# ClemChem



CHAPTER 1

# The Basics

We will look at several of the basics of introductory chemistry in this chapter. These include the rules for determining and working with significant figures, making conversions between metric and English units, and density. You will have plenty of practice problems at the end of the chapter.



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#### Section 1

# Significant Figures

#### THE PLAN

- 1. How do I know what is a significant figure?
- 2. Adding & Subtracting? You have got to be kidding!
- 3. Multiplying and Dividing? Now really!

#### How do I know what is a significant figure?

•Nonzero integers are significant

1, 2, 3, etc... Yep, keep going, and they are all significant.

•Leading zeros are never significant

00.0123...It is exactly what it sounds like it is. These zeroes will appear to the left of nonzero integers. They are sometimes called placeholders. They are never considered to be significant when analyzing a number.

•Captive zeros are always significant

1000000001...Again, it is what it is. These characters are held captive between two nonzero integers. There can be an infinite number of them, by the by.

•Trailing zeros are only significant when there is a decimal present in the number

You guessed it! These kiddos will appear to the right of nonzero integers. The decimal can be anywhere in the number, and then the trailing zero magically becomes significant.

•Exact numbers have an infinite number of significant figures

12 eggs in a dozen...500 sheets in a ream of paper...We just do not worry about their number of significant figures. It goes on and on.

#### **REVIEW 1.1** Significant Figures

How many significant figures are present in 009004.00?



## Adding and Subtracting

Totally serious here. You have a particular way of adding and subtracting and paying attention to the level of precision of the digit. So, what is precision? Check out the image of the dart boards and see if you understand precision and accuracy in that context.



Well, that's all well and good, but that is not the kind of precision that I am talking about. The sort of precision that I am talking about is looking at the decimal place to which a value is carried. For example, 100 is less precise than 100.00. So, the rule for adding and subtracting is as follows...**The answer has the same number of decimal places as the least precise measurement.** 



What is the correct answer when you add the following numbers: 7.2 + 4.841?



REVIEW 1.3 Subtracting		
How about 3.142 - 1?		
<b>A.</b> 2.142		
<b>B.</b> 2.14		
○ C. 2.1		
<b>Ø D.</b> 2		
Check Answer		

**Check Answer** 

### **Multiplying and Dividing**

You guessed it! There is a rule for this stuff, too. This time... The answer has the same number of significant figures as the as the value with the lowest number of significant figures.



**REVIEW 1.5** Dividing

What about when you divide 3.142 by 1?

# Conversions

#### THE PLAN

- 1. Metric to Metric
- 2. Metric to English and Vice Versa
- 3. Temperatures

# **Metric to Metric**

The metric system was well on its way to being used in the United States until the mid 1970s. So, here we sit mired deeply in our English units that even the Brits no longer use exclusively!

First things first, you have to know the prefixes and what they mean. I teach this in a manner quite different from most folks, but I feel that it is a wholly logical method. So, here goes...

- giga(G)-1 x 10<sup>-9</sup>
- mega(M)-1 x 10<sup>-6</sup>
- kilo(k)– 1 x 10<sup>-3</sup>
- hecto(h)– 1 x 10<sup>-2</sup>
- deka(da)– 1 x 10<sup>-1</sup>
- deci(d)-- 1 x  $10^{1}$
- centi(c)-- 1 x 10<sup>2</sup>
- milli(m)-- 1 x 10<sup>3</sup>
- micro( $\mu$ )-- 1 x 10<sup>6</sup>
- nano(n)-- 1 x 10<sup>9</sup>

Each of those prefixes is applied to a base unit of some kind. Examples include

length--meter (m) volume--liter (L) mass--gram (g) time--second (s) Watch the video below and see how logical this method is.

Every time you work with conversions in the metric system, you will relate your units to **one** of the base unit.

• 360 mm = \_\_\_\_m?

