$$
\begin{gathered}
\text { Ghenilstoy: } \\
\text { what you need } \\
\text { to know }
\end{gathered}
$$

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## Measurements and Calculations

Refer to this section as needed throughout your course.

SI Units

Metric units that are useful for everyday measurements differ by a factor of 10. Here is an example for the base unit meter:

| Kilometer $(\mathrm{km})$ | 1000 meters | $10^{3}$ |
| :--- | :--- | :--- |
| Hectometer $(\mathrm{hm})$ | 100 meters | $10^{2}$ |
| Decameter $(\mathrm{dam})$ | 10 meters | 10 |
| Meter $(\mathrm{m})$ | 1 meter | 1 |
| Decimeter $(\mathrm{dm})$ | $1 / 10$ meter | $10^{-1}$ |
| Centimeter $(\mathrm{cm})$ | $1 / 100$ meter | $10^{-2}$ |
| Millimeter $(\mathrm{mm})$ | $1 / 1000$ meter | $10^{-3}$ |

The decameter, or dekameter, is rarely used. Decimeters and hectometers are convenient when people are familiar with them. The system can be extended when we need larger or smaller units. These extended prefixes differ by a factor of 1000 :

| Exa (E) | $1,000,000,000,000,000,000$ | $10^{18}$ |
| :--- | :--- | :---: |
| Peta (P) | $1,000,000,000,000,000$ | $10^{15}$ |
| Tera (T) | $1,000,000,000,000$ | $10^{12}$ |
| Giga (G) | $1,000,000,000$ | $10^{9}$ |
| Mega (M) | $1,000,000$ | $10^{6}$ |
| Kilo (k) | 1,000 | $10^{3}$ |
| Hecto (h) | 100 | $10^{2}$ |
| Deca or Deka (da) | 10 | $10^{1}$ |
| Base unit (m, g, l, etc.) | 1 | $10^{0}$ |
| Deci (d) | $1 / 10$ | $10^{-1}$ |
| Centi $(\mathrm{c})$ | $1 / 100$ | $10^{-2}$ |
| Milli $(\mathrm{m})$ | $1 / 1,000$ | $10^{-3}$ |
| Micro $(\mu)$ | $1 / 1,000,000$ | $10^{-6}$ |
| Nano $(\mathrm{n})$ | $1 / 1,000,000,000$ | $10^{-9}$ |
| Pico $(\mathrm{p})$ | $1 / 1,000,000,000,000$ | $10^{-12}$ |


| Femto (f) | $1 / 1,000,000,000,000,000$ | $10^{-15}$ |
| :--- | :--- | :--- |
| Atto (a) | $1 / 1,000,000,000,000,000,000$ | $10^{-18}$ |

## Scientific Notation

To better manage very large or very small numbers, we use scientific notation. This means that we adjust the number to take up the "ones" place, plus any places after the decimal point as needed, and then multiply it by a power of 10 :
$1000=1 \times 10^{3}$
$500=5 \times 10^{2}$
$14,000=1.4 \times 10^{4}$
$99,325,000=9.9325 \times 10^{7}$
Do not allow the first number in your scientific notation to occupy the "tens" or "hundreds" place. $56 \times 10^{4}$ should be written as $5.6 \times 10^{5}$. If you make the first part of the number 10 times smaller, the second part needs to be 10 times larger so that the actual number stays the same.

One advantage of scientific notation is that numbers with exponents are easy to multiply:
$10^{3} \times 10^{2}=10 \times 10 \times 10 \times 10 \times 10=10^{5}$
When you multiply, add the exponents. Remember that numbers can be multiplied in any order, so rearrange them for your convenience:
$5 \times 10^{4} \times 6 \times 10^{11}=5 \times 6 \times 10^{4} \times 10^{11}=30 \times 10^{15}=3 \times 10^{16}$
To divide numbers with exponents, write them above and below a division line so you can cross things off:

$$
10^{5} \div 10^{3}=\frac{10^{5}}{10^{3}}=\frac{10 \times 10 \times 10 \times 10 \times 10}{10 \times 10 \times 10}=\frac{10 \times 10}{1}=10^{2}
$$

If there are 5 tens above the division line, and 3 tens below, what will be left is 2 tens above the division line. When you divide, subtract the exponents. $5-3=2$.

Sometimes there are more tens below the division line than there are above, and subtraction produces a negative exponent:
$10^{3} \div 10^{5}=\frac{10^{3}}{10^{5}}=\frac{10 \times 10 \times 10}{10 \times 10 \times 10 \times 10 \times 10}=\frac{1}{10 \times 10}=\frac{1}{10^{2}}=10^{-2}$
$3-5=-2$, and $10^{-2}$ means $\frac{1}{10^{2}}$ or $\frac{1}{100}$. Negative exponents can be used to write very small numbers in scientific notation:
$0.1=1 \times 10^{-1}$
$0.03=3 \times 10^{-2}$
$0.25=2.5 \times 10^{-2}$
$0.000004=4 \times 10^{-6}$
$0.0008991=8.991 \times 10^{-4}$
Don't let these negative exponents scare you. The rules are always the same. For multiplication, add the exponents, and for division subtract the exponents.
$4 \times 10^{-6} \times 3 \times 10^{-5}=4 \times 3 \times 10^{-6} \times 10^{-5}=12 \times 10^{-11}=1.2 \times 10^{-10}$
Notice how the exponents add: $-6+-5=-11$.
$\left(8 \times 10^{5}\right) \div\left(2 \times 10^{-2}\right)=\frac{8 \times 10^{5}}{2 \times 10^{-2}}=4 \times 10^{7}$
To divide, subtract the exponents: $5-2=5+2=7$.
Normally, when you add or subtract you automatically adjust your numbers so that their place values line up properly. $6300+200=6500$. You know to add the 2 to the 3 , and not to the 6 .
Now look at the same problem in scientific notation:
$6.3 \times 10^{3}+2 \times 10^{2}=$ ?
When it looks like this, you may be tempted to add the 2 to the 6 , but remember that these numbers have different place values. For addition or subtraction, line up your place values by making the exponents the same. Write the problem like this:
$6.3 \times 10^{3}+0.2 \times 10^{3}=6.5 \times 10^{3}$
Subtraction works the same way:
$8.50 \times 10^{7}-2 \times 10^{5}=8.50 \times 10^{7}-0.02 \times 10^{7}=8.48 \times 10^{7}$

## Conversion Factors

Converting from one unit to another is often quite simple, and you actually do it all the time without even thinking about it. If you only have quarters, you can pay for something that costs $\$ 1.25$ with 5 quarters, or if you are meeting a friend in 30 minutes you may say "See you in half an hour." When the numbers are simple you can just use basic arithmetic, but in chemistry you will often be working with unfamiliar units and awkward numbers. Use conversion factors to avoid errors!

Conversion factors can be written as fractions that have a value of 1.1 hour $=60$ minutes, and you can divide both sides of this equation by 60 minutes:

1 hour $=60$ minutes
$\frac{1 \text { hour }}{60 \text { minutes }}=\frac{60 \text { minutes }}{60 \text { minutes }}$
$\frac{1 \text { hour }}{60 \text { minutes }}=1$
On the other hand, you could also divide both sides by 1 hour:
$1=\frac{60 \text { minutes }}{1 \text { hour }}$
Both $\frac{1 \text { hour }}{60 \text { minutes }}$ and $\frac{60 \text { minutes }}{1 \text { hour }}$ are valid conversion factors. The value of a conversion factor is always 1 . When you multiply any quantity by a conversion factor, you will not change its value because you are multiplying by 1 . Pick your conversion factor so that you are both multiplying and dividing by the unit you want to get rid of:

$$
30 \text { minutes } \times \frac{1 \text { hour }}{60 \text { minutes }}=\frac{30 \text { minutes } \times 1 \text { hour }}{60 \text { minutes }}=0.5 \text { hours }
$$

Be careful not to have your conversion factor upside down because then things don't cancel:

30 minutes $x \frac{60 \text { minutes }}{1 \text { hour }}=$ ??

Conversion factors can be adapted to square and cubic units. Both the number and the unit need to be squared or cubed. For example, there are 12 inches in 1 foot, but when you are dealing with square feet you have to square the conversion factor. When you square
something that means you should multiply it by itself. $\left(\frac{12 \text { inches }}{1 \text { foot }}\right)^{2}$ means
$\frac{12 \text { inches }}{1 \text { foot }} x \frac{12 \text { inches }}{1 \text { foot }}$ which is $\frac{144 \mathrm{in}^{2}}{1 \mathrm{ft}^{2}}$. So, if you have to convert 3 square feet to square inches, do it like this:

3 square feet $x\left(\frac{12 \text { inches }}{1 \text { foot }}\right)^{2}=3 \mathrm{ft}^{2} \times \frac{144 \mathrm{in}^{2}}{1 \mathrm{ft}^{2}}=432 \mathrm{in}^{2}$

## Railroad Tracks (Train Tracks)

When you have a lot of conversion factors in one problem, you can put them all together in a table-like arrangement called a railroad track or train track. The advantages of this are: one single calculation that avoids possible rounding errors, quick check that all the units cancel properly, faster if you know what you are doing, and easy for teachers to grade. Disadvantages: confusing if you're just learning, doesn't show what is happening as you work through the problem, and loss of ability to check the reasonableness of the answer at each step. Personally I never use railroad tracks. If you prefer step-by-step conversions you can still create a track at the top or bottom of your work and fill it in as you go through the steps.

As an example, I will use my effort to make lemonade from instructions I had copied down some years earlier:

30 ml lemon juice / 1 cup water
100 ml sugar / 6 cups water
I used my small milliliter measure to determine that I had 50 ml lemon juice, but once I did that it was dirty and I didn't feel like cleaning and drying it. The sugar would have to be measured in teaspoons or tablespoons.

First draw a railroad track, starting with 50 ml lemon juice:


We can't find the amount of sugar until we know how much water there will be, so use the first conversion factor:
$\frac{50 \mathrm{ml} \text { lemon juice }}{1} \times \frac{1 \text { cup water }}{30 \mathrm{ml} \text { lemon juice }}=1.667$ cups water
Note that I had to round this off at some arbitrary point. The answer seems reasonable as I would expect to need more than 1 cup of water, but less than 2 because I don't have 60 ml of juice. Add the conversion factor you used to your railroad track (but not the calculation):

| 50 ml juice | 1 cup water |  |
| :--- | :--- | :--- |
|  | 30 ml juice |  |

Next, the sugar. Start with what you have, 1.667 cups water, and convert to "sugar needed":
$\frac{1.667 \text { cups water }}{1} \times \frac{100 \mathrm{ml} \text { sugar }}{6 \text { cups water }}=27.78 \mathrm{ml}$ sugar
Again, this seems reasonable because I had a bit less than 2 cups water so I should add less than a third of the amount of sugar required for 6 cups. Add this conversion factor to your track:

| 50 ml juice | 1 cup water | 100 ml sugar |
| :--- | :--- | :--- |
|  | 30 ml juice | 6 cups water |

Now I need that amount of sugar in teaspoons, and there are about 5 milliliters in a teaspoon as my spoon measuring set conveniently informs me:
$\frac{27.78 \mathrm{ml} \text { sugar }}{1} \times \frac{1 \text { teaspoon }}{5 \mathrm{ml}}=5.56$ teaspoons
Add this conversion to your track:

| 50 ml juice | 1 cup water | 100 ml sugar | 1 teaspoon |
| :--- | :--- | :--- | :--- |
|  | 30 ml juice | 6 cups water | 5 ml |

Ughh, about $51 / 2$ teaspoons, which is a fair bit of measuring. But, there are 3 teaspoons in a tablespoon:
$\frac{5.56 \text { teaspoons }}{1} \times \frac{1 \text { tablespoon }}{3 \text { teaspoons }}=1.85$ tablespoons
Add to the track:

| 50 ml juice | 1 cup water | 100 ml sugar | 1 teaspoon | 1 tablespoon |
| :--- | :--- | :--- | :--- | :--- |
|  | 30 ml juice | 6 cups water | 5 ml | 3 teaspoons |

I added just a little less than two tablespoons to my lemonade. It tasted great! When I re-do those calculations on the railroad track, I like to do the top and bottom separately, so I add double lines. You're probably not supposed to do that, but it looks a bit like an equals sign and gives you a place to put those numbers:

| 50 ml juice | 1 cup water | 100 ml sugar | 1 teaspoon | 1 tablespoon | 5000 |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  | 30 ml juice | 6 cups water | 5 ml | 3 teaspoons | 2700 |

Last, I erase any excess line and add the answer before rounding:

| 50 ml juice | 1 cup water | 100 ml sugar | 1 teaspoon | 1 tablespoon | 5000 |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  | 30 ml juice | 6 cups water | 5 ml | 3 teaspoons | 2700 |$=1.85 \mathrm{tbsp}$

## Significant Figures

To chemists and other scientists, zeros that come after the decimal point mean a lot more than they do to mathematicians. When a chemist says that his sample weighs 38.80 grams, he doesn't mean 38.8. That last zero indicates the smallest possible place value digit that can be measured or estimated using a particular measuring device. This zero contains important
information about the weight of the sample, and it is just as significant as the other digits, so don't lose it! When you do calculations with chemistry measurements, the final answer should be just as precise as the original measurements. To accomplish that we have to understand which part of a number is "significant".

You have already learned to use conversion factors, so let's take the measurement 38.80 grams and convert it to kilograms. To do that, we have to know (or look up) that there are 1000 grams in a kilogram. We multiply $38.80 \mathrm{grams} \cdot \frac{1 \mathrm{~kg}}{1000 \mathrm{grams}}$. The unit "grams" cancels out and we are left with $\frac{38.80 \mathrm{~kg}}{1000}=0.03880$ kilograms. There are now more digits in our measured number, but converting the measurement to a different unit doesn't make it more precise. The two zeros in front of the 3 are really just "placeholder zeros" that will not be there if we switch back to grams. We say that 38.80 has 4 significant digits, and so does 0.03880 .

Zeroes that are somewhere in the middle of a number are obviously significant, so 705 has 3 significant digits. The number 12001 has 5 significant digits. Unfortunately however, when there are zeros at the end of a number we sometimes have to guess what kind of measurement was actually made. For example, you may hear people say that the speed of light is $300,000 \mathrm{~km}$ per second. That is an amazingly convenient figure. Does it mean that the speed was measured exactly to the nearest kilometer, and found to be exactly $300,000 \mathrm{~km} / \mathrm{sec}$, or was it rounded off? Actually it was, and there is a far more precise figure available. To the nearest kilometer, the speed of light is $299,792 \mathrm{~km} / \mathrm{sec}$. That gives the speed of light correct to 6 significant figures. Measuring to the nearest meter gives 299792458 meter/sec. This last measurement has 9 significant figures. If you want to show that you have measured something to be precisely 2000 kilometers, you can indicate that by writing 2000. kilometers. The decimal point indicates that the last zero is significant, so your number has 4 significant figures. Some textbooks will place a line under or over ambiguous zeroes to indicate that they are significant. The best way to do things though is to use scientific notation. "Exactly 2000 kilometers" can be written as $2.000 \times 10^{3} \mathrm{~km}$. This clearly shows that the measurement was not rounded off and all those zeroes matter. Ask your teacher what to do when a measurement like 2000 km is not given in scientific notation on a test. Many teachers will direct you to consider 2000 km as having only one significant figure.

Scientific notation also helps by getting rid of those potentially confusing zeroes at the beginning of numbers. If you write 0.03880 in scientific notation, it looks like this:
$0.03880=3.880 \times \frac{1}{100}$

Because $\frac{1}{100}$ can be written as $10^{-2}$, the actual notation used is $3.880 \times 10^{-2}$. Now it is clear that 0.03880 has 4 significant figures. The zeros at the beginning of the number are not involved in showing how precise the measurement was.

When you start doing calculations, you may have a problem if one value was measured much more precisely than another. Suppose a developer wants to buy two adjacent properties, belonging to neighbors Jack and Sam. Jack is a very organized person who has kept all documents about his property. He reports that the area of his land is 8.35 acres. Sam can't find his papers anywhere, but he remembers that he has about 10 acres of land. It would not make much sense to say that buying both properties would give the developer exactly 18.35 acres of land. Sam's figure is only correct to the nearest whole acre. The best we can do when adding or subtracting is to use the lowest place value that the numbers have in common. We report the total to the nearest whole acre, or 18 acres. If Sam had said that he has 10.1 acres of land, we would have our information correct to the nearest tenth of an acre. In that case we would report the total as 18.5 acres $(10.1+8.35=18.45$, which is 18.5 when rounded to the nearest tenth).

When you are multiplying or dividing, keep as many significant figures as practical during your calculations to avoid rounding errors. However, the final result of multiplication and division can have only as many significant figures as the number with the least amount of significant figures that you used as a basis for your calculations. For example: $16.54 \div 19.00 \times 2.7=2.4$ Both 16.54 and 19.00 have four significant figures, but 2.7 only has two. The final result must be rounded off to two significant figures.

Optional: When dealing with logarithms, which are really exponents, you need to consider how logarithms work with scientific notation. The rules for logarithms say that $\log (a b)=\log a+\log$ b. That means that $\log \left(5.21 \times 10^{6}\right)=\log 5.21+\log 10^{6}$. The $\log$ of $10^{6}$ is exactly 6 , or 6.00000000000.... The log of 5.21 is .7168 ..., which we should round to three significant figures just like 5.21. Then use the rule for addition to add the two logs, which gives 6.717. It looks like this has 4 significant figures, but the 6 is really the exponent of the original 10. Going the other way, starting with a log, we look at how many numbers there are after the decimal point. If the log of some number is given as -5.9348 , we find the number by raising 10 to that power:
$10^{-5.9348}=10^{(-5+-0.9348)}=10^{-5} \times 10^{-0.9348}$
$10^{-0.9348}$ is $0.116198 \ldots$, which we should round to four significant figures to match -0.9348 . The first part of the given logarithm, -5 , is an exact exponent so we don't need to count that. The number we need to find is $0.1162 \times 10^{-5}$, or $1.162 \times 10^{-6}$. For logarithms, only count the numbers after the decimal point as significant digits.

## Accuracy, Precision, and Percentage Error

In science, accuracy refers to how close your measurement is to the true value, which may be a generally accepted result.

If you work carefully and measure everything correctly, you can do the same experiment multiple times and get results that are very close to each other. Precision is the closeness of repeated measurements made in the same way. Even if your results are very precise they may not be accurate. For example, scientific scales are sensitive instruments that should be calibrated. If the calibration is off, your results will be wrong even if your measurements are precise. Some students do not know how to measure the level of a liquid in a cylinder or beaker. Make sure that you take such measurements at eye level, and read the value at the bottom of a concave meniscus (most liquids), or at the top of a convex meniscus (mercury).

To determine how accurate a result really is, you should compute the percentage error. The error should be a percentage of whatever the true or accepted value is, so take the difference between that and your own result, and see what percent of the correct value that difference is:
$\frac{\mid \text { Your measurement - true value } \mid}{\text { true value }}$, which is the same as $\frac{\text { absolute value of error }}{\text { true value }}$
The result will hopefully be a small decimal number, which is then multiplied by 100 to convert it to a percentage. For some experiments your error may be more than $100 \%$.

## Percent Composition

In your basic chemistry course, percent composition refers to percent by mass. So, if a sample contains $50 \%$ carbon, then half of the mass of the sample is carbon. One hundred grams of the sample would contain 50 grams of carbon.

To determine the percent composition of a compound if the molecular formula or formula unit is known, first find the weight of 1 mole of the compound. Then find the weight of the individual components. Divide the weight of each component by the total weight to get the percentage by mass of that component.
$\mathrm{NaCl}: 22.99+35.45=58.44$ grams per mole
Na: 22.99 grams per mole. $\frac{22.99 \mathrm{~g} / \mathrm{mole}}{58.44 \mathrm{~g} / \mathrm{mole}}=0.3934 \approx 39 \%$
Cl: 35.45 grams per mole. $\frac{35.45 \mathrm{~g} / \text { mole }}{58.44 \mathrm{~g} / \mathrm{mole}}=0.6066 \approx 61 \%$
Make sure your percentages add up to $100 \%$ !

