Experiment 1 - Mass, Volume and Graphing

In chemistry, as in many other sciences, a major part of the laboratory experience involves taking measurements and then calculating quantities from the results of those measurements. Every measurement involves some error, and it is important to understand the concepts of accuracy and precision, the types of error that can occur, and the meaning of the magnitudes of these errors.

The terms precision and accuracy are often thought to be the same, but in a scientific setting the distinction between the two terms is important. **Precision** refers to the *reproducibility* of the measurement. If several measurements of the same quantity are made, and if the results of those measurements are close to each other, then the data is said to be "precise". For example, if the mass of an object is measured repeatedly and if the results are 14.782 g, 14.785 g, and 14.781 g, the data is precise because the results are very close to each other. **Accuracy**, on the other hand, refers to results that are close to the true value - in other words, the *correctness* of the results. If the true value of the mass of an object is 46.819 g and the experimental results are 46.821 g, 46.818g, and 46.820 g, the results are accurate, because their average is close to the true value. Since these results are also close to each other, they are also precise. Note that it <u>is</u> possible for a set of data to be precise but not accurate, or accurate but not precise. The best situation, of course, is for data to be both accurate and precise. Sometimes the true value will not be known, so one can only speculate on the accuracy of the measurements. However, the precision can be determined by repeating the experiment and noting how close the results are to each other. One can also get a quantitative measure of the precision by calculating the *standard deviation* of the measurements, which will be explained shortly.

Types of Errors

A **personal error** or **blunder** in the measurement occurs when the experimenter makes a mistake in the procedure. Mistakes can include spilling some of the solution or solid, misreading the scale on the measuring instrument, accidentally switching numbers when recording data, and other such activities. If you work carefully, you should not make any blunders. If you suspect that you made a blunder, you should repeat the experiment.

A **systematic error** is often the result of a miscalibrated piece of equipment. For example, a miscalibrated ruler might have the markings of length at the correct spacing, but offset from the end of the ruler by an incorrect amount so that all measurements are off by the same amount in the same direction. If there is a systematic error, the results of repeated experiments might be close to each other (precise), but they will not be accurate (the average will not be close to the true value). Other types of systematic errors may be due to the method used in the experiment. Method errors like these are often due to nonideal chemical and physical properties of the system being studied. For example, there may be errors due to incomplete reactions, unstable reagents, or chemical contaminants in the system. Other method errors may be due to assumptions that we make for the calculations that may not necessarily be true under the experimental conditions used. For example, if we apply the ideal gas law under conditions in which the gas is not behaving ideally, this will introduce error in our result.

Even in the absence of personal errors and systematic errors, there is another type of unavoidable error – *indeterminate* or *random* errors. **Random errors** are unknown and uncontrollable by the experimenter. Random errors cause the data to be off in either direction. In the presence of random errors, we can get a better estimate of the true value of a measurement or quantity by repeating the measurements several times. We can then calculate the average value and the standard deviation of the measurements. The standard deviation gives an indication of the spread or dispersion of the data.

The *mean value* or *average* ($\overline{x}$) is obtained by adding all of the individual measurements (x_i) and dividing by the total number of measurements (n):

$$\overline{x} = \frac{\sum x_i}{n}$$

A measure of the spread of individual values from the mean value is the deviation, δ. The deviation is defined as the difference between the measured value, x_i, and the average value, $\overline{x}$, of a number, n, of measurements.

$$\delta_i = x_i - \overline{x}$$

The smaller the deviations in a series of measurements, the more precise the measurement is.

Another measure of the spread or dispersion in the data is expressed by the *standard deviation, s*:

$$s = \sqrt{\frac{\sum (x_i - \overline{x})^2}{n-1}}$$

To apply this formula, first calculate the average or mean of the data ($\overline{x}$). Then, determine the deviation (δ) of each of the data points from the average. Square each of these deviations, and add up all of the squares. Divide the result by n-1, where n is the number of measurements. Then take the square root of the result to get the standard deviation. The above formula is actually just an estimate of the standard deviation and is used when a small number of data points (usually less than 20) are known.