360 mm x 1 m = 0.36 m $1 \times 10^3 \text{ mm}$ 

• 4.25 x 10<sup>-5</sup> ML = \_\_\_\_nL

 $4.25 \times 10^{-5} \text{ ML x} \underline{1 \text{ L}} \times \underline{1 \times 10^9 \text{ nL}} = 4.25 \times 10^{10} \text{ nL}$  $1 \times 10^{-6} \text{ ML} \text{ l L}$ 

An even sneakier way to make the previous conversion is to realize that the l L divide out. So...

 $4.25 \times 10^{-5} \text{ ML x} \underline{1 \times 10^9 \text{ nL}} = 4.25 \times 10^{10} \text{ nL}$  $1 \times 10^{-6} \text{ ML}$ 

All that you have to know are matched powers of ten to the prefixes, and then it seems like magic.

Now get busy and commit those powers of ten and prefixes to your memory banks



#### Metric to English and Vice Versa

That process of writing what you have and striking through units to get to new units is known as *dimensional analysis*. It is an incredibly useful tool in chemistry, and you will be using it throughout the course. In fact, we are about to use it again right now.

We often need to convert metric units to English units for comprehension purposes; and we often go in the opposite direction to abide by scientific rules that mandate metric units.

When working one of these problems, you must know a conversion factor in order to be successful. Examples of conversion factors that will soon be used are:

1 in = 2.54 cm

1 lb = 454 g

1 mi = 1609 m

1 L = 1.06 qt

Did you notice that there is always one of something in those conversion factors? That is generally how they roll. Shall we try a metric to English conversion?

• 360 mm = \_\_\_\_in?

 $360 \text{ mm x} \underline{1 \text{ x} 10^2 \text{ cm}} \text{ x} \underline{1 \text{ in}} = 14 \text{ in}$  $1 \text{ x} 10^3 \text{ mm} 2.54 \text{ cm}$ 

• 125 lb = \_\_\_kg?

 $125 \implies x 454 g x 1 x 10^{-3} kg = 56.8 kg$  $1 \implies 1 g$  Click on the link below to watch a video below to see how I set this up in real time.

#### Conversions

REVIEW 1.7 Metric to English Conversion

A traditional competitive running distance is a 5k. That actually means 5.00 km. How many miles is this?



#### Temperature

Again, in the United States, we tend to stick with a unit that the rest of the world does not use. That unit is the Fahrenheit. It is what most Americans understand when temperatures are given. It can be troubling when getting off of a plane in Calgary, Alberta, Canada and hearing the the temperature is 25 degrees outside on a sunny July afternoon!

It is traditional in chemistry to use one of two temperature scales that are not the Fahrenheit scale. These two scales are the Celsius and Kelvin scales.

Formulas

Fahrenheit to Celsius:  $(x^{\circ}F - 32^{\circ}F) \times 5^{\circ}C = y^{\circ}C$  $9^{\circ}F$ 

Celsius to Fahrenheit:  $(x \circ C \times 9 \circ F) + 32 \circ F = y \circ F$  $5 \circ C$ 

Celsius to Kelvin:  $x^{\circ}C + 273 = y K$ 

Kelvin to Celsius:  $x K - 273 = y^{\circ}C$ 

• 
$$78^{\circ}F = \__{\circ}C$$
  
( $78^{\circ}F - 32^{\circ}F$ ) x  $5^{\circ}C = 26^{\circ}C$   
 $9^{\circ}F$ 



• 
$$26^{\circ}C = K$$

 $26^{\circ}\text{C} + 273 = 299 \text{ K}^*$ 

\*Note, there is no degree sign with K



#### SECTION 3

# Density

#### THE PLAN

- 1. Volume Formulas
- 2. Density

#### **Volume Formulas**

You might need to recall the formulas of some solid objects in order to work the next few problems.

