Skills to Develop

• To introduce the fundamental mathematical skills you will need to complete basic chemistry questions and problems

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

<table>
<thead>
<tr>
<th>Balance 1</th>
<th>Balance 2</th>
<th>Balance 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.896 g</td>
<td>1.125 g</td>
<td>1.893 g</td>
</tr>
<tr>
<td>1.895 g</td>
<td>1.158 g</td>
<td>1.895 g</td>
</tr>
<tr>
<td>1.894 g</td>
<td>1.067 g</td>
<td>1.895 g</td>
</tr>
</tbody>
</table>

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the average deviation of the measurements as follows:

1. Calculate the average value of all the measurements:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \quad \text{(Eq. 1)}$$

2. Calculate the deviation of each measurement, which is the absolute value of the difference between each measurement and the average value:

$$\text{deviation} = |\text{measurement} - \text{average}| \quad \text{(Eq. 2)}$$

where $|$ means absolute value (i.e., convert any negative number to a positive number).

3. Add all the deviations and divide by the number of measurements to obtain the average deviation:

$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}} \quad \text{(Eq. 3)}$$

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is

$$\left(\frac{1.125 \; g + 1.158 \; g + 1.067 \; g}{3}\right) = 1.117 \; g$$

The deviations are

• $|1.125 \; g - 1.117 \; g| = 0.008 \; g$
• $|1.158 \; g - 1.117 \; g| = 0.041 \; g$, and
• \(|1.067 \; g − 1.117 \; g| = 0.050 \; g\).

So the average deviation is

\[
\frac{0.008 \; g + 0.041 \; g + 0.050 \; g}{3} = 0.033 \; g
\]

The precision of this set of measurements is therefore

\[
\frac{0.033 \; g}{1.117 \; g} \times 100 = 3.0 \%
\]

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

Example \(\PageIndex{1}\)

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

a. a precise but inaccurate set of measurements?

b. an accurate but imprecise set of measurements?

c. a set of measurements that is both precise and accurate?

d. a set of measurements that is neither precise nor accurate?

Example \(\PageIndex{2}\)

a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler’s measurements accurate? Were they precise?

b. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

**SOLUTION**

a. The expected mass of a 2-carat diamond is \(2 \times 200.0 \; mg = 400.0 \; mg\). The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.

The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

\[
\frac{4.9 \; mg}{457.3 \; mg} \times 100 = 1.1 \%
\]

These measurements are rather precise.
b. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of \(-4.5\%\) and \(+17\%\) for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that either there is a significant error in one or both measurements or some other element is present.)

The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which gives an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

\[
\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\% \\
\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\%
\]

**Significant Figures**

No measurement is free from error. Error is introduced by the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and the imperfection of human senses (i.e., detection). Although errors in calculations can be enormous, they do not contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be \(\pm 1\), unless otherwise stated.

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)
5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000...). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

\[
1 \text{ ft} = 12 \text{ in}
\]
An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as \(8.00 \times 10^{-2}\), it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., \(N\)) determines the number of significant figures.

Example \(\PageIndex{3}\)

Give the number of significant figures in each. Identify the rule for each.

a. 5.87  
   b. 0.031  
   c. 52.90  
   d. 00.2001  
   e. 500  
   f. 6 atoms

**SOLUTION**

a. three (rule 1)  
   b. two (rule 3); in scientific notation, this number is represented as \(3.1 \times 10^{-2}\), showing that it has two significant figures.  
   c. four (rule 3)  
   d. four (rule 2); this number is \(2.001 \times 10^{-1}\) in scientific notation, showing that it has four significant figures.  
   e. one, two, or three (rule 4)  
   f. infinite (rule 5)

Example \(\PageIndex{4}\)

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?
Solution

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer. Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

\[
\begin{align*}
3240.7 + 21.2 &= 3261.9 \\
3261.9 &= 3261.9
\end{align*}
\]

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??). Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus, \(42.9 \times 8.323 = 357.057 = 357\). Although the second number in the calculation has four significant figures,
we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in $12.793 \times 12$. In this case, the number of significant figures in the answer is determined by the number 12.973, because we are in essence adding 12.973 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.66666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

Example \(\PageIndex{5}\)

Complete the calculations and report your answers using the correct number of significant figures.

a. $87.25 \text{ mL} + 3.0201 \text{ mL}$

b. $26.843 \text{ g} + 12.23 \text{ g}$

c. $6 \times 12.011$

d. $2(1.008) \text{ g} + 15.99 \text{ g}$

e. $137.3 + 2(35.45)$

f. $\left(\frac{118.7}{2}\right) \text{ g} - 35.5 \text{ g}$

g. $\left(47.23 \text{ g} - \left(\frac{207.2}{5.92}\right) \text{ g}\right)$

h. $\left(\frac{77.604}{6.467}\right) - 4.8$

i. $\left(\frac{24.86}{2.0}\right) - 3.26 (0.98)$

j. $\left((15.9994 \times 9) + 2.0158\right)$

Solution

a. $90.27 \text{ mL}$

b. $39.07 \text{ g}$

c. $72.066$ (See rule 5 under “Significant Figures.”)

d. $2(1.008) \text{ g} + 15.99 \text{ g} = 2.016 \text{ g} + 15.99 \text{ g} = 18.01 \text{ g}$

e. $137.3 + 2(35.45) = 137.3 + 70.90 = 208.2$

f. $59.35 \text{ g} - 35.5 \text{ g} = 23.9 \text{ g}$

g. $47.23 \text{ g} - 35.0 \text{ g} = 12.2 \text{ g}$

h. $12.00 - 4.8 = 7.2$

i. $12 - 3.2 = 9$

j. $143.9946 + 2.0158 = 146.0104$
In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.