

Introduction to the Propagation of Error

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The Problem: Chemists often measure one or more variables, but then use these variables to calculate a chemical or physical parameter. The reliability of the parameter will depend, of course, upon the reliability of the measured variables. This raises a question, "How do you compute the uncertainty in the parameter if you know the uncertainties in each of the measured variables?" The answer to this question is the focus of what scientists refer to as, "Propagation of Error."

Example: Given below are the dimensions of a rectangle, stated as confidence intervals. Calculate the area of the rectangle and its uncertainty:

$$\text{height} = 3.47 \pm 0.10 \text{ cm}$$

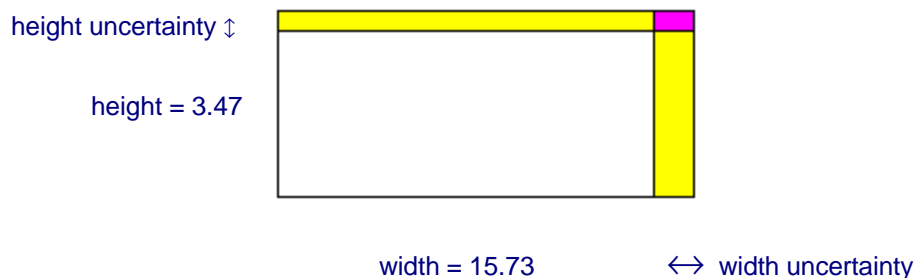
$$\text{width} = 15.73 \pm 0.15 \text{ cm}$$

$$\text{area} = 54.5831 \text{ cm}^2$$

How do we calculate the uncertainty in the area?

Question: The sum of the uncertainties in the height and width is clearly not equal to the uncertainty in the area. Why is this obvious? Hint: consider their units.

Question: The product of the uncertainties in the height and width does have the correct units, but it also is not equal to the uncertainty in the area. Why is this apparent from the figure below? Hint: which rectangle in the figure corresponds to this product?



Examination of this rectangle may suggest that the uncertainty in its area corresponds to the sum of the areas of all of the colored rectangles. This sum, however, overestimates the uncertainty in the rectangle's area since it fails to account for the likelihood that often the errors in the width and height are opposite in sign and tend to cancel each other.

The General Expression: It can be shown that for a function $z = f(x,y)$ the uncertainty in z is related to the uncertainties in x and y as follows (this assumes that the uncertainties in x and y are independent):

$$(\epsilon_z)^2 = \left(\frac{\delta z}{\delta x}\right)^2 \cdot (\epsilon_x)^2 + \left(\frac{\delta z}{\delta y}\right)^2 \cdot (\epsilon_y)^2 \quad \text{Eq (1)}$$

where, the epsilons (ϵ) can be either uncertainties or standard deviations, and $\delta z/\delta x$ and $\delta z/\delta y$ are partial derivatives. (For functions of more than two independent variables, additional terms are added on the right.)

Example (cont.): To apply Eq (1) to our rectangle problem, first change its notation to that of the equation for area, then calculate partial derivatives, and finally substitute the expression for each partial derivative into the modified Eq (1). Beyond this point, what remains is arithmetic.

$$A = h \cdot w \quad \text{(equation for area)}$$

$$(\epsilon_A)^2 = \left(\frac{\delta A}{\delta h}\right)^2 \cdot (\epsilon_h)^2 + \left(\frac{\delta A}{\delta w}\right)^2 \cdot (\epsilon_w)^2 \quad \text{(change Eq (1) notation to A, h & w)}$$

$$\frac{\delta A}{\delta h} = w \quad \text{and} \quad \frac{\delta A}{\delta w} = h \quad \text{(calculate partial derivatives)}$$

$$(\epsilon_A)^2 = w^2 \cdot (\epsilon_h)^2 + h^2 \cdot (\epsilon_w)^2 \quad \text{(substitute for partial derivatives)}$$

$$(\epsilon_A)^2 = (15.73)^2 \cdot (0.10)^2 + (3.47)^2 \cdot (0.15)^2 \quad \text{(substitute numeric values)}$$

$$(\epsilon_A)^2 = 2.474 + 0.2709 \quad \text{(simplify)}$$

Note, although the uncertainty in the width ($\epsilon_w = 0.15$) is 50% greater than the uncertainty in the height ($\epsilon_h = 0.10$), the latter makes a much greater contribution to the uncertainty in the area (ϵ_A). Error propagation calculations help one distinguish between major and minor sources of error.

$$(\epsilon_A)^2 = 2.745 \quad \text{(combine terms)}$$

$$(\epsilon_A) = 1.6 \quad \text{(round to two digits)}$$

Final result: Area = 54.6 ± 1.6 cm²

By convention, the uncertainty in the final result is rounded to two significant digits and the result itself is rounded to the same number of decimal places.

===== **Calculation Template**=====

Calculating partial derivatives of complicated functions is not easy and this can make error propagation calculations intimidating. The template below provides all steps in an example error propagation calculation (on the left), but provides space for you to perform a parallel calculation (on the right). If you need more space, insert it using **[Ctrl] [F9]**. This example consists of calculating density from mass and volume.