V<sub>rectangular prism</sub> = length x width x height

```
V_{cylinder} = \pi r^2 h
```

```
V_{sphere} = \underline{4\pi}r^3
```

#### Density

So, why did I give you the volume formulas? Because density is found by taking an object's mass and dividing by its volume. Some typical units of density include: g/mL, g/cm<sup>3</sup>, g/L

 $D = \underline{m}$ V

If you know density and volume, you can find mass:

m = DV

If you know density and mass, you can find volume:

```
V = <u>m</u>
D
```

Look back at the picture at the beginning of this chapter. Notice how those different liquids are stacked up on each other? Why do you think that is so? A square piece of cobalt glass (glass with cobalt ions mixed into it) has a mass of 12.228 g. Its dimensions are 50. mm x 50. mm x 2.0 mm. What is its density in g/cm<sup>3</sup>?

First convert each of the mm to cm for the volume of the rectangular prism...

V = 5.0 cm x 5.0 cm. 0.20 cm = 5.0 cm<sup>3</sup>

Then divide the given mass by the calculated volume...

 $D = \underline{12.228 \text{ g}} = 2.4 \text{ g/cm}^3$ 5.0 cm<sup>3</sup>

• A cylindrical piece of aluminum metal has a diameter of 12.5 mm and a mass of 16.559 g. The density of aluminum is known to be 2.70 g/cm3. What is its length in mm?

First use the density and the mass to find the volume of the cylinder...

V = <u>16.559 g</u> = 6.13 cm<sup>3</sup>2.70 g/cm<sup>3</sup>

Next convert the diameter to cm and find the radius. Then use the formula for the volume of a cylinder to find the height of the cylinder. This height is the same as the length of the cylinder when it is on its side.

 $6.13 \text{ cm}^3 = \pi (1.25 \text{ cm}/2)^2 \text{h}$ 

h = 5.00 cm...which is 50.0 mm

#### REVIEW 1.10



At the end of each chapter, I will provide a link to at least one pdf practice sheet on my website. Here is the first one:

**Conversions & Density Practice** 

# Matter

This chapter will address classifying matter and separating matter. It is without any mathematics, so give your calculator a break!



# **Classifying Matter**

#### THE PLAN

1. Elements

2. Compounds

#### Elements

Everything that has mass and volume is considered to be matter. A thought is an example of something that is not considered to be matter--no mass and takes up no space even though it seems that thoughts occupy our minds!

The simplest form of matter is an element. Elements are classified as such because they cannot be broken down into simpler forms with physical or chemical means.

This is a good time to learn all names and symbols of the table. From here on out, it is expected that you know both for each element.

Go to webelements for a fantastic web site on the periodic table. Download a periodic table on your phone or tablet, and be a true geek. Here are some free suggestions to find in the Apple App Store: The Chemical Touch (iPhone), 25 Tap Quiz Element Compilation (iPhone), Periodic Table by Jan Dedek (iPad), Periodic Table of the Elements by Kevin Neelands (iPad). Here is a suggestion for an incredibly beautiful periodic table, but it's not free: The Elements: A Visual Exploration (iPad)

Every element that you see on the periodic table does not exist in nature by itself. There are seven that do not exist naturally by themselves. Rather, they exist as compounds.

#### Compounds

Those seven elements exist in nature in a diatomic state, that is a two-atomed substance. In particular, each of them exists with two of the same atom bonded to each other. A silly mnemonic device to help you remember these seven substances is BrINClHOF...pronounced "brink-el-hof." This is not the name of a renowned scientist, it is simply the seven symbols put together in a form that is easily memorized.



So, when you write these seven elements, you will do so by writing a subscript of "2" to the right of each symbol. Bromine is written as  $Br_2$ , iodine as  $I_2$ , nitrogen as  $N_2$  etc.

These seven diatomic molecules are examples of compounds. Compounds are pure substances that can be separated by chemical means, but not by physical means. To go further, you need to know a bit about placement of metals, metalloids, and nonmetals on the periodic table. Look at the stair-stepped elements that start with boron (B) and work their way down to astatine (At). Those elements along the stair steps, excluding aluminum (Al) are the metalloids. They have properties of both metals and nonmetals.

