Chapter 1 BACKGROUND AND BASICS

Greetings. Welcome to General Chemistry.

You are embarking on this course for any of various reasons. Some students simply want to take this course. Many students have to take it for whatever field they are pursuing. Regardless of your own reason, chemistry is a very worthwhile subject:

CHEMISTRY IS CENTRAL TO MANY PARTS OF YOUR WORLD.
WHETHER YOU LIKE IT OR NOT.
WHETHER YOU LEARN IT OR NOT.

I will try to help you do both.

Obviously, a major intention of this text is to help you learn General Chemistry, but this book is also a survival guide and I shall expand on this point below. For many students, a General Chemistry class is not an easy task. This book will try to help you get through this. Another intention of this book is to add interest to the subject and, hopefully, to have some fun with it. Yes, fun. Many people think that chemistry is a nerdy subject and that chemists are nerdy themselves. Well, that's only partly true: some chemists are nerdy, but not all. How do you tell the difference? There are various indicators. For example, if they carry a Periodic Table in their wallet/billfold, then that's one clue. A Periodic Table? We'll get to that in Chapter 2; hold onto that thought.

Before we jump into things, there are two notions which I want to point out.

1.1 The Grand Puzzle

As you go through your school years, you go through many courses on many subjects. In many cases, a pattern develops in a particular area of study whereby you first learn material X which helps you learn material Y which helps you learn material Z, etc. In other words, there is a fairly straightforward, linear path. This doesn't apply in chemistry. I cannot teach chemistry in a linear fashion; it doesn't work that way. The subject of chemistry encompasses many aspects of Nature which are interconnected. It is more like a massive jigsaw puzzle, but not like the old-fashioned ones which you could buy in a store and which have the final picture on the box. In the study of chemistry, you don't know the final picture in advance. But you still must start somewhere. One piece fits at a time. Sometimes you pick up a piece and you can place it in its final position. Sometimes you pick up a piece but you later realize that it doesn't fit the way you thought, so you put it back down for later. You try. You make mistakes. Eventually the picture starts forming. As you go, you can work at different sections of the puzzle. You might have a section in the upper corner, a section in the middle, a section at the right, or whatever. With time, you start to bring together the separate sections. You will start to see the bigger picture when enough pieces from enough sections are in place. You do not need the entire puzzle in order to begin forming the image. Besides, for chemistry, the entire image will forever grow larger as more things are discovered.

So what does this mean? All of this is very important when it comes time to teach and to learn the subject. I cannot present the material to you in a straight line because it does not exist in that manner. I am going to introduce sections and work with them. I may partially build the section and then move to another. This may seem scattered but, with time, I will bring these sections together. In the earlier chapters, I will refer to fuller explanations in the later chapters. If you want to, you can look ahead for more. In the later chapters, I will tie back to the earlier chapters. If you're rusty, go back to those pages and refresh. Sometimes, you will need to go back and read a portion. This approach is not idle repetition. These are the links which will hopefully thread the various sections together. You must understand this process. Nature does not work in isolated bits and pieces. Nature is inherently interconnected. All pieces are part of the Grand Puzzle.

1.2 One REALLY BIG item

Regardless of how well you do in a chemistry course or where your interests lie, there is one REALLY important thing which you should come away with. THIS APPLIES TO YOU. THIS APPLIES TO YOUR WORLD.

BALANCE. I cannot tell you in one paragraph the importance of balance in chemistry. So I will take time throughout the entire book to emphasize this. What we are dealing with in many cases is the balance of opposing processes. Different forces working against each other. Nature's tug-of-war. Again, this is not just chemistry. THERE IS STRUGGLE IN ALL OF NATURE. The expansion of the universe. The population dynamics of a simple ecosystem. So much of your world is the net outcome of different influences, different forces, different directions. Even your own personal finances: earn money, spend money. A lot of people think chemistry is just a fixed subject, black-or-white, yes-or-no. This is wrong. Very wrong. The majority of chemistry is dominated by balance. And in order for you to better understand the subject, you must come to appreciate these opposing influences, these opposing forces, these opposing directions.

There is struggle in all of your world. Nature designed it that way. Keep this in mind. Forever.

1.3 Survival Guide

We will get to some chemistry things later, but I want to give you some pointers about how to learn chemistry and about how a typical first-year course operates.

Before I get to those pointers, let me add a bit more about this text. This book is a "working text". It is called this because you will do work in it. This text contains much of the material for a typical General Chemistry course but it may not contain all. This working text is not necessarily your complete source of material for the course. Other sources may also be available at the direction of your instructor. All of these things together constitute valuable resources for you. Use your resources and use them well.

Now let's go on.

• The first point to note is that, for most students, learning chemistry takes a lot of work and a lot of time. There's no way around this. You have to be ready to work. You have to be ready to put in time and effort. For many students, that means <u>a lot</u> of time and effort. THE PRIMARY RESPONSIBILITY FOR LEARNING LIES WITH YOU, THE STUDENT. But there are other courses, or a job, or a family, or whatever. Your life's responsibilities take time. If you cannot commit enough time to this endeavor at this point in your life, then this may not be the time for you to attempt this course. How much is enough time? Everybody's different. If you're not sure, talk to your instructor or to an advisor.

