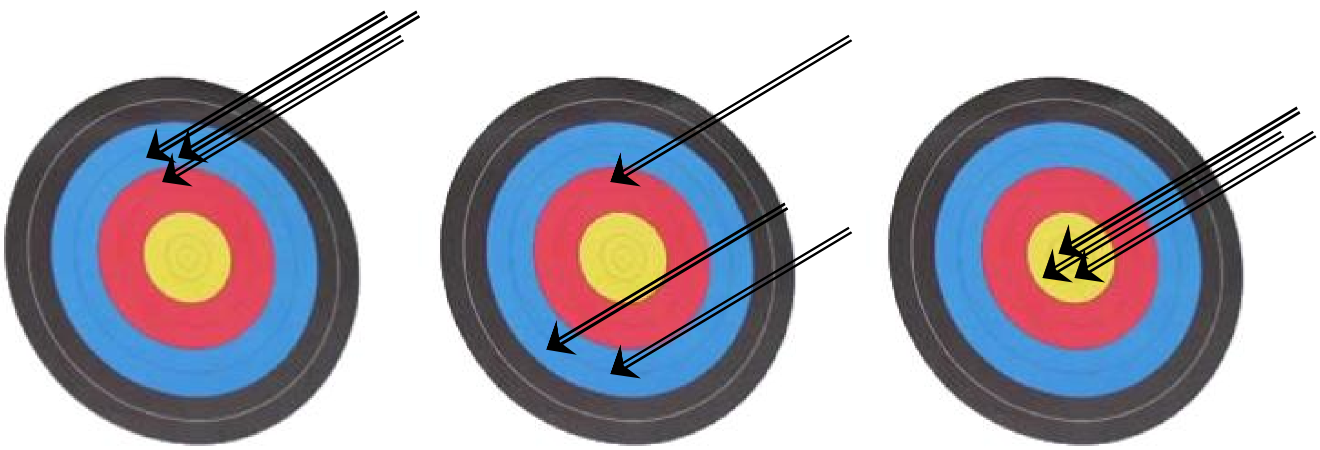
CHAPTER TWO:

MEASUREMENT

2.1 ACCURACY AND PRECISION

In order for valid conclusions to be drawn from quantitative measurements in science, it is essential that those measurements be both repeatable and reliable. The reliability of a measurement refers to how close a value is to the true or accepted value and is called accuracy. Careful selection and calibration of laboratory equipment can go a long way toward ensuring accurate measurements. The repeatability of a measurement is called precision, and is usually talked about in two ways – how close a series of measurements are to one another, and the "fineness" of a particular measurement, which will be discussed momentarily.

The figure below showing the archery targets is a good way to visualize the difference between accuracy and precision. In the first scenario, the arrows all strike the target near one another, but they are all far from the bull's-eye. This would represent an experiment whose data are precise but not accurate since the result is repeatable but not reliable. In the second scenario, none of the arrows hit the center, meaning the results were neither accurate nor precise. On the final target, the results are both accurate and precise as all arrows strike near the bull's-eye.



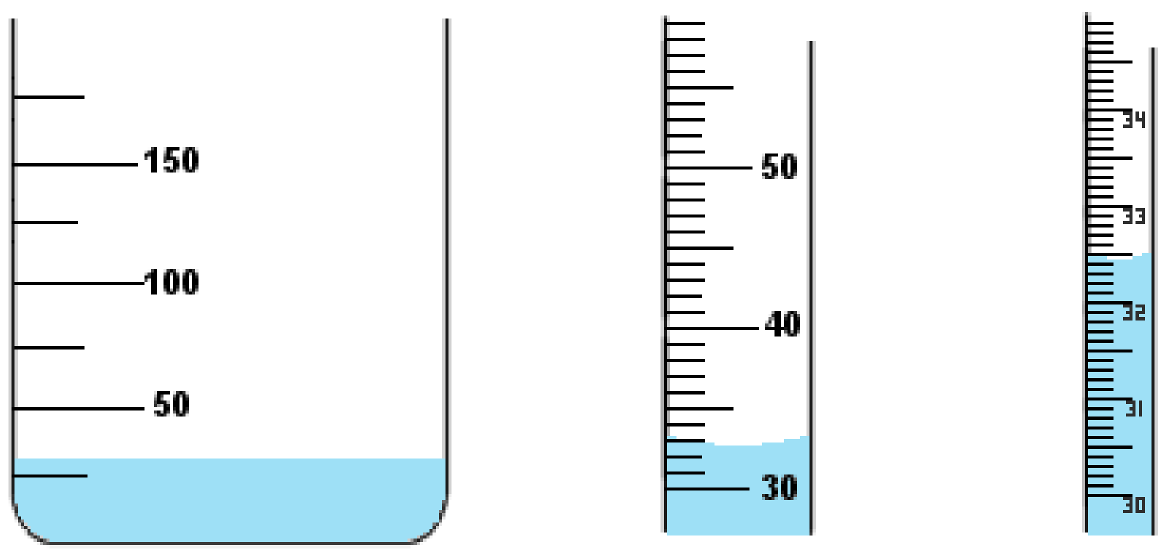
Whenever possible, you should always perform an experiment multiple times. This will eliminate much of the human error involved and produce much more accurate results. In addition, when an experiment is performed repeatedly with the same result, we have confidence that the measurement is accurate. In general, it is assumed that if the measuring instrument is in working order and is properly calibrated, precision is a good indicator of accuracy.