What are those properties of metals and nonmetals? Metals have luster, tend to be in solid phase at room temperature (25 °C), are conductors of heat and electricity, can be malleable, and ductile. Nonmetals are dull when they are solid, can be any phase at room temperature, are typically not conductors of heat and electricity, and solids are brittle.

The majority of the table is made of metals, as they are to the left of the metalloids. The one exception is hydrogen (H). Hydrogen is a nonmetal, while the remaining sixteen nonmetals are those to the right of the metalloids.

Now that you can determine whether an element is a metal, metalloid, or nonmetal, you can determine whether a combination of them makes an ionic compound or a molecular compound.

Ionic compounds are made of a metal and a nonmetal or polyatomic ions. We will get to polyatomic ions later. Would magnesium and sulfur make an ionic compound? Would carbon and hydrogen?

A molecular compound, is also known as a covalent compound. Two or more nonmetals bond to each other to make a molecular compound? Would calcium and oxygen make a molecular compound? Would carbon and oxygen?

# Separating Mixtures

#### THE PLAN

- 1. What is a mixture?
- 2. Decantation
- 3. Filtration
- 4. Centrifugation
- 5. Evaporation
- 6. Distillation
- 7. Chromatography

# What is a mixture?

While elements and compounds are pure substances, mixtures are not.

A homogeneous mixture is a combination of two or more pure substances (elements or compounds) that is uniform throughout. That is, if you take a sample from any part of the mixture, you are guaranteed to match any other sample from that mixture. Another name for homogenous mixtures, is solutions. Sea water is an example of a solution.

In contrast, heterogenous mixtures are a combination of two or more pure substances that is not uniform throughout. You might get two identical samples, but it is not guaranteed. Dirt is an example of a heterogenous mixture.

Unlike elements and compounds, mixtures can be separated by physical means. Six common techniques used to separate mixtures follow.



## Decantation

The pouring off of one substance from another is known as decantation. The process is used for heterogeneous mixtures, and it works due to differences in densi-

ties or particle sizes. You can decant the liquid off of a jar of pickles.



#### Centrifugation

Have you ever noticed how when you are spinning on a merry-goround, you have to hold on lest you be tossed outward? That same principle is at work in separating heterogenous mixtures like blood. A centrifuge is a device that spins



Filtration

The passing of one sub-

stance in a heterogeneous

mixture through a semi-

permeable membrane is

known as filtration. It works

due to differences in particle

through paper and be sepa-

sizes. Dirt can be filtered

rated from water.

phy-061062.blogspot.com

test tubes around in circular motion really quickly (>2000 rpm). The more dense particles will be separated from the less dense particles. In the case of blood, the more dense red

blood cells will lie at the bottom of the tube as a pellet with the remainder of the blood (leukocytes, platelets, and plasma) above that pellet.

#### **Evaporation**

Homogenous mixtures often rely upon differences in boiling point to allow separation. For example, if sea water is left outside to sit, the water will eventually evaporate, leaving behind the salt. What could you do to accelerate this process?

# Distillation Again, differences in boiling point are used in distilling a mixture. While heterogeneous mixtures can be distilled, it is kind of overkill to do so. So-



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lutions are prime candidates for this process. It abides by the same concepts as evaporation, but you can retain multiple components of the mixture...the salt and the water, for example.

#### Chromatography

Some solutions can be separated by differences in the affinity, or likeness, for either a mobile phase or a stationary phase. Paper chromatography is the simplest form of chromatography. For example, black ink is a solution of several colors of ink. Water soluble black ink can be separated by paper chromatography. In the process, colors of ink with greater affinity for the water that creeps through the paper will be separated earlier than those colors that have a greater affinity for the paper. Look at the video below to watch radial paper chromatography separate water-soluble ink.

#### **Chromatography Video**

# Atomic Structure

You will learn about the make-up of an atom and the theories that led us to our present understanding of atomic structure.