• Be aware of your other sources of help and be ready to use them, such as other books, other students, internet, instructional assistants, etc. Many avenues of assistance typically exist. Seek them out. Ask your instructor what's available and then use what's available. And do it before it's too late. Don't wait until you're buried and the exam is tomorrow morning at 8:00 am. (Yes, there are students who do this. You know who you are.)

• There are different students and there are different instructors. Different instructors teach chemistry differently. That should come as no surprise. Each instructor might emphasize different content. Instructors choose their content according to what they believe is best suited for their course and their students. There may not be one single source which exactly fits their course. Instructors may not cover everything in their sources. Some instructors will even add things that aren't covered in the sources. That is their job. It is their responsibility to present what they believe is the most important material for the level of their students for the intention of their course at their school. Another school might do it differently. But that's not your problem.

• In this book, I address those aspects which in my experience warrant specific attention for many students. This means that I am prioritizing topics for inclusion and for exclusion. I cover many of the bigger, important aspects. I may not cover them all. I may exclude minor but still important aspects. I do not intend to cover every topic which is straightforward or which is more readily understood. Those are in your other sources. In this text, we are also going to have some fun as we go. I'll even throw in some references and allusions to make things interesting. At least I hope so.

• Although many people think chemistry is an exact science, it isn't. In fact, it cannot be truly exact. This applies to measurements as well as to other aspects. I already referred to some of this above when I talked about balance. There are actually many aspects in chemistry which have exceptions to "rules". Yes, there are some rules that are always true and I shall indicate them as such. But most things come as trends and tendencies, not as rules. For this reason, I will do a lot of guidelines but not as many rules.

• A lot of people think chemistry is a lot of math. That's only partly true: there is quite a bit of math, but the majority of chemistry is not. You have to be able to do math but you also have to be able to think and to conceptualize. The math requirements in this Part 1 are limited to $+-\times\div$. We'll add logarithms and exponentials, common and natural, starting in Chapter 46 in Part 2. You'll need scientific notation, which I assume you have seen or which is adequately explained in your other sources.

• The language of chemistry can be difficult to master, although not as difficult as a foreign language. Like a foreign language, much of it takes memorization. Common table salt is mostly sodium chloride (with a tad bit of other things thrown in). You will have to know what the words "sodium" and " chloride" mean; there's no way around this. We will cover these things in the early Chapters. Chemistry also uses many words from normal conversational usage. Unfortunately, some such "normal" words have evolved over the centuries to be subtly different or very different in meaning when used in chemistry. I will point these out to you as we go. Just like in society, many communication difficulties arise from failure to understand the meaning behind words in a particular usage.

• How's your toolbox? I don't mean hammer, screwdrivers, wrenches, bandages, antibiotics, etc. I mean your academic toolbox. Your learning tools. The ones you've been accumulating all these years. Have them ready. We'll be using them. By the time most students hit a course such as this, a lot of their tools have been developed. Some of these may not work and you may have to add some. Tools can include conceptualization devices, mathematical devices, memorization methods, etc. The tool you use may be different from the tool another student uses. There are different ways to conceptualize various aspects in chemistry. There are different ways to solve arithmetic problems. There are even different ways for different students to memorize things. Multiple methods. Multiple tools. The more the better. Use the best tool for you for the particular job at hand.

• Feel free to write in this book. Anytime. Anywhere. Write in things. Scratch out ~~things~~. Highlight things. Anything you think might be helpful. Some things are <u>underlined</u>. Some things are ALL CAPITAL LETTERS. Some things are just normal type. Some things are for emphasis. Some things are for lasting importance.

• Since this is a working text, there are things which you must write in yourself. You will need to complete some problems, fill in some tables, etc. If I tell you to mark something, then mark it. If I tell you to flag a paragraph by putting a red star in the margin, then do it. If you don't have red ink with you, then write "red star" in the margin. In some later Chapter, I may send you back there for a reason. If you didn't flag it, then you'll be looking all over for the information.

• There are several catches to learning chemistry. I want to point out three to you up front. Understand them. They will help you.

CATCH #1. NATURE IS IN CHARGE. Humans do not control the planet, let alone the universe. Humans have the ability to learn from experience and from experiment and to apply that knowledge to their world. Humans do modify their world, some for the good and some for the bad. But humans are subject to the same natural laws as is anything else, and many of those laws aren't even understood. In the grand scheme of things, human knowledge is small compared to the whole of knowledge. It is as the Sun once said to the child of eight in her search for the truth:

> “ In this great universe of ours, man is a mere insect, an ant, in his intellect, as compared with the boundless world about him, as measured by the intelligence capable of grasping the whole of truth and knowledge. ”

