Error and uncertainty may seem synonymous with trivial mistakes in the lab, but they are actually well-defined aspects of any numerical measurement in a laboratory experiment.

A number reported without consideration of precision tells an incomplete story, thus a goal in the General Chemistry laboratory is to start thinking about the value and precision of any numerical result—whether it is a laboratory measurement, a survey result, or a sports statistic.

The use of significant digits in calculations is covered in the textbook and is used in the lecture portion of General Chemistry. Significant digits are an approximate approach to treat precision, and they provide rules for addition and multiplication.

This guide will be sufficient for your work in General Chemistry. More information can be found in John R. Taylor’s *An Introduction to Error Analysis.*

**Random and Systematic Error**

One goal for lab work will be controlling the two types of experimental error: systematic error and random error.

**Systematic error** arises from a flaw in experimental design or equipment and can be detected and corrected. This type of error leads to inaccurate measurements of the true value. The best way to check for systematic error is to use different methods to perform the same measurement.

**Random error** is always present and cannot be corrected. It has to do with the precision of measurements in laboratory and is the statistical uncertainty in the last digits of the precision. An example of random error is that which arises from reading a burette, which is somewhat subjective and therefore varies at each reading. Note: “Error” and “uncertainty” are sometimes used interchangeably to mean “random error.” The phrase “error in a measurement” is synonymous with “uncertainty in a measurement.”

One aim will be to eliminate systematic error and minimize random error to obtain a high degree of both accuracy and precision. A goal of the General Chemistry laboratory will be to practice thinking about the largest contributors to both types of error in our experiments.
Random Error in Lab Experiments

Systematic error is corrected for in the lab procedure. Understanding random error comes from repeated measurements to give a set of replicas. The statistics of the set of replicas gives a way to understand the value and error in measurement. The statistical tools to be used are the Mean, the Standard Deviation, and the Standard Deviation of the Mean.

Mean, Standard Deviation, and Standard Deviation of the Mean

The mean, $\bar{x}$, is the simple average of $n$ replicas, each replica signified as $x_i$.

$$\bar{x} = \frac{\sum x_i}{n}.$$  

The standard deviation (SD), $\sigma_x$, is related to the spread in values of replicas in an experiment. We will use the population standard deviation to approximate it:

$$\sigma_x = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}.$$  

The standard deviation of the mean (SDOM), $\sigma_{\bar{x}}$, is also called the estimated standard error. If the full experiment was repeated (all replicas), the spread in the average results should be related to the standard deviation of the mean:

$$\sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{n}}.$$  

Using Excel

Here the discussion is limited to the mean, the standard deviation, and the standard deviation of the mean. For example, when five different volumetric flasks were each used to measure 50.0 mL of water at 25 °C and then each quantity of water was weighed, the following masses in grams were determined: 49.897, 49.938, 49.599, 49.965, 49.771. A spreadsheet was used to calculate the mean, standard deviation and standard deviation of the mean as shown in Figure 1.
Figure 1. The actual appearance of the spreadsheet used to do the calculations is shown to the left and the same spreadsheet appears on the right with the equations used to calculate the quantities shown instead of the numerical result of those calculations.

The number of decimal places shown for the mean, SD, and SDOM were adjusted with the buttons in the toolbar and using the SDOM to decide the last decimal place to report. Remember the $\%$ error is equal to (SDOM/mean) $\times$ 100.

**Reporting Error**

Whenever possible report numerical results with error. The quantity we’ll use to estimate measurement error in General Chemistry is the SDOM, which will be reported with one significant digit. This precision of the error will determine the precision of the measurement (e.g., indicates the last decimal place to the right to report).

**Reporting Absolute Error**

The absolute error has the same units as the measurement. In the example above, the mass of 50.0 mL of water at 25 °C would be reported as 49.8 ± 0.1 g or 4.98 ± 0.01 $\times$ 10$^1$ g in scientific notation. The 0.1 g is the error bar on this measurement and signifies the last decimal place in the measurement to report.