You will be expected to be able find the empirical formula if the percent composition is known. The empirical formula gives the lowest possible ratio of atoms of each element in the compound. Empirical in this case means experimental, since the percent composition is determined by decomposing the compound into its elements and measuring the quantities obtained. The empirical formula may or may not be the same as the actual molecular formula.

If the total mass of the sample is not given, you can arbitrarily use 100 grams to make your calculations easier. For example, if you are told that a sample contains $39.34 \% \mathrm{Na}$ and $60.66 \%$ Cl , you know that 100 grams of such a sample would contain 39.34 grams of Na and 60.66 grams of Cl . Once you have the mass of each element in the sample, you can convert those masses to moles. This allows you to determine the ratios of the different atoms in each molecule or formula unit of the sample.
39.34 grams Na $\frac{1 \mathrm{~mole}}{22.99 \mathrm{~g}} \approx 1.7179$ moles
60.66 grams Cl $\times \frac{1 \text { mole }}{35.45 \mathrm{~g}} \approx 1.7111$ moles

Although the numbers are not exact, we know that there has to be a ratio of whole numbers. If that ratio isn't obvious, divide everything by the smallest number. That will give you 1 , and some numbers that are close to whole numbers. In this case there is one Na for every Cl , and the empirical formula is NaCl .

## Properties of Matter

The mass of a substance is the amount of matter that is present. That is not quite the same as the weight, which is the force of gravity that pulls on a mass. The volume refers to the amount of space occupied by a substance.

Properties like volume, mass, and energy content of a substance are extensive properties that depend on the amount of matter present. Intensive properties like boiling point, density and conductivity can be used to identify the type of substance.

Unlike a physical change, a chemical change involves a change in identity of a substance. Melting is a physical change, while burning results in chemical changes. The substances that change as a result of a chemical reaction are called the reactants. The new substances are called the products of the reaction.

Natural states of matter are solid (densely packed particles), liquid (particles slide past each other), gas (particles are far apart), and plasma (particles become electrically charged). Plasma is found in stars and in fluorescent light bulbs.

The ancient Greeks wondered if matter could be divided up infinitely, or if there was a smallest particle. We now know that all matter is made up of particles that are either molecules or atoms. Molecules are a combination of two or more atoms.

Pure substances have particles that are all the same. Pure substances can be elements, which means that they cannot be decomposed chemically into different substances. All of the atoms in an element are the same. Gold is an element, and all of its particles are gold atoms. Oxygen is an element, and all of its particles are oxygen molecules that are each composed of two oxygen atoms.

Compounds are pure substances made up of more than one kind of atom. They can be decomposed into elements. Pure water is a compound. All of its molecules are the same, but each water molecule contains one oxygen atom and two hydrogen atoms. Water can be decomposed into oxygen gas and hydrogen gas. Table salt, sodium chloride, is also a compound.

Pure substances are not commonly found in nature. Most matter is a mixture of different substances. Mixtures can be homogeneous, which means that the composition is uniform because the substances are mixed at the molecular level. Homogeneous mixtures are also
called solutions. The water that comes out of your tap is a mixture of water molecules and particles of minerals, chloramine, fluoride and other substances. These substances break up into individual atoms and molecules as they dissolve in the water to form a solution. Solutions may be gases or solids. Air is a solution, and so is brass (copper and zinc mixture). Heterogeneous mixtures such as blood or milk may be distinguished from homogeneous mixtures by examining them under a microscope. Red blood cells, white blood cells, or fat globules seen under the microscope show that the composition is not uniform.

A colloid is a heterogeneous mixture with very small "clumps" that don't settle out when the mixture is left undisturbed. Homogenized milk is a colloid. A colloid may look like a solution, but a beam of light shined through it is reflected and scattered by the small bits. This is called the Tyndall effect.

## The Atom

| Name | Location | Charge | Mass (atomic mass units) |
| :--- | :--- | :---: | :---: |
| Proton | Nucleus | +1 | 1.00728 |
| Neutron | Nucleus | 0 | 1.00866 |
| Electron | Around the nucleus | -1 | 0.00055 |

The mass of an atom is less than what would be expected by adding up the mass of the individual particles that make up the atom. This is called the mass deficiency. Some of the mass is lost as energy ( $\mathrm{E}=\mathrm{mc}^{2}$ ) when the atom is formed.

An atomic mass unit (amu) is defined as one twelfth of the mass of an atom of carbon-12, which contains 6 protons, 6 neutrons, and 6 electrons. For your chemistry calculations, use 1 amu as the mass of a proton or a neutron, and ignore the very tiny mass contributed by the electrons. $1 \mathrm{amu} \approx 1.66 \times 10^{-24}$ grams

## Thomson Model

Thomson discovered the electron. Plum Pudding Model: negatively charged electrons are distributed inside a positively charged sphere to create a neutral atom. Not correct.

## Rutherford Model

Rutherford discovered the nucleus. The nucleus contains most of the mass but is extremely tiny compared to the size of the atom. The electrons are located somewhere in the relatively enormous space around the nucleus

## Bohr Model

Rutherford's student Niels Bohr proposed that the electrons orbit the nucleus like planets around the sun. Only certain orbits with fixed energy levels are allowed. Lower energy orbits are closer to the nucleus.

## Quantum Model

When light of a sufficient frequency (visible or ultraviolet) shines on a metal, electrons are emitted. This is called the photoelectric effect. A quantum is the minimum quantity of energy that can be lost or gained by an atom. Photons of light must have a minimum amount of energy (a minimum frequency) to change the atom's energy state. This observation helped scientists to develop the quantum model of the atom. Experiments showed that electrons are like both waves and particles. Schrodinger's wave equations explain that electrons must exist in specific orbitals defined by quantum numbers. The orbitals are not simple rings and can have very complex shapes.

## Molar Mass

By definition, a mole of carbon-12 atoms has a mass of exactly 12 g , just as one carbon- 12 atom is defined to be exactly 12 amu . As a result of this definition, a mole of carbon-12 contains $6.022 \times 10^{23}$ atoms (Avogadro's Number). A mole is a specific number just like a dozen. A mole of oxygen contains $6.022 \times 10^{23}$ molecules of oxygen. A mole of eggs would be $6.022 \times 10^{23}$ eggs.

Molar mass is expressed in grams per mole. Because of our convenient definitions of molar mass and atomic mass, we can use the same number for both. Just look for it in the periodic table.

## Electromagnetic Radiation

Visible light is a small part of the electromagnetic spectrum. Electromagnetic waves travel at the speed of light (c). Their frequency and wavelength can be calculated from the equation $\mathrm{c}=\lambda \nu$ where $\lambda$ (the Greek letter I) is the wavelength, and $v$ (the Greek letter n ) is the number of waves per second (the frequency). A frequency of 1 Hertz means 1 wave per second.

Radio waves have a very long wavelength, and $x$-rays have a very short wavelength. When the wavelength is short the frequency is high, and the radiation is high in energy according to the equation $\mathrm{E}=\mathrm{h} \nu$. Here E is the energy and h is Planck's constant, $6.626 \times 10^{-34}$ Joule sec. (1 Joule $=1 \mathrm{~kg} \cdot \mathrm{~m}^{2} / \mathrm{sec}^{2}$ ). You can combine the two equations $\mathrm{c}=\lambda \nu$ and $\mathrm{E}=\mathrm{h} \nu$ to get $\mathrm{E}=\mathrm{h} \cdot \frac{\mathrm{c}}{\lambda}$.

## The Nucleus

The atomic number is the number of protons in the nucleus, which determines the element. Isotopes are atoms of a particular element that differ in the number of neutrons they contain. The mass number is the total number of protons and neutrons in the nucleus of an atom. Isotopes may be identified by their name and mass number, such as carbon-14. Another notation for isotopes includes both the mass number and the atomic number: ${ }_{6}^{14} \mathrm{C}$. The word nuclide was originally intended to refer to the nucleus, but now refers to the whole atom.

Even though positive charges repel each other, many protons can exist together in the nucleus. The strong nuclear force is an attractive force that acts between the particles in the nucleus and keeps it from falling apart. This force acts over such a short distance that larger nuclei need progressively more neutrons to be stable. Nuclei with too many protons compared to neutrons, or too many neutrons compared to protons are not stable. Also, very heavy nuclei are not stable. The transuranium elements (past Uranium, element 92) are not found in nature and must be made in the laboratory. They are unstable and decay radioactively.

Atoms can lose neutrons and protons through $\alpha$-decay. The nucleus emits an alpha particle $\left({ }_{2}^{4} \mathrm{He}\right)$, which consists of 2 protons and 2 neutrons (an alpha particle has the same composition as the nucleus of a Helium atom). Because protons are lost, the atom is no longer the same element after $\alpha$-decay. Although this is radioactive decay, the relatively heavy alpha particles are not extremely dangerous because they do not travel far and do not penetrate human skin.

Atoms can lose a neutron or a proton through $\beta$-decay. A neutron can split into a proton and an electron. A proton can split into a neutron and a positively charged anti-electron which is called a positron. The electron or positron leaves the nucleus as $\beta$ radiation: $\left({ }_{-1}^{0} \beta\right)$ or $\left({ }_{+}^{0} \beta\right)$. Some metal shielding is required to protect humans from large numbers of these $\beta$ particles.

A nucleus decays because the new nucleus will be more stable than the old one. This means that the new nucleus will be at a lower energy level, so energy will be lost. Gamma rays ( $\gamma$ rays) are a type of high energy radiation produced during nuclear decay. They can penetrate into our bodies and thick lead shielding is required to prevent tissue damage from these rays.

Electron capture allows a nucleus to become more stable by taking one of its own "inner", lower-energy, electrons and combining it with a proton to create a neutron $\left({ }_{-1}^{0} \mathrm{e}+{ }_{+1}^{1} \mathrm{p} \rightarrow{ }_{0}^{1} \mathrm{n}\right)$.

## Half-Life

Although it is impossible to determine when an individual atom with an unstable nucleus will decay, the probability can be determined. When you have a very large number of atoms of a particular kind, you can predict how long it will take for half of them to decay. This time is called the half-life. The radioactive isotope carbon-14 has a half-life of about 5,700 years, and it is used to date fossils up to about 75,000 years old.

## Nuclear Energy

A Uranium-235 atom that gains a neutron can split into lighter elements (fission), with the release of additional neutrons that cause other uranium atoms to split and release yet more neutrons. Together all the lighter fragments have less mass than the original uranium atoms, and the missing mass is released as energy according to the equation $E=\mathrm{mc}^{2}$. The nuclear chain reaction may cause a massive explosion, or it can be controlled inside a nuclear reactor to produce useful energy.

Medium-size nuclei like those of nickel and iron are the most stable, so fission of large nuclei or fusion of lighter nuclei releases energy. Four hydrogen nuclei (protons) can combine to form a helium nucleus and two positrons, which generates a large amount of energy: $4{ }_{1}^{1} \mathrm{H} \rightarrow{ }_{2}^{4} \mathrm{He}+2$ ${ }_{+1}^{0} \beta$. This fusion reaction is what powers the sun. Unfortunately, it takes large amounts of energy to bring nuclei together closely enough that they will combine. Scientists are attempting to create a practical way to use fusion to meet the world's energy needs.

## Electron Configurations

The Schrödinger Wave Equation provides the quantum numbers that describe the orbitals occupied by electrons in the atom.
n : principal quantum number. ( $1,2,3$, etc.) Describes the size of the orbital.
$\ell$ : Angular momentum quantum number. ( $0,1,2, \ldots, n-1$ ). Describes the shape of the orbital. 0 is an s orbital, 1 is a p orbital, 2 is a d orbital, and 3 is an $f$ orbital.
m : Magnetic quantum number. $(-\ell, \ldots, 0, \ldots \ell)$. Determines the way the orbital is oriented in space, e.g. $p_{x}, p_{y}, p_{z}$. The three different $p$ orbitals on each level have magnetic quantum numbers $-1,0$ and 1 .
s: Spin quantum number. $(+1 / 2$ or $-1 / 2)$. Denotes the spin of the electron. Each orbital holds 2 electrons of opposite spin.

| n | $\ell$ | Possible m values | $s$ values | Sublevel | electrons | Total electrons |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 0 | 0 | $+1 / 2,-1 / 2$ | 1s | 2 | 2 |
| 2 | 0 | 0 | $+1 / 2,-1 / 2$ | 2s | 2 | 8 |
|  | 1 | -1, 0,1 | $+1 / 2,-1 / 2$ | 2p | 6 |  |
| 3 | 0 | 0 | $+1 / 2,-1 / 2$ | 3s | 2 | 18 |
|  | 1 | -1,0,1 | $+1 / 2,-1 / 2$ | 3 p | 6 |  |
|  | 2 | $-2,-1,0,1,2$ | $+1 / 2,-1 / 2$ | 3d | 10 |  |
| 4 | 0 | 0 | $+1 / 2,-1 / 2$ | 4s | 2 | 32 |
|  | 1 | -1, 0,1 | $+1 / 2,-1 / 2$ | 4p | 6 |  |
|  | 2 | -2, -1, 0, 1, 2 | $+1 / 2,-1 / 2$ | 4d | 10 |  |
|  | 3 | $-3,-2,-1,0,1,2,3$ | $+1 / 2,-1 / 2$ | 4f | 14 |  |
| 5 | 0 | 0 | $+1 / 2,-1 / 2$ | 5 s | 2 | 50 |
|  | 1 | -1, 0,1 | $+1 / 2,-1 / 2$ | 5p | 6 |  |
|  | 2 | $-2,-1,0,1,2$ | $+1 / 2,-1 / 2$ | 5d | 10 |  |
|  | 3 | $-3,-2,-1,0,1,2,3$ | $+1 / 2,-1 / 2$ | $5 f$ | 14 |  |
|  | 4 | not needed to fill periodic table |  |  |  |  |
| 6 | 0 | 0 | $+1 / 2,-1 / 2$ | 6 s | 2 | 72 |
|  | 1 | -1, 0,1 | $+1 / 2,-1 / 2$ | 6 p | 6 |  |
|  | 2 | $-2,-1,0,1,2$ | $+1 / 2,-1 / 2$ | 6d | 10 |  |
|  | 4 | not needed to fill periodic table |  |  |  |  |
|  | 5 | not needed to fill periodic table |  |  |  |  |
| 7 | 0 | 0 | $+1 / 2,-1 / 2$ | 7s | 2 | 98 |
|  | 1 | -1, 0, 1 | $+1 / 2,-1 / 2$ | 7d | 6 |  |

The number of orbitals for each main energy level is $n^{2}$ ，and since each orbital can hold 2 electrons，the maximum number of electrons in each main energy level is $2 n^{2}$ ．

Aufbau Principle：This is the＂up－building＂principle．Each electron that is added to an atom enters the lowest－energy orbital available．

Pauli Exclusion Principle：Each electron in an atom has a unique set of 4 quantum numbers．
Hund＇s Rule：Orbitals of equal energy，like the three p－orbitals，are each occupied by an electron of the same spin first．After that，electrons of opposite spins are added．

个 — $\uparrow$＿ 1 ＿One electron in each orbital；all electrons have the same spin
ヘ $\downarrow$ ヘ— 1 — The next electron has opposite spin
$\uparrow \downarrow$ ヘ $\downarrow$ ヘ $\downarrow$ All three $p$－orbitals are filled

The different energy levels fill with electrons in a confusing order．Look at the periodic table to see how it works（next section）．

## The Periodic Table

Hydrogen has one electron in the 1s orbital. Each successive element has one more electron. Helium has 2 electrons in the 1 s orbital. Now the orbital is full. The next two elements represent the filling of the $2 s$ level, and so on. There are some glitches in the orderly filling of levels, especially as you go further down the periodic table.


Columns (groups) of the periodic table contain elements with similar electron configurations, which causes them to have similar properties.

The elements of group 1, except hydrogen, are called the alkali metals. Group 2 contains the alkaline earth metals. The "d block" elements are the transition metals (shown in blue above). Lanthanum and the next 14 elements are called the Lanthanides, and the Actinides are Actinium and the 14 elements after it. The halogens are in the second to last group, and the last column contains the noble gases.

The noble gases have the most stable electron configurations. The atoms of elements on the left-hand side of the periodic table can achieve a noble gas configuration by losing electrons, while atoms of elements on the right-hand side can do so by gaining one or more electrons.

## Periodic Trends

Coulomb's Law:
$F=k \frac{q_{1} q_{2}}{r^{2}}$
This says that electrical force is proportional to the charges of two objects ( $q_{1}$ and $q_{2}$ ), and inversely proportional to the distance between them.

As you move across a row of the periodic table from left to right, the atoms get smaller. This is due to electron shielding. The inner electrons shield the outer electrons from the positive charge of the nucleus. Across the row, the positive charge of the nucleus increases while shielding effect from the inner electrons stays the same. This causes atoms to hold on to their existing electrons more tightly. The atomic radius tends to decrease from left to right. As you move down a column, the atoms have more electron shells so they are larger. The outermost electrons in larger atoms are held less tightly because they are shielded from the positive charge of the nucleus by multiple electron shells.

The result of both electron shielding and a greater stability of a noble gas configuration is that atoms in the top right corner of the periodic table, like oxygen and fluorine, tend to gain electrons and hold on to their existing electrons more tightly, while atoms in the bottom left corner lose their outer electrons most readily.

More loosely held outer electrons give elements the properties of metal. Most elements are metals. Except for hydrogen, the non-metals are found in the top right corner of the periodic table. The elements with properties in between metals and non-metals are called metalloids.

The ionization energy (electron binding energy) is the energy required to remove an electron from a neutral atom. It always takes energy to remove an electron, even for elements like sodium and potassium that lose their electrons readily in chemical reactions. Ionization energy is a measure of how tightly an atom holds its outer electrons. As you might expect, ionization energy increases across a row and decreases down a column. The second ionization energy of an atom is the energy required to remove the second electron from what is now a positively charged ion. The second ionization energy is larger than the first.

Electronegativity is a measure of the ability of an atom within a molecule to attract extra electrons toward itself. Electronegativity increases from left to right across the rows of the periodic table, and decreases as you go down a column. Fluorine is the most electronegative element.
[Electron affinity (optional) is the amount of energy released when an electron is added to a neutral atom in the gas state to form a negative ion. Sometimes energy is required to form the negative ion. Periodic trends for electron affinity are not clear-cut, and Chlorine has the highest electron affinity, which means it has the largest release of energy when it gains an electron.]

A high energy photon, such as an x-ray or ultraviolet photon, can knock an electron out of an atom. If we know the energy of the photon, and the kinetic (motion) energy of the ejected electron, we can calculate how much of the photon's energy was used to remove the electron from the atom. This is the electron binding energy, also called the ionization energy. The photoelectron spectrum for a particular atom shows the relative number of electrons in the atom that have a particular electron binding energy. The electrons at the higher energy levels are further away from the nucleus and easier to remove. Their binding energy is lower. You may be asked to identify an atom based on its photoelectron spectrum.

## Bonding

An element is a substance composed of only one kind of atom. Two or more atoms may bond together to form a molecule. (Note that a molecule is sometimes defined as the smallest particle that still retains the properties of a substance, which leads some sources to call the smallest particles of noble gases molecules even though they consist of single atoms). A molecule may contain only atoms of one kind, for example $\mathrm{O}_{2}$, or atoms of different kinds like $\mathrm{H}_{2} \mathrm{O}$. Molecules form when atoms share electrons to create covalent bonds. The sharing of electrons may be unequal, which creates a polar covalent bond.

Sometimes electrons are transferred completely from one atom to another. Both atoms become ions.

Cation: positive ion (lost 1 or more electrons) like $\mathrm{Na}^{+}$. Cations are named like regular atoms, with the name "ion" added. $\mathrm{Na}^{+}$is the sodium ion.

Anion: negative ion (gained 1 or more electrons) like $\mathrm{O}^{2-}$. Anions are named by changing the ending of the element name to "ide". $\mathrm{O}^{2-}$ is the oxide ion.

Notice that a single positive or negative charge is indicated by a + or - sign, while multiple charges are shown by a number followed by + or - .

Cations and anions stick together to form crystals. This is ionic bonding. An example is table salt, NaCl . Salt is composed of crystals rather than individual molecules, so NaCl is not a molecule. Instead, it is a formula unit that indicates the ratio of sodium ions to chloride ions.