CATCH #2. This follows from Catch #1. Since we don't know everything, there is always more to learn. The key point to note here is that CHEMISTRY REPRESENTS OUR UNDERSTANDING OF THINGS BUT OUR UNDERSTANDING IS NOT COMPLETE. I referred to this with the jigsaw puzzle. There are many things which we do not understand. In our attempt to better understand, we develop pictures (sometimes several pictures) to explain things. These pictures are tools which can include models and theories and such. Some of these tools are good and some are not so good. But that may be all we have for now. Sometimes, things don't make sense with one model so we try to formulate another model to explain it. Then we have two models (tools) for the same task. Maybe neither works the way we'd like them to. Our failure to comprehend is not a flaw of Nature. Nature knows what Nature is doing. The problem lies on the human side in the incompleteness of our own understanding. As you go through chemistry, there will be times when one model (tool) is used and then a different model (tool) is used for the same thing. It may appear confusing but this is OK. Be adaptable. Become familiar with the different models and theories. Perhaps someday, someone will straighten out one of these problems. Perhaps that someone is you.

CATCH #3. This is related to Catch #2. Models, theories, and such represent the ideal. They say what should happen. These are very useful but many have limitations. Then reality sets in, and what really happens is different from what should happen. We refer to this as ideal versus real, or ideality versus reality. Be ready for reality checks. They happen. You will see.

• There is one final point to make. The purpose of this book is to help you understand chemistry in general, although this book's approach may differ a bit from that of your instructor. In many cases there are different ways of explaining things and there are different ways of doing the math. This refers to multiple methods, as I noted above. Be mindful of these possible differences, and be mindful if your instructor requires some things a certain way. That is their prerogative.

OK. Let's proceed. We start with several aspects related to numbers and units.

1.4 Measurement

We need to discuss a central issue for all the sciences: measurements. Chemistry is a quantitative and a qualitative science. Quantitative aspects are those which have a numerical value: for example, "the mass of an object is 1.03 g" or "the temperature is 32 °C". Qualitative aspects are non-numerical: for example, "the color of the object is red" or "the liquid smells like vinegar". By their nature, the quantitative aspects are subject to more rigorous definitions and standards. These are all a part of measurement.

The "official" units of measure are called SI units ("Système International" in French or just "International System" in English). These units are principally metric in origin. Although these are supposed to be the "official" units of measure, they are not always adopted in all circumstances and other units remain in use for historical reasons or for simple convenience. As with the metric system, the standard SI units can also be given powers-of-ten prefixes. You are hopefully familiar with some of the prefixes; here are the ones which will be most common for our use.

COMMONLY USED POWERS-OF-TEN PREFIXES

giga-	G	10^9	billion
mega-	M	10^6	million
kilo-	k	10^3	thousand
centi-	c	10^{-2}	one hundredth
milli-	m	10^{-3}	one thousandth
micro-	μ	10^{-6}	one millionth
nano-	n	10^{-9}	one billionth
pico-	p	10^{-12}	one trillionth

SI units are categorized as base or derived units. The base units are fundamental, while derived units are functions of the base units. There are only seven base units but there are many derived units. Some of the base units are common; these can also take a prefix.

Length, *l* The base unit is the meter, m. Related units include km, cm, mm, etc.

Mass, *m* The base unit is the kilogram, kg (which already has a prefix). Other units include g, mg, μg, etc. (In clinical use, μg is also written as mcg.)

Time, *t* The base unit is the second, s. (That's just s, not sec.) Times which are less than a second get a prefix, such as ms. You can also do minute (min), hour (h), etc.

The other base quantities are temperature (below), number of items such as atoms (mole, starting in Chapter 5), electric current (ampere, starting in Chapter 62), and luminous intensity (candela, which I won't mention again because we won't need it).

Derived units are functions of one or more base units. Here are a few common examples.

Speed, *v* Speed is distance (length) per time, so the SI unit is m/s.

Volume, *V* Volume is a length cubed, so the SI unit is m^3. This is one of several SI units which are not used as much by chemists. Chemists typically use a volume based on a liter, L, which leads to mL, μL, etc. The connection to m^3 is $L = 10^{-3}\ m^3$.

Density, *d* Density is mass per volume, *m*/*V*, so the SI unit would be kg/m^3 but chemists don't usually do that one either. The density of a liquid or solid is typically given in g/mL, but the density of a gas is commonly in g/L. (In this text, density will have the symbol *d*, but it is also symbolized by Greek letter ρ.)

While these examples illustrate some of the units to be encountered in typical chemistry applications, there are also the everyday, worldly units such as ounces, pounds, gallons, etc. Connections between these and SI units are made by standard conversion factors, some of which are given on the Conversions and Constants page at the end of the printed text or as a separate link for the online text. Other conversion factors can be found in reference books or reliable online sources. If you are rusty on metric, then you'll need to review it.