**Reporting Relative Error ($\%$ error)**

The relative error is the scale of the error with respect to the value of the measurement. Mathematically, it is the SDOM divided by the mean times 100: $(\frac{\sigma_x}{\bar{x}}) \times 100\%$. The relative error or % error is reported with units of percentage, and it typically has one significant digit. Thus, for the above example, this quantity was calculated in Excel (see Figure 1) thus the mass of 50.0 mL of water at 25 °C would be reported as 49.8 g ± 0.2%.
Significance

In General Chemistry lab, the word “significant” doesn’t always mean “important.” The calculated error bars will be used to gauge the significance of measurements. If two measured values are contained within each other’s error bars, the measured values are the same— with no significant difference between them. If two measured values and their error bars are well separated, then the two values are unique, and their difference is “significant.” There is a grey area between those two extremes, and some results can be inconclusive. A full understanding of the significance of inconclusive results requires other statistical tests such as a t-test. More information can be found on page 150 of Taylor.¹

Multiplying and Adding with Error

Once a measurement has been made some dimensional analysis needs to be done. There are easy rules to follow for multiplication and addition:

**Multiplication/Division**

Multiplication and division *scale* a quantity, so these operations also *scale* the error. The mass of water in the example above can be used to calculate the density of water at 25 °C, by dividing the mass by the volume. The absolute error will be divided by the volume as well:

\[ 49.8 \pm 0.1 \text{ g} \times \frac{1}{50.0 \text{ mL}} = 0.996 \pm 0.002 \frac{\text{g}}{\text{mL}} \]

**Addition/Subtraction**

Addition and subtraction just *shift* a quantity, so they don’t change the error. For instance, if the temperature of the room was measured to be 25.3 ± 0.3 °C, and that value was then converted to Kelvin by adding 273.15 to the measured temperature, as shown below. The absolute error is unchanged because Kelvin and Celsius have the same scale, just a different origin.

\[ 25.3 \pm 0.3 \text{ °C} + 273.15 = 298.4 \pm 0.3 \text{ K} \]
Error in Linear Fits with Excel

One last place to get errors from measurements is from the linear fits done by Excel. For example, using volumetric glassware, different volumes of water were measured and weighed at 25 °C. The following graph was made following the instructions in the Excel Help document.

![Mass versus Volume of Water at 25 °C](image)

**Figure 2.** The mass of water at 25 °C increases linearly with volume, giving a slope of 0.994 ±0.002 g/mL and a y-intercept of 0.06 ± 0.08 g.

Where did ±0.002 g/mL and ± 0.08 g in the figure caption come from? While it’s good to give the R²-value to give a sense for the precision of the fit a better strategy is to use Excel’s LINEST function to calculate the errors in these parameters.

**To Use Excel’s LINEST Function**

1. Highlight an empty block of cells two columns wide (↔) by five rows (↕) high.
2. Immediately type `=LINEST(`
3. Highlight the cells containing the y-values and then type a comma ,
4. Highlight the cells containing the x-values and then type a comma ,
5. Type one more comma ,
6. Type `TRUE)` so your cell should look similar to: `=LINEST(B3:B7,A3:A7,,TRUE)`
7. Hit the command and return buttons 

8. The Excel table below shows exactly what the LINEST generates for output. The top two rows of the LINEST function output contain the value and error for the slope and intercept. These data were needed to make the Figure 2 caption above. Please make sure that the $r^2$ reported for the slope is consistent with the value obtained from the equation for the line in your graph. If you wish, you can look up the meanings of the other quantities reported by LINEST as they are beyond the scope of this course and document.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<td></td>
<td></td>
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<td>Mass(g)</td>
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<td>intercept</td>
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<td>residual SS</td>
</tr>
</tbody>
</table>

**Figure 3.** LINEST output for mass of water versus volume correlation.

**Reference**

**Error Analysis Examples**

Error analysis is often a difficult area for students. However, the careful consideration of experimental error is one of the important skills that we need to learn to be effective scientists. In the following discussion, the errors in a titration experiment are considered. The first section is a detailed look at how to determine the most important errors. The second section is an example of the corresponding text that would be written in a lab report for CH141-142.

