Errors and Uncertainty in Experimental Data

Causes and Types of Errors

Conducting research in any science course is dependent upon obtaining measurements. No measure is ever exact due to errors in instrumentation and measuring skills. If you were to obtain the mass of an object with a digital balance, the reading gives you a measure with a specific set of values. We can assume that the actual measure lies either slightly above or slightly below that reading. The range is the uncertainly of the measurement taken. More accurate instruments have a smaller range of uncertainty. Whenever you take a measurement, the last recorded digit is your estimate. We call digits in a measurement significant figures.

All measurements have inherent uncertainty. We therefore need to give some indication of the reliability of measurements and the uncertainties in the results calculated from these measurements. When processing your experimental results, a discussion of uncertainties should be included. When writing the conclusion to your lab report you should evaluate your experiment and its results in terms of the various types of errors. To better understand the outcome of experimental data an estimate of the size of the systematic errors compared to the random errors should be considered. Random errors are due to the accuracy of the equipment and systematic errors are due to how well the equipment was used or how well the experiment was controlled. We will focus on the types of experimental uncertainty, the expression of experimental results, and a simple method for estimating experimental uncertainty when several types of measurements contribute to the final result.

1. **Random errors**: Precision (Errors inherent in apparatus.)

A random error makes the measured value both smaller and larger than the true value. Chance alone determines if it is smaller or larger. Reading the scales of a balance, graduated cylinder, thermometer, etc. produces random errors. In other words, you can weigh a dish on a balance and get a different answer each time simply due to random errors. They cannot be avoided; they are part of the measuring process. Uncertainties are measures of random errors. These are errors incurred as a result of making measurements on imperfect tools which can only have certain degree of accuracy. They are predictable, and the degree of error can be calculated. Generally they can be estimated to be half of the smallest division on a scale. For a digital reading such as an electronic balance the last digit is rounded up or down by the instrument and so will also have a random error of \pm half the last digit.

2. Systematic errors: Accuracy (Errors due to "incorrect" use of equipment or poor experimental design.)

A systematic error makes the measured value always smaller or larger than the true value, but not both. An experiment may involve more than one systematic error and these errors may nullify one another, but each alters the true value in one way only. Accuracy (or validity) is a measure of the systematic error. If an experiment is accurate or valid then the systematic error is very small. Accuracy is a measure of how well an experiment measures what it was trying to measure. These are difficult to evaluate unless you have an idea of the expected value (e.g. a text book value or a calculated value from a data book). Compare your experimental value to the literature value. If it is within the margin of error for the random errors then it is most likely that the systematic errors are smaller than the random errors.

Examples of Systemic errors:

- Leaking gas syringes.
- Calibration errors in pH meters.
- Calibration of a balance
- Changes in external influences such as temperature and atmospheric pressure affect the measurement of gas volumes, etc.
- Personal errors such as reading scales incorrectly.
- Unaccounted heat loss.
- Liquids evaporating.
- Spattering of chemicals

If it is larger then you need to determine where the errors have occurred. Assuming that no heat is lost in a calorimetry experiment is a systematic error when a Styrofoam cup is used as a calorimeter. Thus, the

measured value for heat gain by water will always be too low. When an accepted value is available for a result determined by experiment, the percent error can be calculated.

Categories of Systematic Errors and how to eliminate them:

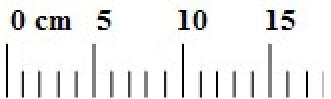
- a. <u>Personal errors</u>: These errors are the result of ignorance, carelessness, prejudices, or physical limitations on the experimenter. This type of error can be greatly reduced if you are familiar with the experiment you are doing. Be sure to thoroughly read over every lab before you come to class and be familiar with the equipment you are using. **Be Prepared!!!**
- b. <u>Instrumental Errors</u>: Instrumental errors are attributed to imperfections in the tools with which the analyst works. For example, volumetric equipment such as burets, pipets, and volumetric flasks frequently deliver or contain volumes slightly different from those indicated by their graduations. Calibration can eliminate this type of error.
- c. <u>Method Errors</u>: This type of error many times results when you do not consider how to control an experiment. For any experiment, ideally you should have only one manipulated (independent) variable. Many times this is very difficult to accomplish. The more variables you can control in an experiment the fewer method errors you will have.