Suppose we set up an experiment in which three students measure the temperature of boiling water using different thermometers. Each student takes a measurement, waits one minute, takes another measurement, and so on until each thermometer has recorded four temperature values. The results shown in Table 2.1:

TABLE 2.1	Student One	Student Two	Student Three
Trial One	99.4ºC	97.3ºC	100.1ºC
Trial Two	102.3ºC	97.4ºC	100.0ºC
Trial Three	101.7ºC	97.4ºC	99.9ºC
Trial Four	101.3ºC	97.3ºC	100.0ºC

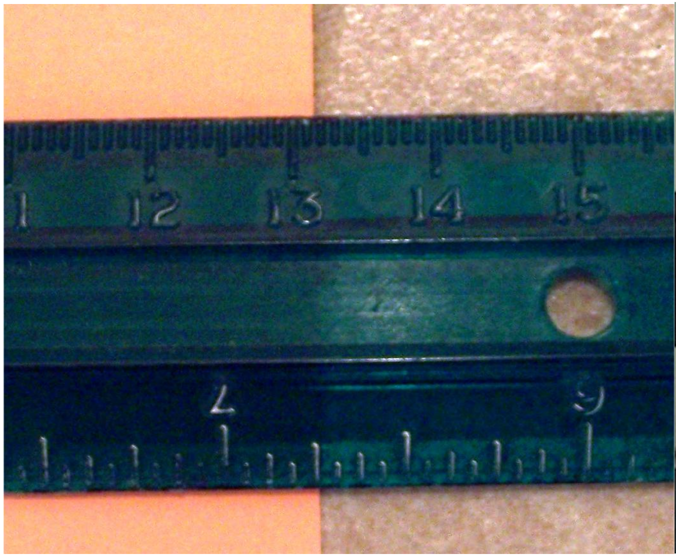
From this information we can determine which experimental data is best – both repeatable and reliable. The true boiling point of water is 100.0ºC, so accurate data would give values at or very near that number. Precise measurements are repeatable, as indicated by the results from students Two and Three. So let us analyze the data shown here: The first student's data is neither accurate nor precise. This could be due to errors made by the experimenter, or perhaps the thermometer is faulty in some way. The second student's data is precise, but is not accurate. This is likely due to an incorrectly calibrated thermometer that gives consistently low temperature readings. The third student recorded temperatures close to the true value (accurate) and reported similar temperatures repeatedly (precise).

As mentioned earlier, the second use of the term precision refers to the "fineness" of a measurement. To illustrate this concept, consider a beaker, a graduated cylinder, and a buret each filled with the same quantity of water:



As we look at the markings on the beaker, we see that the smallest increments are 25 mL. When reading a measurement, we can always make a "guess" as to the very last digit in the number. We can estimate one decimal place smaller than the smallest increment on the instrument. In this case, the smallest increment is 25, so the best approximation we can make is to the tens place. Perhaps a good approximation for this volume would be 30 mL. It is impossible to know the volume in the beaker more *precisely* than this. For this reason, beakers are rarely used for measuring volume. In the graduated cylinder, the smallest increment between markings is one milliliter, so we can approximate one decimal place smaller than one, the one-tenths place. As a general rule, if the markings are too close together to approximate ten smaller markings, then estimate by halves. Since the meniscus of the water in the cylinder rests between 32 and 33 mL, then we could report this volume as 32.5 mL. Different graduated cylinders have different increments, but these are the best tool we have for making fairly precise measurements quickily. In the buret to the left, the smallest marking is 0.1 mL, so we can estimate the one-hundredths place. Again the markings are too close together to divide each increment by ten, so we will do half. The meniscus lies between 32.4 and 32.5 mL, so the volume is 32.45 mL. Burets and volumetric pipets are used when it is important to know the volume as precisely as possible.