**Determining the Important Errors**

- **The purpose** of the error analysis section of the lab report is to determine the most important errors and the effect that those errors have on the final result.

- **Random Errors**: Random errors cause positive and negative deviations from the average value of a measurement. Random errors cancel by averaging, if the experiment is repeated many times. Upon averaging many trials, random errors have an effect only on the precision of a measurement. The effect of random errors is primarily on the precision. Every non-integer experimental measurement is a source of random error. The random error is estimated from the readability of the device. A table of typical measurements and the associated precision, under practical circumstances, is given below. For instrument readings, to avoid round-off error, report one extra significant figure and then underline the digit that is not significant.

<table>
<thead>
<tr>
<th>Volumetric flasks and pipettes</th>
<th>precision (relative)</th>
<th>significant figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mL</td>
<td>± 0.03 mL</td>
<td>3 i.e. 10.0 mL</td>
</tr>
<tr>
<td>25 mL</td>
<td>± 0.03 mL</td>
<td>3 25.0 mL</td>
</tr>
<tr>
<td>50 mL</td>
<td>± 0.05 mL</td>
<td>3 50.0 mL</td>
</tr>
<tr>
<td>100 mL</td>
<td>± 0.08 mL</td>
<td>4 100.0 mL</td>
</tr>
</tbody>
</table>

**Auto-pipettors**

| 10 µL                           | ± 0.05 µL (0.5%)     | 3 i.e. 10.0 µL      |
| 100 µL                          | ± 0.3 µL (0.3%)      | 3 100. µL           |
| 1000 µL                         | ± 2 µL (0.2%)        | 3 1000. µL          |

**Analytical Balance**

| 0.1000 g                        | ± 0.0001 g           | 4 e.g. 0.3456 g    |
| 1.0000 g                        | ± 0.0001 g           | 5 2.3456 g         |
| 10.0000 g                       | ± 0.0001 g           | 6 12.3456 g        |

**Spectrophotometer (Spectro-Viz*)**

| 0.100                           | ± 0.003 (± 3%)       | 2 e.g. 0.123       |
| 0.500                           | ± 0.003 (± 0.6%)     | 2 0.456            |
| 1.000                           | ± 0.004 (± 0.4%)     | 3 1.123            |
| 1.500 (1 sign. fig. for A>2)    | ± 0.015 (± 1%)       | 2 1.567            |

**pH Meter**

| 7.00                            | ± 0.02               | ~3 e.g. 6.123      |

**Electronic Pressure Sensor**

| 1.0 atm (760 torr)              | ± 0.0005 atm (± 0.4 torr) | 3-4 e.g 826.4 torr |

**Constant Current Power Supply**

| 0.400 amp                       | ± 0.0004 amp (± 0.1 %)  | 3 0.4162 amp       |

* Spectro-Viz plus photometric accuracy is ± 13%, but standard curve calibration decreases the systematic error to approximately equal the averaged precision (about 3 sign. figures), assuming the range of A is 0.1 to 1.0.
• **Systematic Errors:** Without any changes in the procedure, systematic errors are repeated if the experiment is repeated. Systematic errors have a biased effect on the final results; systematic errors make the final result high or low, but not both. Instrument calibration errors are examples of systematic errors. Environmental effects can also be causes of systematic error, for example a change in lab temperature changing the calibration of a balance or the volume of a flask. An example of a systematic error from the CaCO\(_3\) precipitation experiment is that small particles pass through the glass frits in a Gooch crucible, making the final precipitate mass too small. Systematic errors affect the accuracy of the final results.

A given measurement can contribute to both random and systematic error. Non-integer measurements always contribute to the random error. For example, a miscalibrated balance is a source of random and systematic error. Systematic errors are often corrected by completing a determination using a different method or by comparing results among different laboratories.