Example Problem:

Student Calculations:

Step #1. Define the function whose uncertainty you wish to compute. Be sure to list the independent variables in parentheses on the left.

$$d(m, V) := \frac{m}{V}$$

Step #2. Change the notation of Eq (1) to that of your function. (The equal sign used here is the **[Ctrl] [=]**.)

$$(\epsilon_z)^2 = \left(\frac{\delta z}{\delta x}\right)^2 \cdot (\epsilon_x)^2 + \left(\frac{\delta z}{\delta y}\right)^2 \cdot (\epsilon_y)^2$$

$$(\epsilon d)^2 = \left(\frac{\delta d}{\delta m}\right)^2 \cdot (\epsilon m)^2 + \left(\frac{\delta d}{\delta V}\right)^2 \cdot (\epsilon V)^2$$

Step #3. Calculate partial derivatives. Enter the derivative symbol **[Shift] [?]** once for each independent variable. Enter each independent variable into a denominator placeholder, and **Copy** and **Paste** your function into the argument placeholders. Select each expression, enter **[Ctrl] [.]** and hit **[Enter]**.

$$\frac{d}{d m} d(m, V) \rightarrow \frac{1}{V}$$

$$\frac{d}{d V} d(m, V) \rightarrow \frac{-m}{V^2}$$

Step #4. Derive the final equation by substituting the expression for each partial derivative obtained in Step #3 into the equation obtained in Step #2. (Use **Copy** and **Paste.**)

$$(\epsilon d)^2 = \left(\frac{\delta d}{\delta m}\right)^2 \cdot (\epsilon m)^2 + \left(\frac{\delta d}{\delta V}\right)^2 \cdot (\epsilon V)^2$$

$$(\epsilon d)^2 = \left(\frac{1}{V}\right)^2 \cdot (\epsilon m)^2 + \left(\frac{-m}{V^2}\right)^2 \cdot (\epsilon V)^2$$

This equation provides the relationship between the uncertainty (or standard deviation) in the density and the uncertainties (or standard deviations) in both mass and volume; which is what we wanted. What remains now is only arithmetic.

Step #5. Provide values for all independent variables and their uncertainties.

$$m := 10.2943$$

$$\epsilon m := 0.0010$$

$$V := 10.000$$

$$\epsilon V := 0.020$$

Step #6. Compute separately the value of each term on the right hand side of the equation you derived in Step #4. This allows one to compare the relative contribution of each independent variable to the total error. (Use **Copy** and **Paste**.)

$$\text{term1} := \left(\frac{1}{V}\right)^2 \cdot \epsilon m^2$$

$$\text{term1} = 1 \cdot 10^{-8}$$

$$\text{term2} := \left(\frac{-m}{V^2}\right)^2 \cdot \epsilon V^2$$

$$\text{term2} = 4.239 \cdot 10^{-6}$$

Notice that the volume error term is over 400 times as large as the mass error term.

Step #7. Compute the square root of the sum of the terms. (Use the backslash key \ to obtain the square root function.)

$$\epsilon d := \sqrt{\text{term1} + \text{term2}}$$

$$\epsilon d = 2.061 \cdot 10^{-3}$$

$$d(m, V) = 1.02943$$

Step #8. Round the uncertainty to two significant digits, and then round the result to as many decimal places as the uncertainty. Use **[Alt] [0177]** (with Num Lock ON) from the number keypad to produce the plus/minus sign (\pm).

$$\text{density} = d = 1.0294 \pm 0.0021 \quad \text{this is a line of text}$$

If desired, units can be included in all of the calculations above.

Footnote: Often equations like the one derived in Step #4 mask the fundamental relationship between the uncertainties. Sometimes a simpler expression can be derived by dividing this equation by the square of the original function, i.e., $z^2 = f(x,y)^2$

Step #9. Divide the equation derived in Step #4 by the square of the original equation from Step #1 (use **Copy** and **Paste** and **[Ctrl] [=]**). Select the equation that results and from the **Symbolics** menu choose **Simplify**. (Additional simplification may be necessary).

$$(\epsilon d)^2 = \left(\frac{1}{V}\right)^2 \cdot (\epsilon m)^2 + \left(\frac{-m}{V^2}\right)^2 \cdot (\epsilon V)^2$$

$$d^2 = \left(\frac{m}{V}\right)^2$$

$$\frac{(\epsilon d)^2}{d^2} = \left(\frac{1}{V}\right)^2 \cdot \frac{(\epsilon m)^2}{\left(\frac{m}{V}\right)^2} + \left(\frac{-m}{V^2}\right)^2 \cdot \frac{(\epsilon V)^2}{\left(\frac{m}{V}\right)^2}$$

$$\frac{\epsilon d^2}{d^2} = \frac{(\epsilon m^2 \cdot V^2 + m^2 \cdot \epsilon V^2)}{(m^2 \cdot V^2)}$$

The latter can be further simplified (by hand) to:

$$\left(\frac{\epsilon d}{d}\right)^2 = \left(\frac{\epsilon m}{m}\right)^2 + \left(\frac{\epsilon V}{V}\right)^2$$

This result indicates that the square of the relative error in density is equal to the sum of the squares of the relative errors in mass and volume.

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