Keep in mind that the estimation of the last digit is an acceptable practice for every piece of laboratory equipment, including beam-balances and rulers. See if you can correctly read the measurements in the photos below:



2.2 SIGNIFICANT FIGURES

Since the instrument itself determines the degree of precision, it follows that all measurements are understood to contain a certain amount of error, either human or instrumental. It is impossible to measure exactly five and one-half grams of table salt, for example. We may be able to measure 5.5 grams, 5.50 grams, or even 5.500 grams, but none of these measurements represents *exactly* five grams. The first is accurate to only the tenths place – somewhere between 5.4 and 5.6 grams. The last is much more precise – between 5.499 and 5.501 grams – but it is still not exact. The final reported digit of any measurement is *uncertain*. It is an approximation, just like in the previous section where we estimated between graduations on an instrument. A measurement contains two kinds of *significant figures*, those that are known and one final approximated digit. The more significant figures a number has, the more precise the measurement is.

Determining the Number of Significant Figures:

This is actually a fairly simple process, as long as the rules for significant figures are understood. These rules are:

1) All nonzero digits are considered significant
   ex: The measurement 546 grams has three sig-figs
2) Zeros between significant figures are considered significant
   ex: The measurement 3.502 seconds has four sig-figs
3) Trailing zeros after a decimal are considered significant
   ex: The measurement 22.50 pounds has four sig-figs
4) Zeros that serve as placeholders are not significant
   ex: The measurements 100 mL and 0.05 ft each have only one sig-fig

There are some numbers, however, that are exact, having an infinite number of significant figures. These numbers are counting numbers (exactly 12 eggs in one dozen), defined constants (exactly 2.54 centimeters in one inch), and metric definitions (one kilometer is exactly 1000 meters).

Calculations Involving Measurements:

Significant figures indicate the degree of precision in any measurement, and when those measurements are used in calculations, the precision remains with it. This means a set of data can only be as precise as its least precise value. Let's take a simple calculation as an example: density. Density is defined as the amount of mass an object has divided by its volume. Suppose we have a 5.50 gram wooden block with a volume of 7.3 cubic centimeters. If we divide the mass by the volume, we get the value 0.753424658 g/cm^3. How can the density be known to a greater precision than either the mass or the volume? Quite simply, it can't. The mass is known to three significant figures, and the volume to two significant figures. Therefore the density can only be known to the same degree as the least precise measurement used to calculate it, two. The density of the block is 0.75 g/cm^3.

While accounting for the propagation of uncertainties is sometimes a complicated task, the following rules for significant figures generally suffice:

- When multiplying or dividing measurements, the result must be given with the same number of significant figures as the measurement with the fewest significant figures.
- When adding or subtracting measurements, the result will have the same number of decimal places as the measurement with the fewest decimal places.

Table 2. 2

From	To	Distance
McKinney	Allen	8.32 miles
Plano	Dallas	19 miles
Melissa	McKinney	7.3 miles
Allen	Plano	7.31 miles

To illustrate the second rule, suppose four students were sent out to measure distances between cities. There results are in the table to the left. If we wanted to know the distance from Melissa to Allen we would simply need to add the distance from Melissa to McKinney and the distance from McKinney to Allen. The sum of 7.3 miles and 8.32 miles is 15.62 miles, but since the least precise measurement is known only to the nearest tenth of a mile, we can only report the distance as 15.6 miles. Also, the distance from Melissa to Dallas could be obtained by adding all four measurements together, getting a total of 41.93 miles. The correct sum, however, would be 42 miles since the distance from Plano to Dallas is only known to the nearest mile. It is important to remember that rounding to the correct number of significant figures should only be done after every calculation has been performed to reduce the error introduced by excessive rounding.

2.3 LE SYSTÈME INTERNATIONAL

In any quantitative measurement, the number is only part of the value. All measurements have both a quantity and a unit, each as important as the other. If you ask someone how much pizza they ate last night and they respond "6," what does that mean? Six pizzas? Slices? Pounds? Kilograms? Ounces? Cups? Dozen? The numerical value is essentially useless without knowing the unit that is associated with it. And just as important is to know the general scale of each unit. Is six ounces of pizza a reasonable amount? Which is larger – six pounds of pizza or six kilograms of pizza?