There is one SI base unit which I will elaborate upon at this time: temperature, T. The most common everyday units are Fahrenheit (°F) and Celsius (°C). These two systems were set up differently; they differ in the size of their degree units and in their zero points. Let's look at the boiling and freezing temperatures for water in the two scales, and the difference between them.

water boils at:	100 °C	212 °F
water freezes at:	0 °C	32 °F
difference:	100 °C units	180 °F units

The size of a Celsius unit is bigger than the size of a Fahrenheit unit, by a multiplier of 180/100 or 9/5. (This is like saying the size of an inch is bigger than the size of a centimeter, although they both measure length. For these, the ratio is 2.54.) Historically, the zero point for Celsius was defined as the freezing point of water, and this corresponds to 32 °F. Celsius/Fahrenheit conversions are straightforward (plug-and-chug) by standard equations, one of which is given below.

$$T(°\mathrm{F}) = \frac{9}{5}\,T(°\mathrm{C}) + 32$$

This equation includes the 9/5 factor (for the different degree sizes) and also the 32 (for the zero offset, 0 °C = 32 °F).

Celsius is very commonly used in chemistry, but it's not right when it comes to using temperatures in mathematical equations. For this, we typically use the absolute temperature scale, which is also called the Kelvin scale. The kelvin unit is symbolized K and this is the SI base unit. That's just K, not °K; the Kelvin scale does not use the degree (°) symbol. In fact, they're called "kelvins", not "degrees kelvin". The Kelvin scale is the absolute temperature scale since its zero point is defined as absolute zero. That means that there are no negative temperatures in the Kelvin system. Some people aren't real comfortable with the notion of an absolute zero and the lack of any negative temperatures, but that is a result of our familiarity with Celsius and Fahrenheit.

Let me explain this absolute zero business. Consider some sample of a given identity and a given size; its temperature is a measure of the amount of heat (thermal) energy which it contains. For purposes of this explanation, let me sidestep momentarily so we can talk about a more visible form of energy: light. Imagine being in a room which has a lamp but which is closed from all outside light. The lamp produces some amount of light energy. Now, make the light dimmer: this means there's less light energy. Turn off the lamp completely: you have absolute darkness. We can define "absolute darkness" as the point at which there is no light energy. You cannot go any further. There is nothing darker. All rooms, spaces, caves, etc. which possess zero light energy are all equally, absolutely dark. OK? Now let's come back to heat energy. Imagine that we start with an item at some temperature which corresponds to some total thermal energy. Now remove some of the heat energy: this lowers the temperature and makes the item colder. Remove more heat energy: it gets even colder. Keep removing more, more, more heat energy: the item gets colder, colder, colder. If you continued removing the heat energy, you would reach a point where there was no more heat energy left. You cannot go further. There is nothing colder. This is absolute zero. This is zero kelvin, 0 K. Zero kelvin is the point of no heat (thermal) energy.

While the kelvin scale is the official SI temperature scale, the Celsius scale still finds wide use. The modern connection between the Kelvin scale and the Celsius scale sets 0 °C to exactly 273.15 K. Fortunately, the kelvin unit is the same size as the °C unit, so the only difference between the two is the zero offset.

$$T(\mathrm{K}) = T(°\mathrm{C}) + 273.15$$

The modern Celsius scale includes a slight tweak to the freezing and boiling temperatures for water: now, water freezes at 0.002519 °C and boils at 99.974 °C, at normal pressure. Those values are clearly very close to the historical values, so those still work in the majority of applications.

This ends our section summarizing some basic measurements and units. Now we change gears; we will talk about just how good a measurement is and how to convey that information.

1.5 Can we ever be sure about uncertainty?

This is not a simple question. In the real world, there are errors and there is uncertainty. In this usage, the word "error" carries a normal dictionary definition. "Uncertainty", however, carries a more careful meaning: uncertainty refers to the limit of certainty. Uncertainty in a number is like being unsure about the number: you think the number is right but you may be a little off. The uncertainty is how far off you may be.

Let me tell you some things about how numerical data are obtained. There're basically two ways: counting and measuring. Counting and measuring are fundamentally different, and it's important that you see the difference. This is important in quantitative studies in any scientific area, not just chemistry.

Counting gives a number of items. In principal, it can be done exactly with no errors. That means you can be fully certain of the number and that means there is no uncertainty. Let's say we have six beakers on the bench. This is a count. It's exact.

Measuring gives an estimate of some quantity. Let's say we place a beaker on a balance and the balance says the mass is 36.03 g. This is a measurement. It's not a count. The true number could be 36.0287401.... g. Or it could be 36.0316597.... g. Or it could be 36.0296933.... g. Or it could be any one of a zillion possibilities. There is some uncertainty here. We can't know the mass exactly. We can only know it within some reasonable limit. This is our limit of certainty.

Measuring an object on a balance is a single step operation, but some measurements can have multiple steps. Regardless of the number of steps, measuring procedures can be characterized as having some degree of accuracy and some degree of precision. These contribute to uncertainty. The term accuracy refers to the correctness of the result: in other words, it's how close you are to the true answer. Precision refers to the repeatability of the result: if you repeat the measurement, it's how close the separate results agree with each other. You might think that you should always get the same answer whenever you follow the same steps for a measurement. Well, that depends on the process and the instrument(s) involved. It's not unusual to get slightly different results; the variation is your indication of precision.

