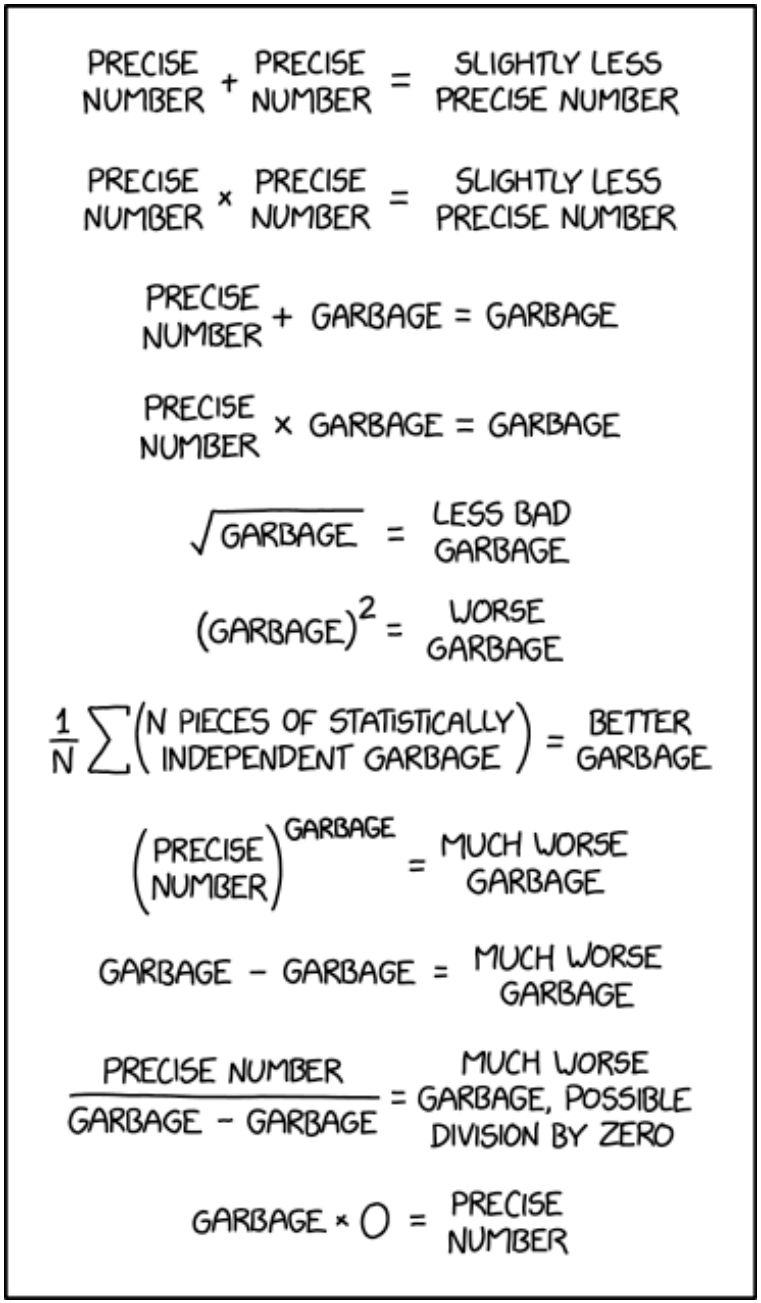
What is "propagation of error?"



- Usually the phrase refers to propagation of *uncertainty*
- Bias can also propagate; nonlinear transformations of unbiased measurements actually introduces bias
- Some transformations (as shown in the figure) can greatly amplify uncertainty
- Goal: knowing the uncertainty in the input measurements, predict the uncertainty of the value(s) calculated from those measurements.

Propagation of Random Error

How does the error from one variable propagate to another?

Let y be a value calculated from one or more random variables,

$$y = f(x_i)$$

The uncertainty from the original random variable(s) propagates as

$$\sigma_y^2 = \sum_i \left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_i^2 = \left(\frac{\partial y}{\partial x_1}\right)^2 \sigma_1^2 + \left(\frac{\partial y}{\partial x_2}\right)^2 \sigma_2^2 + \cdots$$

Assumptions in this equation:

- y is a linear function of the random variable(s) x_i
- If there are 2 or more random variables, their uncertainties are independent

Example Calculation

Calculate the standard free energy change, ΔG°, and its uncertainty for a keto-enol tautomerization reaction based on the data in the table.

$$\Delta G^\circ = -RT \ln K$$

Quantity, units	Value	SD
R, J/mol K	8.314 459 8	1×10^{-7}
T, K	300	2
K_c	1.50	0.01

Applying the propagation of error formula leads to:

$$\sigma^2_{\Delta G} \approx (-T \ln K)^2 \sigma^2_R + (-R \ln K)^2 \sigma^2_T + \left(\frac{-RT}{K}\right)^2 \sigma^2_K$$

Generalization to Other Intervals

If I am using a measure of uncertainty other than the standard deviation, does the error propagation formula still work?

- Yes, we can use the same formula to propagate other measures of uncertainty, such as the MAD or IQR
- In some cases we can even propagate MOE (ie, confidence intervals)

The general formula can be written as

$$(\Delta y)^2 = \sum_i \left(\frac{\partial y}{\partial x_i}\right)^2 (\Delta x_i)^2$$

where Δy and Δx_i are quantitative measures of uncertainty in variables y and x_i.

Propagation of Random Error

Do I really need to do partial differentiation to do propagation of error?

- You can do step-by-step calculations using the following table for each step
- Use RSD or SD depending on which is easier (then calculate the other quantity) for each step

Case	**SD_y**	**RSD_y**
$y = x_1 \pm x_2$	$\sigma_y^2 = \sigma_1^2 + \sigma_2^2$	
$y = x \pm k$	$\sigma_y = \sigma_x$	
$y = kx$	$\sigma_y = \lvert k \rvert \sigma_x$	$RSD_y = RSD_x$
$y = x_1 \times x_2$		$RSD_y^2 \approx RSD_1^2 + RSD_2^2$
$y = x_1 \div x_2$		
$y = x^k$		$RSD_y \approx \lvert k \rvert RSD_x$
$y = k^x$		$RSD_y \approx \ln(k)\sigma_x$
$y = \log_k x$	$\sigma_y \approx \frac{RSD_x}{\ln(k)}$	

Class exercise: Calculate the uncertainty in ΔG for the keto-enol tautomerization using the table above.

Monte Carlo Method of Error Propagation

Is there any other method of doing propagation of error? If so, let's see it.

- Illustrate with the keto-enol problem using 10,000 random values
- Advantage: works with non-linear transformations, and can examine effect of transformation on the distribution
- Advantage: can identify problems when using standard deviation
- Partition variability by "zero-ing out" all but one variable (and repeating for all variables)