Crystals can also be formed when atoms share electrons. Diamonds are crystals composed of carbon atoms that are sharing their electrons in covalent bonds. The atoms of a metal readily share their electrons among themselves so that electrons can move from atom to atom (metallic bonding).

The electrons that participate in bonding are called valence electrons. These are the atom's "outer" electrons, usually the $s$ and $p$ electrons in the highest occupied energy level.
Transition metals may have additional d valence electrons. Atoms tend to gain or lose electrons in such a way that they end up with the same electron arrangement as the closest noble gas. This occurs because noble gas configurations are the most stable. Transition metals do not follow this simple rule and usually form more than one kind of ion. Configurations that result in an exactly half-filled or a completely filled subshell are more stable.

## Covalent vs Ionic Compounds

Your course will likely ask you to classify bonds as covalent or ionic, and various compounds as covalent (molecular) compounds or ionic compounds. You should understand that there is a range of unequal electron distribution in various bonds, so that there is not a sharp distinction between a covalent and a polar covalent bond, or between a highly polar covalent bond and an ionic bond. The character of a particular bond can be calculated from the difference in electronegativity of the atoms involved, with your textbook supplying some arbitrary values as lines between covalent, polar covalent, and ionic. In general, if a compound contains only nonmetals you should consider it covalent, and if it contains a metal atom the compound is ionic. Acids are normally covalent compounds that react to varying degrees with water to form ions. If no separate "acid" category is available, classify them as covalent. Ionic compounds may contain complex ions that have covalent bonds within them. For example, the ionic compound $\mathrm{Na}_{2} \mathrm{SO}_{4}$ contains the sulfate ion, $\mathrm{SO}_{4}{ }^{2-}$, which has covalent bonds between the sulfur and the oxygen atoms.

## Naming Ionic Compounds

Many ionic compounds contain only two kinds of atoms. These binary ionic compounds are named using the name of the cation (the element name), followed by the name of the anion (the element name with the ending changed to "ide"). The easiest way to remember this is to think of table salt: NaCl is sodium chloride. When the charges on the ions are predictable, we can infer the formula and it is not necessary to indicate how many atoms of each element are present. For example, magnesium chloride will have one magnesium ion $\left(\mathrm{Mg}^{2+}\right)$, and two chloride ions ( $\mathrm{Cl}^{-}$) to balance the charges. The formula unit of magnesium chloride is $\mathrm{MgCl}_{2}$.

The charges on ions are not always predictable, because some elements can form more than one kind of ion. In that case, Roman numerals following the cation indicate the ion's charge. Roman numerals are used for all of the transition metals except Ag , which is almost always $1+$. Since Zn and Cd almost always have a $2+$ charge their Roman numerals are sometimes omitted even though they are transition metals. Sn (Tin), Pb (Lead), and Bi (Bismuth) are not transition metals but they still form more than one kind of ion, so use Roman numerals for these metals too.

Examples: Iron(III) oxide, $\mathrm{Fe}_{2} \mathrm{O}_{3}$
Iron(II) oxide, FeO

$$
\begin{aligned}
& \mathrm{Tin}(\mathrm{IV}) \text { chloride, } \mathrm{SnCl}_{4} \\
& \mathrm{Tin}(\mathrm{II}) \text { chloride, } \mathrm{SnCl}_{2}
\end{aligned}
$$

Ionic compounds may contain polyatomic ions like acetate $\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$.
The most common polyatomic oxyanion of each kind is given a name ending in "ate":

| Sulfate $\mathrm{SO}_{4}{ }^{2-}$ | Nitrate $\mathrm{NO}_{3}{ }^{-}$ |
| :--- | :--- |
| Phosphate $\mathrm{PO}_{4}^{3-}$ | Carbonate $\mathrm{CO}_{3}{ }^{2-}$ |

When one less oxygen atom is present the ending "ite" is used, and if one less than that is present we use the prefix "hypo". If there is one more oxygen atom than what is present in the most common oxyanion, the prefix "per" is added:

| Prefix | Suffix | Example |
| :--- | :--- | :--- |
| Hypo | ite | Hypochlorite $\mathrm{ClO}^{-}$ |
|  | ite | Chlorite $\mathrm{ClO}_{2}^{-}$ |
|  | ate | Chlorate $\mathrm{ClO}_{3}{ }^{-}$ |
| Per | ate | Perchlorate $\mathrm{ClO}_{4}{ }^{-}$ |

Bleach is a solution containing sodium hypochlorite, NaClO . Sodium chlorite helps disinfect your drinking water. Sodium chlorate bleaches paper to make it nice and white. Potassium chlorate is a disinfectant that can also be used as an ingredient in explosives and firecrackers. Potassium perchlorate, $\mathrm{KClO}_{4}$, is used in fireworks and sparklers.

Manganate, $\mathrm{MnO}_{4}{ }^{2-}$, and permanganate, $\mathrm{MnO}_{4}^{-}$, have the same number of oxygen atoms but different charges. In this case the "per" prefix is used because the manganese atom is relatively more "oxidized", which is a term that you will learn about later in your course.

## Important lons

| $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | Acetate |
| :--- | :--- |
| $\mathrm{CN}^{-}$ | Cyanide |
| $\mathrm{CO}_{3}{ }^{2-}$ | Carbonate |
| $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ | Oxalate |
| $\mathrm{ClO}^{-}$ | Hypochlorite |
| $\mathrm{ClO}_{2}{ }^{-}$ | Chlorite |
| $\mathrm{ClO}_{3}{ }^{-}$ | Chlorate |
| $\mathrm{ClO}_{4}^{-}$ | Perchlorate |
| $\mathrm{CrO}_{4}{ }^{2-}$ | Chromate |


| $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ | Dichromate |
| :--- | :--- |
| $\mathrm{HCO}_{3}{ }^{-}$ | Hydrogen Carbonate |
| $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$ | Dihydrogen Phosphate |
| $\mathrm{MnO}_{4}^{-}$ | Permanganate |
| $\mathrm{NH}_{4}^{+}$ | Ammonium |
| $\mathrm{NO}_{2}{ }^{-}$ | Nitrite |
| $\mathrm{NO}_{3}{ }^{-}$ | Nitrate |
| $\mathrm{OH}^{-}$ | Hydroxide |
| $\mathrm{PO}_{4}{ }^{3-}$ | Phosphate |
| $\mathrm{SO}_{4}{ }^{2-}$ | Sulfate |
| $\mathrm{SO}_{3}{ }^{2-}$ | Sulfite |
| $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ | Thiosulfate |

## Naming Binary Covalent Compounds

Binary covalent compounds contain two kinds of atoms that are covalently bonded. The best example to remember is $\mathrm{CO}_{2}$, carbon dioxide.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| :---: | :--- | :--- | ---: | ---: | ---: | ---: | ---: | ---: | :--- |
| mono | di | tri | tetra | penta | hexa | hepta | octa | nona | deca |

- Write the name of the first element in the formula.
- The second element is named as an anion: "-ide", e.g. hydrogen $\rightarrow$ hydride, carbon $\rightarrow$ carbide
- Use the prefixes shown above to indicate the number of atoms.
- Mono- is never used for the first element.
- When there are two vowels next to each other drop the a or the o (but never the i) at the end of the prefix. Write nonoxide instead of nonaoxide. Similarly, write monoxide and tetroxide.

Using these rules, water is called dihydrogen monoxide. Hydrogen sulfide, $\mathrm{H}_{2} \mathrm{~S}$, is a common
compound that could technically be called dihydrogen monosulfide, but no one bothers.

Naming Practice

1. NaBr
2. $\mathrm{CaSO}_{4}$
3. $\mathrm{K}_{2} \mathrm{~S}$
4. $\mathrm{Ni}\left(\mathrm{NO}_{3}\right)_{2}$
5. $\mathrm{Mg}_{3} \mathrm{~N}_{2}$
6. $\mathrm{Fe}_{2}\left(\mathrm{CO}_{3}\right)_{3}$ $\qquad$
7. $\mathrm{Cr}_{2} \mathrm{O}_{3}$ $\qquad$
8. $\mathrm{Ti}\left(\mathrm{ClO}_{4}\right)_{4}$
9. $\mathrm{AlCl}_{3}$ $\qquad$
10. $\mathrm{PbC}_{2} \mathrm{O}_{4}$ $\qquad$
11. CO
12. $\mathrm{CO}_{2}$ $\qquad$
13. $S_{2} F_{6}$ $\qquad$
14. $\mathrm{P}_{4} \mathrm{O}_{10}$ $\qquad$
15. $\mathrm{N}_{2} \mathrm{O}_{4}$ $\qquad$
16. $\mathrm{NCl}_{3}$ $\qquad$
17. $\mathrm{PBr}_{5}$ $\qquad$
18. $\mathrm{SiS}_{2}$ $\qquad$
19. $\mathrm{N}_{2} \mathrm{~F}_{4}$
20. $\mathrm{SeBr}_{2}$
$\qquad$
$\qquad$
21. $\mathrm{FeCl}_{2}$ $\qquad$
22. $\mathrm{Al}\left(\mathrm{NO}_{3}\right)_{3}$ $\qquad$
23. $\mathrm{Fe}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ $\qquad$
24. $\mathrm{Cd}\left(\mathrm{MnO}_{4}\right)_{2}$ $\qquad$
25. $\mathrm{Mg}\left(\mathrm{PO}_{4}\right)_{2}$ $\qquad$
26. $\mathrm{N}_{2} \mathrm{H}_{4}$ $\qquad$
27. SiC
28. $\mathrm{NH}_{4} \mathrm{Cl}$ $\qquad$
29. $\mathrm{PbO}_{2}$
30. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$

## Answers

1. sodium bromide
2. calcium sulfate
3. potassium sulfide
4. nickel(II) nitrate
5. magnesium nitride
6. iron(III) carbonate
7. chromium(III) oxide
8. titanium(IV) perchlorate
9. aluminum chloride
10. lead(II) oxalate
11. carbon monoxide
12. carbon dioxide
13. disulfur hexafluoride
14. tetraphosphorus decoxide
15. dinitrogen tetroxide
16. nitrogen trichloride
17. phosphorus pentabromide
18. silicon disulfide
19. dinitrogen tetrafluoride
20. selenium dibromide
21. iron(II) chloride
22. aluminum nitrate
23. iron(II) phosphate
24. cadmium permanganate
25. magnesium phosphate
26. dinitrogen tetrahydride
27. silicon carbide
28. ammonium Chloride
29. lead(IV) oxide
30. sodium thiosulfate

## Write the Formula

1. sodium nitrate
2. aluminum sulfate
3. magnesium carbonate
4. ammonium dichromate
5. potassium permanganate
6. $\mathrm{NaNO}_{3}$
7. $\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$
8. $\mathrm{MgCO}_{3}$
9. $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$
10. $\mathrm{KMnO}_{4}$

## More Naming

## Acids

A simple definition of an acid is that it is a compound that releases hydrogen ions when dissolved in water.

Binary acids consist of hydrogen and one other element. An example of a binary acid would be HCl , hydrochloric acid. To name binary acids, start with hydro-, followed by the name of the other element with its ending changed to -ic. HF is hydrofluoric acid, which is a weak acid. Hydrogen sulfide, $\mathrm{H}_{2} \mathrm{~S}$, is a weak acid when dissolved in water. To name it as an acid, call it hydrosulfuric acid.

## Optional

A negatively charged ion that contains oxygen is called an oxyanion. We have already seen the names of some common oxyanions. For hydrogen-containing oxyanions, add hydrogen or dihydrogen depending on the number of hydrogen atoms. Examples:
$\mathrm{HCO}_{3}{ }^{-}$hydrogen carbonate
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$dihydrogen phosphate.
Oxyacids contain oxygen atoms. The prefix hydro is not used for oxyacids. Only the names of the oxyanions are used to construct a name for the acid. If the oxyanion ends in -ate, its ending is changed to -ic. If the oxyanion ends in -ite, the ending is changed to -ous.

| Acid | Oxyanion | Anion Name | Acid Name |
| :--- | :--- | :--- | :--- |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $\mathrm{SO}_{4}{ }^{2-}$ | Sulfate | Sulfuric acid |
| $\mathrm{H}_{2} \mathrm{SO}_{3}$ | $\mathrm{SO}_{3}{ }^{2-}$ | Sulfite | Sulfurous acid |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | Acetate | Acetic acid |
| $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $\mathrm{PO}_{4}{ }^{3-}$ | Phosphate | Phosphoric acid |
| $\mathrm{HNO}_{2}$ | $\mathrm{NO}_{2}{ }^{-}$ | Nitrite | Nitrous acid |

## Covalent Bonding: Lewis Dot Diagrams

1. If C is present it is usually in the center. H is very unlikely to be in the center because it normally only forms one bond. Many compounds have a single atom of one kind in the center, surrounded by several atoms of a second kind. If it is not obvious which atom should be in the center, choose the least electronegative atom.
2. Count how many valence electrons you have. Be careful if you have an ion - account for the charge!
3. Determine how many valence electrons you need. Most atoms prefer 8 valence electrons. Hydrogen wants 2, Beryllium 4, and Boron 6 or 8. Atoms that have d subshells can sometimes accommodate more than 8 , such as $\mathrm{P}, \mathrm{S}, \mathrm{Cl}, \mathrm{I}$ and Xe ; when you see these larger atoms consider that they want at least 8 valence electrons.
4. Calculate the difference between what you have and what you need. "Create" the extra electrons by sharing: Each bond gives you two extra electrons. For example, if you are short 8 electrons, place 4 bonds in your diagram.
5. Add additional bonds if needed to connect all the atoms. The central atom may have more than 8 valence electrons, which may include non-bonding electron pairs.
6. Place remaining electrons around atoms to make sure each atom is happy with what it has. Oxygen can form two bonds, but one bond is fine so long as there are 8 electrons around the oxygen atom.
7. If you drew the diagram for an ion, place square parentheses around it and indicate the charge in the upper right corner outside the parentheses e.g. [ ... ] $]^{2-}$.
8. Many molecules and ions have some double bonds that result in more than one possible Lewis dot structure. The true structure of these molecules or ions is intermediate between the possible Lewis structures, so you need to draw all of the resonance (alternate) structures.

## Molecular Geometry

The carbon atom has 4 valence electrons ( $2 s^{2} 2 p^{2}$ ) so it forms four bonds. Once the bonds are made the 2 s orbital and the three 2 p orbitals are full. When one carbon bonds to four other atoms, for example in $\mathrm{CH}_{4}$, the four orbitals that hold the bonding electrons are all the same, so we call them hybrid orbitals. Since one s orbital and three p orbitals are used to create these hybrid orbitals, we call them $\mathrm{sp}^{3}$ hybrids. Other hybrid orbital configurations include sp and $\mathrm{sp}^{2}$.

The Valence Shell Electron Pair Repulsion theory (VSEPR), explains the observed geometry of molecules. The valence shell electron pairs spread out as much as possible. If there are nonbonding electron pairs, they spread out a little more since they are only attracted to one nucleus instead of two. This spreading out causes a slight compression of the other bond angles. If there are double or triple bonds the geometry is the same as if the bonds were single. Multiple bonds do take up a bit more space and cause a slight compression of the other bond angles.

The table below shows how non-bonding electron pairs affect molecular geometry.
When there are 5 electron pairs around the central atom, any non-bonding electron pairs occupy the equatorial (middle) position where the $120^{\circ}$ angles are located. This gives these non-bonding pairs more room, as the top and bottom angles are $90^{\circ}$.

If there are 6 electron pairs around the central atom they spread apart to form an octahedron. This is a perfectly symmetrical shape and all of the bond angles are the same, which means that it doesn't matter which position a non-bonding pair occupies. If there are two non-bonding pairs they will be on opposite sides to be as far apart as possible, and drawings usually show them at the top and the bottom.

| Electron pairs | Basic Shape | Bond Angles | 1 non-bonding pair | 2 non-bonding pairs | 3 nonbonding pairs |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | $\begin{gathered} \text { linear } \\ \mathrm{Cl}-\mathrm{Be}-\mathrm{Cl} \end{gathered}$ | $180^{\circ}$ |  |  |  |
| 3 | trigonal planar | $120^{\circ}$ |  |  |  |
| 4 | tetrahedral | $109.5^{\circ}$ | trigonal pyramidal | bent |  |
| 5 | trigonal bipyramidal | $\begin{aligned} & 90^{\circ} \\ & 120^{\circ} \end{aligned}$ | seesaw | t-shape | linear |
| 6 | octahedral | $90^{\circ}$ | square pyramidal | square planar |  |

## Sigma Bonds and Pi Bonds

Although there are exceptions, for the purpose of your course all single bonds are sigma ( $\sigma$ ) bonds. These bonds are formed by a "head-on" overlap of $s$ and/or $p$ orbitals. The $p_{x}, p_{y}$, and
$p_{z}$ orbitals are all at right angles to each other, so only one of them can point directly at the other atom to form a sigma bond. After the sigma bond has been made, if there is a second bond it will be a pi ( $\pi$ ) bond. This involves a "sideways" overlap of two $p$ orbitals that are at right angles to the sigma bond. If you draw a line between the nuclei of the atoms, the pi bond will be located in two regions - above and below this line. If there is a third bond it is made from a "sideways" overlap of the p-orbitals at right angles to those forming the second pi bond. Pi bonds are usually weaker than sigma bonds, meaning that it takes less energy to break them.

As an example, consider acetylene (ethyne), $\mathrm{C}_{2} \mathrm{H}_{2}$. This molecule has a triple bond between the two carbon atoms. The triple bond consists of one sigma and two pi bonds. According to the valence bond theory, the sigma $\mathrm{C}-\mathrm{H}$ bonds are formed from the joining of an s orbital of the hydrogen atom with an sp hybrid orbital of the carbon atom. The sigma $\mathrm{C}-\mathrm{C}$ bond is an overlapping of two sp hybrid orbitals. The two additional $\mathrm{C}-\mathrm{C}$ bonds are pi bonds, formed by the overlap of $p$ orbitals.

## Infrared Radiation and Bonding

We tend to think of molecules as static structures made of atoms that are joined by bonds of a fixed length, at fixed angles. However, many molecules can absorb infrared radiation of a specific wavelength to change both their bond length and bond angles. After the surface of the Earth has been warmed by the sun, it emits infrared radiation. If all of that radiation passed straight into space, the Earth would be very cold. In our atmosphere, carbon dioxide, methane and water vapor molecules absorb much of the infrared radiation from the Earth's surface, and re-emit it in all directions. This keeps our planet warm. Infrared absorption can be used to study covalent bonding inside molecules.

## Reactions

## Decomposition Reactions

A substance decomposes into two or more elements or compounds.
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{H}_{2}+\mathrm{O}_{2}$
$\mathrm{CaCO}_{3} \rightarrow \mathrm{CaO}+\mathrm{CO}_{2}$

## Synthesis Reactions

A synthesis reaction is the reverse of a decomposition reaction. A compound is synthesized from one or more products.

```
\(2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}\)
\(4 \mathrm{Fe}+3 \mathrm{O}_{2} \rightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3}\) (rust)
```


## Combustion Reactions

A fuel reacts with oxygen or fluorine (the most electronegative elements). Most combustion reactions involve oxygen.

$$
2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}
$$

Hydrocarbon $+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$

$$
\text { Carbohydrate }+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

## Single Displacement Reactions

A compound reacts with another substance, and one of the components of the compound is replaced by the other substance.
$\mathrm{H}_{2} \mathrm{~S}+\mathrm{Zn} \rightarrow \mathrm{ZnS}+\mathrm{H}_{2}$
$\mathrm{CuSO}_{4}+\mathrm{Fe} \rightarrow \mathrm{FeSO}_{4}+\mathrm{Cu}$
A Reactivity Series (or Activity Series) can help you predict if a single displacement reaction will occur. Elements listed near the top are more "active" than elements near the bottom, and a more active element will displace a less active element. The position of H or $\mathrm{H}_{2}$ in the series does not reflect displacement reactions with water. Na is the least reactive metal that will displace $\mathrm{H}_{2}$ in cold water. Elements below Na but above H will still displace the hydrogen atoms of an acid in solution because they give up electrons to $\mathrm{H}^{+}$ions to produce $\mathrm{H}_{2}$ gas. What you see when you add elements above H to water or to an acid solution is that gas is formed, sometimes violently, so that the element seems "reactive".