Accuracy and precision are independent of each other. Ideally, you want high accuracy and high precision, but you may not get both and sometimes you may not get either. For example, balances need to be properly calibrated in order to correctly relate the weight and mass of an object. If not properly calibrated, the balance will give wrong readings and therefore wrong results. That's poor accuracy. Balances also need to be in good shape; if there is a flaw in its movements or a flaw in an electronic component, then you might get different numbers when measuring the same object different times. This gives less precision to the measurement. You can gauge the level of precision by repeating the measurement process several times. Unfortunately, it may not be possible to gauge accuracy, and you may never know how correct your answer is.

For now, we focus on uncertainty overall, regardless of its origin. For any single instrument, how do you know its uncertainty? Well, it's built into its design.

There are actually two points to note regarding all instruments of measurement: <u>every measuring instrument has an inherent uncertainty and a range of applicability</u>. These are determined by the design of the instrument. One of the simplest instruments is the 12" ruler. That's not exactly high tech, but a ruler is a simple measuring device. Typical rulers show lines to 1/16". Some go finer but we'll stick with this. With a good ruler and good eyesight, we can measure a length to 1/16" and be certain of this within another 1/16" or so. This becomes our "uncertainty", which we can represent as ±1/16". The ruler also has a range of applicability. It's OK to measure length from ~1/16" up to 12", but it's no good for measuring 1/1000" and it's no good for measuring 4.2 miles. Although uncertainty and range of applicability are designed into every instrument, I'm still emphasizing uncertainty right now.

Let's return to our beaker on the balance. Many balances measure to two decimal places and a typical uncertainty for this type of balance would be ±0.01 g. So, if the balance says the beaker's mass is 36.03 g, then the measurement means the 36.0 part is certain but the second decimal place is uncertain. The mass is within 36.02 - 36.04 g.

This is the reality of life in the world of measurements. Uncertainty is everywhere in every field of science wherever instruments are used. When a scientist reports her/his measurement data, s/he gives some indication of the uncertainty involved. This can extend beyond the measurement itself: it includes calculations which use those measurements. Let me illustrate this with an example.

We'll keep our beaker with a mass of 36.03 g and its uncertainty of ±0.01 g. Now let's separately determine the mass of a penny, but we'll use an expensive balance which measures out to five decimal places. Let's say we measure the mass of our penny to be 2.46836 g. We look up the uncertainty in the manufacturer's information and we find the uncertainty for the balance is ±0.00003 g. Thus, the uncertainty for the penny is in the fifth decimal place.

Now here's a simple question: what is the combined mass of the penny in the beaker?

If you do this on your calculator, it will tell you the combined mass is 38.49836 g. Now there's a word for an answer like that and that word is "dumb". Calculators are fast, but they are dumb. Let me show you why this is a dumb answer. Look at the problem this way:

mass of beaker	36.03???....
mass of penny	2.46836....
calculator's answer	38.49836

Remember! We have no idea at all of the values for the ?'s in the beaker mass. We have no clue as to what they are. The calculator simply assumed these were zeros, which was dumb. The answer 38.49836 is WRONG. The correct answer is written as 38.50. This reflects the fact that digits were at least available to the second decimal in all of the values being added. By writing the answer as 38.50, we properly convey that the uncertainty in the answer begins in the second decimal place.

In general, final answers from measurements and their calculations should only contain uncertainty in the last (rightmost) digit. In other words, numbers should be rounded off so that only one uncertain digit is conveyed. There are some exceptions and technicalities here, but we will not go into those; this is good enough for our purposes.

The penny in the beaker example involves a single, simple calculation. Calculations can get quite complicated, and we still need to convey the proper sense of uncertainty in the final answer. But how do we do this? There are several systems available.

1.6 Sigfigs

There are exact and very tedious methods for determining the manner by which a final numerical result from a calculation should be presented, but these methods can be a pain in the butt to use every time. So chemists typically use a compromise system for routine applications. This compromise system adequately covers the need to portray uncertainty in most cases, although the most exacting work still requires the exact and very tedious methods. The compromise system is much more convenient to use, although it still takes time to get used to.

The system is commonly referred to as "significant figures". "Significant" is used here in its normal dictionary usage as "meaningful". It can also be interpreted for our purposes here as "can be trusted". "Figure" refers to the digits which make up the number, such as the four digits within the number 36.03. Thus, a "significant figure" is any one digit within a numerical value which can be considered meaningful and which can be trusted. Look at the example above with the sum of the beaker + penny. When we present the result as 38.50, we mean to say that all four of those digits are meaningful and can be trusted. They are "significant", although we accept that there is uncertainty in the rightmost digit (the "0").

To simplify things, I'll start referring to significant figures as sigfigs. It's just easier.

When you do number-crunching, especially on a calculator, you can get some digits which are meaningful and some which are not. You need to be able to decide which are which and you then round-off accordingly. Up above, I said that the sigfig system is a compromise system; sigfigs are not the completely, totally true method. That allows for some variations to have developed over the years. These variations are minor. I will present the system as we will use it in this book. Your instructor may have a slight difference. As far as your grade is concerned, go with your instructor.