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#### Democritus (460-370 BC)



Democritus was the first person to propose that matter is not infinitely divisible. That is, we cannot just get smaller and smaller particles with no end. He called the smallest particles that exist *atomos*, and he proposed that matter was empty space through which *atomos* move.

http://www.findabout.net/

#### Aristotle (384-322 BC)

Then along came Aristotle who proved to be much more influential than Democritus was. Aristotle disagreed with the empty space idea that Democritus had put forth and rejected Democritus's idea of atomic theory. Rather he believed all matter was fire, earth, air, and water! And



http://www.counter-currents.com/

folks believed him...for over two thousand years!

## John Dalton (1766-1844 AD)

Aristotle's beliefs were supported until John Dalton proposed his theory of the atom in 1803. The following are the tenets of Dalton's Atomic Theory:

• All matter is made of atoms.



www.biography.com

- All atoms of a given element are identical and are different from atoms of other elements.
- Atoms cannot be created, destroyed, or divided into smaller particles.
- Atoms combine in simple whole number ratios to make compounds.
- In a chemical reaction, atoms are separated, combined, or rearranged.

Two of these parts of the theory have been slightly amended over the last two hundred years.

• All atoms of a given element are different from atoms of other elements. Did you notice that the *identical* part is missing? This is because Dalton did not know of isotopes when he wrote this theory. There will be more on isotopes later.

• Atoms cannot be created, destroyed, or divided into smaller particles by physical or chemical means. This is because we know of the existence of subatomic particles, while Dalton did not.

#### J.J. Thomson (1856-1940 AD)



Joseph John Thomson worked with cathode ray tubes (CRTs), which are glass tubes with electricity flowing through them. It was he who first deduced that the negatively charged particles flowing through the CRTs were electrons...hence the first subatomic particle was discovered.

#### www.chemicaheritage.org

In 1904, Thomson proposed a model of an atom to explain the neutrality of an atom, and he called his model the Plum Pudding Model. Plum pudding is a rich pudding that contains raisins, currants, and spices. It is rather like the fruitcakes of today.

The Plum Pudding Model is illustrated to the upper right. Notice that Thomson proposed that the bread represented a diffuse positive charge that spread throughout the sphere, while the electrons were just placed randomly amidst the bread.

His model was an Sphere of positive improvement on previous models vps.prenhall.com with his discovery of electrons. Alas, his model was short-lived.

#### Ernest Rutherford (1871-1937 AD)



Rutherford was a graduate student of Thomson, and he set out to prove the **Plum Pudding** Model to be true. He inadvertently disproved the Plum Pudding Model!

Electron

charge

www.daviddarlinginfo.com

He fired alpha particles (positively charged) at a thin sheet of gold foil. He expected the alpha particles to blow right

through the gold atoms and be detected as doing so. However, he found that some alpha particles were deflected at large angles. This caused him to believe that the alpha particles encoun-

tered very strong positive charge that was concentrated rather than diffuse. In 1909, it was Rutherford who first proposed that the atom had a tiny, dense central por-



tion, and that electrons move through empty space around the nucleus. He later stated that *protons* were in the nucleus.

#### Niels Bohr (1885-1962 AD)



In 1913 as a student of Rutherford, Bohr proposed a quantum model of the atom in which the electrons followed distinct orbits around the nucleus, modifying Rutherford's model with regard to the electrons. This is the model that most folks think an atom looks like.

In the 1920's the Quantum Mechanical Model of the atom was introduced by some very famed and talented scientists. Albert Einstein, Neils Bohr, Louis de Broglie, P. A. M. Dirac, Max Planck, Werner Heisenberg, and Erwin Schrödinger. These chaps were not all fans of their work. In fact Bohr said, "Anyone who is not shocked by quantum mechanics has not understood it." While Schrödinger wrote, "I don't like it, and I'm sorry I ever had anything to do with it."

(http://www.nytimes.com/2005/12/26/science/27eins\_side. html) Albert Einstein disbelieved the very theory he helped create. In fact, Einstein attempted to disprove quantum mechanics—without success—until he died.



