

REPORTING PRECISION OF EXPERIMENTAL DATA

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SIMPLE CONCEPTS OFTEN receive the comment, "but everyone knows that!" Unfortunately, *everyone* seldom includes all persons. In particular, we feel this generalization applies to one of the basic responsibilities of the scientific community—reporting the precision of experimental data. Many times in theses, dissertations and even in technical papers this straightforward, mathematically obvious exercise is either ignored or applied improperly.

The concept of precision is precisely defined and is a statistical quantity not to be confused (though it frequently is) with the equally precise concept of accuracy. Precision is a measure of the experimental reproducibility, that is, of the random errors associated with the apparatus and operator. The accuracy is a measure of the absolute quality of the data, that is, how closely the data approximate the true values of the observables. We can calculate precision by standard statistical techniques (and approximations), but we must estimate accuracy based upon knowledge of the apparatus, calibration against known standards, and confidence in its operation.

The standard deviation is the preferred representation of precision and is defined as the square root of the variance of the data. For example, if z is an observable, its variance is the expected value of the square of the deviation between the observed quantity and its expected value:

$$\text{var}(z) = \langle (z - \langle z \rangle)^2 \rangle \quad (1)$$

Assume we are collecting data which meet the usually-satisfied continuity requirements allowing $z - \langle z \rangle$ to be approximated by a Taylor series truncated to first order,

$$z - \langle z \rangle \approx \sum_i \left(\frac{\partial z}{\partial x_i} \right)_{x_i} (x_i - \langle x_i \rangle) \quad (2)$$

where the x_i are the independent variables determining z . To obtain an estimate of the standard deviation, square each side of equation (2):

$$\begin{aligned} (z - \langle z \rangle)^2 \approx & \sum_i \left(\frac{\partial z}{\partial x_i} \right)_{x_i}^2 (x_i - \langle x_i \rangle)^2 \\ & + 2 \sum_{\substack{i,j \\ j>i}} \left(\frac{\partial z}{\partial x_i} \right)_{x_i} \left(\frac{\partial z}{\partial x_j} \right)_{x_j} (x_i - \langle x_i \rangle) (x_j - \langle x_j \rangle) \end{aligned} \quad (3)$$

then take the expected value of the result (assuming the derivatives are exact):

$$\begin{aligned} \text{var}(z) \approx & \sum_i \left(\frac{\partial z}{\partial x_i} \right)_{x_i}^2 \text{var}(x_i) \\ & + 2 \sum_{\substack{i,j \\ j>i}} \left(\frac{\partial z}{\partial x_i} \right)_{x_i} \left(\frac{\partial z}{\partial x_j} \right)_{x_j} \text{cov}(x_i, x_j) \end{aligned} \quad (4)$$

The standard deviation of z , σ_z , is simply the square root of equation (4).

Unfortunately, we rarely have even an estimate of $\text{cov}(x_i, x_j)$. Fortunately, we seldom need one. The covariance represents a correlation, or interdependence, between the subject variables (in this case x_i, x_j). The observables are usually measured independently, therefore the covariance is zero and the variance of z reduces to

$$\text{var}(z) \approx \sum_i \left(\frac{\partial z}{\partial x_i} \right)_{x_i}^2 \text{var}(x_i) \quad (5)$$

Using equation (5) requires knowledge of z as a function of the x_i and of the variances of the x_i . The data themselves satisfy the first requirement, although a more convenient situation would be to have a mathematical function $z = z(x_1, x_2, \dots)$ which can be differentiated. The

variances of the x_i are seldom available, but can be replaced with estimated errors of the x_i , ϵ_i^2 . The equation for estimating the standard deviation then becomes

$$\sigma_z \approx \left(\sum_i \left(\frac{\partial z}{\partial x_i} \right)^2 \epsilon_i^2 \right)^{0.5} \quad (6)$$

An attractive and valid geometric model for the additivity of variances results from considering z as uncertainly located in n -space, with the uncertainty arising from the errors in the n independent variables, which combine orthogonally if each independent variable acts along its own coordinate of the space. (Correlations, in this model, correspond to non-orthogonality of the error-component vectors.)

Reviewing the assumptions involved in equation (6):

- $z - \langle z \rangle$ can be approximated by a first-order Taylor expansion;
- errors in the independent variables, x_i , are not correlated;
- variances of the independent variables may be approximated by their apparent experimental errors, ϵ_i .

(Along with the third assumption, we caution that there are occasional cases where badly skewed or bimodal error distributions make simple addition of the variances, or second moments, inadequate.)