The problem lies in the fact that there are dozens of systems of measurement used around the world, and the basis for those measurements have changed throughout history. In ancient India, length was measured with units such as the dhanus, krosa, and jojana. The ancient Mesopotamian system was based on the cubit, the distance from the elbow to the middle finger. Unfortunately this was different for every person. The Greeks and Romans inherited the foot from the Egyptians. The pace, equivalent to five Roman feet, was used to determine the mile (1000 paces). Queen Elizabeth the First of England changed the mile to 5280 feet in order to be equivalent to 8 furlongs, each furlong being 40 rods of 5.5 yards each. The meter was once defined as one ten-millionth the distance from the North Pole to the equator along a meridian. Mass was originally measured by comparing the weight of an object to the weight of a grain of wheat. Later masses were compared to standard stones with units such as the mina, sheckel, talent, and eventually the pound. And don't forget the ounce, carat, long ton, short ton, hundredweight, gram, and countless others.

When scientific discovery really began to take off and become an endeavor that had little to do with geopolitical borders, it became obvious that a standardized system of measurement was essential. In 1875 seventeen nations signed the *Convention du Mètre* and established the General Conference on Weights and Measures (CGPM) and the International Committee for Weights and Measures (CIPM) to establish and oversee measurement standards around the world. The United States governmental body the National Institute of Standards and Technology (NIST) has a permanent seat on the CIPM which continuously updates standards of measurement.

In 1960, the 11th General Conference laid down the standards for a new system of units that would become the Système International d'Unitès, commonly referred to as SI. The SI established six base units (the seventh was added in 1971) from which all other measurements could be derived, as well as prefixes and rules for writing abbreviations. These units pertinent to chemistry are listed in Table 2.3, as well as the standard on which they are based. All seven base units are based on a universal physical constant except the kilogram, which is also the only base unit with a prefix.

Table 2. 3

Unit	Abbrev.	Quantity	Standard
Meter	m	Length (l)	The distance traveled by light in the time interval of 1/299792458 of a second
Second	s	Time (t)	The duration of 9192631770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of the Cs-133 atom
Kilogram	kg	Mass (*m*)	The mass of the international prototype stored in a vault in Sèvres, France. The cylinder is a platinum/iridium alloy stored beneath three bell jars to limit exposure to the atmosphere.
Kelvin	K	Temperature (T)	The fraction 1/273.16 the temperature at the triple point of water. To convert degrees Celsius to Kelvin, simply add 273.15. Zero Kelvin is Absolute Zero
Mole	mol	Amount	The amount of substance in which there are as many elementary entities (atoms, molecules, ions, particles, etc) as there are in exactly 12 grams of carbon-12. This number is the constant called Avogadro's Number (N_A) and is equal to $6.022x10^{23}$

The International Prototype Kilogram. There are also six official copies stored in the same vault and additional copies around the world.

While every country in the world has officially adopted the International System, a few (the United States being one of them) are reluctant to initiate change due to public resistance. Distances in inches, feet, and miles will be familiar to you since they are accepted in U.S. culture, but the scientific community and most of the world rarely use these units. The same is true for the Fahrenheit temperature scale and masses in pounds and ounces. To help you get a better understanding of the International System of Units, Table 2.4 contains some conversions between the International System and units commonly used in the United States:

Table 2. 4

LENGTH					
1 mile	=	1.61 kilometers	1 kilometer	=	0.621 miles
1 yard	=	0.914 meters	1 meter	=	1.09 yards
1 foot	=	30.5 centimeters	1 centimeter	=	0.394 inches
1 inch	=	2.54 centimeters*			
MASS					
1 carat	=	200 milligrams*	1 gram	=	0.0352 ounces
1 ounce	=	28.4 grams	1 kilogram	=	2.20 pounds
1 pound	=	0.454 kilograms			
VOLUME					
1 Tablespoon	=	14.8 milliliters	1 milliliter	=	1 cubic centimeter*
1 cup	=	237 milliliters	1 liter	=	1 cubic decimeter*
1 quart	=	0.946 liters	1 liter	=	0.264 gallons
1 gallon	=	3.79 liters			
TEMPERATURE					
0ºC = 32ºF = 273.15 K*					
100ºC = 212ºF = 373.15 K*					
ºC = (9/5)(ºF - 32)					
K = ºC + 273.15					
* denotes an exact number					

You may have noticed that some of the units in the table to the right include prefixes such as milli-, centi-, and deci-. These occur because there are many occasions on which using the standard base unit in the SI is impractical due to the magnitude of the measurement. For example, you wouldn't want to measure the mass of an electron in kilograms (approximately 0.000 000 000 000 000 000 000 000 000 000 0091 kg) or the distance from the sun to Jupiter in meters (778 330 000 000 m). The numbers would be either very large or very small and extremely cumbersome. There are two ways of solving this problem – using scientific notation, or altering the magnitude of the unit by changing the prefix.