## Double Displacement Reactions

A double displacement reaction is an exchange of components between two compounds.
$\mathrm{AgNO}_{3(\mathrm{aq)}}+\mathrm{HCl}_{(\mathrm{aq)}} \rightarrow \mathrm{HNO}_{3(\mathrm{aq)}}+\mathrm{AgCl}_{(\mathrm{s})}$
If one or both of the new compounds are not soluble in water, a precipitate may form. It may help to know that all compounds with group I elements (the alkali metals) are soluble. Also, acids like HCl and $\mathrm{HNO}_{3}$ are soluble. See "Solubility Rules" in the Equilibrium section if you need more information.

In the reaction above, a precipitate forms when two solutions are mixed. The net ionic equation is $\mathrm{Ag}^{+}{ }_{(\text {aq })}+\mathrm{Cl}_{(\text {aq })} \rightarrow \mathrm{AgCl}_{(\mathrm{s})}$. $\mathrm{NO}_{3}^{-}$and $\mathrm{H}^{+}$do not participate in the reaction that forms the precipitate. They are considered spectator ions.

## Acid-Base Reactions

1. An acid reacts with a base to create a salt and water:
$\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{HCl}+\mathrm{KOH} \rightarrow \mathrm{KCl}+\mathrm{H}_{2} \mathrm{O}$
2. Neutralization with formation of a gas. The base may be an anion (proton acceptor), such as $\mathrm{HCO}_{3}{ }^{-}, \mathrm{S}^{2-}$, or $\mathrm{SO}_{3}{ }^{2-}$. Such bases may form a gas when they are neutralized:
$2 \mathrm{HCl}(\mathrm{aq})+\mathrm{Na}_{2} \mathrm{~S}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+2 \mathrm{NaCl}(\mathrm{aq})$
$\mathrm{Na}_{2} \mathrm{SO}_{3}(\mathrm{~s})+2 \mathrm{HCl}(\mathrm{aq}) \rightarrow 2 \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{SO}_{3} \rightarrow 2 \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{SO}_{2}(\mathrm{~g})$
Sulfurous acid, $\mathrm{H}_{2} \mathrm{SO}_{3}$, seems to immediately decompose into water and sulfur dioxide.
$\mathrm{NaHCO}_{3}(\mathrm{~s})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightarrow \mathrm{NaCH}_{3} \mathrm{COO}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{NaCH}_{3} \mathrm{COO}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
Here baking soda combines with acetic acid (vinegar), to form carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$, which then decomposes to release carbon dioxide.

If you take a straw and blow into a glass of water, the carbon dioxide from your breath will react rapidly with water to form carbonic acid:
$\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g}) \rightleftarrows \mathrm{H}_{2} \mathrm{CO}_{3} \rightleftarrows \mathrm{H}^{+}+\mathrm{HCO}_{3}^{-}$
Use a home-made pH indicator (boiled red cabbage juice) to see this reaction. The color change disappears slowly as the carbonic acid decomposes, with the $\mathrm{CO}_{2}$ escaping into the air.

## Stoichiometry

## Balancing Reactions

The object here is to make sure that you have the same number of atoms of each kind on both sides of the reaction. While it may seem tempting to start with the simplest reactants or products, it is actually easier to go for the most complicated molecule and balance its components first. Afterwards you can more easily adjust the quantities of the simpler molecules or elements.

Note that charges should also be balanced on both sides of the reaction.
If $\mathrm{O}_{2}$ is part of the reaction, it supplies an even number or oxygen atoms. When you balance such a reaction and need an odd number, don't hesitate to write something like $1.5 \mathrm{O}_{2}$. Once you have the reaction balanced, simply multiply everything by 2 to get nice whole numbers.

## Ratios and Limiting Reactant

For the reaction $2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$, two moles of hydrogen gas react with one mole of oxygen gas to produce two moles of water. Your teacher can keep you busy restating this fact in various ways:

2 moles of hydrogen react with 1 mole of oxygen: the ratio is $2: 1$
2 moles of water are produced for every mole of oxygen used: the ratio is $2: 1$
2 moles of water are produced for 2 moles of hydrogen used: the ratio is 1:1
Sometimes one of the reactants is available in large quantities, while the other one is limited. For example, consider the combustion of table sugar: sucrose $+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$. The oxygen is supplied by air, and the amount of sugar is limited. Sucrose is considered to be the limiting reactant (or limiting reagent) because its quantity limits the amount of the products produced. Problems of this kind often don't make it clear which reactant is the limiting one. You just have to look at the number of available moles of each one, and decide which reactant will be completely used up (the limiting one), and which one will have some amount left over (the excess reagent).

Problems with this topic are often caused by complex-looking numbers with decimals, and additional mole to gram conversions. It may help to consider the following simple example:

I am decorating some cupcakes with fresh blueberries. I want to put 3 blueberries on each iced cupcake to produce a nicely decorated cupcake. Looking at my supplies, I see that I have a dozen cupcakes, and 42 fresh blueberries. What is the limiting reagent?

If you think about this, you'll realize that I'll have 6 blueberries left after I am done. There are too many blueberries, so blueberries are the excess reagent. Since the ratio is 3 blueberries per 1 cupcake, 42 blueberries would be enough to decorate 14 cupcakes. I can't actually do that because there are not enough cupcakes. The final product number is limited by the number of cupcakes that I have. Cupcakes is the limiting reagent.

## Oxidation - Reduction Reactions

Oxidation - Reduction, or redox reactions, involve a transfer or partial transfer of electrons. Many, but definitely not all, reactions are redox reactions. Oxygen is the most common element in reactions to gain electrons. When something loses electrons, we say that it has been oxidized, even if oxygen is not actually involved. Whatever is responsible for the loss of electrons is called the oxidizing agent. When something gains electrons, it has been reduced (by the reducing agent).

Oxidation numbers are somewhat arbitrary numbers assigned to each atom to allow chemists to keep track of electrons in reactions. Note that the + or - sign is placed in front of the number, unlike for real charges where the sign comes after the number. To assign oxidation numbers, consider how many valence electrons are present, and use the following rules:

1. The sum of the oxidation numbers is zero for a neutral compound or equals the charge on an ion.
2. Assign all shared electrons to the most electronegative atom, or distribute them equally if both atoms are the same.
3. $F$ is the most electronegative atom, and it completes its valence shell with 1 electron. Give it a -1 oxidation number when it combines with another element.
4. O is the next most electronegative atom. It completes its valence shell with 2 electrons so give it a -2 oxidation number, except when it combines with F , or forms a peroxide like $\mathrm{H}_{2} \mathrm{O}_{2}$. $\mathrm{H}_{2} \mathrm{O}_{2}$ has a total of 14 valence electrons. If you assign them all to the 2 oxygen atoms, each O gets 7 , for an oxidation number of -1 .
5. H usually shares its single electron with a more electronegative atom, so it gets a +1 oxidation number. Sometimes H combines with a less electronegative metal (metal hydride); in that case assign it both shared electrons for a -1 oxidation number.

Oxidation numbers are useful for balancing complex oxidation-reduction reactions. Assign oxidation numbers to all atoms. Usually only some atoms will show a change in oxidation number. Because the number of electrons "lost" must equal the number of electrons "gained", the reaction can be balanced. There are two methods available:

The Arrow Method: Draw arrows connecting atoms of each element with a changed oxidation number. Adjust coefficients to get the same number of atoms of that element on both sides. Above the arrows, write the number of electrons gained or lost. Adjust coefficients so the number of electrons lost equals the number of electrons gained. Then balance the remaining compounds. If you need additional oxygen atoms, read the problem to see if the solution is acidic or basic. For acidic solutions, add $\mathrm{H}_{2} \mathrm{O}$ to the side requiring more O , then add $2 \mathrm{H}^{+}$to the other side to balance the H . For basic solutions, add $\mathrm{OH}^{-}$to the side needing O , using twice as much as you need. Then balance the H by adding $\mathrm{H}_{2} \mathrm{O}$ to the other side. Alternatively, you can pretend that the reaction is taking place in an acidic solution. Balance it that way, and then add enough $\mathrm{OH}^{-}$ions to neutralize all $\mathrm{H}^{+}$and turn it into $\mathrm{H}_{2} \mathrm{O}$. This will result in $\mathrm{H}_{2} \mathrm{O}$ on one side, and an excess of $\mathrm{OH}^{-}$on the other as would be expected in a basic solution.

The Half-Reaction Method: First write the ionic equation. Identify the atoms that show a change in oxidation number. Then write separate oxidation and reduction half-reactions Balance the atoms in each half-reaction. If you need additional oxygen atoms, read the problem to see if the solution is acidic or basic. For acidic solutions, add $\mathrm{H}_{2} \mathrm{O}$ to the side requiring more O , then add $2 \mathrm{H}^{+}$to the other side to balance the H . For basic solutions, add $\mathrm{OH}^{-}$ to the side needing O , using twice as much as you need. Then balance the H by adding $\mathrm{H}_{2} \mathrm{O}$ to the other side. Alternatively, you can pretend that the reaction is taking place in an acidic solution. Balance it that way, and then add enough $\mathrm{OH}^{-}$ions to neutralize all $\mathrm{H}^{+}$and turn it into $\mathrm{H}_{2} \mathrm{O}$. Adjust coefficients so the number of electrons lost in one half-reaction equals the number of electrons gained in the other. Now add each separate half-reaction, and eliminate items that appear on both sides of the equation.

## States of Matter

## Intermolecular Forces

Intramolecular forces hold atoms or ions together in covalent (polar or non-polar), ionic or metallic bonds. Intermolecular forces act between molecules. Cohesion refers to intermolecular forces between identical molecules, while adhesion refers to attraction between different types of molecules. Capillary action is the ability of a liquid to flow upwards in narrow channels against gravity. This is a result of cohesion between the molecules of the liquid and adhesion between the liquid molecules and molecules of the material that make up the capillary channel.

Dipole-Dipole Forces are attractions between polar molecules. Because one end of the molecule is a bit negative, and the other end is a bit positive, oppositely charged parts of molecules attract each other.

Dipole-Ion Forces are attractions between polar molecules and ions. Positive ions are attracted to the negative part of a polar molecule, and negative ions are attracted to the positive end of the polar molecule. These forces cause salt to dissolve in water, and remain active while the ions are in solution.

Hydrogen bonds are an especially strong type of dipole-dipole force. They occur between molecules that have a hydrogen atom bonded to an oxygen, fluorine or nitrogen atom. Because oxygen is highly electronegative, the hydrogen bonds between water molecules are quite strong. Note that the bond between oxygen and hydrogen inside of a water molecule is a polar covalent bond. Hydrogen bonds occur between different molecules. They may be indicated by a dotted line drawn between molecules in diagrams.

London Dispersion Forces occur between non-polar molecules (or atoms). Even if molecules have no fixed positive and negative regions, there are temporary distortions in their electron clouds. Such temporary dipoles can induce distortion in the electron cloud of another molecule, creating another temporary dipole. The two molecules (or atoms) then attract each other. As you would expect, this is a weaker force than the dipole-dipole force if all other factors are equal. Molecules with larger electron clouds experience stronger dispersion forces, and large non-polar molecules may have stronger intermolecular forces between them than small polar molecules.

## Phase Changes

When a gas changes into a liquid, the process is called condensation. Water forms hydrogen bonds as it enters the liquid phase. Deposition is the change of a gas into a solid. Water vapor may deposit directly on trees and windows as frost when it is cold and humid. A solid substance can enter the gas phase directly without first becoming a liquid in a process called sublimation. Sublimation occurring in a freezer causes ice cubes to shrink without melting.

Phase changes absorb or release energy. If you heat a solid substance until it reaches its melting point, the temperature will not increase until all of the substance is melted. The heat of fusion is the amount of heat needed, per unit of mass, to melt the substance. An equal amount of energy is released when the liquid solidifies again. As a liquid boils, its temperature stays constant until all of the liquid has evaporated. Use the known heat of evaporation for a particular substance to calculate the energy required to change the liquid into a gas.

If you take an open flask and seal it, the pressure inside is equal to the pressure of the atmosphere. If you then inject a liquid into it, some molecules will escape from the liquid on the bottom and enter the air above, even when the liquid is not heated. As a result, the pressure in the flask increases. This increase in pressure is called the vapor pressure of the liquid, and it measures the tendency of a liquid to evaporate. Boiling occurs when the vapor pressure equals the atmospheric pressure. If the atmospheric pressure is lower, such as occurs at higher elevations, boiling points are correspondingly lower. Experimentally, you can make water boil at room temperature if you lower the pressure sufficiently.

## Phase Diagrams

Phase diagrams allow you to see what phase a substance will be in at any given temperature and pressure. The pressure is graphed along the vertical axis while the horizontal axis shows the temperature. Because you will not have much experience with substances at pressures other than 1 atmosphere, you may find it less confusing to start at this point and look at what happens to the substance as the temperature increases and the pressure stays constant. Water predictably changes from a solid to a liquid and then to a gas.

At very low pressures substances are normally gaseous, since gases are less dense than solids or liquids. As temperatures increase substances are less likely to be solid or liquid, so you will see the gas phase occupying more space in the right bottom corner of the diagram.

The space above the gas phase is divided into solid and liquid. When the temperature is low, a substance is more likely to be solid than liquid. Therefore you will see the solid phase on the left and the liquid phase on the right.


The diagram shows three lines that divide the three phases. The point where all three lines intersect is the triple point. This is the balance point between solid, liquid and gas phases, and all three can coexist at this point. At temperatures below the triple point the liquid phase usually does not exist. Lowering the pressure or increasing the temperature causes the substance to change from a solid directly into the gas phase.

Increasing the pressure on a liquid at a constant temperature may cause it to turn into a solid, because solids are more dense. An important exception here is water, which is less dense as a solid than as a liquid. If you start at the conditions of the triple point and increase the pressure
while keeping the temperature the same, all of the water will become a liquid (its densest state). You can recognize the phase diagram of water because the line between liquid and solid slopes backward rather than forward.

The phase diagram ends at the critical point. At temperatures and pressures above the critical point substances form a supercritical fluid. Supercritical fluids have properties of both gases and liquids and they have important commercial uses. Supercritical carbon dioxide is used to make decaffeinated coffee and tea.

## Solutions

Suspensions are not true solutions. Suspended particles are relatively large and will settle out if left undisturbed, or if you are in a rush you can filter the mixture to separate the suspended particles from the liquid.

A colloid such as milk may look like a solution, but it is actually a mixture containing particles that are not quite large enough to settle out. Colloids cannot be separated by using a filter. They come in many forms such as whipped cream (gas in liquid), marshmallows (gas in solid) and clouds (liquid in gas). A dilute colloid can look like a solution, but it can be distinguished from a true solution by the Tyndall effect, which causes light to scatter when it hits the suspended particles.

Although we usually think of solutions as liquid, they can also exist as gases or solids.

The solute dissolves in the solvent. In case of a solid solute, the process can be speeded up by breaking up the solute into smaller pieces so that more surface area is available. Stirring helps the solute dissolve faster, and so does increasing the temperature. Polar solutes dissolve best in polar solvents, and non-polar solutes dissolve best in non-polar solvents ("Like dissolves like"). Once as much solute as possible has been dissolved, the solution is saturated. Letting a saturated solution cool slowly can produce a supersaturated solution.

A substance that conducts electricity when dissolved in water is called an electrolyte. The electrolyte breaks up into ions when it dissolves, and those ions are responsible for the conduction of electric current. Table salt is an electrolyte because it breaks down into $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions when it dissolves. Sugar dissolves well in water but does not form ions, so it doesn't conduct electricity.

## Factors Affecting Solubility

## 1. Temperature

The heat of solution refers to the energy change that results when the solute dissolves in the solvent. The solution process may be endothermic (absorbing heat), or exothermic (producing heat). Increasing the temperature often allows more of a solid solute to dissolve because this process is often endothermic. If the solution process is exothermic for a particular solid, it should be more soluble at lower temperatures. Gases are more soluble at lower temperatures.

Warm soda tastes flat because it has lost dissolved carbon dioxide bubbles.

## 2. Pressure

Henry's Law: the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

## 3. Solute-Solvent Interactions

Polar solutes dissolve best in polar solvents, and non-polar solutes dissolve best in non-polar solvents.

## Concentration

There are several different ways to express how much solute is present in a solution. One of the most commonly used ones is molarity (M), which tells you the number of moles of solute that are present in one liter of solution. Molarity is useful in a chemistry lab, where a chemist might need a certain amount of a particular substance. By measuring out the calculated volume, the required number of grams or moles can be easily obtained from a stock bottle.

For example, suppose that we have a 0.500 M solution of NaCl , and we want to use that to make 100 ml of 0.125 M NaCl . The question then is how much we should take from the bottle that has the 0.500 M solution. Once we know that we will take this amount and add enough water to make 100 ml of our more dilute solution.

## Using conversion factors:

If we want 100 ml of a 0.125 M solution, that means that we need $\frac{0.125 \mathrm{moles}}{1 \mathrm{~L}} \times 100 \mathrm{ml}=$ $\frac{0.125 \text { moles }}{1000 \mathrm{ml}} \times \frac{100 \mathrm{ml}}{1}=0.0125$ moles of NaCl .

How can we get 0.0125 moles? Take them out of the bottle that has the 0.500 M solution. 0.500 M means $\frac{0.500 \text { moles }}{1 \mathrm{~L}}$, and we can turn that around as needed: $\frac{1 \mathrm{~L}}{0.500 \mathrm{moles}}$.
0.0125 moles $\times \frac{1 \mathrm{~L}}{0.500 \mathrm{moles}}=\frac{0.0125 \mathrm{moles}}{1} \times \frac{1000 \mathrm{ml}}{0.500 \mathrm{moles}}=25.0 \mathrm{ml}$.

The 25 ml will contain our 0.0125 moles, so now add water to get 100 ml .

## Using the Shortcut Formula:

$\mathrm{M}_{1} \mathrm{~V}_{1}=\mathrm{M}_{2} \mathrm{~V}_{2} \quad \mathrm{M}$ stands for molarity, V stands for volume.
$(0.125 \mathrm{M})(100 \mathrm{ml})=(0.500 \mathrm{M})($ ml)

The unknown amount will be $12 \cdot 5 / 0.500=25.0 \mathrm{ml}$.
The answer appears, but you may not really understand what you are doing. Many times students attempt to use this formula in cases where it doesn't apply.

Molality ( $m$ ) indicates the number of moles of solute per kilogram of solvent. Although one liter of pure water weighs almost exactly one kilogram, molality is not equal to molarity even if the solvent is water. Molality is important when we are considering how a dissolved substance affects the properties of a solution, since it provides information about the ratio between solute and solvent molecules.

## Colligative Properties

If you add salt to water, the freezing point is lowered and the boiling point is elevated. Colligative properties of a solution (freezing point depression, boiling point elevation, osmotic pressure, and lowering of vapor pressure) depend on the concentration of particles of solute rather than the type of solute present.

The change in freezing point is $\Delta \mathrm{T}_{f}=\mathrm{k}_{f} \cdot \mathrm{~m}$, where m is the molality of the solution.
The change in boiling point is $\Delta T_{b}=k_{b} \cdot m$.
For water, $\mathrm{k}_{\mathrm{f}}=-1.86^{\circ} \mathrm{C} / \mathrm{m}$ and $\mathrm{k}_{\mathrm{b}}=0.51^{\circ} \mathrm{C} / \mathrm{m}$, for a non-volatile non-electrolyte solute.
One mole of NaCl contributes two moles of particles, so it lowers the freezing point and raises the boiling point about twice as much as a molecular compound like sugar.

All of these calculations will be more accurate for solutions that are not too concentrated.

## Alloys

An alloy is a solid solution, or a mixture of two or more such solutions. Alloys can be a mixture of two metals, or a metal and another element. In a substitutional alloy, the solute atoms are similar in size and have displaced some of the solvent atoms from their usual position in the lattice. In an interstitial alloy, the solute element is typically a small non-metal that fits in the holes in the lattice. Filling these holes makes the metal stronger and more rigid. Steel is an alloy of iron and carbon, with the carbon atoms fitting in between the iron atoms to create an interstitial alloy.