Estimating and Reducing Errors through Proper Measurement Technique

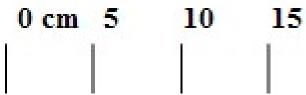
- Scientists make a lot of measurements. They measure the masses, lengths, times, speeds, temperatures, volumes, etc.
- When they report a number as a measurement the number of digits and the number of decimal places tell you how exact the measurement is
 - o For example: 121 is less exact than 121.5
 - o The difference between these two numbers is that a more precise tool was used to measure the 121.5.
 - o If a scientist reports a number as 121.5 they are saying that they were able to measure that quantity up to the tenths place.
 - o If a scientist reports a number as 121 they are saying that they were able to measure that quantity up to the ones place.
 - O The total number of digits and the number of decimal points tell you how precise a tool was used to make the measurement.
- Reporting measurements:
- a. There are 3 parts to a measurement:
 - 1. The measurement
 - 2. The uncertainty
 - 3. The unit
- b. Example: 5.2 ± 0.5 cm
 - 1. Which means you are reasonably sure the actual length is somewhere between 4.7 and 5.7
- c. No measurement should be written without all three parts.
- d. The last digit in your measurement should be an estimate
 - 1. If the smallest marks on your tool are .001 apart (as they are on a meter stick that has millimeters marked) then your last digit should be in the ten-thousandths place (i.e. 0.0010)*

*This is true for measurements that don't fluctuate. If the tool you use fluctuates then your estimated digit will probably not be smaller than the smallest hash mark on the tool but should indicate how sure you are of the exactness of your measurement. See below for how to deal with this situation.

2. Logic:

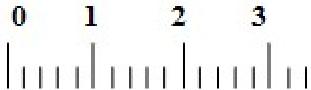


In the above, you would report the length of the bar as 31.0 ± 0.5 cm (assuming the big marks are centimeters). The bar appears to line up with the 31st mark and you know it's more than 1/2 way from the 30 mark and less than 1/2 way from the 32nd mark. So you can be reasonably sure the actual length of the bar is between 30.5 and 31.5 cm.



In the above, you would report the length of the bar as 31 ± 2 cm. You know the bar is longer than 30 cm and the last digit is your best guess. You are reasonably sure the actual bar length is between 30 and 33 cm.

- e. The uncertainty is 1/2 the amount between the smallest hash marks. Notice in the above 2 examples that this is the case.
 - 1. This rule may change depending on the book you look at or the teacher you work with.
 - 2. Some uncertainties are determined by the manufacturer. (e.g. electronic balances, probes)
 - 3. Some uncertainties are determined based on what you, as the experimenter decide:

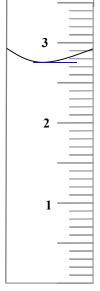


In this case, the divisions between the mark = 0.2 cm which makes estimating a digit trickier. If you say the measurement is right on the 6.2 mark than according to the above rules you should report the measurement as 6.20 cm. However, the uncertainty, according to the rules above is 1/2 the distance between the smallest two marks, or 0.2/2 = 0.1. It doesn't make sense to say 6.20 ± 0.1 cm because your uncertainty is so much bigger than the estimated digit (the zero). So, we need to go back to the most important idea of reporting uncertainties. We need to report a measurement that we are reasonably sure of. I am reasonably sure that the blue bar is bigger than 6.1 cm and less than 6.3, in which case you would report the measurement as 6.2 ± 0.1 cm, but you could also argue that the blue bar is bigger than 6.15 and less than 6.25 cm. In which case you would report 6.20 ± 0.05 cm. This is where you, as the experimenter, have to make the decision. Consider what another experimenter would get if he/she measured the blue bar again. Consider the implications of stating a too precise number.

f. from data provided by the manufacture (printed on the apparatus). Temperature probes for example state that the uncertainty is 0.2° C.

g. from the last significant figure in a measurement (as for a digital balance). Since our digital balances measure to .01 g, (or 0.001 g) we assume that the unseen digit is rounded either up or down, so the uncertainty is \pm 0.01 g (\pm 0.001 g)

- h. Measurements can sometimes be difficult to determine. The following are some important techniques.
 - 1. When measuring liquids that have a curve at the surface, measure from the bottom of the meniscus. The meniscus is the curve formed at the surface of a liquid due to attraction of the liquid for the sides of the container (adhesion). Measuring from the bottom \tilde{n} you should get 2.75 ± 0.05 mL (assuming #id marks represent milliliters).