The standard deviation is used to express the *confidence interval* of the data. There is a 68% probability of the true value being plus or minus one standard deviation from the mean. There is a 95% probability that the true value will be within two standard deviations from the mean.

The following example demonstrates the calculation of the standard deviation and its significance.

Example:
An object is weighed repeatedly. The measured values for the mass measurement are 3.55 g, 3.52 g, 3.50 g, 3.61 g, and 3.56 g.

The average (mean) of these values is calculated as follows:

$$\overline{x} = \frac{3.55 + 3.52 + 3.50 + 3.61 + 3.56}{5} = \frac{17.74}{5} = 3.548$$

The deviations and squares of deviations are summarized in the following chart:

Measured value (x_i)	Deviation ($x_i - \bar{x}$)	Square of deviation $(x_i - \bar{x})^2$
3.55 g	0.002 g	0.000004 g^2
3.52 g	- 0.028 g	0.000784 g^2
3.50 g	- 0.048 g	0.002304 g^2
3.61 g	0.062 g	0.003844 g^2
3.56 g	0.012 g	0.000144 g^2
Σ = 17.74 g	Σ = 0.000	Σ = 0.00708 g^2

The standard deviation is calculated to be:

$$s = \sqrt{\frac{0.00708\ \text{g}^2}{(5-1)}} = 0.042\ \text{g}$$

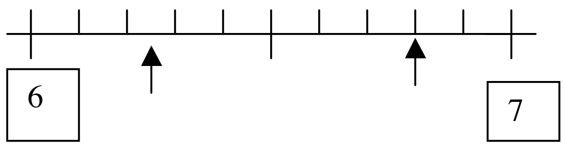
Since each of the data points was measured to two decimal places, the standard deviation should also be shown to two decimal places. Therefore, the standard deviation should be expressed as 0.04 g. The overall result of the measurement should be expressed as 3.55 ± 0.04 g. The confidence intervals can be expressed as follows: We are 68% confident that the true value of the measurement is within one standard deviation of the mean, so we are 68% confident that the true value is between 3.51 and 3.59 g. We are 95% confident that the true value is within two standard deviations of the mean. In this case, we are 95% confident that the true value is between 3.47 and 3.63 g.

Precision of Laboratory Equipment

The magnitude of the error in a measurement depends partly on the measuring device used. For example, some balances measure mass to the nearest centigram (±0.01 g), while other balances measure mass to the nearest milligram (±0.001 g) or even to the nearest tenth milligram (±0.0001 g). Therefore, the result of a mass measurement would depend on which balance was used to make the measurement. Typical uncertainties for different types of equipment are given in Table 1 below.

In an experiment, when you make a measurement, you must indicate the uncertainty in the measurement either explicitly by stating or writing it, for example "±0.01 g") or it can be stated indirectly by writing down the correct number of significant figures. Significant figures include all certain digits of a measurement and one digit that is uncertain. For example, if you measured the length of an object using a ruler that had divisions every 0.1 cm, you could measure length to the nearest 0.01 or 0.02 cm by interpolating between the lines. The following diagram shows a close-up view of a section of a ruler. If the object is lined up with the end of the ruler and if it comes to the position of the first arrow, one can see that the length is definitely between 6 and 7 cm. One can also see that the length is definitely between 6.2 and 6.3 cm. The first two digits are thus certain digits. Further, one can see that the length is mid-way between 6.2 and 6.3 cm. If you estimate between the lines, you can come up with a length of 6.24 or 6.25 cm. Determining the last digit involves making an estimate, and thus the last digit is uncertain. However, including this last digit gives you more information than not including it. In general, measurements that are given are assumed to have an error of plus or minus one in the last digit, unless the error is specifically stated by the experimenter.