## Gases

The Kinetic Molecular-Theory explains the behavior of gases. It states that gases consist of constantly moving small particles that are so far apart that they don't interact significantly. The kinetic energy of these particles is given by the expression $1 / 2 \mathrm{mv}^{2}$, where $v$ is the velocity of an individual particle. As the temperature increases, the average kinetic energy increases. This means the gas particles are moving faster, on average, at higher temperatures. If two particles with different masses have the same kinetic energy, $1 / 2 \mathrm{mv}^{2}$, the heavier particle will move more slowly than the lighter particle. As $m$ increases, $\mathrm{v}^{2}$ has to decrease to keep the energy the same.

## Pressure

The pressure exerted by a gas is due to the collisions of the gas particles with a surface or with the wall of a container. The gases in the earth's atmosphere create enough pressure to raise a column of mercury to a height of 760 mm at sea level. $1 \mathrm{~atm}=760 \mathrm{~mm} \mathrm{Hg}$. An open-end mercury manometer can compare the pressure of a particular gas or gas mixture in a container against the atmospheric pressure that pushes on the mercury at the open end. The height difference of the two columns is the amount that the gas pressure is greater than or less than 760 mm of mercury.

Dalton's Law of Partial Pressures tells us that if there is a mixture of gases, the total pressure is equal to the sum of the partial pressures of the individual gases.

## Avogadro's Law

When a current is passed through water, bubbles form at both electrodes as the water is decomposed. An inverted glass or test tube filled with water can be placed above the bubbles to collect them. The two separate gases collected are hydrogen and oxygen, and the volume of the hydrogen gas is twice that of the oxygen gas. From this observation, scientists correctly concluded that water contains twice as many hydrogen atoms as oxygen atoms. When gas is collected in a flexible container, such as an inverted test tube or a balloon, the volume of the gas is proportional to the number of particles (molecules or atoms) of which the gas is composed.
$\mathrm{V}=\mathrm{k} \mathrm{n}$, where k is some constant and n is the number of particles of the gas. This is known as Avogadro's Law. Collisions between the gas particles and the flexible boundary of a container provide the pressure that causes the container to expand.

## Charles's Law

If you increase the temperature of a gas, the particles move faster and more collisions with the wall of the container occur. If the container is flexible, it will expand. This is easy to demonstrate by inflating a balloon and then placing it in your freezer. The balloon decreases in size as it cools, and increases in size again after it is removed from the freezer. The volume is proportional to the temperature. $\mathrm{V}=\mathrm{kT}$, where k is some constant and T is the temperature measured in degrees Kelvin to avoid negative values. This relationship is known as Charles's Law.

## Gay-Lussac's Law

If the gas is confined to a container that cannot expand, the pressure of the gas will increase if the temperature is increased. The container could eventually explode if it is not strong enough to withstand the pressure. The pressure is proportional to the temperature. $\mathrm{P}=\mathrm{kT}$, where k is some constant, and T is measured in degrees Kelvin. This is Gay-Lussac's Law.

## Boyle's Law

A gas confined in a container can be compressed by decreasing the volume of the container. This is often demonstrated by compressing air in a syringe. As the volume of the container decreases, the pressure of the confined gas increases. As you might expect, the pressure is inversely proportional to the volume ( $\mathrm{P}=\mathrm{k} \frac{1}{\mathrm{~V}^{\prime}}$, where k is some constant). This is known as Boyle's Law.

## The Ideal Gas Law

All of the relationships above can be combined into the Ideal Gas Law:
$P V=n R T$

Here $R$ is a constant that combines all of the constants above and makes sure that the units match. If you measure pressure in atmospheres, R is $0.08206 \mathrm{~L}-\mathrm{atm} / \mathrm{mol}-{ }^{-} \mathrm{K}$. If the pressure is given in mmHg (or Torr), you can just convert that to atmospheres by knowing that $1 \mathrm{~atm}=760$ mm Hg ( 760 Torr). The volume of the gas should usually be in Liters, which is the unit that goes with the R value $0.08206 \mathrm{~L}-\mathrm{atm} / \mathrm{mol}{ }^{\circ} \mathrm{K}$. T is always measured in degrees Kelvin - be careful because that is easy to forget!

PV = nRT is called the ideal gas law because real gases deviate from this relationship due to the interactions between the particles of the gas, and the size of these particles. If the gas is not very dense the ideal gas law usually gives a good approximation of the actual values.

Standard temperature and pressure of a gas are considered to be 273 degrees Kelvin ( 0 degrees Celsius, which is the freezing point of water) and 1 atmosphere of pressure. These conditions are abbreviated as STP. At STP, the volume of 1 mole of gas is about 22.4 Liters, as you can calculate by using the equation $\mathrm{PV}=\mathrm{nRT}$

The number of moles $n$ of a pure substance is equal to its mass $m$ divided by the molar mass M :
$\mathrm{n}=\frac{\mathrm{m}}{\mathrm{M}}$
We can substitute this into the ideal gas law so that we can find the molar mass or the mass of a particular gas when all the other factors are known:
$P V=\frac{m}{M} R T \quad$ or $\quad P V=\frac{m R T}{M}$
Density is mass $\div$ Volume, so we can rearrange this equation to find the density of a gas. Divide both sides by V , and then substitute $\mathrm{D}=\frac{\mathrm{m}}{\mathrm{V}}$ :
$P=\frac{m R T}{V M}$ so $P=\frac{D R T}{M}$
Now solve for D:
$D=\frac{M P}{R T}$

## Collecting Gases Over Water

An amazing consequence of the Ideal Gas Law is that we can calculate the number of moles of a particular gas in a specified volume just by knowing the pressure of that gas, and the temperature. Gases that are produced during a reaction are often collected over water, which results in a mixture of the gas of interest and a small amount of evaporated water. The vapor pressure of water at different temperatures is known, and tables are available.

Total Pressure = Pressure of Gas + Pressure of Water Vapor
To find the pressure of the gas of interest, just subtract the pressure of the water vapor from the total given pressure. Next, consider only the gas that you are interested in. It is present in the container, which has a specified volume and temperature, and it has a partial pressure that you just calculated. Now you can find how many moles of this gas are present. If PV = nRT, then $n=\frac{P V}{R T}$, where $P$ is the partial pressure of the gas. Be careful to match up units for the value of $R$. For example, if you are using $R=0.08206 \mathrm{~L}$-atm/mol- ${ }^{\circ} \mathrm{K}$, your volume should be in liters and the pressure has to be in atmospheres. Temperature should always be in degrees Kelvin if you are using the Ideal Gas Law.

## Graham's Law of Effusion

If gas leaves a container through a small opening, we call the process effusion. The rate of effusion depends on the speed of the gas particles. The average kinetic energy of these particles is $1 / 2 m v^{2}$ and depends on the temperature of the gas. We can use this to find the velocity and compare the rate of effusion of two different gases under the same conditions:
$\frac{\text { Rate of effusion of gas } A}{\text { Rate of effusion of gas } B}=\frac{\sqrt{M_{B}}}{\sqrt{M_{A}}}$ where $M$ is the molar mass of each gas
This somewhat complex looking equation is obtained by applying simple algebra to compare the velocity of gas A particles ( $\mathrm{v}_{\mathrm{A}}$ ) to the velocity of gas B particles ( $\mathrm{v}_{\mathrm{B}}$ ). If two gases are at the same temperature, then the average kinetic energy of a particle of gas $A$ is equal to the average kinetic energy of gas B:
$1 / 2 m_{A} v_{A}^{2}=1 / 2 m_{B} v_{B}^{2}$, where $m$ is the actual mass of a gas particle.
$m_{A} V_{A}{ }^{2}=m_{B} V_{B}{ }^{2}$ (multiply both sides by 2 )
$\mathrm{V}_{\mathrm{A}}{ }^{2}=\frac{\mathrm{m}_{\mathrm{B}} \mathrm{V}_{\mathrm{B}}{ }^{2}}{\mathrm{~m}_{\mathrm{A}}} \quad$ (divide both sides by mA )
$\frac{\mathrm{v}_{\mathrm{A}}{ }^{2}}{\mathrm{v}_{\mathrm{B}}{ }^{2}}=\frac{\mathrm{m}_{\mathrm{B}}}{\mathrm{m}_{\mathrm{A}}} \quad$ (divide both sides by $\mathrm{v}_{\mathrm{B}}{ }^{2}$ )
$\frac{\mathrm{v}_{\mathrm{A}}}{\mathrm{v}_{\mathrm{B}}}=\sqrt{\frac{\mathrm{m}_{\mathrm{B}}}{\mathrm{m}_{\mathrm{A}}}}=\frac{\sqrt{\mathrm{m}_{\mathrm{B}}}}{\sqrt{\mathrm{m}_{\mathrm{A}}}}$ (take the square root on both sides) $\rightarrow \frac{\text { Rate of effusion of } A}{\text { Rate of effusion of } B}=\frac{\sqrt{\mathrm{m}_{\mathrm{B}}}}{\sqrt{\mathrm{m}_{\mathrm{A}}}}$
Instead of the mass of an individual particle we use the molar mass of that particular gas. The rate of effusion is inversely proportional to the square roots of the molar mass of the gases. "Heavier" gasses effuse more slowly, as would be expected.

## Root Mean Square Speed

Your course may require you to calculate the root mean square speed, which is a measure of the average speed of an individual gas molecule or atom. This is somewhat interesting because gas molecules move surprisingly fast. The formula that you will need is:
$V_{\text {rms }}=\sqrt{\frac{3 R T}{M}}$
Here $M$ is the molar mass of the gas, and $R$ is the gas constant $R$. Because you might like to have the speed in units that make sense, like meters per second, you'll want to use the appropriate value of R , which in this case would be $8.314 \mathrm{~J} / \mathrm{mol}{ }^{\circ} \mathrm{K}$. The Joule, J, is a unit of energy. It is the amount of energy expended when a force of 1 Newton moves an object a distance of 1 meter. The Newton is a unit of force. It is the amount of force required to give a 1 kilogram object and acceleration of 1 m per second per second, which is $1 \mathrm{~m} / \mathrm{sec}^{2}$. So, 1 Joule is $1 \mathrm{~kg} \mathrm{~m} / \mathrm{sec}^{2}$ times 1 m or $1 \mathrm{~kg} \mathrm{~m}^{2} / \mathrm{sec}^{2}$. This shows you that when you consider the molar mass $M$, it needs to be in kilograms, which is a bit of a large unit. $1 \mathrm{~kg}=1000 \mathrm{~g}$. Notice that the speed depends only on temperature and molar mass.

Although unlikely, it is possible that you might be asked to find the average kinetic energy of an individual gas particle. Since the kinetic energy is $1 / 2 \mathrm{mv}^{2}$, you can use the root mean square speed and the actual mass of the gas particle. The mass must be expressed in kilograms so that the answer will be in Joules. The mass numbers in the periodic table are not just in grams per mole for the molar mass M ; they also indicate the atomic mass in amu. An average atom of carbon has a mass of about 12.011 amu , and $1 \mathrm{amu}=1.66 \times 10^{-27} \mathrm{~kg}$. You could also use the
formula Kinetic Energy $=\frac{3}{2} n R T$, so that you can calculate the total kinetic energy for 1 mole of particles $(\mathrm{n}=1)$. Again, you would use $\mathrm{R}=8.314 \mathrm{~J} / \mathrm{mol}{ }^{\circ} \mathrm{K}$. Then you can divide by $6.022 \times 10^{23}$ particles per mole to get the kinetic energy of a single particle.

## Equilibrium

Many reactions can proceed in either direction. At some point, the rate of the backwards reaction equals the rate of the forward reaction, and there is no longer a net change. The reaction has reached a state of equilibrium. At equilibrium the change in available energy, called $\Delta \mathrm{G}$, is zero because no energy is absorbed or produced by the reaction.

We can quantify this equilibrium state by finding the equilibrium constant $K_{c}$, according to the following formula:

For the reaction $\mathrm{aA}+\mathrm{bB} \rightleftarrows \mathrm{cC}+\mathrm{dD}$ :
$\mathrm{K}_{\mathrm{c}}=\frac{[\mathrm{C}]^{\mathrm{C}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$
The subscript c in $\mathrm{K}_{\mathrm{c}}$ stands for concentration. Units are not used with equilibrium constants.
For example, for the reaction $\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightleftarrows 2 \mathrm{NH}_{3}, \mathrm{~K}_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}$
The value of $K$ depends on the reaction and the temperature, but it is constant for a particular reaction at a given temperature. The mechanism of the reaction doesn't matter; you only need to look at the balanced equation for the reaction. If a catalyst is present equilibrium is reached faster, but K stays the same. The concentration of reactants or products that are liquids or solids does not change during the reaction, so these components are simply omitted from the equilibrium expression.

If $K$ is larger than 1, there are more products than reactants at equilibrium. A reverse reaction just flips the equation around so that $\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$ turns into $\frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}}$. This means that $\mathrm{K}_{\text {reverse }}=\frac{1}{\mathrm{~K}_{\text {forward }}}$

If all components of the reaction are gases, we can use the partial pressures, usually in atmospheres, to express the equilibrium constant:
$K_{p}=\frac{\left(P_{C}\right)^{c}\left(P_{D}\right)^{d}}{\left(P_{A}\right)^{a}\left(P_{B}\right)^{b}}$ where $p$ stands for pressure. $P_{A}$ is the partial pressure of gas $A$.
$P V=n R T$, so $P=\frac{n}{V} R T$, and $\frac{n}{V}$ is the concentration (moles per Liter). For each component we can calculate the partial pressure by multiplying the concentration by RT. Since we would normally use atmospheres here, use $\mathrm{R}=0.08206 \mathrm{~L}-\mathrm{atm} / \mathrm{mol}-{ }^{\circ} \mathrm{K}$. If the number of moles of the products is the same as the number of moles of the reactants, all of the multiplications by RT cancel out and $k_{p}$ will have the same value as $K_{c}$. Otherwise, you can use the formula $K_{p}=K_{c}(R T)^{\Delta n}$, where $\Delta n$ is the change in the number of moles: number of moles of products the number of moles of reactants.

The reaction quotient, Q , refers to the concentrations of the products and reactants at any given time, not just at equilibrium. Once the system reaches equilibrium $Q=K$.

For the reaction $\mathrm{aA}+\mathrm{bB} \rightleftarrows \mathrm{cC}+\mathrm{dD}$ :
$\mathrm{Q}=\frac{[\mathrm{C}]^{\mathrm{C}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$

## Le Châtelier's Principle

Le Châtelier's Principle states that if a stress is placed on a system at equilibrium, the system will move in the direction that relieves the stress. Please note that such changes are due to physical and mathematical principles that govern equilibrium rather than a desire of the system to reduce stresses.

The equilibrium constant, $\mathrm{K}_{\text {eq }}$, is directly affected by temperature. Endothermic reactions require heat, and product formation is favored at higher temperatures:

Reactants + heat $\rightleftarrows$ Products
Le Châtelier's Principle helps you remember that the reaction shifts to the right if you add heat, although you might guess that it would if you just think about it.

In the case of an exothermic reaction, the reverse reaction is endothermic. If you add heat, reactants are favored:

Reactants $\rightleftarrows$ Products + heat

If you increase the concentration of one or more of the reactants, a new equilibrium will be achieved with a higher concentration of product. This is consistent with Le Châtelier's Principle, as well as the rules of mathematics:

For $\mathrm{aA}+\mathrm{bB} \rightleftarrows \mathrm{cC}+\mathrm{dD}, \quad \mathrm{K}_{\mathrm{c}}=\frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$
The equilibrium constant $K$ stays the same at a given temperature. If you increase the concentration of $A, B$, or both, then the concentration of the products must increase in order for $K$ to stay the same. Some of the reactants $A$ and $B$ will be consumed to form products, until a new equilibrium is reached that allows $K$ to have the same value. In the same way, if you increase the concentration of $C, D$, or both, the concentration if the reactants must increase. Then the reaction proceeds more quickly in the reverse direction, until there is a greater quantity of reactants than there was originally.

For reactions involving gases, the concentration of the gases is directly proportional to their partial pressures. If K is constant then T is constant. Increasing the pressure by decreasing the volume of the container will increase the concentration of a gas. This will affect the concentrations of all the gases in the container equally. However, for the reaction $A+B \rightleftarrows C$ there is a difference between the total number of particles of product and reactants. Doubling the concentration of all gases disturbs the equilibrium $K_{c}=\frac{[C]}{[A][B]}$.
$\frac{2[\mathrm{C}]}{2[\mathrm{~A}] 2[\mathrm{~B}]}=\frac{2[\mathrm{C}]}{4[\mathrm{~A}][\mathrm{B}]}=\frac{[\mathrm{C}]}{2[\mathrm{~A}][\mathrm{B}]}$, which does not have the same value as $\frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}$. Some of the reactants must be converted to product to reach the original $K_{c}$ value. The equilibrium shifts to the side with the fewest molecules. Using Le Châtelier's Principle, you would reason that the system relieves the increased pressure by shifting so that there are fewer molecules, which lowers the pressure.

On the other hand, increasing the pressure of the system by adding an inert gas does not change the partial pressures (or the concentrations) of any of the other gases. Even though there is a "stress" on the system from added pressure, there is no way for the system to respond to relieve that stress and the equilibrium is not affected. Le Châtelier's Principle is a useful generalization, but this particular exception will probably appear on your test.

## Solubility

When a solid dissolves in a liquid, only so much of it can go into solution. Once there is more
solute than what the solution can hold, an equilibrium is set up. Some of the solid solute continues to dissolve, while some of the already dissolved solute precipitates.

For $\mathrm{CaSO}_{4(\mathrm{~s})} \rightleftarrows \mathrm{Ca}^{2+}{ }_{(\mathrm{aq})}+\mathrm{SO}_{4}{ }^{2-}{ }_{(\mathrm{aq})}, \mathrm{k}_{\mathrm{eq}}=\frac{\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{SO}_{4}{ }^{-}\right]}{\left[\mathrm{CaSO}_{4}\right]}$
However, $\mathrm{CaSO}_{4}$ is a solid, so its "concentration" is constant. We can ignore it and consider only the product of the ion concentrations, which is the solubility product constant indicated by $K_{\text {sp }}$.
$\mathrm{K}_{\text {sp }}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2-}\right]$
This is an equilibrium situation, and $\mathrm{K}_{\text {sp }}$ is constant at a given temperature. If the product [Ca $\left.{ }^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2-}\right]$ in a particular solution exceeds the value of $\mathrm{K}_{\text {sp }}$, solid $\mathrm{CaSO}_{4}$ will precipitate until equilibrium is achieved. If the concentration of $\mathrm{Ca}^{2+}$ or $\mathrm{SO}_{4}{ }^{2-}$ is decreased, additional $\mathrm{CaSO}_{4}$ will dissolve until there is an equilibrium again, or until all of the solid $\mathrm{CaSO}_{4}$ is gone.

You can easily predict if there will be a precipitate in a solution by comparing the product of the concentration of the ions with the given $\mathrm{K}_{\text {sp }}$ for the particular solid. You can also figure out how many moles per liter of a particular solid will dissolve in water if you know the $\mathrm{K}_{\text {sp }}$.
$K_{\text {sp }}$ values are only useful for solids that are slightly soluble, so that ion concentrations are very low at equilibrium and ion interactions are not significant.

When considering how much solute will dissolve in a given solution, consider any ions that may already be present in the solution. Less $\mathrm{CaSO}_{4}$ can dissolve in a solution of $\mathrm{CuSO}_{4}$ than would dissolve in water, due to the fact that there are already $\mathrm{SO}_{4}{ }^{2-}$ ions present. This is the common ion effect.

## Example 1

The $\mathrm{K}_{\text {sp }}$ for calcium fluoride is given as $5.3 \times 10^{-9}$ at a particular temperature. Find the molar solubility of calcium fluoride.

For each mole of $\mathrm{CaF}_{2}$ that dissolves, there will be 1 mole of $\mathrm{Ca}^{2+}$ and 2 moles of $\mathrm{F}^{-}$in the solution. $\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}$. Let's say that x moles of calcium fluoride will dissolve in 1 Liter of solution to give $x$ moles of $\mathrm{Ca}^{2+}$ and 2 x moles of $\mathrm{F}^{-}$:
$\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}$
$5.3 \times 10^{-9}=(x$ moles per liter $) \cdot(2 x \text { moles per liter })^{2}=x \cdot 4 x^{2}=4 x^{3}$
$5.3 \times 10^{-9}=4 x^{3}$
$1.325 \times 10^{-9}=x^{3}$
$\mathrm{x}=1.1 \times 10^{-3}$ moles per liter, so the solubility of $\mathrm{CaF}_{2}$ is $1.1 \times 10^{-3} \mathrm{moles} / \mathrm{L}$.