- Meniscus 50
- 2. Sometimes the measurement on an electronic balance will fluctuate. Start with the numbers that are not fluctuating and then make your best guess as to what the next digit would be. Say for example you are weighing something on a balance and you get the following readings:
 - 1. 12.345
 - 2. 12.320
 - 3. 12.349
 - 4. 12.357
 - 5. 12.327

This should be reported as a measurement of 12.34 ± 0.05 . If you use a balance containing a shield the fluctuations will be greatly reduced.

Remember: when reporting measurements, you need to do 3 things

- 1. give the measurement (the magnitude)
- 2. tell how good a tool you used to measure it (this is given by the number of significant figures and uncertainty)
- 3. State the units

Dealing with Uncertainties

Now you know the kinds of errors, random and systematic, that can occur with physical measurements and you should also have a very good idea of how to estimate the magnitude of the random error that occurs when making measurements. Now we can deal with the question, "what do we do with the uncertainties when we add or subtract two measurements? Or divide/multiply two measurements?"

When you mathematically manipulate a measurement you must take into consider the precision. If you add two measurements the result CANNOT be more precise than your measures. It just doesn't make sense. Here's an example.

Let's say you make the following measurements for the mass of a copper weight in a small cylinder:

• Mass of empty container: 2.3 g

• Mass of container with copper: 22.54 g

What is the mass of the copper? 22.54 - 2.3 = 20.24 gAnswer to report: 20.2 g

Why 20.2 g and not 20.24g?

Since you only measured the container to the tenths place then the 3 is really an estimate. Perhaps the actual value was 2.2 or 2.4 g, then the mass of copper could be (22.54-2.3 or 22.54-2.4) 20.34 or 20.14 g. As you can see the difference in the tenths place is far more significant than the hundredths place. So the mass you should report is 20.2 g

Remember that when making measurements there are three parts to a measurement:

- The measurement
- The uncertainty
- The unit

To take into consideration precision

- 1. For single measurements
 - a. For the measurement $\tilde{\mathbf{n}}$ use significant figures
 - b. For the uncertainty ñ use error propagation
 - c. It doesn't make sense to talk about a unit's precision
- d. Once you have the determined the value and uncertainty, make sure the significant figures and uncertainty match.

Resource: Significant figures & Uncertainties

The uncertainty of a calculated value, and therefore the possible random error, can be estimated from uncertainties of individual measurements which are required for that particular calculation. In a calorimetry experiment, for example, the uncertainty in the amount of heat produced depends on the uncertainties in the mass, temperature and specific heat measurements. The estimation of an overall uncertainty from component parts is called Error Propagation.

- 2. For a set of the trials for which you are finding the average
 - a. Use the average and standard deviation for both the measurement and the uncertainty.

Another measure of uncertainty or precision arises when an experiment is repeated many times, yielding several results from which an average value can be calculated. The precision is a measure of how close the results are to the average value. The uncertainty (here called experimental uncertainty) is a measure of how far apart the results are from the average. This usually is calculated either as the average (and percent average) deviation or as the standard deviation compared to the average of the final results. The average value should always be the average of the final results calculated from each trial, rather than the average of the raw data or results of intermediate calculations. This uncertainty of an experiment is a measure of random error. If the uncertainty is low, then the random error is small.

**You should never take the average of beginning measurements (raw data) or intermediate data. Only final results should be averaged.

Example 1: Standardization of NaOH by titration

The following concentrations, in mol / dm³, were calculated from the results of three trials:

0.0945, 0.0953, 0.1050

The average value is 0.0983 and the standard deviation is 0.0048

Since uncertainties are meaningful only to one sig. fig., the results should be reported as follows:

Concentration = $0.098 \pm 0.005 \text{ mol / dm}^3$

Significant Figures and Rounding Answers:

Every physical measurement is subject to a degree of uncertainty that, at best, can be decreased only to an acceptable level. When numerical data are collected, the values cannot be determined exactly, regardless of the nature of the scale or instrument or the care taken by the operator. If the mass of an object is determined with a digital balance reading to 0.1 g, the actual value lies in a range above and below the reading. This range is the uncertainty of the measurement. Remember every time you take a measurement, the last digit recorded represents a guess. If the same object is measured on a balance reading to 0.001 g the uncertainty is reduced, but can never be completely eliminated.

