Introduction

This tutorial is a follow-up to the tutorial on *Significant Figures in Calculations, tutorial* #4. The significant figure rules outlined in tutorial # 4 are only approximations; a more rigorous method is used in laboratories to obtain uncertainty estimates for calculated quantities. This method relies on partial derivates from calculus to propagate measurement error through a calculation. As before we will only consider three types of operations: 1) multiplication/division/power functions, 2) addition/subtraction and 3) logarithmic/exponential functions.

The mathematical formulas used in this tutorial are based on calculus; their derivation is not necessary for you to learn when and how to apply the correct formula. The conditions for their use are: 1) the random errors assigned to each measured value are independent of each other and 2) they follow a normal (Gaussian) distribution, and 3) there is negligible or no covariance between the errors. These conditions should easily be met under most conditions encountered in a general chemistry lab.

As before, **APLY THE FORMULAS PRESENTED BELOW TO EVERY MATHEMATICAL OPRATION IN A SEQUENTIAL MANNER**. Again you cannot be lazy!

Basic formula for propagation of errors

The formulas derived in this tutorial for each different mathematical operation are based on taking the partial derivative of a function with respect to each variable that has uncertainty. As a base definition let *x* be a function of at least two other variables, *u* and *v* that have uncertainty.

$$x = f(u, v, \ldots)$$

The variance of *x*, σ_X^2, with respect to the variance in *u* and *v* can be approximated using partial derivatives.

$$\sigma_X^2 \simeq \sigma_u^2 \left(\frac{\delta x}{\delta u}\right)^2 + \sigma_v^2 \left(\frac{\delta x}{\delta v}\right)^2 + \ldots \qquad (1)$$

This function applies under all circumstances and can be used directly as stated once each partial derivative is found and mathematically evaluated. Below are a few examples where the partial derivatives are easy to evaluate. **Remember, to apply this formula you must have values for all variances in each independent variable. These variances can come from a standard deviation calculation. Th equipment manufacturer, or an estimation based on a scale reading.**

1. Addition and Subtraction

If *x* is the sum or difference of *u* and *v*.

$$x = u \pm v$$

The partial derivatives equal 1, and equation (1) becomes

$$\sigma_x^2 = \sigma_u^2 + \sigma_v^2 .$$

In general, when adding or subtracting n numbers:

$$\sigma_x^2 = \sigma_u^2 + \sigma_v^2 + \ldots \sigma_n^2$$

1. Example.
   The volume delivered by a buret is the difference between the final (R_f) and initial readings

(R_i). Each reading has an uncertainty of ±0.02 mL according to the buret manufacturer.

$$V = R_f - R_i;\ \sigma_V^2 = \sigma_{R_f}^2 + \sigma_{R_i}^2 = (0.02mL)^2 + (0.02mL)^2 = 0.0008mL^2 .$$

So, the error in the volume delivered, σ_V , is $\sigma_{V=}\sqrt{\sigma_V^2} = \sqrt{0.0008mL^2} = 0.028mL$.

a. Example. The volume delivered by a 100-mL graduated cylinder is also the difference between the final and initial readings. In this case each reading has an uncertainty of ±0.5 mL.

$$V = R_f - R_i;\ \sigma_V^2 = \sigma_{R_f}^2 + \sigma_{R_i}^2;\ \sigma_V^2 = (0.5mL)^2 + (0.5mL)^2 = 0.5mL^2 .$$

So, the error in the volume delivered is $\sqrt{\sigma_V^2} = \sqrt{0.5mL^2} = 0.71mL$.

2. Multiplication and division

If x is the product or quotient of u and v.

$$x = uv \text{ or } x = \frac{u}{v}$$

The partial derivatives are no longer 1. A simplified formula can be found with some rearrangement. Consider $x = uv$. Equation (1) becomes

$$\sigma_x^2 = \sigma_u^2(v^2) + \sigma_v^2(u^2) .$$

Dividing both sides by $x^2 = (uv)^2$

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_u^2(v^2) + \sigma_v^2(u^2)}{x^2} = \frac{\sigma_u^2(v^2) + \sigma_v^2(u^2)}{(uv)^2} = \frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2} .$$

Thus, the relative variance in x^2, $\frac{\sigma_x^2}{x^2}$, is the sum of the relative variances in each parameter, u, and v.

