. The latter quantities are assumed to be mutually independent. Let their uncertainties, usually in the form of 95 percent confidence limits, be designated $\Delta(x)$, $\Delta(y)$, $\Delta(z)$, etc. The value of $F$ is determined by substituting the experimentally determined values of $x$, $y$, $z$, etc., into a mathematical formula, which we write symbolically as

$$F = f(x, y, z, \ldots)$$  \hspace{1cm} (32)

The issue to be discussed here is how one can estimate the uncertainty of the final result $F$, usually in the form of a 95 percent confidence limit.

Infinitesimal changes $dx$, $dy$, etc., in the experimentally determined values will produce in $F$ the infinitesimal change $dF$, where

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy + \frac{\partial F}{\partial z} dz + \ldots$$  \hspace{1cm} (33)

If the changes are finite rather than infinitesimal, but are small enough that the values of the partial derivatives are not appreciably affected by the changes, we have approximately

$$\Delta F = \frac{\partial F}{\partial x} \Delta x + \frac{\partial F}{\partial y} \Delta y + \frac{\partial F}{\partial z} \Delta z + \ldots$$  \hspace{1cm} (34)
This is equivalent to a Taylor expansion in which only the first-power terms have been retained. Now suppose that \( \Delta x \) represents the experimental error \( \epsilon(x) \) in the quantity \( x \):

\[
\Delta x = \epsilon(x) \equiv x \text{ (measured)} - x \text{ (true)}
\]  

(35)

Such errors will produce an error in \( F \),

\[
\Delta F = \epsilon(F) = F \text{ (calculated from measured } x, y, z, \ldots) - F \text{ (true)}
\]  

(36)

the value of which is given by

\[
\epsilon(F) = \frac{\partial F}{\partial x} \epsilon(x) + \frac{\partial F}{\partial y} \epsilon(y) + \frac{\partial F}{\partial z} \epsilon(z) + \ldots
\]  

(37)

*PROPAGATION OF RANDOM ERRORS*

In the case of random errors, we do not know the actual values of \( \epsilon(x), \epsilon(y), \ldots \), and we cannot determine the actual value of \( \epsilon(F) \). However, we have already assigned to each experimental variable an estimated standard deviation \( S \) or a confidence limit \( \Delta \). We now wish to deduce the corresponding uncertainty in the final result \( F \), taking into consideration the high probability that the errors in the several variables will tend somewhat to cancel one another out. Let us square both sides of Eq. (37):

\[
[\epsilon(F)]^2 = \left( \frac{\partial F}{\partial x} \right)^2 [\epsilon(x)]^2 + \left( \frac{\partial F}{\partial y} \right)^2 [\epsilon(y)]^2 + \ldots + 2 \left( \frac{\partial F}{\partial x} \right) \left( \frac{\partial F}{\partial y} \right) \epsilon(x) \epsilon(y) + \ldots
\]  

(40)

Now let us average this expression over all values expected for \( \epsilon(x), \epsilon(y), \ldots \), in accordance with the normal frequency distribution. Since the \( \epsilon(x) \) independently have average value zero, we expect the cross-terms to vanish. However, the squared terms are always positive and will not vanish. If we replace the average of each squared error by the variance, we obtain

\[
S^2(F) = \left( \frac{\partial F}{\partial x} \right)^2 S^2(x) + \left( \frac{\partial F}{\partial y} \right)^2 S^2(y) + \ldots
\]  

(41)

It can be seen immediately that the variance in the mean of \( N \) measurements \( S^2(\bar{x}) = S^2(x)/N \), which was discussed previously, can be obtained as a trivial example of Eq. (41) by taking

\[
F = \bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i
\]
Equation (41), which is not limited to normal distributions, is an equation that can be used when all or substantially all of the experimental variables are means of sets of measurements from which statistical measures of variance are available. From $S(F)$ a confidence limit $\Delta(F)$ can be derived if the total number of degrees of freedom can be ascertained. In some cases this may be the sum of the number of degrees of freedom from all of the experimental variables; in general it will be larger than the number of degrees of freedom from any one variable. This complicated problem may be bypassed by assuming that the central limit theorem is at work: the error probability distribution in $F$ is more closely normal than are the error probability distributions in the experimental variables. Thus, to a satisfactory approximation, the value of $t$ to be used can be taken to be that for $\nu = \infty$: For $P = 95$ percent, $t = 1.96$.