If the object comes to the position of the second arrow, it appears to be right on the 6.8 cm line. In a case like this, if you are interpolating to the nearest ± 0.01 cm and the measurement is right on the line, you must state the length as 6.80 cm instead of just 6.8 cm. The extra zero at the end indicates that the measurement has an uncertainty of ± 0.01 cm rather than just ± 0.1 cm.



The precision of various pieces of laboratory equipment is given below. These uncertainties are limitations that are inherent in the equipment. They do not reflect any systematic errors.

Table 1
Typical Uncertainties in Laboratory Equipment

Instrument	Typical Uncertainty
Platform balance	± 0.5 g
Triple-beam (centigram) balance	± 0.01 g
Digital centigram balance	± 0.01 g
Top-loading semimicro balance	± 0.001 g
Analytical balance	± 0.0001 g
100-mL graduated cylinder	± 0.2 mL
10-mL graduated cylinder	± 0.1 mL
50-mL buret	± 0.02 mL
25-mL pipet	± 0.02 mL
10-mL pipet	± 0.01 mL
Thermometer (10°C to 110°C, graduated to 1°C)	± 0.2°C
Mercury barometer	± 0.5 torr

Significant Figures and Propagation of Error in Calculations

Significant figures in a measurement include all certain digits and one uncertain digit. When you record a measurement in your laboratory notebook, make sure to include the estimated digit. If you do not record your data in this way, make sure to indicate the uncertainty by writing it next to the measurement, for example "25.7 ± 0.2 mL".

When you perform calculations using numbers that were obtained by measurement, the result of the calculation also has some uncertainty. The uncertainty of the measurements limits the precision of the resulting calculation. A simplified system of determining the precision of the results is given in the rules for significant figures. Briefly, the rules are as follows:

For **multiplication and division**, count the number of significant figures in each of the measurements used in the calculation. The number of significant figures in the result should be the same as that in the measurement with the smallest number of significant figures. For example, multiplying 1.40 by 5.667 gives 7.9338. The first measurement (1.40) has three significant figures, and the second one (5.667) has four. The result should be rounded to three significant figures, and should be written as 7.93.

For **addition and subtraction**, count the number of decimal places in each of the measurements. The number of significant figures in the result should be the same as that in the measurement with the fewest numbers behind the decimal point. For example, subtracting 4.601 from13.88 gives 9.279. The first measurement has three decimal places (an uncertainty of ± 0.001) and the second one has two (an uncertainty of ± 0.01). The second measurement has fewer decimal places (and a larger uncertainty), so the result should also have two decimal places. The result should be rounded to 9.28.

See the appendix of this laboratory manual and your textbook for more information on significant figures.

Graphing

(Note: please refer to the appendix of this laboratory manual for more details regarding graphing.)

A graph is a pictorial representation that shows the relationship between two variables. Graphs are used quite often in the sciences, and in many laboratory experiments, you will need to draw graphs and extract information from them.

In order to be useful, a graph must include a descriptive title, axes that are clearly labeled with the quantity, numbers, and units, a well-chosen scale, plotted points that are visible, and a line or smooth curve drawn among the points that shows the relationship between the variables under study. A brief description will be given of each of these aspects of a graph. An example of a graph will be shown at the end of this section.

The **title** of a graph must be a clear and concise description of what is being studied. Examples of good titles are: "Absorbance at 447 nm vs. concentration of $FeSCN^{2+}$" and "Volume vs. Temperature for a Trapped Sample of Air". Examples of unhelpful titles are "Experiment 2" and "Volume vs. Temperature".

There are several considerations for the **axes**. The first quantity given in the title of the graph should be along the y axis and the second quantity goes along the x axis. If the instructions are to make a graph of absorbance vs. concentration, then the absorbance is on the vertical axis (the y axis) and the concentration is on the horizontal (x) axis. The axes must be clearly labeled with the quantity (such as volume, temperature, absorbance, concentration, or length), numbers, and units (such as mL, °C, M, cm, etc.). Numbers written along the axes should be spaced so that they are easy to read.