Let's say you have a numerical value to work with. For example, this could be a number given to you in a problem as a measurement or it could be a measurement you actually did in the lab. It could also be an exact number which carries no uncertainty whatsoever. The FIRST TASK is to understand which digits in that number are significant. We will break up numbers into two types: measured values and exact values. We will first consider the rules for distinguishing significant from non-significant digits. The rules as presented here are fairly common to all sigfig variations.

• NUMBERS WHICH CONVEY MEASUREMENT

Most numbers which convey a measured value are straightforward. The only confusion lies in zeros since zeros can be part of the measurement itself or they can just be used as place-holders. Zeros which are part of the measurement itself are significant digits. Place-holders are not. Let's show some numbers and explain how they are interpreted. Remember that uncertainty is allowed only in the rightmost digit; the other digits are for sure and they have no uncertainty.

A. 4.761 This number implies that uncertainty lies in the third decimal. All four digits are meaningful and significant. We say there are four sigfigs in the value.

B. 10.2 This number implies that uncertainty lies in the first decimal. The zero is part of the measured value. All three digits are meaningful and significant. We say there are three sigfigs in the value.

C. 0.0631 This number implies that uncertainty lies in the fourth decimal. The zeros act as place-holders; the number could be written as 6.31×10^{-2} and still retain its full meaning. Only the digits 631 are meaningful and significant. We say there are three sigfigs in the value.

D. 2.480 This number implies that uncertainty lies in the third decimal. The zero is part of the measured value. All four digits are meaningful and significant. We say there are four sigfigs in the value.

E. 190 There is an ambiguity here which leaves two interpretations depending on whether the zero is meant to be significant or not. Let's look at these two interpretations.

1. This number could mean that the uncertainty lies in the ones column if the zero is part of the measured value. In other words, the uncertainty is ±1 or so. In this case, there are three sigfigs. The number would be written in scientific notation as 1.90×10^2.

OR

2. If the zero is not part of the measurement and it is only place-holding, then the uncertainty lies in the tens column. In other words, the uncertainty is ±10 or so. In this case, there are two sigfigs. The number would be written in scientific notation as 1.9×10^2.

Do we care? The number with an uncertainty of ±1 is more meaningful than the number with ±10. It may not look like it even matters but, yes, it really does. Notice that the ambiguity is eliminated by using scientific notation, since scientific notation eliminates place-holding zeros. Another method in these cases uses a terminal decimal. You show a terminal decimal point when a zero in the ones column is meant to be significant. In this manner "190." (with the decimal shown) implies that the zero is also significant and the uncertainty is ±1 or so. "190" (without the decimal) means there are only two sigfigs and the uncertainty is ±10 or so. You may need to check with your instructor on this since not everyone uses the terminal decimal distinction. I will use the terminal decimal practice in this text.

Here's another way of looking at beginning and ending zeros. We'll use examples C and D above and we'll consider a balance and mass again for illustration purposes. If the balance said the mass of an object is 0.0631 g, then only the "631" part registered with the balance; the "0.0" part never even registered with the balance because the sample mass was below 0.1 g. Thus, the "0.0" part carries no weight except to hold a decimal place. On the other hand, if the balance said the mass is 2.480 g, then the balance did register the zero; the measured value is between 2.479 and 2.481 g, and the zero in 2.480 conveys that meaning.

As you can see by these five examples, different numbers can be interpreted in terms of their significance. We can put these to rules as follows; these are lettered to fit the above examples.

A. Nonzero digits are significant.
B. Zeros between nonzeros are significant.
C. Zeros to the left of the first nonzero are not significant.
D. Zeros that end a number to the right of the decimal place are significant.
E. Zeros that end a number to the left of the decimal place can be ambiguous unless a terminal decimal is shown. (Check with your instructor on this one.)

• EXACT NUMBERS

OK, now we'll consider exact values. These are easy. Since they are exact, they have no uncertainty. There are two types: defined values and counts. A dozen is 12. That's absolutely, exactly 12. There's no uncertainty in this. There are 1000 mL in a L. That's absolutely, exactly 1000. No uncertainty here either. Earlier I used the example of 6 beakers on the bench as a count. That's absolutely, exactly 6. Since they have no uncertainty at all, exact numbers do not influence round-off decisions.

Circle the last sentence. It's important.

Now that you know which digits are significant, this ends the FIRST TASK. The SECOND TASK to the sigfig system occurs after number-crunching: the answer must be rounded off in order to properly convey the uncertainty within the result. The method of rounding depends on the arithmetic operation involved in the string. We'll list addition/subtraction and multiplication/division rules now. There are rules for other operations (such as logarithms) which we don't need yet.

Addition/subtraction rule: At the end of an addition/subtraction string for a series of values, round off the answer according to the decimal place. Which decimal place do you round at? You look at the original values, and you go by the input value with the fewest decimal places. That's the number of decimal places in your final answer.