The same formula is found for the quotient of u and v.

In general, when multiplying or dividing n numbers:

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2} + \ldots \frac{\sigma_n^2}{n^2}$$

2. Example.
   The volume of room is given by the length, width and height, *LxWxH*. A room has measurements of 12.5(1) ft by 10.3(1) ft by 7.8(1) ft. (The uncertainty in the last digit of each length is given in parenthesis.) Find the volume of the room and the uncertainty in the volume.

$$V = LxWxH = (12.5ft)(10.3ft)(7.8ft) = 1004ft^3 .$$

$$\frac{\sigma_V^2}{V^2} = \frac{\sigma_L^2}{L^2} + \frac{\sigma_W^2}{W^2} + \frac{\sigma_H^2}{H^2} = \frac{(0.1ft)^2}{(12.5ft)^2} + \frac{(0.1ft)^2}{(10.3ft)^2} + \frac{(0.1ft)^2}{(7.8ft)^2} = 3.2x10^{-4} .$$

So, the variance in the volume is

$$\sigma_V^2 = \left(\frac{\sigma_V^2}{V^2}\right)V^2 = (3.1x10^{-4})(1004\,ft^3)^2 = 325\,ft^6 .$$

The uncertainty in the volume is $\sqrt{\sigma_V^2} = \sqrt{325\,ft^6} = 18\,ft^3$.

Final answer: $V = 1004(18)\,ft^3$.

3. Addition and Subtraction with weighting constants

If x is the sum or difference of u and v with weighting constants a and b.

$$x = au \pm bv$$

The partial derivatives include the weighting constants, and equation (1) becomes

$$\sigma_x^2 = a^2\sigma_u^2 + b^2\sigma_v^2 .$$

In general, when adding or subtracting n numbers with weighting constants:

$$\sigma_x^2 = a^2\sigma_u^2 + b^2\sigma_v^2 + \ldots n^2\sigma_n^2 .$$

3. Example.
   Let P be the perimeter of a rectangle with dimensions *L=15.70(5) cm* and *W=5.65(5) cm*.

$$P = 2L + 2W = 2(15.70cm) + 2(5.65cm) = 42.70cm .$$

$$\sigma_P^2 = 2^2\sigma_L^2 + 2^2\sigma_W^2 = 4(\sigma_L^2 + \sigma_W^2) = 4\left[(0.05cm)^2 + (0.05cm)^2\right] = 0.02cm^2 .$$

The uncertainty in the perimeter is $\sqrt{\sigma_P^2} = \sqrt{0.02cm^2} = 0.14cm$.

Final answer: $P = 42.70(14)cm$.

4. Multiplication and division with weighting constants

If x is the product or quotient of u and v with weighting constant a;

$$x = a(uv) \text{ or } x = a\frac{u}{v}$$

Even though the partial derivatives include the weighting constant, the relative variance in x reduces to the same formula we derived without weighting constants.

In general, when multiplying or dividing n numbers with weighting constant *a*:

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2} + \ldots \frac{\sigma_n^2}{n^2} .$$

4. Example.
   Let A be the area of a triangle with a base *b=15.70(5) cm* and height *h=5.65(5) cm*.

$$A = \tfrac{1}{2}bh = \tfrac{1}{2}(15.70cm)(5.65cm) = 44.35cm^2 .$$

$$\frac{\sigma_A^2}{A^2} = \frac{\sigma_b^2}{b^2} + \frac{\sigma_h^2}{h^2} = \frac{(0.05cm)^2}{(15.7cm)^2} + \frac{(0.05cm)^2}{(5.65cm)^2} = 8.8x10^{-5} .$$

So, the variance in the area is

$$\sigma_A^2 = \left(\frac{\sigma_A^2}{A^2}\right)A^2 = (8.8x10^{-5})(44.35cm^2)^2 = 0.17cm^4 .$$

The uncertainty in the area is $\sqrt{\sigma_A^2} = \sqrt{0.17cm^4} = 0.42cm^2$.

Final answer: $A = 44.35(42)cm^2$.