The **scale** should be set up so that all of the plotted points will fit on the graph. In order to obtain the most accurate information from the graph, the region of plotted points should take up most of the page. For this reason, many graphs should not start at (0,0), otherwise the region of plotted points will take up a very small area of the graph and it will be very difficult to estimate between the lines with precision. To facilitate estimation between the lines on the graph, each square on the graph should represent 2,5, or 10 units of the variable.

The **data points** should be plotted once the axes and scale are set up. They should be clearly visible. You may wish to draw a small circle around each data point to make it more visible.

Once the data points are plotted, a **line** or **smooth curve** should be drawn. If the data points appear to lie on a straight line, use a ruler to draw one unbroken straight line among the points that best represents the trend. The data points might not lie exactly on this line. (*Do not* draw a zigzag line connecting the dots). If the data points appear to lie on a curve, draw a smooth curve among the data points.

If the graph is linear, you may want to calculate its slope and y-intercept in order to determine the equation of the line. Recall that the equation of a straight line is in the form $y = mx + b$, where m represents the slope of the line and b is the y-intercept (the y-intercept is the value of y when x = 0). After you have drawn the best straight line among the data points, choose two points on the straight line that are far apart from each other, and estimate the coordinates of these points. (The points do not have to be data points, but they must be on the line.) If the coordinates of the points are expressed as (x_1, y_1) and (x_2, y_2), the slope of the line may be calculated as:

$$m = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

Once you have calculated the slope, use the equation of the straight line $y = mx + b$ and the coordinates of one of the points on the line, and calculate the value of b.

On the next page is an example of a well-drawn graph. Note the following characteristics:

- It has a descriptive title.
- The axes are labeled with quantities, numbers, and units.
- The scales are chosen so that the data points are spread out on the page. The graph does not start at (0,0).
- Each square along the vertical axis represents 1 g. Each square along the horizontal axis represents 1 mL. This will make it easy to estimate between the lines when reading the graph. (Other examples of good choices for intervals: 1, 2, 5, 10, 20, 50, 100, 200, 500, 0.1, 0.2 0.5, 0.01, 0.02, 0.05, etc.)
- The data points are visible.
- The best straight line is drawn among the data points.

The slope of the line is calculated as follows. First, two points are chosen that are on the line and far apart from each other. (These points are shown as circles on the following graph.) The coordinates of the first point are estimated to be (1.0 mL, 62.9 g) and the second point's coordinates are estimated as (23.0 mL, 77.0 g). Note that an extra zero is added when the point appears to be right on the line.

The slope is calculated as:

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{77.0 \text{ g} - 62.9 \text{ g}}{23.0 \text{ mL} - 1.0 \text{ mL}} = \frac{14.1 \text{ g}}{22.0 \text{ mL}} = 0.641 \text{ g/mL}$$

Using the value of m calculated above, the coordinates of the first point (1.0 mL, 62.9 g) and the equation of a straight line ($y = mx + b$), the y-intercept b is calculated as follows:

$$6.29 \text{ g} = (0.641 \text{ g/mL})(1.0 \text{ mL}) + b$$
$$62.9 \text{ g} = 0.641 \text{ g} + b$$
$$62.3 \text{ g} = b$$

The equation of the line is thus: $y = (0.641 \text{ g/mL})x + 62.3 \text{ g}$

Safety Precautions:

- All of the materials for this experiment are harmless.

Waste Disposal:

- There is no waste for this experiment.

Procedure

Part 1: Mass Measurement

Pennies minted in the United States in 1981 and earlier are significantly different from pennies dated 1983 and later. We would like to determine if it is possible to tell the difference between these two kinds of pennies by weighing them.