Scientific Notation:

Sometimes called exponential notation, this method of writing numbers makes use of the fact that our numbering system is a *decimal* system, meaning groups of ten. If you have the number nine and add one, we don't put "10" in the ones place, but rather "1" in the tens place and start over with "0" in the ones place. The same is true for the tens place – when we reach ten "tens," we create the hundreds place and start over with zero again in the tens place. It works the same way on the other side of the decimal with the tenths and hundredths place. Other numerical systems, such as binary and hexadecimal (based on 2 and 16, respectively) are more difficult to work with because we are used to working in tens. Scientific notation simply expresses any value as a number between 1 and 10 multiplied by a factor of ten. For example, 1 000 000 would be expressed as 1×10^{6} and 0.000 000 01 would be 1×10^{-7}. When expressing a number in scientific notation, the number of significant figures should be the same as in the original number. To illustrate this, the mass of an electron from above would be 9.1×10^{-31} kg and the distance to Jupiter would be 7.7833×10^{11} m.

The power of ten can be obtained by counting the number of places the decimal must be moved to get a number between one and ten, with positive exponents representing values greater than 1 and negative exponents representing values less than 1.

Prefixes:

The alternative to scientific notation for measurements is to use a prefix that serves the same purpose as the power of ten. For example, kilo- means 1000 (10^3), so 8.3 kilometers is simply 8.3×10^3 m, or 8300 meters. Additional prefixes are in Table 2.5. Using these prefixes, we could express the distance from the sun to Jupiter in, say, terameters (Tm) or gigameters (Gm). Unfortunately we don't have a prefix small enough to represent the mass of an electron so we'll have to stick to scientific notation for that one.

Table 2.5	Prefixes		
tera-	T	Trillion	10^{12}
giga-	G	Billion	10^{9}
mega-	M	Million	10^{6}
kilo-	k	Thousand	10^{3}
hecto-	h	Hundred	10^{2}
deca-	da	Ten	10^{1}
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deci-	d	Tenth	10^{-1}
centi-	c	Hundredth	10^{-2}
milli-	m	Thousandth	10^{-3}
micro-	μ	Millionth	10^{-6}
nano-	n	Billionth	10^{-9}
pico-	p	Trillionth	10^{-12}

2.4 DIMENSIONAL ANALYSIS

It is useful to have a quick and straightforward way to express a measurement with different units without having to measure again and again. Once a measurement has been taken, it can be converted to any system using a process called dimensional analysis. Any unit can be converted to any other unit as long as there exists a known relationship between the two. Let's assume we measured the length of a sheet of paper and found it to be 8.5 inches. What is this value in centimeters? We can solve this or any other computational problem using dimensional analysis.

We know that a relationship exists between the unit we have (inches) and the unit we want (centimeters) – one inch is equal to exactly 2.54 centimeters. If we create a ratio, the value is fundamentally equal to one since both 1 in and 2.54 cm are the same quantity.

$$\frac{1\ \text{in}}{2.54\ \text{cm}} = 1 \qquad \frac{2.54\ \text{cm}}{1\ \text{in}} = 1$$

Multiplying the original measurement by one of these ratios will not change the physical quantity, only the units with which it is being expressed. So how do we know which ratio to use? Just like in algebraic equations, when a value or unit appears in both the numerator and the denominator, it can be cancelled out. Since we want to remove the unit "inches"