• **Student Mistakes:** Student mistakes are just student mistakes; they are neither random nor systematic errors. Examples in this category are spills, misreading a device such as a burette, misinterpretation of the procedure, incorrect handling of a micro-pipettor, and forgetting to rinse out a beaker when doing a quantitative transfer. These errors are known and easily preventable, if the experiment is repeated. Systematic errors occur with each repetition of the experiment, assuming no changes in instrumentation. Mistakes should be noted in the Results section of your report as mistakes.

**Example:** *Titration of an Unknown Acid:*

A 25.0-mL sample of an unknown acid is titrated with 15.67 mL of 0.1042 M NaOH. The volume of the acid is determined using a volumetric pipette and the burette used in the experiment has scale divisions every 0.1 mL. The standard base solution was made using an analytical balance and a 100.0-mL volumetric flask. The end point is determined by visually detecting the pink color of phenolphthalein.

**Answer:**

**Random Measurement Errors:** Every measurement is a source of random error. However, we must identify those errors that have a significant effect on the final result. The effects on the final result are determined using significant figure rules. The concentration of the unknown acid is:

\[
M_{\text{unknown}} = \frac{V_{\text{titrant}}M_{\text{titrant}}}{V_{\text{unknown}}} = \frac{0.01567 \text{ L}(0.1042 \text{ mol/L})}{0.0250 \text{ L}} = 0.4821 \text{ M}
\]

Since only multiplications and divisions are involved, the number of significant figures in the final result is equal to the smallest number of significant figures of the terms in the calculation. We next discuss the errors associated with each term.

**Volumetric Glassware and Analytical Balance Measurements:** Large volume standard volumetric glassware typically has a precision and accuracy of four significant figures. The accuracy and precision of mass measurements on an analytical balance are also typically to four significant figures (±0.0001). The expected precision in the NaOH solution, using the analytical balance and volumetric glassware, is four significant figures. The number of significant figures in the 25.0-mL volumetric pipette is three. At best the final concentration is known to three significant figures.

**Measurements that are Interpolated between Scale Markings:** The burette readings are not as precise. To determine the volume of titrant delivered, two readings are made. Each reading is
recorded to the nearest 0.01 mL. However, visually estimating the volume to better than ±0.02 mL is difficult. Consequently the precision of the volume delivered by the burette is poorer than ±0.02 mL, since two readings are necessary. Correspondingly in the titration example, the volume delivered by the burette at best is 15.67 ± 0.03 mL, or three significant figures. Correspondingly, the final unknown concentration is officially known to three significant figures. The conclusion is that the precision is determined primarily by the random error in the burette readings and pipette. The random error in the other volume and mass determinations are not consequential.

**Systematic Measurement Errors:** Every measurement is a potential source of systematic error. However, with thoughtful construction of the procedure many measurements can be discounted as significant sources of systematic error. So while the calibration of the glassware and the balance used in a titration experiment are technically sources of systematic error, these errors are easily avoided. The calibration of the balances is periodically checked using a registered calibration mass. Standard volumetric glassware is certified by the manufacturer through calibration against National Institute of Standards and Technology (NIST) traceable procedures. In a titration experiment the only significant systematic errors are in the purity of the reagents and the visual determination of the end point. The purity of the reagents also includes absorption of moisture from the ambient air. So reagents that are susceptible to atmospheric moisture absorption are usually kept in low humidity desiccators. In a titration, the primary systematic error is the endpoint determination. The difference between the equivalence point and the measured end point is called the titration error. A visual end point is always slightly beyond the equivalence point because of the necessity of seeing the color change by eye. The result is that the volume of titrant delivered is too large, giving a larger final concentration than the true value. The conclusion is that the accuracy is determined primarily by systematic error in the end point.

**Example Lab Report Section on Error Analysis**

The discussion, above, gives the complete thought process for determining the most important errors in the experiment. The section in the lab report that presents your conclusions is disappointingly short, by comparison. For the titration example:

The precision is dominated by the random error of the volume readings of the burette and volumetric pipette. The other volumetric glassware contribute insignificant random error. The accuracy is determined by the systematic error in the visual detection of the end point. The visual end point is at a volume larger than the equivalence point, giving a higher final result than the true concentration value.