Work in pairs for this part of the experiment. One of you will find four pennies dated 1981 and earlier, and the other partner will find four pennies from 1983 or later. Weigh each of your four pennies on the analytical (digital) balance to at least ± 0.001 g. Record the mass and date of each of the pennies, and then write down your partner's data.

Calculate the average value and the standard deviation for each of the sets of pennies (pre-1981 and post-1983). *Does there appear to be a significant difference in the average mass of the two groups of pennies? If so, what is a likely explanation for this difference?*

Part 2: Volume Measurement

Using a ruler, measure the length, width, and height of a soy milk container to the nearest ± 0.1 cm. Record the values. Calculate the volume of the container in cm^3. Convert this volume to liters and to quarts. Compare to the volume printed on the container.

In the hood, there will be two partially filled graduated cylinders. Reading the bottom of the curved surface of the liquid (the meniscus) at eye level, determine the volume of liquid in the small and the large graduated cylinders. Read the volume of the smaller cylinder to the nearest ± 0.01 mL, and the larger one to the nearest ± 0.1 mL. Record your readings, and report the two values to the instructor. If they are not correct, the instructor will show you how to read the meniscus correctly.

Part 3: Graphing

Collect four beakers of different sizes and a piece of string. Use the piece of string to measure the circumference of each of these beakers. To do this, hold the string snugly around each beaker and mark the overlapped ends of the string with a pen. Measure the distance between the marks on the string with a ruler to determine the circumference. Record this value. Measure the diameter of each beaker by placing the edges of two books or blocks of wood against the beaker on opposite sides. Then carefully remove the beaker and measure the distance across the gap with a ruler. Record each diameter.

Make a table of the diameters and circumferences of the beakers. Draw a graph of circumference vs. diameter of the beakers. (Circumference is the vertical (y) axis, and diameter is the horizontal (x) axis.) Draw a line through the plotted points. Pick two points on the line (located near the ends of the line) and determine the slope of the line, where

$$slope = \frac{\Delta y \text{ (circumference)}}{\Delta x \text{ (diameter)}}$$

Is the numerical value of the slope, the ratio of the circumference to the diameter of a circle, what you expected it to be? (Reminder: the circumference of a circle = $2\pi r$, where r is the radius of the circle.)

Questions:

(Always show your work and/or explain your reasoning.)

1. To demonstrate that the rules for significant figure propagation do give an estimate of the uncertainty in the answer, consider a block with rectangular sides whose dimensions have been measured with a millimeter ruler.
   height: 254.7 mm width: 136.8 mm depth: 25.3 mm

   a. Determine the volume of the block in cubic millimeters.
   b. Determine the volume of the block if you assume that each of the above measurements should actually be 0.1 mm higher than listed.
   c. With which digit do the answers to parts a and b begin to differ? If you report the volume using all of the digits that are the same in parts a and b plus one more digit where the two values do not agree, how many digits should you report?

d. How many digits would you report according to the rules for significant figures? Is this the same as in part c?

2. The density of water is very close to 1.00 g/mL at room temperature. If you determined the density of a 25-mL sample using a centigram balance and a graduated cylinder, you could determine the density to three significant figures. This is because the mass would be known to 4 significant figures (the mass would be about 25 g and it would be known to ± 0.01 g, for example 25.00 g) and the volume would be known to 3 significant figures (the volume would be about 25 mL and it would be known to ± 0.1 mL, for example 25.0 mL) Dividing mass by volume would give a result with three significant figures in this case. Table 1 shows the typical uncertainties for some common measuring instruments in the laboratory. How many significant figures should you report for the density if you used:

a. an analytical balance for measuring mass and a 25-mL pipet for the volume measurement?

b. a centigram balance and a pipet?

c. an analytical balance and a graduated cylinder?

3. Calculate the mean and the standard deviation of the following set of data: 4.578 g, 4.581 g, 4.572 g, 4.573 g, 4.601 g, 4.577 g. State the 68% and 95% confidence intervals for this data.