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blogs.nature.com

The current model looks curiously like the Bohr Model, but the orbits of the electrons are not circular or ellipsoidal. They are like clouds.



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#### **Atomic Theories Practice**

CHAPTER 4

# Isotope Formulas, Electron Configurations & Orbital Diagrams

I mentioned isotopes in the previous chapter, and now you will learn how to write their formulas and understand their differences. You will also learn about the locations of electrons within their clouds by writing electron configurations and orbital diagrams.



# Isotopes

### THE PLAN

- 1. Subatomic Particles
- 2. Mass Number
- 3. Atomic Number
- 4. Number of Subatomic Particles

## **Subatomic Particles**

By this point in your life, you know that protons, electrons and neutrons exist. You probably know that protons are positively charged; electrons are negatively charged; and neutrons are neutral, or without charge.

Different forms of the same element can have different numbers of neutrons. They must have the same number of protons in order for them to be considered the same element, however. This differing number of neutrons results in the existence of isotopes, atoms of the same element with different number of neutrons.

An isotope formula provides an element's symbol, mass number, and atomic number.

• **Mass number**--the number of protons plus the number of neutrons. It is written as a superscript to the left of the element's symbol. It is always a whole number.

 $mass\#=\#p^++\#n$ 

• Atomic number--the number of protons or the number of electrons. It is written as a subscript to the left of the element's symbol and is always a whole number.

atomic# =  $\#p^+$  or  $\#e^-$ 

mass # atomic #

#### Number of Subatomic Particles

Carbon has two naturally occurring isotopes. They are reported as carbon-12 and carbon-13. The number after the element's name indicates the mass number, sum of protons and neutrons, for that isotope. Look at a periodic table to determine the atomic number of carbon and then you can see its isotope's formulas would be...

$$^{12}_{6}$$
C and  $^{13}_{6}$ C

How many neutrons does carbon-12 have? To answer this, simply subtract the atomic number from the mass number. In this case 12 - 6, and you get 6 neutrons. How many neutrons does carbon-13 have?

You can be given the mass number or the number of neutrons and write an isotope's formula. For example...

Hydrogen with 2 neutrons...

 $_{1}^{3}\mathrm{H}$ 

You can be given an isotope formula and then be asked to name the number of subatomic particles. For example...

18 9 F...

There are 9 protons, 9 electrons, and 9 neutrons.



# **Electron Configurations**

### THE PLAN

- 1. Valence Electrons
- 2. Aufbau Principle
- 3. Pauli Exclusion Principle
- 4. Hund's Rule
- 5. Energy Levels
- 6. Sublevels
- 7. Number of Electrons
- 8. Writing the Electron Configurations
- 9. Learning the Periodic Table
- 10. Shorthand Electron Configurations
- 11. Exceptional Electron Configurations

## Valence Electrons

We now know that electrons reside in the cloud that surrounds the nucleus. We care so much about electrons because they are what will interact with other atoms. In particular, the outermost electrons, or those living farthest from the nucleus, are the ones that will bond to make compounds. We call these outermost electrons valence electrons. There are three tenets that govern where within the cloud electrons will be found.

- **Aufbau Principle**--electrons will occupy lower energy orbitals before higher energy orbitals.
  - So, what is an orbital? Think of it as an electron's house.
- **Pauli Exclusion Principle**--no more than two electrons may occupy an orbital. If two electrons do occupy an orbital, then they must have opposite spins.
  - Think of it as a maximum of two electrons can live in the house. If two of them happen to live in the house, then one lives upstairs, and one lives downstairs.
- **Hund's Rule**--when occupying orbitals of equal energy, parallel spinning electrons must occupy first and then the oppositely spinning electrons may enter.
  - Okay, this is the difficult one. It will make more sense when you draw orbital diagrams a bit later. For now, think of it as you have houses on the same street and

electrons must occupy the downstairs of each house before the upstairs can have an occupant.