5. Powers

If x is obtained by raising the variable u to power b with weighting constant a

$$x = au^b.$$

The partial derivative of x with respect to u,

$\frac{\delta x}{\delta u} = \pm abu^{\pm(b-1)}$. This can be simplified by multiplying by $\frac{x}{au^b} = 1$;

$\frac{\delta x}{\delta u} = \frac{\pm xabu^{\pm(b-1)}}{au^b}$ that reduces to:

$\frac{\delta x}{\delta u} = \pm\frac{bx}{u}$. Rearranging, $\sigma_x = \left(\pm\frac{bx}{u}\right)\sigma_u$. Dividing both sides by x,

$\frac{\sigma_x}{x} = b\frac{\sigma_u}{u}$. This is the simplest formula for powers.

5. Example.
   The volume of a sphere is given by $\frac{4}{3}\pi r^3$. Let r = 2.65(5) cm.

   $V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(2.65cm)^3 = 78.0cm^3$.

   Finding the relative error, $\frac{\sigma_V}{V} = 3\left(\frac{\sigma_r}{r}\right) = 3\left(\frac{0.05cm}{2.65cm}\right) = 0.057$.

   So the error in the volume is,

   $\sigma_V = \left(\frac{\sigma_V}{V}\right)V = (0.057)77.95cm^3 = 4.4cm^3$.

   $V = 78.0(4.4)\text{cm}^3$

6. Exponential functions

Let x be obtained by raising the natural base, e, to power u with weighting constants a and b,

$$x = ae^{\pm bu}.$$

The partial derivative of x with respect to u is

$\frac{\delta x}{\delta u} = \pm b\left(ae^{\pm bu}\right) = \pm bx$. Rearranging; $\sigma_x = (\pm bx)\sigma_u$. Dividing by x

The relative error in x is $\frac{\sigma_x}{x} = b\sigma_u$.

If the base is not e, a similar formula can be derived for any base y.

$$x = ay^{\pm bu} \rightarrow \frac{\sigma_x}{x} = b\ln(y)\sigma_u.$$

6. Example.
   The activity of a radioactive source after some time period t is given by the formula

$A_t = A_0 e^{-kt}$ where A_t is the activity at time *t*, A_0 is the initial activity, and *k* is the decay constant. Assuming a negligible error in A_0 and *k*, the uncertainty in the activity is determined by any uncertainty in the time.

$$\frac{\sigma_{A_t}}{A_t} = k\sigma_t$$

Let *t* = 3.00(4) days, *k* = 0.0547day^{-1}, and A_0 = 1.23x10^3/s.

The activity after 3 days: $A_t = 1.230x10^3/_s\, e^{-\left(0.0547/_{day}\right)(3.00day)} = 1.044x10^3/_s$.

The relative error in the activity: $\frac{\sigma_{A_t}}{A_t} = 0.0547/_{day}(0.04day) = 0.0022$.

So the uncertainty in A_t is

$$\sigma_{A_t} = \left(\frac{\sigma_{A_t}}{A_t}\right)A_t = 0.0022\left(1.044x10^3/_s\right) = 2/_s .$$

A_t = 1.044x10^3(2)/s.

7. Logarithmic functions

Let *x* be obtained by taking the natural logarithm of *u* with weighting constants *a* and *b*,

$$x = a\ln(\pm bu) .$$

The partial derivative of *x* with respect to *u* is

$$\frac{\delta x}{\delta u} = \frac{a}{u} .$$

Rearranging, $\sigma_X = a\frac{\sigma_u}{u}$.

If we use base 10 logarithms

$$\sigma_X = a\frac{\sigma_u}{2.303u} .$$

7. Example.
   In chemistry lab we measure the pH of a solution as –log[H$^+$], where [H$^+$] is the concentration of hydrogen ions in solution in units of molarity, M = moles/liter. Given [H$^+$] = 0.0023(1) M, find the pH and uncertainty in the pH.

   pH = -log(0.0023) = 2.64.

   The uncertainty in the pH: $\sigma_X = \frac{a\sigma_u}{2.303u} = \frac{0.0001}{2.303(0.0023)} = 0.02$.

   Final answer: pH = 2.64(2).

Summary

Several formulas were presented for propagating random errors through calculations using partial derivatives from calculus. The formulas assume a normal distribution of random errors and no correlation between errors. The simplified formulas are summarized below. For complicated functions, the user may well have to numerically evaluate the partial derivatives with respect to each uncertainty explicitly, and not rely on the simplified formulas.