Table 2.6: Orders of Magnitude

		METERS	SECONDS	GRAMS
10^{12}	TERA-	Sun to Jupiter	32 millennia	The Great Pyramid
10^{11}		*Earth to Mars*	*Time passed since David became king of Israel*	*Fully loaded supertanker*
10^{10}		*Total length of all US roads*	*1686 to present*	*The Titanic*
10^{9}	GIGA-	3x distance to the moon	32 years	The Space Shuttle
10^{8}		*2.5x Circumference of Earth*	*Length of war with Japan 1941-1945*	*Blue Whale*
10^{7}		*Diameter of Earth*	*4 months*	*Elephant*
10^{6}	MEGA-	Dallas to St. Louis	11 days 14 hrs	Passenger Car
10^{5}		*Dallas to Oklahoma border*	*1.2 days*	*Adult male*
10^{4}		*Custer Rd. to Dallas North Tollway*	*Length of typical blockbuster movie*	*Dog*
10^{3}	KILO-	5-6 city blocks	17 minutes	1 Liter soft drink
10^{2}	*HECTO-*	*Height of the Statue of Liberty and Pedestal*	*Duration of the "Minute Waltz"*	*Human kidney*
10^{1}	*DECA-*	*Length of Killer Whale*	*World Record time in the 100m dash*	*Lethal dose of caffeine for an adult*
10^{0}		Length of arm	Time for light to travel from Earth to the moon	Paperclip
10^{-1}	*DECI-*	*Cell phone*	*Blink of an eye*	*One-half carat diamond*
10^{-2}	*CENTI-*	*Fingernail*	*Camera shutter speed*	*1.5 teaspoons of air*
10^{-3}	MILLI-	Grain of sand	Duration of camera flash	Mosquito
10^{-4}		*Thickness of hair*	*Sampling interval for telephone audio*	*A "Hit" of LSD*
10^{-5}		*Cell diameter*	*Sampling interval for CD audio*	*Small grain of sand*
10^{-6}	MICRO-	Cellular organelles	Cycle time for typical AM radio signal	Lethal dose of botulin toxin (Botox)
10^{-7}		*Wavelength of visible light*		*Smallest detectable amount of marijuana per mL of urine*
10^{-8}		*DNA supercoils*		*Amount of DNA needed for genetic fingerprinting*
10^{-9}	NANO-	Width of DNA	Time for light to travel one foot	Human cell
10^{-10}		*Radius of atom*		*Amount of dioxin in one hamburger*
10^{-11}		*Wavelength of gamma rays*		*Mass of 10 bacteria*
10^{-12}	PICO-	100x diameter of nucleus	Time for light to travel 0.3 cm	2.5 billion Uranium nuclei

**All measurements are approximations and are meant to provide a general size comparison* and replace it with "centimeters," we will choose the second ratio so that inches cancels out. Then we simply multiply and round the answer to the correct number of significant figures.

$$8.5 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 21.59 \text{ cm} = 22 \text{ cm}$$

This method can be used with practically every problem in chemistry. It provides a standard approach to problem solving and is also easy to double check for accuracy. As long as the conversion factors are correct and the units cancel out, we can be certain of the outcome. Dimensional analysis is not limited to one-step conversions, nor is it limited to units within the same measurement scheme. Here are some additional examples to emphasize the utility of this method.

Example 1: Express the quantity 3.2 kg in milligrams.

We don't immediately know the relationship between kg and mg, but we do know that 1 kg is 1000 g and 1 g is 1000 mg. So we will first convert from kg to g, then from g to mg:

$$3.2 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{kg}} \times \frac{1000 \text{ mg}}{1 \text{g}} = 3\,200\,000 \text{ mg} = 3.2 \times 10^{6} \text{ mg}$$

Example 2: A ream of paper weighs 5.0 kg and costs \$2.50. What is the price of one gram of paper?

If we listed out the relationships we know, we would find that 1 ream = 5.0 kg, 1 ream = \$2.50, and 1 kg = 1000 g. We will convert from grams to kilograms, then from kilograms to reams, then from reams to dollars:

$$1 \text{g} \times \frac{1 \text{kg}}{1000 \text{ g}} \times \frac{1 \text{ream}}{1 \text{kg}} \times \frac{\$2.50}{1 \text{ream}} = \$0.0025$$

Example 3: How many milliseconds in 25 centuries?

There are 1000 ms in one second, 3600 s in one hour, 24 hours in a day, 365 days in a year, and 100 years per century:

$$25 \text{ cent.} \times \frac{100 \text{ yr}}{1 \text{cent.}} \times \frac{365 \text{ d}}{1 \text{yr}} \times \frac{24 \text{ h}}{1 \text{d}} \times \frac{3600 \text{ s}}{1 \text{h}} \times \frac{1000 \text{ ms}}{1 \text{s}} = 7.884 \times 10^{13} \text{ ms} = 7.9 \times 10^{13} \text{ ms}$$