Multiplication/division rule: At the end of a multiplication/division string, you round off according to how many sigfigs. How many sigfigs are to be in the answer? You look at the original values and see which input value has the fewest sigfigs. That's the number of sigfigs in your final answer.

Let's illustrate. We already did the addition/subtraction rule: this was our penny in the beaker example earlier. Go back and look at it. You can see that we rounded according to decimal place, consistent with the addition/subtraction rule. Now let's do a new example for multiplication/division. We'll still use our penny and its mass of 2.46836 g. Let's say we measure its volume and find that it is 0.344 mL. What is the density (in g/mL) of the penny?

$$d = \frac{\text{mass}}{\text{volume}} = \frac{2.46836 \text{ g}}{0.344 \text{ mL}}$$

Your calculator will tell you the answer is "7.1754651" g/mL, but that is another dumb answer. According to the multiplication/division rule, we round-off according to fewest sigfigs. The value 2.46836 has six sigfigs; the value 0.344 has three sigfigs. By the multiplication/division rule, we must restrict to the fewest sigfigs, so the answer is rounded to three sigfigs. We write the answer as 7.18 g/mL.

REMEMBER!

- Rounding for addition/subtraction goes by decimal place.
- Rounding for multiplication/division goes by number of sigfigs, regardless of decimal place.

(ASIDE. Why are the rules different for the different operations? It has do to with absolute error versus relative error and how the exact and tedious method deals with these. I'm not going there. If you are familiar with some of that, fine. Otherwise, stick with the rules as given.)

So what happens when the problem requires a combination of addition/subtraction and multiplication/division operations? You round off at the end of each type of operation before continuing into the next one. Here's an example. Suppose we need the answer to the following calculation.

$$\frac{17.28}{2.31 \times (9.2 + 2.06)}$$

To do this, we first do the parenthetical addition and then we do the remaining multiplication/division. We will round off at the end of the addition since it takes one rule, before continuing to the multiplication/division which takes another rule.

Addition: $(9.2 + 2.06) = 11.3$

Multiplication/division: $\frac{17.28}{2.31 \times 11.3} = 0.662$

If you do not round off after the addition operation, your final answer is 0.664. Does it matter? Is that wrong? Yes, it can matter. Whether it's completely wrong depends on who's grading your exam. When dealing with mixed operations such as in this example, things can get fairly complicated. We will follow this method but there will be some shortcuts in some cases. Your instructor may do their own method. That is their prerogative.

So far, we've talked quite a bit about rounding off in general, but there are rules for that also. Actually, there are several different rules for rounding, depending on different technical programs and sources. We start with three rules that are very general.

1. When you are rounding off and the leading digit to be dropped is less than 5, then always round down. Examples:

Round off 6.2814 to the second decimal.
You must lose the 14. The lead digit to drop is 1; since it is less than 5, the answer rounds down to 6.28.

Round off 207,499 to three sigfigs.
You must lose the 499. The lead digit to drop (4) is less than 5, so the answer rounds down to 207,000.

2. When you are rounding off and the leading digit to be dropped is more than 5, then always round up. Examples:

Round off 6.2878 to the second decimal.
You must lose the 78. Since the lead digit to drop (7) is more than 5, the answer rounds up to 6.29.

Round off 207,601 to three sigfigs.
You must lose the 601. The lead digit to drop is 6; since that is greater than 5, the answer rounds up to 208,000.

3. When you are rounding off and the leading digit to be dropped is a 5, and there are one or more nonzero digits anywhere after the 5, then always round up. Examples:

Round off 3.6851 to the second decimal.
You must lose the 51. The lead digit to drop is 5, and it is followed by a nonzero digit (1), so the answer rounds up to 3.69.

Round off 3.68500001 to three sigfigs.
You must lose the 500001. The lead digit to drop is 5; this is followed (eventually) by a nonzero digit (1), so the answer rounds up to 3.69.

The fourth rule deals with dropping a 5 by itself or a 5 followed by any number of zeros. This is where you can find variations in different sources. In this text, I will follow the odd/even practice.

4. When you are rounding off and the digit to be dropped is just a 5, or a 5 followed by any number of zeros, then...
   a. if the original 5 follows an even digit, round down;
   b. if the original 5 follows an odd digit, round up. Examples:

Round off 6.2850 to the second decimal.
You must lose the 50. Since the 50 follows an even digit (8), the answer rounds down to 6.28.

Round off 207,500 to three sigfigs.
You must lose the 500. Since the 500 follows an odd digit (7), the answer rounds up to 208,000.

This convention is also called the round-to-even rule, since the final digit after rounding ends up as an even number either way. Although I will be following this practice, your instructor may round 5's differently and, again, that is their prerogative. Just be aware that it may change some answers in this text (by a small amount).

By the way, there are two points to note when rounding off in general. Be sure to round-off at the end of the string of operations and not in the middle. Also, be sure to use all sigfigs as given to you. If the value 4.086 is given, don't be lazy and round it to 4.1. Those mistakes lead to "round-off errors".

This concludes our section on uncertainty and its representation. We now turn to problem-solving methods.