#### **Energy Levels**

I have explained orbitals, but we need to understand that orbitals are always part of an energy level. Think of the energy level as the city in which the houses are located. Energy levels are denoted by positive integers, 1, 2, 3, 4, etc. A larger integer means that energy level is located farther away from the nucleus than a smaller integer. Thus, the energy level closest to the nucleus is the 1st; and the 7th energy level is quite far away from the nucleus.

## Sublevels

Within energy levels, there are sublevels. Think of these sublevels as the streets of the city upon which the houses are located. The sublevels are referred to by letters: s, p, d, and f. If you go beyond f, then you will continue in the alphabet from that point, i.e. the next one would be g. The sublevels stack up in the energy levels successively. That is, the 1st energy level only has an s sublevel; whereas, the 2nd energy level has an s and a p sublevel. The 3rd energy level will have one of each, s, p, and d. Finally, the 4th energy level will have all four sublevels in it.

#### Number of Electrons

Since the sublevels are like streets within the city, there may be a certain number of houses on each street. *s* sublevels only

have one house. That means that the *s* sublevel has only one orbital. That orbital may only hold a maximum of two electrons (Pauli Exclusion Principle). From that, we get that the maximum number of electrons in an *s* sublevel is two.

Remember that the 1st energy level only has an s sublevel. That means that the 1st energy level can only hold a maximum of two electrons. When we move into the 2nd energy level which is just farther away from the nucleus than the 1st energy level, we will have both s and p sublevels. A p sublevel can have three houses on its streets. Therefore, a p sublevel can have three orbitals, each with two electrons as a maximum; so, there is a maximum of six electrons in the p sublevel.

We do not encounter the p sublevel until we get into the 2nd energy level. The 2nd energy level contains both s and p sublevels. That means a maximum of 2 from the s and 6 from the p, for a total maximum in the 2nd energy level of 8 electrons.

As we keep going, the 3rd energy level holds one each of s, p, and d. A d sublevel can hold a maximum of 5 houses, or orbitals. Thus, 10 electrons is the maximum number of electrons that can be held in the d sublevel. If we have s, p, and d sublevels in the 3rd energy level, the we have respectively, a maximum of 2, 6, and 10 electrons within the houses. The 3rd energy level can hold a maximum of 18 electrons.

And finally, the *f* sublevel greets us. We do not encounter the *f* sublevel until the 4th energy level. Within the 4th energy level, there is one of each type: *s*, *p*, *d*, and *f*. An *f* sublevel

can hold a maximum of 7 houses, or orbitals. Which means that there can be a maximum of 14 electrons within the f sublevel. So, in the 4th energy level, we have houses that can hold 2, 6, 10, and 14 electrons, or a total of 32 electrons.

ENERGY LEVEL	SUBLEVEL	MAX # OF ELECTRONS
1	S	2
2	S	2
	р	6
3	S	2
	р	6
	d	10
4	S	2
	р	6
	d	10
	f	14
5	S	2
	р	6
	d	10
	f	14
	g	18

See if the table that follows helps to summarize all this confusing stuff.

The table could keep going, but I hope that you get the point by now.

#### Writing the Electron Configurations

Now we get to write electron configurations, which are notations that tell us where electrons reside within the electron cloud. Within an electron configuration, you will be given the energy level(s), the sublevel(s), and the number of electrons present in each sublevel. Below you see the electron configuration for hydrogen. Look at a periodic table. Hydrogen has an atomic number of 1, thus it has 1 electron.

 $1S^1$ 

Reading this electron configuration from right to left, we understand that there is one electron living in the *s* sublevel of the first energy level.

We will do helium's electron configuration next. There are two electrons living in the *s* sublevel of the first energy level...this follows the Aufbau Principle and the Pauli Exclusion Principle. Thus, we write its configuration as 1s<sup>2</sup>.