However, we are usually working in situations where many or most of the uncertainties in the experimental variables are estimated on the basis of judgment and experience. On the assumption that the errors in such variables are distributed in a roughly normal manner, we may resort to the following approximate expression in terms of confidence limits:

$$\Delta^2(F) = \left(\frac{\partial F}{\partial x}\right)^2 \Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2 \Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2 \Delta^2(z) + \ldots$$

(42)

In certain cases, the propagation of random errors can be carried out very simply:

1. For $F = ax \pm by \pm cz$,

$$\Delta^2(F) = a^2\Delta^2(x) + b^2\Delta^2(y) + c^2\Delta^2(z)$$

(43)

2. For $F = axy$ (or $axy/2$ or $ax/yz$ or $a/xyz$),

$$\frac{\Delta^2(F)}{F^2} = \frac{\Delta^2(x)}{x^2} + \frac{\Delta^2(y)}{y^2} + \frac{\Delta^2(z)}{z^2}$$

(44)

3. For $F = ax^2$,

$$\frac{\Delta^2(F)}{F^2} = n^2 \frac{\Delta^2(x)}{x^2} \rightarrow \frac{\Delta(F)}{F} = n \frac{\Delta(x)}{x}$$

(45)

4. For $F = ae^x$,

$$\Delta^2(F) = a^2e^{2x} \Delta^2(x) \rightarrow \frac{\Delta(F)}{F} = \Delta(x)$$

(46)

5. For $F = a \ln x$,

$$\Delta^2(F) = \frac{a^2}{x^2} \Delta^2(x) \rightarrow \Delta(F) = a \frac{\Delta(x)}{x}$$

(47)
Examples

Given below are three numerical examples of a propagation of errors treatment.

Example 1. The first example is related to the optical rotation measurement described as a case study in the next section. The formula for calculating the specific rotation $[\alpha]$ is

$$[\alpha] = \frac{V}{Lm} \alpha$$

where $V$ is the volume of the solution in cubic centimeters, $L$ is the length of the polarimeter tube in decimeters, $m$ is the mass of solute contained in volume $V$, and $\alpha$ is the rotation angle in degrees. Values of these four independent variables together with their 95 percent confidence limits are as follows:

<table>
<thead>
<tr>
<th>$V$</th>
<th>$L$</th>
<th>$m$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.00 cm$^3$</td>
<td>2.000 dm</td>
<td>1.7160 g</td>
<td>+20.950°</td>
</tr>
<tr>
<td>$\Delta = 0.02$ cm$^3$</td>
<td>0.002 dm</td>
<td>0.0003 g</td>
<td>0.016°</td>
</tr>
</tbody>
</table>

The confidence limits for the first three variables were estimated on the basis of judgment and experience. The last was determined from a statistical analysis of data from 10 individual measurements with Eqs. (8) and (29). From Eq. (51) we calculate

$$F = [\alpha]^2_{D} = \frac{25.00}{2.000 \times 1.7160} \times 20.950 = 152.61 \text{ deg dm}^{-1} (\text{g cm}^{-3})^{-1}$$

We observe that Eq. (51) is of the type for which Eq. (44) is applicable. Therefore

$$\Delta^2([\alpha]) = [\alpha]^2 \left[ \frac{\Delta^2(V)}{V^2} + \frac{\Delta^2(L)}{L^2} + \frac{\Delta^2(m)}{m^2} + \frac{\Delta^2(\alpha)}{\alpha^2} \right]$$

$$= 152.61^2 \left( \frac{0.02^2}{25.00^2} + \frac{0.002^2}{2.000^2} + \frac{0.0003^2}{1.7160^2} + \frac{0.016^2}{20.950^2} \right)$$

$$= 2.33 \times 10^4 (64 + 100 + 3 + 58) \times 10^{-8} = 0.0524$$

$$\Delta ([\alpha]) = 0.23 \text{ deg dm}^{-1} (\text{g cm}^{-3})^{-1}$$

One would report this result as $[\alpha] = 152.61 \pm 0.23 \text{ deg dm}^{-1} (\text{g cm}^{-3})^{-1}$ or $1.5261 \pm 0.0023 \text{ deg m}^2 \text{ kg}^{-1}$ in SI units.