A common and less defensible technique for assigning precision to data is to use the derivatives themselves as weighting factors. Assuming $z = z(x_1, x_2, \dots)$,

$$dz = \sum_i \left(\frac{\partial z}{\partial x_i} \right) dx_i \quad (7)$$

dz is assumed to be σ_z and the dx_i are all replaced with ϵ_i . Of course, the partial derivatives and ϵ_i can be negative; so the absolute values are commonly used:

$$\sigma_z \approx \sum_i \left| \left(\frac{\partial z}{\partial x_i} \right) \epsilon_i \right| \quad (8)$$

Equation (8) is often said to provide the "maximum error estimate." This statement has no valid theoretical basis; a defensible worst-case error estimate would actually be $3\sigma_z$ from equation (6). Furthermore, when absolute values are used, physical significance becomes obscure, and geometrical significance is destroyed. Effectively, equation (8) contains all the assumptions of equation (6) plus one more—that the square root of a sum is the sum of the square roots. This latter assumption is not generally valid—

$$\sqrt{4 + 9 + 16} = \sqrt{29} = 5.4 \\ 2 + 3 + 4 = 9$$

Now consider some examples, the first involving the precision in measuring liquid composition by interferometry. Kirwan (1967) provides the difference between interface composition and that of the bulk liquid

$$Y = y_o - y_w = \frac{\Delta N \lambda_o}{2t} \left(\frac{\partial n}{\partial y} \right)_T^{-1} \quad (9)$$

where ΔN is the fringe shift at the interface, λ_o is the wavelength of the light, t is the thickness of the optical wedge and n is the refractive index. Kirwan also reports that the percentage errors in ΔN , λ_o , t and $(\partial n / \partial y)_T$ are respectively 20%, <0.1%, 10% and 5%. In this case (when all observables appear as multiples in the equation), it is convenient to divide both sides of equation (6) by the dependent variable:

$$\frac{\sigma_y}{y} = \left[\left(\frac{\epsilon_{\Delta N}}{\Delta N} \right)^2 + \left(\frac{\epsilon_t}{t} \right)^2 + \left(\frac{\epsilon_n}{\partial n / \partial y} \right)^2 \right]^{0.5} \quad (10)$$

Now percentage errors can be substituted directly, yielding $\sigma_y / Y = 0.23$. From equation (8), the value would be $\sigma_y / Y = 0.35$.

A second example involves a PvT experiment. For illustration, assume a van der Waals gas with the properties $T_c = 356.37\text{K}$, $P_c = 3.700\text{MPa}$, $a = 1.000 \times 10^{-6}$, $b = 1.000 \times 10^{-4}$ and the gas

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constant, $R = 8.3143 \times 10^{-6}$ MPa m³/mol K. We desire the precision in determining the volume at 360.82K and 100.0MPa. The following equation is applicable:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Note that the observables do not appear as simple multiples, so an equation similar to equation (10) does not exist. Using $\epsilon_T = 0.01K$ and $\epsilon_p = 0.01$ MPa (both reasonable values for these measurements), equation (6) estimates $\sigma_v = 1.3 \times 10^{-9}$, or 0.0011, while equation (8) produces $\sigma_v = 1.7 \times 10^{-9}$, or 0.0015%. These precisions are reasonable because the gas is in a low compressibility region.

Our third example concerns measurement of oxygen concentration with the Westinghouse concentration-cell sensor (Updike, Dammann, and Bowers, 1968). The response of this device is Nernstian, and may be described by the relation

$$\Delta E = \frac{RT}{nF} \ln \frac{f_{\text{ref}}}{f_{\text{O}_2}} \quad (12)$$

where ΔE is the cell output voltage; R and F are the gas constant and Faraday's constant; T is absolute temperature of the zirconia electrolyte; n is the number of electrons transferred in the electrode reaction; and f is the fugacity of oxygen in reference and sample stream, as indicated by the subscripts. Equation (14) can be rearranged conveniently, with substitutions for the fugacities, to the form

$$y_{\text{O}_2} = y_{\text{ref}} \left(\frac{P_{\text{samp}}}{P_{\text{ref}}} \right) \left(\frac{\phi_{\text{samp}}}{\phi_{\text{ref}}} \right) \left(e^{-\frac{nF\Delta E}{RT}} \right) \quad (13)$$

$$= y_{\text{ref}} \alpha \beta e^{\gamma \Delta E/T} \quad (13a)$$

where P_{samp} and P_{ref} are total pressures in the sample and reference regions; ϕ_{samp} and ϕ_{ref} are

the corresponding fugacity coefficients; and α , β and γ are introduced for convenience as shown in form (13a).

