Significant Figures and Errors

Two recruiters for high tech companies are sitting in a bar after work. One says, “Today I interviewed five Ph.D.’s for the same job, and all their resumes looked the same to me.” The other asks, “Which one did you hire?” And the first recruiter replies, “The one who had error bars on her data, of course!”

In science, knowing the accuracy of a measurement is arguably as important as the result of the measurement itself. Later in the course, we’ll talk about a Nobel prize winning discovery that happened only because of careful error analysis. Your future Nobel prize, whatever it is about, will likely have something to do with understanding the accuracy of your measurement or theoretical calculations. From a more immediately practical point of view in Chemistry 12H, we will take points off your quizzes and exams if you mess up on significant figures. Significant figures are our shorthand way of keeping track of errors in measurements and calculations.

Significant figures

Generally, we assume that the last digit quoted in a measured value is the one that has some uncertainty. For example, let’s say you weigh a sample on a balance and get a value of 44.2239672 g. The accuracy of the balance (determined by several weighings of the same object) is ± 0.1 mg = 0.0001 g. We can write the result like this:

\[ \text{Weight} = 44.2239672 \pm 0.0001 \]

This means that the true weight of the sample is most likely between 44.2240672 and 44.2238672. It is clear that the “72” at the end of the number has essentially no meaning, and that the “6” before it has limited meaning. This number should be properly written as:

\[ \text{Weight} = 44.2240 \text{ (rounding off to the nearest 0.0001 g)} \]

or

\[ \text{Weight} = 44.22396 \]

In the latter case we keep the “6” but acknowledge that we don’t know much about this decimal place. This is helpful for minimizing round off error in subsequent calculations. In either case we say we know the weight to 6 significant figures.

Error propagation

There is a rigorous way to do error propagation, which we will discuss at the end of this section for the interested student. For the purposes of Chem 12H, we can do a reasonably good job of error propagation just by keeping track of significant figures. The following example (taken from a problem in Chapter 1 of BLB) illustrates the idea.

Let’s say we have an irregularly shaped lump of iron pyrite (foolsgold, FeS\(_2\)), and wish to measure the density by using Archimedes’ principle.
Step 1: Weigh the rock. \( M_{\text{solid}} = 32.65 \text{ g} \) (known to 4 significant figures)

Step 2: Tare a beaker, put in the rock, add toluene up to the 50.00 mL mark, and weigh again.

Density of toluene = 0.864 g/mL (3 sig. figs.)

Calculating the density

We have four equations:

\[
\begin{align*}
\text{(1)} & \quad \rho_{\text{solid}} = \frac{M_{\text{solid}}}{V_{\text{solid}}} \\
\text{(2)} & \quad V_{\text{total}} = 50.00 \text{ mL} = V_{\text{solid}} + V_{\text{liquid}} \\
\text{(3)} & \quad \rho_{\text{liquid}} = 0.864 = \frac{M_{\text{liquid}}}{V_{\text{liquid}}} \\
\text{(4)} & \quad M_{\text{liquid}} = M_{\text{total}} - M_{\text{solid}}
\end{align*}
\]

Starting from (4), we solve for \( M_{\text{liquid}} \)

\[
M_{\text{liquid}} = \frac{58.58 \text{ g}}{32.65 \text{ g}} - \frac{25.93 \text{ g}}{25.93 \text{ g}}
\]

From (3), \( V_{\text{liquid}} = M_{\text{liquid}}/\rho_{\text{liquid}} = \frac{25.93 \text{ g}}{0.864 \text{ g/mL}} = 30.0_{116} \text{ mL (3 sig. figs)} \)

From (2), \( V_{\text{solid}} = V_{\text{total}} - V_{\text{liquid}} \)

\[
V_{\text{solid}} = \frac{50.00 \text{ mL}}{30.0_{116} \text{ mL}} = 19.9_{884} \text{ mL (3 sig. figs)}
\]

And finally, from (1), \( \rho_{\text{solid}} = \frac{32.65 \text{ g}}{19.9_{884} \text{ mL}} = 1.63_{34} = 1.63 \text{ g/mL} \)

In this example, we used three rules for keeping track of significant figures:

1. Addition (subtraction): truncate the answer at the last digit that is known with certainty for all the numbers being added (subtracted).
2. Multiplication (division): the number with the fewest significant figures determines the number of significant figures in the product (dividend).
3. Keep all the insignificant figures until the end and then round off appropriately.
What does the answer $\rho_{\text{solid}} = 1.63 \text{ g/mL}$ mean? If the uncertainty is $\pm 1$ in the last digit, it means that, to the accuracy of our measurement, $\rho_{\text{solid}}$ is somewhere between 1.62 and 1.64.

We can test this idea by taking the high and low limits in the last step of the calculation:

$$\rho_{\text{solid}} = \frac{32.65 \pm .01}{20.0 \pm 0.1}$$

Largest

$$\frac{32.65 + .01}{20.0 - 0.1} = \frac{32.66}{19.9} = 1.64_{12}$$

Smallest

$$\frac{32.65 - .01}{20.0 + 0.1} = \frac{32.64}{20.1} = 1.62_{38}$$

So the range of possible values is $1.63 \pm 0.01$.