## Example 2

If one of the ions is already present in the solution before you start dissolving the solid, you can add the amount " $x$ " to what is already present. For example, if you are trying to dissolve solid $\mathrm{CaF}_{2}$ in a solution that already has $\mathrm{Ca}^{2+}$ at a concentration of 0.01 M , the new concentration of $\mathrm{Ca}^{2+}$ would be $0.01+\mathrm{x}$. An "ICE" table is the most efficient way to keep track of things. ICE stands for "Initial", "Change", and "End". The initial concentration of Ca ${ }^{2+}$ is 0.01 , while the initial concentration of $\mathrm{F}^{-}$is zero. Once the solid dissolves, the $\mathrm{Ca}^{2+}$ concentration will increase by $x$, while the $F^{-}$concentration increases by $2 x$ :

|  | $\left[\mathrm{Ca}^{2+}\right]$ | $\left[\mathrm{F}^{-}\right]$ |
| :--- | :---: | :---: |
| Initial | 0.01 | 0 |
| Change | x | 2 x |
| End | $0.01+\mathrm{x}$ | 2 x |

Because $K_{\text {sp }}$ values are usually quite small, the new concentration of $\mathrm{Ca}^{2+}$ will normally not be significantly larger after x moles per liter are added. Calculations can be simplified like this:
$\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}$
$5.3 \times 10^{-9}=(0.01+x) \cdot(2 x)^{2} \approx 0.01 \cdot 4 x^{2}=0.04 x^{2}$
$5.3 \times 10^{-9}=.04 x^{2}$
$1.325 \times 10^{-7}=x^{2}$
$x=3.6 \times 10^{-4}$ moles per liter
Notice that less of the solid dissolves than in Example 1. Also, you can now see that the amount $x$ is very small compared to the initial concentration of $\mathrm{Ca}^{2+}$. As a rule of thumb you can ignore the added $x$ if the original concentration of the ion divided by the $\mathrm{K}_{\text {sp }}$ is greater than 1000. In this case $0.01 \div 5.3 \times 10^{-9}=1.9 \times 10^{6}$.

## Example 3

If both ions are already present in the solution, calculations can get complex so we use a trick. Suppose that 300 ml of a 0.10 M solution of NaF is mixed with 200 ml of a 0.10 M solution of $\mathrm{CaSO}_{4}$. What are the final concentrations of $\mathrm{Ca}^{2+}$ and $\mathrm{F}^{-}$? Here we could start with the initial concentrations of the two ions and subtract $x$ and $2 x$ to get $(0.1-x)(0.1-2 x)^{2}$, but the problem with that is that it would lead to a cubic equation that is difficult to solve. We can also not ignore the x's here because then we would have no $x$ left to find a value for. The trick we use is to imagine that the ions first completely precipitate into a solid, and then the solid dissolves. To use this trick you must keep track of the number of moles of each ion needed to form the solid, and account for what is left over.
$\mathrm{Ca}^{2+}+2 \mathrm{~F}^{-} \rightarrow \mathrm{CaF}_{2}$. 2 moles of $\mathrm{F}^{-}$are needed to react with 1 mole of $\mathrm{Ca}^{2+}$. There are 0.300 L x 0.10 moles $/ \mathrm{L}$ or 0.030 moles $\mathrm{F}^{-}$and $0.200 \mathrm{~L} \times 0.10$ moles $/ \mathrm{L}$ or 0.020 moles of $\mathrm{Ca}^{2+}$. 0.020 moles of $\mathrm{Ca}^{2+}$ would need 0.040 moles of $\mathrm{F}^{-}$, so there isn't enough. If we used all 0.030 moles of $\mathrm{F}^{-}$, that would use up 0.015 moles of $\mathrm{Ca}^{2+}$, and 0.005 moles $\mathrm{Ca}^{2+}$ would be left over. Although this is not what actually happens, you can imagine that you have only the solid, and some $\mathrm{Ca}^{2+}$ in solution. 0.005 moles of $\mathrm{Ca}^{2+}$ in a total of 0.500 L amounts to an initial concentration of 0.01 M . Now you can imagine that the solid starts dissolving until an equilibrium is reached. Proceed as in example 2:

|  | $\left[\mathrm{Ca}^{2+}\right]$ | $\left[\mathrm{F}^{-}\right]$ |
| :--- | :---: | :---: |
| Initial | 0.01 | 0 |
| Change | x | 2 x |
| End | $0.01+\mathrm{x}$ | 2 x |

## Solubility Rules (for Reference Only)

The following generalized rules are listed here to help you quickly estimate whether a precipitate is likely to form. For the purpose of these rules, substances are classified as insoluble if a precipitate forms when equal volumes of 0.1 M solutions of their components are mixed. This is relatively arbitrary, and you should consider the actual $\mathrm{K}_{\mathrm{sp}}$ values.

1. All compounds of Group IA elements (the alkali metals) are soluble.
2. All salts of $\mathrm{NH}_{4}{ }^{+}$are soluble.
3. Salts of nitrate $\left(\mathrm{NO}_{3}^{-}\right)$, chlorate $\left(\mathrm{ClO}_{3}^{-}\right)$, perchlorate $\left(\mathrm{ClO}_{4}^{-}\right)$, and acetate $\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$, are soluble.
4. Chloride $\left(\mathrm{Cl}^{-}\right)$, bromide $\left(\mathrm{Br}^{-}\right)$, and iodide $\left(\mathrm{l}^{-}\right)$salts are soluble except for those containing $\mathrm{Ag}^{+}$, $\mathrm{Pb}^{2+}$, and $\mathrm{Hg}_{2}{ }^{2+}$. AgCl is often used as an example of an insoluble salt.
5. All sulfate $\left(\mathrm{SO}_{4}{ }^{2-}\right)$ compounds are soluble except those of $\mathrm{Ba}^{2+}, \mathrm{Sr}^{2+}, \mathrm{Ca}^{2+}, \mathrm{Pb}^{2+}$, and $\mathrm{Hg}_{2}{ }^{2+}$. Sulfate compound containing $\mathrm{Hg}^{2+}, \mathrm{Ca}^{2+}$ and $\mathrm{Ag}^{+}$are moderately soluble.
6. All hydroxide $\left(\mathrm{OH}^{-}\right)$compounds are insoluble except those of Group I-A (rule 1) and $\mathrm{Ba}^{2+}$, $\mathrm{Ca}^{2+}$, and $\mathrm{Sr}^{2+}$.
7. All sulfide $\left(\mathrm{S}^{2-}\right)$ compounds are insoluble except those of Groups I-A (rule 1) and Group II-A.
8. All sulfites $\left(\mathrm{SO}_{3}{ }^{2-}\right)$, carbonates $\left(\mathrm{CO}_{3}{ }^{2-}\right)$, chromates $\left(\mathrm{CrO}_{4}{ }^{2-}\right)$, and phosphates $\left(\mathrm{PO}_{4}{ }^{3-}\right)$ are insoluble except for those of Group I-A (rule 1) and $\mathrm{NH}_{4}{ }^{+}$(rule 2).

## Acids and Bases

A water molecule can break apart into $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$, and these two ions can combine again to form $\mathrm{H}_{2} \mathrm{O}$. This process is called the auto-ionization of water. As a result, there is always a tiny bit of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$present in pure water. $\mathrm{H}^{+}$is just a single proton, which can "stick" to one or more adjacent water molecules $\left(\mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}\right)$. The concentration of $\mathrm{H}^{+}$, written as $\left[\mathrm{H}^{+}\right]$, in pure water is $1 \times 10^{-7}$ moles per liter, and $\left[\mathrm{OH}^{-}\right]$is also $1 \times 10^{-7} \mathrm{M}$. Adding an acid will increase the concentration of $\mathrm{H}^{+}$, and adding a base will increase the concentration of $\mathrm{OH}^{-}$, however the product of the two concentrations always remains constant:
$\left[\mathrm{H}^{+}\right] \times\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14}=\mathrm{K}_{\mathrm{w}}$.
When the concentration of $\mathrm{H}^{+}$in a solution is $1 \times 10^{-7}$, the solution is considered neutral. If $\left[\mathrm{H}^{+}\right]$ is greater than $1 \times 10^{-7}$ the solution is acidic, and if $[\mathrm{H}+]$ is less than $1 \times 10^{-7}$ the solution is basic.

To calculate the pH from a given concentration of $\mathrm{H}^{+}$, take the negative log of the $\mathrm{H}^{+}$ concentration. If the concentration of $\mathrm{H}+$ in a solution is $1 \times 10^{-7}$, the pH is $-\log \left(1 \times 10^{-7}\right)=7$.

To calculate $\left[\mathrm{H}^{+}\right]$from a given pH , reverse the above operation. The inverse of the $\log$ is $10^{x}$, and you must reverse the sign again since you originally took the negative log. If the pH is 7 , then the $\mathrm{H}+$ concentration is $10^{-\mathrm{pH}}=10^{-7}=1 \times 10^{-7}$

If you know $\left[\mathrm{H}^{+}\right]$and you want $\left[\mathrm{OH}^{-}\right]$, use $\mathrm{K}_{\mathrm{w}}:\left[\mathrm{H}^{+}\right] \times\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14}$. Divide both sides by $\left[\mathrm{H}^{+}\right]$to get $\left[\mathrm{OH}^{-}\right]=\frac{1 \mathrm{x} 10^{-14}}{\left[\mathrm{H}^{+}\right]}$.

The pOH is the negative log of the $\mathrm{OH}^{-}$concentration. $\mathrm{pH}+\mathrm{pOH}=14$. (Logarithms are exponents, and when you multiply you add the exponents.)

The functional definition of acids and bases is that when dissolved in water, an acid increases the concentration of $\mathrm{H}^{+}$ions, and a base increases the concentration of $\mathrm{OH}^{-}$ions.

## Arrhenius Acids and Bases

The original definition was that acids are substances that release $\mathrm{H}^{+}$when dissolved in water, and bases release $\mathrm{OH}^{-}$. Examples would include HCl and NaOH .

## Bronsted-Lowry Acids and Bases

An acid is a proton donor, and a base is a proton acceptor. Under this broader definition,
ammonia, $\mathrm{NH}_{3}$, is a base because it accepts a proton to turn into $\mathrm{NH}_{4}{ }^{+}$:
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{4}{ }^{+}+\mathrm{OH}^{-}$

## Lewis Acids and Bases

This is the broadest and most complex definition. It includes all acids and bases. An acid is a substance that accepts an electron pair, and a base is an electron-pair donor. Under this definition, $\mathrm{CO}_{2}$ is an acid. It reacts reversibly with water to form carbonic acid: $\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow$ $\mathrm{H}_{2} \mathrm{CO}_{3}$. One of the electron pairs around the carbon atom gets displaced to the attached oxygen, allowing the carbon to take on an extra electron pair from the oxygen atom on the water molecule.

A substance that can act as either an acid or a base is called amphoteric. Water is amphoteric.
A monoprotic acid can only donate a single proton $\left(\mathrm{H}^{+}\right)$, while polyprotic acids can donate more than one $\mathrm{H}^{+}$. Diprotic and triprotic acids can donate two and three $\mathrm{H}^{+}$respectively. $\mathrm{H}_{3} \mathrm{PO}_{4}$ is a triprotic acid. Bases can also be monoprotic or polyprotic, meaning that they can accept one or more protons.

If you have already studied the topic "Equilibrium", you can see that it is closely related to pH. The acid dissociation constant, $\mathrm{K}_{\mathrm{a}}$, is the equilibrium constant for an acid. For the generic acid HA that dissociates to form $\mathrm{H}^{+}$and $\mathrm{A}^{-}$:
$K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
The acid HA dissolves in water, even when it is not dissociated. Individual molecules of HA are present in an aqueous state, which is different from the case where we are dissolving a solid in water. The concentration of HA varies because it is not a solid, so it is not omitted from the equilibrium expression.

The $\mathrm{pK}_{a}$ is the negative log of the $\mathrm{K}_{\mathrm{a}}$. A strong acid would have a relatively high $\mathrm{K}_{\mathrm{a}}$, which means that the $\mathrm{pK}_{\mathrm{a}}$ would be relatively low.
$\mathrm{K}_{\mathrm{b}}$ is the base dissociation constant. For the reaction $\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HA}+\mathrm{OH}^{-}$:
$\mathrm{K}_{\mathrm{b}}=\frac{[\mathrm{HA}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{A}^{-}\right]}$

The concentration of $\mathrm{H}_{2} \mathrm{O}$ is not included in this expression because it is a liquid and its concentration doesn't change significantly.
$K_{a} \times K_{b}=K_{w}=1.0 \times 10^{-14}$. That last part is true because if you multiply the expressions for the dissociation of the acid and the protonation of the base you get the expression for the dissociation of water, $\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$.

Example: At what pH will a 0.10 M solution of $\mathrm{CaCl}_{2}$ form a precipitate of $\mathrm{Ca}(\mathrm{OH})_{2}$ ? The given $\mathrm{K}_{\text {sp }}$ of calcium hydroxide is $5.5 \times 10^{-6}$.
$\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^{-}\right]$
$5.5 \times 10^{-6}=(0.10)(x)^{2}$
Be careful: x is simply the unknown concentration of $\mathrm{OH}^{-}$ions. Even though x moles of the solid would dissolve to give 2 x moles of $\mathrm{OH}^{-}$, that is not relevant here. We are only trying to find the actual concentration of $\mathrm{OH}^{-}$needed to create a precipitate.
$x=0.00742$ moles per liter $\mathrm{OH}^{-}$
$\mathrm{pOH}=-\log 0.00742=2.1 \mathrm{pH}=14-\mathrm{pOH} \quad \mathrm{pH}=11.9$

Example: You have a 1 M solution and a 0.01 M solution of a hypothetical acid HA with a $\mathrm{K}_{\mathrm{a}}$ of $1.0 \times 10^{-6}$. Compare the dissociation of the acid in these two solutions.

The acid will dissociate to form x moles of $\mathrm{H}^{+}$and x moles of $\mathrm{A}^{-}$. For the 1 M solution:
$\mathrm{K}_{\mathrm{b}}=\frac{[\mathrm{HA}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{A}^{-}\right]}$
$1.0 \times 10^{-6}=\frac{x \cdot x}{1-x} \approx \frac{x^{2}}{1}$ so $x=1.0 \times 10^{-3}$
For the 0.01 M solution, which is 100 times more dilute:
$\mathrm{K}_{\mathrm{b}}=\frac{[\mathrm{HA}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{A}^{-}\right]}$
$1.0 \times 10^{-6}=\frac{x \cdot x}{0.01-x} \approx \frac{x^{2}}{0.01}$
$1.0 \times 10^{-8}=x^{2} \quad$ so $\mathrm{x}=1.0 \times 10^{-4}$

Making the solution 100 times more dilute resulted in a hydrogen ion concentration only 10 times less, rather than 100 times less. A greater percentage of the acid is dissociated in the dilute solution, as you might expect.

## Conjugate Acid and Base

When an acid is added to water, it dissociates to a variable degree. Weak acids release protons from some of their molecules, while others remain intact. Strong acids release protons from practically all of their molecules. HCl is a strong acid: $\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-}$. An example of a weak acid is acetic acid: $\mathrm{CH}_{3} \mathrm{COOH} \rightleftarrows \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+}$.

Notice that when the acid dissociates there is always a proton plus something else. That other part is called the conjugate base, because it acts as the base when you reverse the reaction (it absorbs $\mathrm{H}^{+}$, which increases the $\mathrm{OH}^{-}$concentration in the solution). Strong acids have a very weak conjugate base, which means that the reverse reaction doesn't take place to any significant degree. NaCl is neutral in aqueous solution because $\mathrm{Cl}^{-}$doesn't take protons away from water to form HCl . An extremely weak acid has a strong conjugate base. In the middle range, a moderately weak acid has a moderately weak base. When your chemistry course talks about a weak acid, it is referring to a moderately weak acid that has a weak conjugate base. An acid that is weak enough to have a strong conjugate base has almost negligible acidity, so you wouldn't really call it an acid. An example of that is $\mathrm{H}_{2} \mathrm{O}$, which has the conjugate base $\mathrm{OH}^{-}$.
$\mathrm{CH}_{3} \mathrm{COOH}$, acetic acid, is a common example of a weak acid. Sodium acetate, $\mathrm{NaCH}_{3} \mathrm{COO}$, is weakly basic when dissolved in water because $\mathrm{CH}_{3} \mathrm{COO}^{-}$is able to accept protons from water to form acetic acid.

The weaker the acid, the stronger the conjugate base. It works the same for bases: the stronger the base the weaker the conjugate acid.

## Titration

If you mix an acid and a base, the $\mathrm{H}^{+}$from the acid and the $\mathrm{OH}^{-}$from the base will combine to form water. This is called a neutralization reaction.
$\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{Cl}^{-}+\mathrm{Na}^{+}$

The remaining ions form a salt. A salt in chemistry is any ionic compound resulting from the neutralization reaction that occurs when an acid and a base are mixed.

Titration can be used to find how much acid is present in a solution. A standard base, usually NaOH , is added to the solution slowly, and the pH is monitored. At first the pH changes slowly, as the base reacts with some of the acid. When the reaction is nearly complete, the pH changes very rapidly. At the center of the rapid pH change on the graph is the equivalence point. At this point equal amounts of acid and base are present, so that all of the acid is neutralized. Mixing equivalent amounts of acid and base doesn't necessarily result in a solution with a pH of zero! If you are titrating a moderately weak acid such as hydrofluoric acid, the conjugate base that is left when the neutralization is complete is moderately basic.
$\mathrm{HF}+\mathrm{NaOH} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{F}^{-}+\mathrm{Na}^{+}$

Hydrofluoric acid is a weak acid and therefore its conjugate base $\mathrm{F}^{-}$is a weak base. It reacts with water to create $\mathrm{OH}^{-}$ions:
$\mathrm{F}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HF}+\mathrm{OH}^{-}$

The solution will be basic when the neutralization reaction is complete, so the pH will be above 7 at the equivalence point.

When a strong acid is mixed with a strong base, that leaves a really weak conjugate base and a really weak conjugate acid. Neither one of these will react with water to any significant degree. The solution will have a pH of about 7 at the equivalence point. As you are interpreting acid titration curves on an exam, look at the pH of the equivalence point to see if a strong acid or a weak acid is being titrated. The initial pH may be quite low even for a weak acid, because it depends on the concentration of the acid as well as its strength.

The titration curve of a strong acid with a strong base shows an initial slow but steady increase in pH . That initial rate of increase is larger than it looks because each unit increase in pH represents a 10 -fold decrease in the $\mathrm{H}^{+}$concentration (the pH scale is a logarithmic scale). The initial part of the titration curve of a weak acid with a strong base is more complex because initially most of the acid is not dissociated. At the start of the titration the base consumes the $\mathrm{H}^{+}$ions and leaves the conjugate base alone. Because there is already some conjugate base in solution, the acid dissociates more slowly, releasing less $\mathrm{H}^{+}$than you would expect. This is the common ion effect (see "Equilibrium - Solubility"). The pH rises more rapidly at first. As you add more base, you create a buffer situation where the acid and its conjugate base are present in nearly equal amounts. The pH stays fairly stable. Once the buffer is exhausted the pH rises rapidly to the equivalence point.

Indicators are weak acids or weak bases that have different colors depending on whether they are dissociated or not. They can be used to measure the pH of a solution over a certain range. When you are doing titrations you can calculate or estimate the pH at the equivalence point, and choose an indicator accordingly.

## Buffers

Buffer solutions contain a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid, preferably in equal amounts. This allows the buffer solution to resist changes in pH . When an acid and its conjugate base are present in equal amounts, the pH of the buffer is equal to the $\mathrm{pK}_{\mathrm{a}}$ of the acid:
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
From this equation you can see that if $\left[\mathrm{A}^{-}\right]=[\mathrm{HA}]$ then $\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}}$. When the hydrogen ion concentration is higher than the $\mathrm{K}_{\mathrm{a}}$, more HA is formed, and when it is lower more of the acid dissociates.