For the factors in equation (13a), the uncertainties are estimated as

$$\epsilon_{y_{\text{ref}}} = 0.001, \epsilon_{\alpha} = 0.002, \epsilon_{\beta} = 0.001, \epsilon_{\Delta E} = 0.0001 V, \text{ and } \epsilon_T = 3K \text{ (at } 1123K \text{).}$$

(The pressure and fugacity ratios are handled as single variables because errors in these terms are, by design compensating.) The expression for the estimated standard deviation results from differentiation of equation (13) and substitution in equation (6); the derivatives are conveniently developed from the concise form (13a). Substitution of these derivatives into equation (6) yields

$$\sigma_{y_{\text{O}_2}} = y_{\text{O}_2} \left[\left(\frac{\epsilon_{y_{\text{ref}}}}{y_{\text{ref}}} \right)^2 + \left(\frac{\epsilon_{\alpha}}{\alpha} \right)^2 + \left(\frac{\epsilon_{\beta}}{\beta} \right)^2 + \left(\frac{\gamma \epsilon_{\Delta E}}{T} \right)^2 + \left(\frac{\gamma \Delta E \epsilon_T}{T^2} \right)^2 \right]^{0.5} \quad (14)$$

Thus, at $y_{\text{O}_2} = 0.500$, and $\Delta E = 0.0210$ volts

$$\sigma_{y_{\text{O}_2}} = \left[(5.7 + 1.0 + 0.3 + 4.3 + 1.3) \times 10^{-6} \right]^{0.5} = 0.0035$$

This third example shows several points:

(a) the exponential factor does not allow the simple combination of percentage errors which was possible in the first case; (b) the independent variables contribute unequally to the overall uncertainty, and equation (6) displays clearly the minor contribution of uncertainties in β (the fugacity ratio); (c) with more error contributors, the ratio between the more defensible estimate of equation (6) and that of equation (8) has increased; (d) expected correlations were handled by using ratios of variables in factors α and β ; and (e) because of the exponential form, the error level changes with y_{O_2} and y_{ref} —arguing for care in the choice of the reference gas concentration when this sensor is used.

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allowed to cool in a draught proof perspex case, the principal mode of heat loss being natural convection. The temperature of the fluid and the surroundings are noted for an hour or two. Again a transient (heat) balance yields the desired model:—

$$-MC_p \frac{d\theta}{dt} = hA (\theta - \theta_a) \quad (6)$$

whose integrated form can be represented by a straight line on log-linear graph paper. An extension of the basic theory which allows for the dependence of heat transfer coefficient with temperature difference where:

$$h \propto (\theta - \theta_a)^{0.25} \quad (7)$$

can also be made.

All of the experiments can be repeated using different initial heights, concentrations and temperatures respectively. The results then for, say, all the fluid flow experiments lie on the same line if the normalized ordinate (H/H_0) is used. Indeed if the normalized abscissa (Kt) is also used then the results from different diameter capillary experiments also can be reduced to a one line representation. This dimensionless plotting is yet another important concept for the student to grasp.

CONCLUSION

WE HAVE FOUND THAT these three inexpensive and simple experiments have aided our student's comprehension of, and belief in, the analogous behaviour of the various forms of transport phenomena. Equally importantly, the writing of full engineering reports on their findings provides useful training prior to their early industrial baptism. Perhaps as a postscript we can also mention two further experiments which are given to our first year men which again are governed by:

$$\frac{dy}{dx} = ky \quad (8)$$

these being the transient mass balance over a stirred tank containing acid diluted with water and a rig on the rates of batch sieving.

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NOTATION

A	Area
C_s, C	(Saturation), concentration
C_p	Specific heat

d	Capillary diameter
g	Acceleration due to gravity
H_0, H	(Original), height
h	Heat transfer coefficient
K, k	Constants
K_L	Mass transfer coefficient
l	length of capillary
M	Mass
N	Rotational speed
t	Time
V	Volume
$\theta_a, \theta_i, \theta$	(Ambient, initial), temperature
ρ	Density
μ	Viscosity

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Equation (8) approximates σ_z as greater than the more valid estimate of equation (6). The difference depends on the number of error-contributing independent variables and on the derivative-weighted contributions of each. For the common case where three or four factors each contribute comparably to the overall variance, the linearly-additive equation (8) produces estimates not more than twice the orthogonally-additive estimate of equation (6); for only one major contributor, results are essentially the same. Since the calculation required is only negligibly greater, the theoretically defensible equation (6) should always be used.

We hasten to add that nothing new is presented here. Equation (6) is available in many references, for example Mickley, Sherwood and Reed (1957); but we find that an overwhelming majority of students—and even colleagues!—use equation (8). This communication is an attempt to advocate the more rigorous, well documented, largely neglected approach. □

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