Assume $x = f(u, v, \ldots)$.

$$\sigma_x^2 \simeq \sigma_u^2 \left(\frac{\delta x}{\delta u}\right)^2 + \sigma_v^2 \left(\frac{\delta x}{\delta v}\right)^2 + \ldots$$

Specific formulas:

$x = au \pm bv$:	$\sigma_x^2 = a^2\sigma_u^2 + b^2\sigma_v^2 + \ldots n^2\sigma_n^2$
$x = a(uv)$ or $x = a\frac{u}{v}$:	$\frac{\sigma_x^2}{x^2} = \frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2} + \ldots \frac{\sigma_n^2}{n^2}$
$x = au^b$	$\frac{\sigma_x}{x} = b\frac{\sigma_u}{u}$
$x = ae^{\pm bu}$:	$\frac{\sigma_x}{x} = b\sigma_u$
$x = ay^{\pm bu}$	$\frac{\sigma_x}{x} = b\ln(y)\sigma_u$
$x = a\ln(\pm bu)$:	$\sigma_x = a\frac{\sigma_u}{u}$
$x = a\log(\pm bu)$:	$\sigma_x = a\frac{\sigma_u}{2.303u}$

Self-Test

Complete the following calculations. Find the uncertainty in each calculated value by the propagation of errors method. Check your answers by reviewing the next page. These are the same problems from tutorial #4. I have added uncertainties to the measured values.

1. It takes 10.5(1) s for a sprinter to run 100.00(5) m. Calculate the average speed of the sprinter in meters per second and mi/hr.

2. The mass of an empty 10-mL graduated cylinder is 25.442(2) g. After adding 8.5(1) mL of liquid the mass increases to 32.402(2) g. Calculate the density of the liquid in g/mL and kg/L.

3. The radius of an iodine atom is 140(5) pm. Find the volume of one iodine atom in pm^3 and cm^3.

4. pH is defined as –log[H^+] where [H^+] is the molarity (M) of hydrogen ions in an aqueous solution. If the molarity of hydrogen ions is 1.32(2)x10^{-3} M, find the pH.

5. A solution has a pH of 10.72(2). Find the concentration of hydrogen ions in solution.

6. A Cu/Al alloy contains 95.6(2)% copper by mass. How many milligrams of aluminum are in a 2.7332(2) g sample of this alloy?

Answers to Self-Test

1. It takes 10.5(1) s for a sprinter to run 100.00(5) m. Calculate the average speed of the sprinter in meters per second and mi/hr.

$$\frac{100.00m}{10.5s} = 9.52\frac{m}{s}$$

Convert to km/hr: $9.5\underline{2}4\frac{m}{s}\left(\frac{1km}{1000m}\right)\left(\frac{1mi}{1.6093km}\right)\left(\frac{3600s}{1hr}\right) = 21.3\frac{mi}{hr}$

Uncertainty calculations.

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_t^2}{t^2} + \frac{\sigma_d^2}{d^2} = \frac{(0.1s)^2}{(10.5s)^2} + \frac{(0.05m)^2}{(100.00m)^2} = 9.1x10^{-5}$$

$$\sigma_X^2 = \left(\frac{\sigma_x^2}{x^2}\right)x^2 = 9.1x10^{-5}\left(9.52\, {}^{m}\!/\!{}_{s}\right)^2 = 0.0082\, {}^{m^2}\!/\!{}_{s^2}$$

$$\sigma_X = \sqrt{\sigma_X^2} = \sqrt{0.0082\, {}^{m^2}\!/\!{}_{s^2}} = 0.09\, {}^{m}\!/\!{}_{s}$$

$$Speed = 9.52(9)\, {}^{m}\!/\!{}_{s} = 21.3(2)\, {}^{mi}\!/\!{}_{hr}$$

2. The mass of an empty 10-mL graduated cylinder is 25.442(2) g. After adding 8.5(1) mL of liquid the mass increases to 32.402(2) g. Calculate the density of the liquid in g/mL and kg/L.