**Error propagation by the root mean square (rms) method**

If you take a statistics class or an advanced class in analytical chemistry, you will learn that a more mathematically defensible procedure for propagating error uses root mean square (rms) calculations. This derives from the fact that random error is ordinary described by a gaussian probability curve. Root mean square means that you add up the squares of the individual errors and then take the square root of the sum. For addition and subtraction, use the absolute errors, and for multiplication and division, use the relative error, which is the absolute error divided by the value. Let’s do the same density example by the rms method:

1. $M_{\text{liquid}} = (58.58 \pm 0.01) - (32.65 \pm 0.01) = 25.93 \pm ?$

   \[ \text{rms error} = \sqrt{(0.01)^2 + (0.01)^2} = 0.014 \]

2. $V_{\text{liquid}} = \frac{25.93 \pm 0.014}{0.864 \pm 0.001} = 30.0116 \pm ?$

   relative error in numerator = $0.014/25.93 = 5.4 \times 10^{-4}$
   relative error in denominator = $0.001/0.864 = 1.16 \times 10^{-3}$
   rms relative error = $\sqrt{(5.4 \times 10^{-4})^2 + (1.16 \times 10^{-3})^2} = 1.28 \times 10^{-3}$
   error in dividend = $(1.28 \times 10^{-3})(30.0116) = \pm 0.04$
   $V_{\text{liquid}} = 30.01 \pm 0.04 \text{ mL}$

3. $V_{\text{solid}} = (50.00 \pm 0.01) - (30.01 \pm 0.04) = 19.99 \pm ?$

   \[ \text{rms error} = \sqrt{(0.01)^2 + (0.04)^2} = 0.04 \text{ mL} \]

4. $\rho_{\text{solid}} = \frac{32.65 \pm 0.01}{19.99 \pm 0.04} = 1.6334 \pm ?$
Relative error in numerator = \( \frac{0.01}{32.65} = 3.0 \times 10^{-4} \)
Relative error in denominator = \( \frac{0.04}{19.99} = 2.0 \times 10^{-3} \)
RMS relative error = \( \sqrt{(3.0 \times 10^{-4})^2 + (2.0 \times 10^{-3})^2} = 2.2 \times 10^{-3} \)
Error in dividend = \( (2.2 \times 10^{-3})(1.6334) = \pm 0.004 \)
\( \rho_{\text{solid}} = 1.633 \pm 0.004 \text{ g/mL} \)

From this we conclude that, within the accuracy of our measurement, \( \rho_{\text{solid}} \) is between 1.629 and 1.637 g/mL.

From this example, we see that the RMS error in the final answer (0.004) is about half that (0.01) estimated by the significant figure method. The significant figure method thus errs “on the safe side” for most calculations. In terms of the math involved, it is much simpler and is thus the method we will use in Chem 12H.

Questions:

1. How many significant figures are there in (a) 9.14, (b) 9.014, (c) 4137.98, (d) 7.00 \times 10^{-4}, (e) 0.0063, (f) 1.0063, (g) 2.3 \times 10^5, (h) 77200?

2. How many significant figures are there in (a) 322.2 \times 14.1, (b) 23.0 + 0.112, (c) 211.23-207.6, (d) 1051 \div 4.122

3. You need 1.00 mL of a 1.00 M solution of silver nitrate (\( \text{AgNO}_3 \), FW = 169.87 g/mol) for an analytical experiment. You must first make the \( \text{AgNO}_3 \) solution by weighing out the solid and then adding an appropriate amount of water. The accuracy of your balance is \( \pm 0.1 \text{ mg} \). You are able to measure large volumes (50-150 mL) to an accuracy of \( \pm 0.1 \text{ mL} \) by using a buret, and you also have a 0.50 mL pipet that has an accuracy of \( \pm 0.02 \text{ mL} \). Your TA suggests that you start by making 100 mL of the \( \text{AgNO}_3 \) solution, but your lab partner thinks that 2 mL should be enough. Who is right, and why?

4. Carbon dioxide emissions are now thought to be a major cause of global warming. One of the problems with predicting future global \( \text{CO}_2 \) levels and mean temperatures, however, is the uncertainty in projections of populations, energy use, and energy efficiency. The Kaya equation (see M. Hoffert, Nature, 1998, 395, 882-881)

\[ M_c = N(GDP/N)(E/GDP)(M_c/E) \]

estimates the mass of \( \text{CO}_2 \) released into the atmosphere per year, \( M_c \), as the product of the world population (\( N \)), the per capita annual gross domestic product (\( GDP/N \)), the primary energy density (\( E/GDP \)) and the carbon intensity of the energy produced (\( M_c/E \)). These values are known with less certainty for predictions made farther into the future. Assuming we can predict the values of each of the four terms in the equation in the year 2026 to an accuracy of \( \pm 15\% \), and the calculated value of \( M_c \) for that year is 8.5 gigatons of carbon, what is the uncertainty in \( M_c \)?