The term precision is used to describe the reproducibility of results. It can be defined as the agreement between the numerical values of two or more measurements that have been made in an identical fashion. The terms precision and reliability are inversely related to uncertainty. Where uncertainty is relatively low, precision is relatively high. Every measurement you make in the lab should tell you the magnitude (size) of the object and the precision (reliability) of the instrument used to make the measurement. The number of subdivisions on the instrument can indicate the precision of the instrument.

Precision = Reliability = Significant Digits

Rules for Determining Degrees of Precision in a Measurement (sig. figs).

	Rule	Example: Significant figures are in bold	# of Significant Figures
1	All non-zero digits are significant	1234.5667	8
2	Zeroes after a decimal point AND after a non-zero digit are significant	12.0 0.0020	3 2
3	Zeroes between non-zero digits are significant	102	3
4	Zeroes at then end of numbers punctuated by a decimal point or line are significant.	120. 12Ō0 (1.20 x 10 ³) 1200	3 3 2
5	When adding and subtracting, your answer needs to have the same number of decimal places as the number with the fewest decimal places	12.0 + 5.23 =17.2 14.56 - 0.02 = 14.54 75 - 5.5 = 70.	1 dec. place 2 dec. place 0 dec. place, but zero is significant

6	When multiplying and dividing, your answer needs to have the same number of significant figures as the number with the fewest significant figures	$ \begin{array}{l} 12 \times 2 = 20 \\ 5.00 \times 7.0 = 35 \\ 2.00/6.0 = .33 \end{array} $	1 2 2
7	Exact numbers can be treated as if they have an infinite number of significant figures. (example, you know you have 5 quantities of something you are adding together)	$3.2 \times 2 = 6.4$	2
8	When doing more than one calculation, do not round numbers until the end.	13.2 x 2 / 5 = 5 (not 6)	

Error Propagation

In data collection, estimated uncertainties should be indicated for all measurements. These uncertainties may be estimated in different ways:

- 1. from the smallest division (as for a measuring cylinder)
- 2. from the last significant figure in a measurement (as for a digital balance)
- 3. from data provided by the manufacture (printed on the apparatus)

The amount of uncertainty attached to a reading is usually expressed in the same units as the reading. This is then called the Absolute uncertainty. eg. 25.4 ± 0.1 s. The symbol for absolute uncertainty is dx, where x is the measurement:

In the example: x = 25.4 and dx = 0.1

The absolute uncertainty is often converted to show a Percentage or Fractional uncertainty. For the above example, this would be: $25.4 \pm 0.4\%$ s (0.1 s / 25.4s x 100% = 0.4%). The symbol for fractional uncertainty is: dx/x

**Note that uncertainties are themselves approximate and are not given to more than one significant figure, so the percentage uncertainty here is 0.4%, not 0.39370%.

Multiple Readings

If more than one reading of a measurement is made, then the uncertainty increases with each reading.

Example 3:

For example: 10.0 cm^3 of acid is delivered from a 10cm^3 pipette ($\pm 0.1 \text{ cm}^3$), repeated 3 times. The total volumes delivered is

- $10.0 \pm 0.1 \text{ cm}^3$
- $10.0 \pm .0.1 \text{ cm}^3$
- $10.0 \pm 0.1 \text{ cm}^3$

Total volume delivered = 30.0 ± 0.3 cm³

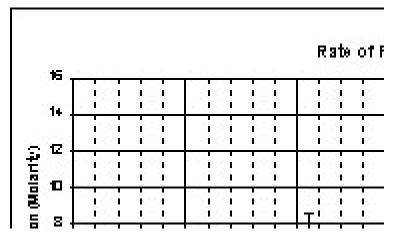
Example 4:

When using a burette (\pm 0.02 cm³), you subtract the initial volume from the final volume. The volume delivered is:

Final volume = 38.46 ± 0.05 cm³ Initial volume = 12.15 ± 0.05 cm³

Total volume delivered = 26.31 ± 0.04 cm³

	Rule	Example	
1	When adding or subtracting uncertain values, add the absolute uncertainties	Initial temp. = 34.50° C (± 0.05) Final Temp. = 45.21° C (± 0.05) Δ T = $45.21 - 34.5 = 10.71^{\circ}$ C (± 0.05 + 0.05 = ± 0.1°C) Δ T should be reported as $10.7 \pm 0.1^{\circ}$ C	
2	When multiplying or dividing add the percentage uncertainties	Mass = 9.24 g (± 0.005 g) Volume = 14.1cm3 (± 0.05 cm3)	
	a Make calculations	Density = 9.24/14.1 =0.655 g/cm3	
	b Convert absolute uncertainties to percentage/fractional/ relative uncertainties	Mass: 0.005/9.24x100 = 0.054% Vol: 0.05/14.1 x 100 = 0.35 %	
	c Add percentage uncertainties	0.054 + 0.35 = 0.40 % Density = $0.655 \text{ g/cm}^3 (\pm 0.40\%)$	
	d Convert total uncertainty back to absolute uncertainty	0.655 *0.4/100 = 0.00262 Density = 0.655 ± 0.003 g/cm3	
3	Multiplying or dividing by a pure (whole) number: multiply or divide the uncertainty by that number.	$4.95 \pm 0.05 \times 10 = 49.5 \pm 0.5$	
4	Powers: When raising to the nth power, multiply the % uncertainty by n When extracting the nth root, divide the % uncertainty by n.	$(4.3 \pm .5 \text{ cm})^3 = 4.33 \pm (.5/4.3)*3$ = 79.5 cm ³ (± 0.349%) = 79.5 ± 0.3 cm ³	
5	Formulas: Follow the order of operations: find uncertainties for numbers added and subtracted. Use that new uncertainty when calculating uncertainty for multiplication and division portion of formula, etc. This can be very complex. See example below.		
	Graphing Graphing is an excellent way to average a range of values. When a range of values is plotted each point should have error bars drawn on it. The size of the bar is calculated from the uncertainty due to random errors. Any line that is drawn should be within the error bars of each point. If it is not possible to draw a line of "best" fit within the error bars then the systematic errors are greater than the random errors.		



Example of Error Propagation with Formula

- 1. A student performs an experiment to determine the specific heat of a sample of metal. 212.01 g of the metal at 95.5°C was placed into 150.25 g of 25.2 °C water in the calorimeter. The temperature of the water went to 27.5°C. Given: $CH_2O = 4.18 \text{ J/g}$ -°C. The thermometer was marked in 1 oC increments and the balance was digital.
 - a. Calculate the specific heat of the metal Cm using the following equation:
 - b. Calculate the uncertainty in the
 - i. Temperature

(absolute uncertainty is \ddagger distance between smallest mark, for this thermometer which measures to the nearest fC, uncertainty is $0.5^{\circ}C$)

- 1. Tf = 27.5 ± 0.5 °C
- 2. Ti (H2O) = 25.2 ± 0.5 °C
- 3. Ti (metal) = 95.5 ± 0.5 oC
- 4. $\Delta T (H_2O) = (27.5-25.2) \pm (0.5+0.5) = 4.3 \pm 1 \, ^{\circ}C$ % = 1/4.3*100 = 23%
- 5. $\Delta T \text{ (metal)} = (95.5-27.5) \pm (0.5+0.5) = 68 \pm 1 \text{ °C}$ % =1/68*100 =1.5%
- ii. Mass

(absolute uncertainty for electronic balance half of smallest decimal place)

- 1. $H_2O = 150.25 \pm 0.05 g$
- %=.033%
- 2. $metal = 212.01 \pm 0.05 g$
- %=.024%
- iii. specific heat capacity
 - 1. assume there is no uncertainty in numbers used as constants. So no uncertainty in water's specific heat capacity.
 - 2. (metal) add % uncertainties for all quantities involved in the calculation of the heat capacity

$$0.033 + 23 + .024 + 1.5 = 24.6 \%$$

$$0.1002 \text{ J/g-}^{\circ}\text{C} (\pm 24.6\%) = .10 \pm .02 \text{ J/g-}^{\circ}\text{C}$$

- c. Calculate the percent error if the literature value is 0.165 J/g-°C.
- d. Comment on the error. Is the uncertainty greater or less than the percent error? Is the error random or systemic? Explain

Since percent error is much greater than the uncertainty and the literature value does not fall in the range of uncertainty ($.10 \pm 0.02 \, \text{J/g-}^{\circ}\text{C}$), than systematic errors are a problem. Random error is estimated by the uncertainty and since this is smaller than the percent error, systematic errors are at work and are making the measured data inaccurate.

Resource: <u>Statistical Calculations</u>

Resource Calculating standard deviation with a calculator (TI-83)