1.7 Problem solving

There are many variations to problem-solving for mathematical operations. Some of these are fairly common; other methods, however, can be more individual as a student develops their own methods and skills over the years. One common type is dimensional analysis or factor-label method. This involves executing a series of multiplication/division steps as one big string, one step at a time. Let's illustrate the method with an Example. We'll do an English-metric conversion problem.

. . . .

Example. How many ounces are in 2.04 L?

. . . .

In order to begin, we need an English-metric conversion factor; from the Conversions and Constants page, we have one conversion available, and it's L = 1.057 qt. There are two important things to note about conversion factors: <u>their ratio is one</u> and <u>they can be used fractionally right-side-up or upside-down</u>.

So if you are given $$\text{L} = 1.057\ \text{qt}$$

then this means $$1 = \frac{1.057\ \text{qt}}{\text{L}} \qquad \text{OR} \qquad 1 = \frac{\text{L}}{1.057\ \text{qt}}$$

When doing a problem, both ratios of the conversion factor are available. Use the one that fits the problem at hand.

In order to do the problem, start with your given information and then plot your path to where you are going. Take one step at a time, converting one unit into another. Each step must correspond to one available conversion factor. At each step, <u>look at the unit you have and choose a conversion factor which has that unit in it for the next step</u>. Look at all your available conversion factors and <u>know what's available</u>. Plug in the numbers, using the right-side-up or upside-down version to cancel the unit from the prior step. Since conversion factors equal one, you can multiply/divide by as many conversion factors as are needed to get to the desired units.

Alright, let's get this problem started. We need to take liters to ounces. We have a conversion factor with liters and quarts in it, but we don't have a direct conversion factor for liters and ounces. Let's go ahead with the L/qt or qt/L ratio as above, since this allows us to convert metric L into English qt. This provides the first step of the path.

path: $\text{L} \rightarrow \text{qt}$

The arrow represents a conversion step. You can plug in the numbers so far.

$$2.04\ \text{L} \times \underbrace{\frac{1.057\ \text{qt}}{\text{L}}}_{\text{conversion factor}}$$

Notice that the conversion factor which we used was chosen from the two options above so that L would cancel. (Go ahead, cross out the L's.) Following this step, the remaining unit is qt and we still have to go to oz. How many ounces are in a quart? 32. This gives us two more conversion ratios.

$$32\ \text{oz} = \text{qt}$$

This means $$1 = \frac{32\ \text{oz}}{\text{qt}} \qquad \text{OR} \qquad 1 = \frac{\text{qt}}{32\ \text{oz}}$$

We will use one of these to go from qt to oz. This will complete our path for the units.

path: $\text{L} \rightarrow \text{qt} \rightarrow \text{oz}$

Add the new conversion to the previous string.

$$2.04\ \text{L} \times \frac{1.057\ \text{qt}}{\text{L}} \times \frac{32\ \text{oz}}{\text{qt}}$$

Take your calculator, plug it in and punch it out. Your calculator will tell you "69.00096" which is not right. Round it off. Where? The multiplication/division rule says you must go by the fewest sigfigs. The number 2.04 has three sigfigs and the number 1.057 has four sigfigs. The fewest is three, and that's where we round off. The proper answer is 69.0 oz.

path: $\text{L} \rightarrow \text{qt} \rightarrow \text{oz}$

$$2.04\ \text{L} \times \frac{1.057\ \text{qt}}{\text{L}} \times \frac{32\ \text{oz}}{\text{qt}} = 69.0\ \text{oz}$$

What about the 32? Why didn't we consider it for rounding off? Go back to the sentence which you circled earlier and answer that by yourself.

This one example is meant to illustrate dimensional analysis without spending excessive time on it. The fact remains that, in general, there are <u>multiple methods</u> available for solving mathematical problems in chemistry. Many people use dimensional analysis but some don't. There are also many problems in chemistry which are not suitable for dimensional analysis. BOTTOM LINE: It's a tool. Use it when it's appropriate.

Problems (Answers are in Appendix D.)

1. True or false.
   a. One billion millimeters equal one kilometer.
   b. One million micrometers is the same as one hundred centimeters.
   c. One Fahrenheit degree unit is larger than a Celsius degree unit.
   d. If the temperature of an object increases by 10 °C, then this corresponds to an increase of 10 K.
   e. Precision is a measure of how close an experimental value is to the correct answer.
   f. The value 0.06030010 has six significant figures.
   g. The value 2.4060 has five significant figures.

2. Check your calculations and your sigfigs.
   a. $18.3 - 0.6394 + 86.9 =$
   b. $(18.3 \div 0.6394) \times 86.9 =$
   c. $\dfrac{18.3 - 0.6394}{86.9} =$

3. Common human body temperature is 37.0 °C. Convert this to °F and to K. (FYI: The numbers used in the temperature conversion equations in Section 1.4 are exact. 37.0 is not exact.)

4. A molecule of oxygen in the air is about to collide with your face at 444.1 m/s. How fast is that in miles per hour?