$$\frac{32.402g - 25.442g}{8.5mL} = \frac{6.96\underline{0}g}{8.5mL} = 0.81\frac{g}{mL}\ \text{(2 sig figs)}$$

Convert to kg/L: $0.8\underline{1}9\frac{g}{mL}\left(\frac{1kg}{1000g}\right)\left(\frac{1mL}{10^{-3}L}\right) = 0.82\frac{kg}{L}$

Uncertainty calculations.

$$\sigma_{mass}^2 = \sigma_{mass1}^2 + \sigma_{mass2}^2 = 2(0.002g)^2 = 8.0x10^{-6}$$

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_{mass}^2}{mass^2} + \frac{\sigma_{vol}^2}{vol^2} = \frac{8.0x10^6 g^2}{(6.960g)^2} + \frac{(0.1ml)^2}{(8.5ml)^2} = 1.4x10^{-4}$$

$$\sigma_x = \sqrt{\left(\frac{\sigma_x^2}{x^2}\right)}x = \sqrt{1.4x10^{-4}}\left(0.81\, {}^{g}\!/\!{}_{mL}\right) = 0.01\, {}^{g}\!/\!{}_{mL}$$

$$Density = 0.81(1)\, {}^{g}\!/\!{}_{mL} = 0.81(1)\, {}^{kg}\!/\!{}_{L}$$

3. The radius of an iodine atom is 140(5) pm. Find the volume of one iodine atom in pm^3 and cm^3.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(140\,pm)^3 = 1.15x10^7\,pm^3$$

Uncertainty calculations

$$\frac{\sigma_V}{V} = 3\frac{\sigma_r}{r} = 3\frac{5\,pm}{140\,pm} = 0.11$$

$$\sigma_V = \left(\frac{\sigma_V}{V}\right)V = 0.11(1.15x10^7\,pm^3) = 0.12x10^{-7}\,pm^3$$

$$V = 1.15(12)x10^7\,pm^3 = 1.15(12)x10^{-23}\,cm^3$$

4. pH is defined as –log[H^+] where [H^+] is the molarity (M) of hydrogen ions in an aqueous solution. If the molarity of hydrogen ions is 1.32(2)x10^{-3} M, find the pH.

   pH = -log[H^+] = -log(1.32x10^{-3}) = -(-2.879) = 2.879.

   Uncertainty calculations

   $$\sigma_{pH} = \frac{\sigma_M}{2.303M} = \frac{0.02x10^{-3}\,M}{2.303(1.32x10^{-3}\,M} = 0.007$$

   pH = 2.879(7)

5. A solution has a pH of 10.72(2). Find the concentration of hydrogen ions in solution.

   Rearranging and using the properties of logarithms:

   log[H^+] = -pH. $10^{\log[H^+]} = [H^+] = 10^{-pH} = 10^{-10.72} = 1.91x10^{-11}\,M$

   Uncertainty calculations

   $$\frac{\sigma_x}{x} = b\ln(y)\sigma_u = (1)\ln(10)0.02 = 0.046$$

   $$\sigma_x = \left(\frac{\sigma_x}{x}\right)x = (0.046)1.9x10^{-11}\,M = 0.09x10^{-11}\,M$$

   $$[H^+] = 1.91(9)x10^{-11}\,M$$

6. A Cu/Al alloy contains 95.6(2)% copper by mass. How many milligrams of aluminum are in a 1.0332(2) g sample of this alloy?

   Al% in the alloy: (100%-95.6%) = 4.4%.

   $$1.0332gAlloy\left(\frac{4.4gAl}{100gAlloy}\right)\left(\frac{1mg}{10^{-3}g}\right) = 45mgAl$$

   Uncertainty calculations

   $$\sigma_{\%}^2 = (0.2\%)^2 = 0.04$$

   $$\frac{\sigma_{mg}^2}{mg^2} = \frac{\sigma_{\%}^2}{\%^2} + \frac{\sigma_{mass}^2}{mass^2} = \frac{0.04}{4.4^2} + \frac{(0.0002g)^2}{(1.0332g)^2} = 0.0021$$

   $$\sigma_{mg} = \sqrt{\left(\frac{\sigma_{mg}^2}{mg^2}\right)}mg = \sqrt{0.0021}(45mg) = 2mg$$

   $$Mass = 45(2)mg$$