The Henderson-Hasselbalch Equation can be used to calculate the pH of a buffer:
$\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right] \cdot \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
$\log K_{a}=\log \left[\mathrm{H}^{+}\right]+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
$-\log \left[\mathrm{H}^{+}\right]=-\log \mathrm{K}_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
If [ $\mathrm{A}^{-}$] is exactly equal to [HA], the pH of the buffer is equal to the $\mathrm{pK}_{\mathrm{a}}$ of the acid, because the log of 1 is 0 . This can be used to select a particular acid and its conjugate that is most suitable for the pH that you want to maintain.

## Energy and Thermodynamics

Specific Heat

Heat is energy that flows from a warmer object to a cooler object, and it increases the temperature of the cooler object. Heat is measured in Joules, or rather in kilojoules, kJ, because a Joule is a fairly small amount of energy. The specific heat (also called the specific heat capacity) of a substance is the amount of heat energy required to raise the temperature of 1 gram of that substance by 1 degree Celsius (or Kelvin). The specific heat of water is about $4.184 \mathrm{~J} / \mathrm{g}-{ }^{\circ} \mathrm{K} .4 .184$ Joules of energy will raise the temperature of 1 gram of water by 1 degree, and this amount of energy is called one calorie. Because 1 calorie is quite small, the energy content of food is normally expressed in Calories, with a capital C. One Calorie $=1000$ calories.

For calculations, use the formula $q=c m \Delta T$, where $q$ is the heat energy gained or lost, $c$ is the specific heat of a substance (which you can look up in a table), $m$ is the mass and $\Delta T$ is the change in the temperature. You can also just think about what is going on so you won't need to memorize the formula.

## Hot Metal Added to Water

You place 300.0 g of water in a coffee-cup calorimeter and the temperature of the water is $22.3^{\circ} \mathrm{C}$. A 94.5 g piece of silver metal is heated to $100^{\circ} \mathrm{C}$ and added to the water in the calorimeter. What will be the final temperature of the silver and the water? The specific heat of silver is $0.235 \mathrm{~J} / \mathrm{g}{ }^{\circ} \mathrm{C}$

When I do these kinds of problems I like to think about ideas rather than formulas. If the silver is warmer than the water, there is an excess amount of heat energy that will be redistributed. First I imagine that both the water and the silver could have the same temperature, 22.3 degrees. The silver is actually $100-22.3$ or 77.7 degrees warmer, which is extra heat that we can redistribute over both the water and the metal. To raise the temperature of 94.5 g of silver by 77.7 degrees would take ( 94.5 times 0.235 times $77.7=$ 1725.52 J ). I have 1725.52 J of extra heat energy available to redistribute (significant figures later). Next, I distribute that extra heat energy over both the water and the silver. To raise the temperature of this combination of materials by 1 degree would take 300 gx 4.184 (water) plus
$94.5 \mathrm{~g} \times 0.235$ (silver) $=1277.41 \mathrm{~J}$. That is for 1 degree. Since I have 1725.52 J available I can raise the temperature of the water/silver combination by 1725.52/1277.41 = 1.35 degrees above the base temperature of 22.3 degrees. Final temperature is 23.65 , round to 23.7 degrees.

You can do the same thing in a fancier way by considering the final temperature $\mathrm{T}_{\mathrm{f}}$, which lies somewhere between 22.3 and 100 degrees. The silver will lose heat to change its temperature from 100 to $\mathrm{T}_{\mathrm{f}}$. The water will gain heat to change its temperature from 22.3 to $\mathrm{T}_{\mathrm{f}}$. The heat gained must be equal to the heat lost:

Heat lost by silver: $94.5 \mathrm{~g} \times 0.235 \times\left(100-\mathrm{T}_{\mathrm{f}}\right)$
Heat gained by water: $300 \mathrm{~g} \times 4.184 \times\left(\mathrm{T}_{\mathrm{f}}-22.3\right)$
When I set these two expressions equal to each other and solved for $\mathrm{T}_{\mathrm{f}} \mathrm{I}$ also got 23.65 degrees, but it was a lot more work than doing it the other way. The first method is a fairly simple idea that you can easily remember for a long time.

## Enthalpy

An open system can exchange matter and energy with the surroundings. A closed system can exchange only energy with the surroundings. An isolated system doesn't exchange either matter or energy with its surroundings, but we can only approximate that (for example by a closed thermos). Energy gets added to or leaves a closed system as heat (q), work (w), or a combination of these two quantities:
$\Delta E=q+w$
This says that the change in energy is the sum of the heat transfer and the work done. The internal energy of a system increases when heat is transferred into it, and when work is done on the system. The system's energy decreases when heat is lost to the surroundings, or when the system does work on the surroundings. [Since work can be a positive or negative quantity, you may see $\Delta \mathrm{E}=\mathrm{q}-\mathrm{w}$, depending on how we define "positive" work.]

The equation above was developed from the study of steam engines, where work is done when hot steam generates pressure that moves pistons. The chemical reactions we study are usually taking place in open containers in the constant pressure of the environment, and any work that could be done would be due to a change in volume caused by expanding gases. Gases that are produced push aside the surrounding air, which represents a small amount of work.

While it is relatively easy to measure the heat produced or absorbed by a chemical reaction, the work done by any escaping gasses is not so easy to quantify. To make things simpler, scientists have defined a quantity called enthalpy. The change in energy minus any work done is the enthalpy:
$\Delta E=q+w$
$\Delta \mathrm{E}-\mathrm{w}=\mathrm{q}$
$\Delta \mathrm{E}-\mathrm{w}$ is the change in enthalpy, $\Delta \mathrm{H}$.
$\Delta H=q$
The change in enthalpy is equal to the change in heat content (q) of a system under constant pressure. Now we can measure and compare changes in enthalpy for various reactions. The total energy change for a reaction is very close to $\Delta H$ because little or no work is done by the system that constitutes the reactants and the products.

The change in enthalpy that occurs as the result of a reaction is $\mathrm{H}_{\text {products }}-\mathrm{H}_{\text {reactants }}$. If the heat content of the product(s) is lower than that of the reactant(s), heat is produced as the result of the reaction. Enthalpy has decreased, so $\Delta H$ is negative. We say that the reaction is exothermic. If $\Delta H$ is positive for a given reaction, the reaction is endothermic; energy is absorbed from the environment as the reaction proceeds. If an endothermic reaction occurs in a solution in a beaker, the beaker will feel cold because the reaction absorbs heat energy from the solution and the container.
$H$ itself can't be measured directly, but since all we need is $\Delta H$ we can start from pure elements and just measure the changes as they react to form compounds. Hess's Law of heat summation says that we can calculate $\Delta H_{\text {reaction }}$ from any series of steps that theoretically would lead to the product(s), since the enthalpy depends only on the current state of a system and not on how it got there. Values for enthalpy changes can be found in tables, which show specific changes in enthalpy under defined standard conditions. These conditions are: all substances are in their pure form, the pressure is 1 atmosphere, and a set temperature is given (usually 25 degrees Celsius). The standard enthalpy change is written as $\Delta H^{\circ}$. We can measure the heat of formation, $\Delta H_{f}$, of compounds from their component elements. $\Delta H_{f}{ }^{\circ}$ is the standard enthalpy of formation. It represents the change in enthalpy that occurs when one mole of a compound is formed from its elements under standard conditions. If an element exists in more than one form under standard conditions, the most stable form is usually chosen to calculate $\Delta H_{f}{ }^{\circ}$.

Using values from a table, we can create imaginary steps that break the reactants into their components, and then build the products from those components. This is not really that hard, if you keep a couple of things in mind:

1. Enthalpy of formation is stated in the table for 1 mole of product, since the units are normally $\mathrm{kJ} / \mathrm{mol}$. You may see fractional coefficients, like this: $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ $\Delta H_{f}{ }^{\circ}=-285.8 \mathrm{~kJ}$ (heat is released).
2. If your reaction produces 2 moles of water, multiply the enthalpy change by 2 :
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ (I) $\Delta \mathrm{H}_{\mathrm{f}}{ }^{0}=-571.6 \mathrm{~kJ}$
3. If you reverse the reaction to break water into its components, you must reverse the sign of the enthalpy change: $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \Delta \mathrm{H}^{\circ}=285.8 \mathrm{~kJ}$
4. Consider the state of the reactants and the products, because that affects the enthalpy. If we consider the formation of water in the gas state rather than as a liquid we have:
$\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}=-241.8 \mathrm{~kJ}$.
5. By definition, $\Delta H_{f}{ }^{\circ}$ of an element in its most stable form is zero. For example, $\Delta H_{f}{ }^{\circ}$ of $\mathrm{O}_{2(\mathrm{~g})}$ is 0.

Breaking down the reactants and making the products from their components may seem confusing for more complex reactions, and having to change the sign of $\Delta H_{f}$ can trip you up. There is an easier way to get the answer:

$$
\Delta H_{\text {reaction }}=\Delta H_{f}(\text { products })-\Delta H_{f}(\text { reactants })
$$

## Entropy

It may seem odd that an endothermic reaction would proceed spontaneously. What favors such reactions is that they result in an increase in entropy, or randomness. The universe "favors" increases in entropy because disorder is statistically more likely to occur than order. The symbol used for entropy is $S$, and the change in entropy is written as $\Delta S$.

More movement of particles means more entropy. Gases have more entropy than liquids, and liquids have more entropy than solids. Molecules have more entropy than atoms, because the atoms in molecules can slightly change their position relative to each other (vibration), and spin around in various ways (rotation). Complex molecules have more entropy than simple molecules. At a higher temperature particles have more energy to move, vibrate and rotate, so entropy increases with increasing temperature. A perfect crystal at a temperature of zero
degrees Kelvin would have an entropy of zero. Scientists are able to determine the actual values for S for different substances under various conditions.

$$
\Delta S_{\text {reaction }}=S_{\text {products }}-S_{\text {reactants }}
$$

If the products have more entropy than the reactants, $\Delta \mathrm{S}$ is positive, which favors the reaction.

## Gibbs Free Energy

Some reactions result in both a decrease in enthalpy (exothermic) and an increase in entropy, which means they always occur spontaneously. Endothermic reactions that result in an increase in entropy may or may not proceed spontaneously depending on the temperature. Gibbs free energy is a measure that allows us to predict whether the reaction will be spontaneous. The Gibbs free energy, originally called the available energy, is also a measure of the useful work that could potentially be done by the reaction. If the reactants contain more free energy than the products, the reaction proceeds from a higher energy level to a lower energy level, so it is spontaneous. That means that the change in free energy, $\Delta G$, is negative, since the change is measured as free energy of products minus free energy of reactants:
$\Delta \mathbf{G}=\mathbf{G}_{\text {products }}-\mathrm{G}_{\text {reactants }}$
Even though a reaction is spontaneous when $\Delta G$ is negative, the rate can be extremely slow. It is thermodynamically favorable for a diamond to decompose into graphite, but fortunately this reaction is negligibly slow.

Just like enthalpy, the Gibbs free energy can't be measured in absolute terms, but we can measure the change in G as a compound is formed from the elements that compose it. $\Delta \mathrm{G}_{\mathrm{f}}{ }^{\circ}$, the standard entropy change of formation, is available in tables for common products and reactants. Standard means all substances are pure, solutions are at 1 M concentration, pressure is 1 atm , and a particular temperature (usually $25^{\circ} \mathrm{C}$ ) is specified. Since $\Delta \mathrm{G}^{\mathrm{f}}{ }^{\circ}$ is the energy change when a substance is formed from its elements, $\Delta \mathrm{G}_{\mathrm{f}}{ }^{0}$ is zero for elements. So, to find $\Delta \mathrm{G}^{0}$ for a reaction, add up $\Delta \mathrm{G}_{\mathrm{f}}{ }^{\circ}$ of the products and then subtract the sum of $\Delta \mathrm{G}_{\mathrm{f}}{ }^{0}$ of the reactants. You still won't know any actual values of G , but as long as you have a baseline (the elements), you can know the change in $\mathrm{G}, \Delta \mathrm{G}$.
$\Delta \mathrm{G}^{0}=\sum \mathrm{n} \Delta \mathrm{G}^{0}{ }_{\mathrm{f}}$ (products) $-\sum \mathrm{m} \Delta \mathrm{G}^{0}{ }_{\mathrm{f}}$ (reactants)
where n and m are coefficients in the balanced reaction, and the symbol $\Sigma$ stands for sum.
$\Delta \mathrm{G}$ is also given by the equation:
$\Delta G=\Delta H-T \Delta S$

You can see from this equation that $\Delta G$ is more likely to be negative when $T$ is high.
Endothermic reactions are more likely to be spontaneous at higher temperatures, which makes sense.

Most problems will refer to reactions taking place under standard conditions. Tables will provide $\Delta H_{f}{ }^{\circ}$ and $S^{\circ}$ at a given temperature (usually $25^{\circ} \mathrm{C}$ ). Unfortunately, tables give $\Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}$ in kilojoules, while the entropy, S , is in Joules. Make sure you convert so you have the same units before you put these values together into the formula $\Delta G^{\circ}=\Delta H^{\circ}-T \Delta S^{\circ}$

Although you can just calculate $\Delta \mathrm{G}_{\mathrm{f}}{ }^{\circ}$ from the equation, it will probably be in the table also, along with S and $\Delta H_{f}{ }^{\circ}$. Remember that to calculate $\Delta \mathrm{G}_{\mathrm{f}}{ }^{\circ}$ you must use $\Delta \mathrm{S}^{\circ}$ rather than $\mathrm{S}^{\circ}$. For a pure element in its regular state $\Delta \mathrm{H}_{f^{0}}$ is zero by definition, so $\Delta \mathrm{G}_{\mathrm{f}}{ }^{0}$ is also zero since there is no change in entropy. Because $\Delta H_{f}{ }^{0}$ and $\Delta S^{\circ}$ don't change that much with temperature, you can calculate $\Delta G_{f}$ at say $37^{\circ} \mathrm{C}$ by just changing T to $310^{\circ} \mathrm{K}$ in the equation $\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$.

The actual free energy change $\Delta \mathrm{G}$ at non-standard concentrations is related to the standard Gibbs free energy change $\Delta \mathrm{G}^{\circ}$, by the equation:
$\Delta G=\Delta G^{0}+R T \ln Q$
Where $Q$ is the reaction quotient (which uses the actual concentrations of the reactants and the products at a given time). Here you will use the value of $R$ that goes with Joules, 8.314 $\mathrm{J} / \mathrm{mol}-{ }^{\circ} \mathrm{K}$. Be really careful, because $\Delta \mathrm{G}^{\circ}$ will be in kilojoules instead of Joules!

As long as $\Delta \mathrm{G}$ is negative the reaction proceeds forward and the concentration of the products increases. Once the reaction is at equilibrium (see section on Equilibrium), Q is equal to K , the equilibrium constant, and $\Delta \mathrm{G}=0$ :
$0=\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln \mathrm{K}$
$\Delta \mathbf{G}^{\mathbf{o}}=-\mathbf{R T} \ln \mathrm{K} \quad$ (Once you have $\ln \mathrm{K}$, raise the number e to this power to get K )
In this equation $R$ will be 0.008314 kJ , and for K you can use $\mathrm{K}_{\mathrm{c}}$ for reactions in solution or $\mathrm{K}_{\mathrm{p}}$ for gases. This means that $\Delta G^{\circ}$ can be calculated if $K_{c}$ or $K_{p}$ is known, and you can find $\Delta G^{\circ}$ if you know the equilibrium constant.

## Energy Diagrams

Energy diagrams show the reactants at a certain level, and then the products are placed higher or lower on the diagram depending on $\Delta H$ for the reaction. The activation energy shows up as a "bump". The overall energy change for a reaction is approximately equal to the energy it takes to break and form bonds, which can be calculated from bond energies.

## Born-Haber Cycle (Optional)

This is a way to see energy changes and calculate lattice energy. Lattice energy is the energy released when an ionic solid forms.

## Electrochemistry

Ions of different metals differ in how strongly they attract electrons. Copper ions attract electrons more strongly than zinc ions, and as a result copper ions can remove electrons from zinc metal. If solid zinc metal is placed in a solution containing copper ions, the zinc will dissolve in the solution as zinc ions, and solid copper will precipitate. Another way of looking at this is that zinc "does something" if you put it in a solution of copper ions, while copper does nothing if you put it in a solution of zinc ions. We can say that zinc is more reactive than copper. An activity series shows which metals are relatively more "active" in terms of giving up their electrons.

Electrons move from a solid metal to ions of a less reactive metal spontaneously, so energy is released, in this case in the form of heat. The energy from this type of process can also be harnessed to provide electricity. We can construct a voltaic cell (a battery) by creating a barrier that prevents the direct movement of electrons from one atom to another and force those electrons to run through a wire instead. The electron flow can then power a device, much as a river can power a water wheel. The barrier must be porous to allow ions to balance the flow of electrons, otherwise the build-up of charges would stop the flow of current.

In an alkaline battery, electrons move from zinc atoms to the manganese ions in $\mathrm{MnO}_{2}$. A mercury battery uses the flow of electrons from zinc atoms to mercury (II) oxide to generate liquid mercury.

The part of either a voltaic cell or an electrolytic cell that supplies electrons is called the anode (negative electrode). Those electrons must come from somewhere, which means that oxidation takes place at the anode. The part of the cell that consumes electrons is called the cathode (positive electrode). Reduction occurs at the cathode. The flow of electrons is called the current. 1 coulomb of electrical charge is equivalent to about $6.24 \times 10^{18}$ electrons, and a current of 1 amp means that $6.24 \times 10^{18}$ electrons are passing by a given point every second. A mole of electrons is $6.022 \times 10^{23}$ electrons, which is equivalent to 96,485 Coulombs of charge. Due to an unfortunate convention, current is considered to flow from positive to negative, which is opposite to the actual flow of electrons. Do not be confused by diagrams showing the direction of current flow; pay attention to which way the electrons are going instead.

Electrical potential, E , or emf (electromotive force) is expressed in volts. One volt is the electrical potential difference that imparts 1 Joule of energy to a charge of 1 coulomb. A table of reduction potentials allows you to calculate the voltage generated by a voltaic cell, based on
the voltage of each half reaction. To get these reduction potentials chemists use a standard hydrogen electrode (SHE), which provides the equilibrium $\mathrm{H}_{2}(\mathrm{~g}) \rightleftarrows 2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$. Both the forward and reverse half-reactions for this electrode are assigned a value of OV , and other half-reactions are measured against this. The standard conditions for these measurements involve using a 1 M concentration for all ions in solution, as concentration affects the voltage. To find an oxidation potential instead of a reduction potential just reverse the reaction and the sign of the voltage. A positive voltage indicates that the reaction is favored in the direction it is written.

These voltages are a measure of the "pull" on the electrons, much as the height of a waterfall affects the water that goes over it. If more water flows, the height of the waterfall stays the same. When more atoms and electrons are involved, the reduction potential is still the same; there is just more current (flow of electrons). Do not multiply the voltage by the coefficient in the reaction!

One way to calculate the net voltage of a voltaic cell is by writing the half-reactions in the way that they occur, and reversing the sign of the reduction potential for the oxidation halfreaction, as shown below. Then just add the voltages:

Alkaline battery:

| $\mathrm{Zn}+2 \mathrm{OH}^{-} \rightarrow \mathrm{ZnO}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$ | +1.28 V | $\left(\mathrm{E}^{0}{ }^{\text {red }}=-1.28 \mathrm{~V}\right)$ |
| :--- | :--- | :--- |
| $\underline{2 \mathrm{MnO}_{2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{Mn}_{2} \underline{\mathrm{O}}_{3}+2 \mathrm{OH}^{-}}$ | $+\mathbf{+ 0 . 1 5 \mathrm { V }}$ |  |
| $\mathrm{Zn}+2 \mathrm{MnO}_{2} \rightleftarrows \mathrm{ZnO}+\mathrm{Mn}_{2} \mathrm{O}_{3}$ | +1.43 V |  |

Another way is to use the actual reduction potential for both half-reactions:

$$
\mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0} \text { (cathode) }-\mathrm{E}_{\text {red }}^{0} \text { (anode) }
$$

For the alkaline battery shown above, the anode is where the electrons are produced, so that is $\mathrm{Zn}+2 \mathrm{OH}^{-} \rightarrow \mathrm{ZnO}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}, \mathrm{E}_{\text {red }}=-1.28 \mathrm{~V}$. Subtract that from the reduction potential at the cathode, $\mathrm{E}^{0}$ red $=+0.15 \mathrm{~V}$ :
$E^{0}$ cell $=+0.15 \mathrm{~V}--1.28 \mathrm{~V}=+1.43 \mathrm{~V}$
An element that loses electrons very easily is a strong reducing agent, and an element that gains electrons easily is a strong oxidizing agent. This applies to all elements rather than just to metals, and reduction potentials for many non-metals will also be listed in your table.

Example shorthand notation for voltaic cells:
$\mathrm{Zn}\left|\mathrm{Zn}^{2+}\right|\left|\mathrm{Cu}^{2+}\right| \mathrm{Cu}$
$\mathrm{Pt}(\mathrm{s})\left|\mathrm{Fe}^{2+}(\mathrm{aq}), \mathrm{Fe}^{3+}(\mathrm{aq})\right|\left|\mathrm{Br}_{2}, \mathrm{Br}^{-}(\mathrm{aq})\right| \mathrm{Pt}(\mathrm{s})$ [Note that the substance that is losing electrons is written closest to the electrode]

Just as spontaneous electron flow generates electricity, we can also use electrical energy to force electrons to run through a wire in the reverse direction. This allows an energetically unfavorable reaction to take place. Electrolytic cells are used for electroplating. Rechargeable batteries also use this principle. In an electrolytic cell, electrons are also produced at the anode (by oxidation), and consumed at the cathode (reduction occurs here). In order to drive these processes, the positive terminal of a battery or other power source must be connected to the anode to pull electrons away from it, while the negative terminal must be connected to the cathode to supply the electrons consumed there. Electrolytic cells do not require separate halfcells connected by a salt bridge, because the reaction will not occur spontaneously inside the solution.

Your course may require you to be able to calculate how many grams of a metal can be electroplated out if a particular current runs through the circuit for a specified length of time. Earlier we said that 1 Amp of current $=6.24 \times 10^{18}$ electrons per second.

## Current x time $=$ Total number of electrons moved

Convert this number of electrons to moles by using Avogadro's number, $6.022 \times 10^{23}$. Alternatively, you can say that $1 \mathrm{Amp}=1$ Coulomb/sec, and then convert from Coulombs to moles of electrons if you know that 1 mole electrons $=96,485$ Coulombs.

The energy generated by the movement of electrons depends on both the voltage (potential) and the total charge that is moved by that voltage. 1 joule $=1 \mathrm{~V} \times 1$ Coulomb.
$\Delta \mathrm{G}^{\circ}=-\mathrm{nFE}{ }^{\circ}$
Here $\Delta \mathrm{G}$ is in Joules and E is in volts. n is the number of moles of electrons. To find n , write the balanced reaction and see how many electrons are transferred. F is the Faraday constant, which represents the electrical charge carried by one mole of electrons ( 96,485 Coulombs). F has the units Coulombs/mole, or equivalently, Joules/Volt-mole, since 1 Coulomb = 1 Joule/1V.
$\mathrm{F}=96,485 \mathrm{C} / \mathrm{mol}=96,485 \mathrm{~J} / \mathrm{V}-\mathrm{mol}$

The minus sign shows that the change in the Gibbs free energy will be negative, which means the reaction is thermodynamically favorable, if the voltage $E$ is positive.

You can use the equation $\Delta \mathrm{G}^{\circ}=-\mathrm{nFE}{ }^{\circ}$ to find the energy generated by a voltaic cell in which the electrolyte concentrations are at 1 M . However, even if you start out with 1 M solutions the concentrations will change as the reaction proceeds. You can use Le Châtelier's Principle to predict what will happen to the voltage of a cell under non-standard conditions, when the concentration of the ions in solution is not 1 M . The voltage decreases with a decreasing concentration of the reactants and an increasing concentration of the products, as you would expect. Eventually the voltage drops to zero, and energy can no longer be generated.

In the chapter on Energy, we saw that $\Delta \mathrm{G}^{\circ}$ is also equal to $-\mathrm{RT} \ln \mathrm{K}$. Putting those two equations together we get $E^{\circ}=\frac{R T}{n F} \ln K$. Once you know $\ln K$, you can find the equilibrium constant $K$ by raising e to that power: $e^{\ln K}=K$.

## The Nernst Equation

For non-standard conditions (concentrations not at 1 M ), you can use the equation $\Delta G=\Delta G^{\circ}+R T \ln Q$ to find the energy change as a result of a reaction. Here $Q$ is the reaction quotient, which is the current concentration of products over the concentration of reactants. As the reaction progresses, Q changes until equilibrium is reached. At that point, $\mathrm{Q}=\mathrm{K}$. Also, at equilibrium no more free energy is available from the reaction, and $\Delta G=0$. Substituting those values into the equation $\Delta G=\Delta G^{\circ}+R T \ln Q$ gives $\Delta G^{\circ}=-R T \ln K$.

We can substitute $\Delta \mathrm{G}^{\circ}=-\mathrm{nFE}{ }^{\circ}$ and $\Delta \mathrm{G}=-\mathrm{nFE}$ into the equation $\Delta \mathrm{G}=\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln \mathrm{Q}$ to get $-n F E=-n F E^{\circ}+R T \ln \mathrm{Q}$, and rearrange that to get the Nernst Equation:
$E=E^{0}-\frac{R T}{n F} \ln Q$
This equation can also be converted to use a base 10 logarithm: $E=E^{0}-\frac{2.303 R T}{n F} \log Q$, and at the standard temperature of $25^{\circ} \mathrm{C}$ or $298 \mathrm{~K}, \frac{2.303 \mathrm{RT}}{\mathrm{F}}$ is equal to 0.0592 Volts. The form of the Nernst equation that you will be using is:
$E=E^{0}-\frac{0.0592 \mathrm{~V}}{\mathrm{n}} \log \mathrm{Q}$ (only at 298 K )

A concentration cell uses two the same half-reactions but with the ions at different concentrations. $\mathrm{E}^{0}$ for this type of cell is zero, but E is not zero because of the concentration difference. The reaction proceeds until the concentration of the ions is equal in each half cell.

## Kinetics

Rate of reaction $=k[\text { Reactant } A]^{a}[\text { Reactant } B]^{b} .$. where the exponents are the order. The overall order of a reaction is the sum of individual orders. If a reaction is first order in A , and first order in $B$, the overall order is 2 . The reaction order may be a fraction, or zero.

Reactions usually depend on collisions between molecules (or atoms), so we can expect the rate to depend on the concentration of the reactants. Higher concentrations mean more frequent collisions. If a solid is involved, increasing the available surface area will increase the number of collisions.

In order for a particular collision to actually contribute to the reaction, the particles must collide with sufficient energy to overcome the activation energy for the reaction. The particles must also have the right orientation in order to break or form bonds.

At higher temperatures the average kinetic energy of particles is higher, which means more frequent and more energetic collisions. Reaction rates increase with an increase in temperature.

Exponents in a rate law must be determined experimentally, unlike for equilibrium. This is because reactions often take place in several steps, which are called elementary reactions. The slowest step determines the reaction rate, and therefore the rate law. If all other factors are equal, the slowest step will be the one with the highest activation energy. The number of molecules that come together in the rate-determining step is called the molecularity. Depending on the number of molecules involved, the elementary reactions may be unimolecular, bimolecular, or termolecular. Because termolecular steps require three molecules to come together in the proper orientation they are very rare. An intermediate compound may be formed in one step and consumed in another. Do not put an intermediate in the rate law - see if it is in fast equilibrium with one or more of the reactants, and substitute those into your proposed rate law.

The rate constant $(\mathrm{k})$ for a particular reaction is affected by temperature and the presence of a catalyst. A catalyst is a substance that is present at the beginning of a reaction, and then appears unchanged at the end of the reaction. A catalyst can speed up a reaction by providing a new mechanism for the reaction that has a lower activation energy, or by helping to create the proper orientation of the reactants. Enzymes are large protein molecules that catalyze reactions in living organisms.

When you talk about the overall rate of a reaction, you have to think about how you will express it. For example, for the reaction $2 \mathrm{~A} \rightarrow \mathrm{~B}$, you can measure how fast A decreases, or how fast $B$ forms. However, in terms of moles per unit of time, $A$ disappears at a higher rate than $B$ appears, by a factor of 2. For a reaction of the form $a A+b B \rightarrow c C+d D$, the overall rate of the reaction may be expressed in terms of the disappearance of one of the reactants (negative):
rate $=-\frac{1}{a} \frac{\Delta[\mathrm{~A}]}{\Delta \mathrm{t}} \mathrm{M} / \mathrm{sec}=-\frac{1}{b} \frac{\Delta[\mathrm{~B}]}{\Delta \mathrm{t}} \mathrm{M} / \mathrm{sec}$
Or in terms of the appearance of one of the products (positive):
rate $=\frac{1}{c} \frac{\Delta[\mathrm{C}]}{\Delta \mathrm{t}} \mathrm{M} / \mathrm{sec}=\frac{1}{d} \frac{\Delta[\mathrm{D}]}{\Delta \mathrm{t}} \mathrm{M} / \mathrm{sec}$.
Partial pressure of a gas can be used as a unit of concentration in the rate laws because we know from the ideal-gas law that the pressure is directly proportional to the number of moles per unit volume.

## Zero Order Reactions

For a zero order reaction, the rate is constant and independent of the concentration of the reactants. Example: a gas decomposing on the surface of a solid.
$-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k} \quad$ where k is a constant
The minus sign in the equation is present because $A$ is disappearing, which makes $\frac{\Delta[A]}{\Delta t}$ a negative quantity. The minus sign turns k into a positive constant.

Even without calculus, we can figure out that in this case the concentration of $A$ decreases from its initial value, $[A]_{0}$, at a nice steady rate:

$$
[\mathrm{A}]_{\mathrm{t}}=-\mathrm{kt}+[\mathrm{A}]_{0}
$$

Here $[A]_{t}$ stands for the concentration of $A$ at any given time $t$. This is an equation for a straight line, $y=m x+b$. Graph $[A]$ against $t$, so that the slope is $-k$, and the $y$-intercept is $[A]_{0}$.

## First Order Reactions

In a first order reaction, the rate is directly proportional to the concentration of a single reactant. The rate keeps slowing down as the concentration of that reactant is decreasing:
$-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k}[\mathrm{A}]$
Although $\Delta$ means "the change in", if we consider the change in concentration over a given interval we only get the average rate, because that rate is always changing. To get the actual rate at a given moment, we would need to consider an infinitely small change in the concentration that happens over an infinitely small interval of time. This is the instantaneous rate. The instantaneous rate at time $t=0$ is called the initial rate. An instantaneous rate can't be measured directly but is determined from a tangent line to a concentration vs. time graph.

Calculus allows us to work backwards from knowing how $A$ is changing to finding the actual concentration of A at a given time. This gives us the integrated rate law:
$\ln [A]_{t}=-k t+\ln [A]_{0}$
If you graph $\ln [A]$ against $t$, you get a straight line with a slope of $-k$ and a $y$-intercept of $\ln [A]$.

The half-life is the amount of time it takes for the concentration of $A$ to be reduced to one-half of its initial value. Just substitute $[A]_{t 1 / 2}=\frac{1}{2}[A]_{0}$
$\ln \frac{1}{2}[\mathrm{~A}]_{0}=-k t_{1 / 2}+\ln [\mathrm{A}]_{0}$
$\ln \frac{1}{2}[\mathrm{~A}]_{0}-\ln [\mathrm{A}]_{0}=-k t_{1 / 2}$
$\ln \frac{\frac{1}{2}[\mathrm{~A}]_{0}}{[\mathrm{~A}]_{0}}=-k t_{1 / 2} \quad$ (using the rules of logarithms: $\ln \mathrm{a}-\ln \mathrm{b}=\ln \frac{\mathrm{a}}{\mathrm{b}}$ )
$\mathrm{t}_{1 / 2}=-\frac{\ln \frac{1}{2}}{\mathrm{k}} \approx \frac{.693}{\mathrm{k}}$

## Second Order Reactions

For a second order reaction, the rate depends on the concentration of one reactant squared (or the concentration of two reactants):
$-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k}[\mathrm{A}]^{2}$
The reaction rate decreases more quickly than it does for a first order reaction. The integrated rate law for this is:
$\frac{1}{[\mathrm{~A}]_{\mathrm{t}}}=\mathrm{kt}+\frac{1}{[\mathrm{~A}]_{0}}$
If you graph $\frac{1}{[A]}$ against $t$, you will get a straight line with a slope of $k$ and a y-intercept of $\frac{1}{[A]_{0}}$.
(Note that k is the rate constant relative to [A]. However, as explained earlier, if the reaction equation shows that 2 moles of $A$ are consumed then the rate constant for the overall reaction is only $1 / 2$ the value of $k$ that you get from this equation:
For $a \mathrm{~A} \rightarrow b \mathrm{C}$ the overall rate is $-\frac{1}{a} \frac{\Delta[\mathrm{~A}]}{\Delta \mathrm{t}} \mathrm{M} / \sec$ or $\frac{1}{b} \frac{\Delta[\mathrm{~B}]}{\Delta \mathrm{t}} \mathrm{M} / \mathrm{sec}$.)
To express the half-life in terms of $[\mathrm{A}]_{0}$, substitute $[\mathrm{A}]_{\mathrm{t} 1 / 2}=\frac{1}{2}[\mathrm{~A}]_{0}$ :
$\frac{1}{[\mathrm{~A}]_{\mathrm{t} 1 / 2}}=\mathrm{kt}_{1 / 2}+\frac{1}{[\mathrm{~A}]_{0}}$
$\frac{1}{\frac{1}{2}[\mathrm{~A}]_{0}}=\mathrm{kt}_{1 / 2}+\frac{1}{[\mathrm{~A}]_{0}}$
$\frac{2}{[\mathrm{~A}]_{0}}=\mathrm{kt}_{1 / 2}+\frac{1}{[\mathrm{~A}]_{0}}$
$\mathrm{t}_{1 / 2}=\frac{1}{\mathrm{k}[\mathrm{A}]_{0}}$

## Beer's Law

Because spectroscopy can be used to measure the concentration of a substance while a reaction progresses, you may need to know Beer's Law (Beer-Lambert Law). The absorbance of
light, $A$, relates directly to the concentration $c: A=\varepsilon b c$ (sometimes expressed as $A=\varepsilon \mid c$ ). Here $b$ is the length of the path the light travels, and $\varepsilon$ is a constant that depends on the particular substance and the specific wavelength of light.

## The Arrhenius Equation (Optional Topic)

Usually the rate of a reaction increases when the temperature increases. Although you might expect that there would be a linear relationship between rate and temperature, that is not normally the case. Arrhenius realized that the rate of most reactions depends on the following factors:

1. The number of molecules that have a kinetic energy that is at least equal to the activation energy for the reaction, $\mathrm{E}_{\mathrm{a}}$. This depends on the temperature T .
2. The number of collisions that take place between molecules, and the proportion of those collisions that have the right orientation. This factor is represented by $A$, the frequency factor. A remains approximately constant as the temperature is varied.

The Arrhenius Equation relates the rate constant k to the temperature T :
$\mathrm{k}=\mathrm{A} e^{\frac{-E_{a}}{R T}}$
Here $R$ is the gas constant 8.314 Joules $/ \mathrm{Mol}{ }^{\circ} \mathrm{K}$, and T is measured in degrees Kelvin. If you measure the reaction rate and the temperature, you can calculate the activation energy. You may think that you would also need to know $A$, that is not necessary if you take multiple measurements at different temperatures.

To make the Arrhenius Equation easier to work with, we can take the natural logarithm In on both sides:
$\ln \mathrm{k}=\ln \left(\mathrm{A} e^{\frac{-E a}{R T}}\right) \quad$ Using the fact that $\ln (\mathrm{ab})=\ln \mathrm{a}+\ln \mathrm{b}$, we get:
$\ln k=\ln A+\ln e^{\frac{-E_{a}}{R T}}$
The natural logarithm is the inverse of the exponential function, so they cancel each other out, leaving only $\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}$ :
$\ln \mathrm{k}=\ln \mathrm{A}+\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}$
Because $A$ is (pretty much) constant and $\frac{1}{\mathrm{~T}}$ is a variable, we prefer to write this equation as $\ln k=\frac{-E_{a}}{R T}+\ln A$, so we can relate it to the equation of a straight line $y=m x+b$. When you take multiple measurements and plot $\ln k$ against $\frac{1}{T^{\prime}}$ you can find the activation energy $E_{a}$ from the slope, while $\ln \mathrm{A}$ is the y -intercept.

If you have only two measurements, you have the following situation:
$\ln \mathrm{k}_{1}=\ln \mathrm{A}+\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}_{1}}$
$\ln \mathrm{k}_{2}=\ln \mathrm{A}+\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}_{2}}$
Now you can just subtract the bottom equation from the top one, or vice versa:
$\ln \mathrm{k}_{1}-\ln \mathrm{k}_{2}=\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}_{1}}-\frac{-\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}_{2}} \quad$ Factor out $-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}:$
$\ln \mathrm{k}_{1}-\ln \mathrm{k}_{2}=-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}_{2}}\right) \quad$ Remove the minus sign by switching $\frac{1}{\mathrm{~T}_{1}}$ and $\frac{1}{\mathrm{~T}_{2}}$ :
$\ln \mathrm{k}_{1}-\ln \mathrm{k}_{2}=-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(-\frac{1}{\mathrm{~T}_{2}}+\frac{1}{\mathrm{~T}_{1}}\right) \quad$ and factoring out -1 :
$\ln \mathrm{k}_{1}-\ln \mathrm{k}_{2}=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{2}}-\frac{1}{\mathrm{~T}_{1}}\right) \quad$ Also use the fact that $\ln \left(\frac{\mathrm{a}}{\mathrm{b}}\right)=\ln \mathrm{a}-\ln \mathrm{b}$ :
$\ln \left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{2}}\right)=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}_{2}}\right)$

## Calculus for Rate Laws (Reference Only)

Zero Order Reactions: $-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k}$

Consider an infinitely small time interval dt, during which the concentration of A changes by an infinitely small amount d[A]:
$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}=\mathrm{k}$
$d[A]=-k d t$
Integrate both sides:
$\int \mathrm{d}[\mathrm{A}]=\int-\mathrm{kdt}$
$[\mathrm{A}]=-\mathrm{kt}+\mathrm{C}$
At time $t=0$ the concentration of $A$ is $[A]_{0}:[A]_{0}=-k t+C$.
So the value of $C$ is $[A]_{0}$, and at any time $t$ the concentration of $A$ is given by:
$[\mathrm{A}]=-\mathrm{kt}+[\mathrm{A}]_{0}$

First Order Reactions: $-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k}[\mathrm{A}]$
$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{A}]$
$\frac{1}{[A]} d[A]=-k d t$
$\int \frac{1}{[\mathrm{~A}]} \mathrm{d}[\mathrm{A}]=\int-\mathrm{kdt}$
$\ln [\mathrm{A}]=-\mathrm{kt}+\mathrm{C}$
At time $t=0$ the concentration of $A$ is $[A]_{0}: \ln [A]_{0}=-k t+C$.
So the value of $C$ is $\ln [A]_{0}$ :
$\ln [A]=-k t+\ln [A]_{0}$
Second Order Reactions: $-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\mathrm{k}[\mathrm{A}]^{2}$
$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{A}]^{2}$
$\frac{1}{[A]^{2}} d[A]=-k d t$
$\int[\mathrm{A}]^{-2} \mathrm{~d}[\mathrm{~A}]=\int-\mathrm{k} \mathrm{dt}$
$-[\mathrm{A}]^{-1}=-\mathrm{kt}+\mathrm{C}_{1}$
$\frac{1}{[\mathrm{~A}]}=\mathrm{kt}+\mathrm{C}_{2}$
At time $\mathrm{t}=0$ the equation becomes: $\frac{1}{[\mathrm{~A}]_{0}}=\mathrm{C}_{2}$.
So the value of $\mathrm{C}_{2}$ is $\frac{1}{[\mathrm{~A}]_{0}}$
$\frac{1}{[\mathrm{~A}]}=\mathrm{kt}+\frac{1}{[\mathrm{~A}]_{0}}$