#### Learning the Periodic Table

Let's take a look at the periodic table and learn some more about it.





www.elementsdatabase.com

The rows on the table are called periods, and the columns are called groups. I will refer to them as such from here on. Notice that there are 7 periods because Cerium's and Thorium's periods are really a part of the 6th and 7th periods.

In your mind's eye, move helium over to be above beryllium and next to hydrogen. Now notice that there are two groups that poke up on the left side of the table. There are six groups that poke up on the right side of the table. Keep going...there are ten groups that are in the middle of the table, and there are fourteen groups that are pulled out at the bottom. The following schematic offers the groups that I just mentioned with the energy level that corresponds to each. Notice that the s and p sublevels' energy levels agree with their period numbers. The d sublevels' energy levels are always one less than their respective period numbers, and the d sublevel elements are called the transition metals. The f sublevels' energy levels are two less then their period numbers, and they are called the inner transition metals.





So, as we continue to write electron configurations, we will look at lithium and know that it has 3 electrons. The first 2 of those 3 electrons will live in the same place as helium's 2 electrons live...that is in the 1s. Since an *s* sublevel can only hold a maximum of 2 electrons, and it is the only sublevel in the 1st energy level, we must place the 3rd electron in the 2nd energy level and start with its *s* sublevel. Thus, we get  $1s^22s^1$  for lithium's electron configuration.

If you add the superscripts you will get the total number of electrons, by the by. We translate this electron configuration by reading from right to left as we did earlier. Therefore, there is one electron living in the 2*s* sublevel, and there are two electrons living in the 1*s* sublevel. Aufbau and Pauli Exclusion Principles are upheld.



When we move to boron, we will have to move into the p sublevel since the 2s sublevel will be filled with its two electrons. Boron's electron configuration is  $1s^22s^22p^1$ . Notice that the sum of the superscripts is still boron's total number of electrons.

You will find carbon through neon below.

C... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>2</sup>

N... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>

- O... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>
- F... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>5</sup>

## Ne... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>

The next element is sodium. It resides on the 3rd period in the *s* sublevel area. Let the periodic table on page 31 guide you, and notice that with neon, you have now filled the 2p sublevel with six electrons. Thus, you must move into the 3s sublevel to get to sodium's eleventh electron. The first ten of sodium's electrons live in the same place as neon's ten electrons. So we get

Na... 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>1</sup>

INTERACTIVE **4.3** Electron Configurations

### What is the electron configuration of magnesium?



# Shorthand Electron Configurations

As you can imagine, the length of an electron configuration can become ridiculously long. There is a shorthand notation that is advisable to use when you have any element that is beyond neon in the periodic table. To use this shorthand technique, you simply find the noble gas (group 18) that

precedes the element whose configuration you are tackling. Place the symbol of that noble gas in brackets, and then continue to write the electron configuration as normal from the point just beyond that noble gas. Here are a few shorthand notations:

Na...[Ne]3s1

Ar...[Ne]3s<sup>2</sup>3p<sup>6</sup>

 $Ca...[Ar]4s^2$ 

Notice that the valence electrons (those in the outermost energy level) are essentially pointed out to you with the shorthand electron configuration. Na has 1 valence electron, Ar 8 , and Ca 2.

Once you get beyond calcium, it starts to get a little weird. Look at the periodic table on the bottom right side of page 31 and notice that after calcium, we begin to enter the 3*d* sublevel. As mentioned before, the *d* sublevel's energy level will always be one less than its period. Thus, scandium has one electron in the 3*d* sublevel.

# Sc...[Ar]4s<sup>2</sup>3d<sup>1</sup>

Scandium only has 2 valence electrons, as the outermost energy level is the 4th. If you keep going across the periodic table on the 4th period, you simply count across the d sublevel until you reach 10. Recall that the maximum number of electrons that can be in a d sublevel is 10.

# Zn...[Ar]4s<sup>2</sup>3d<sup>10</sup>

When you get to gallium, you have gone into the 4p sublevel. Write the electron configuration in the order of electrons' filling.

# Ga...[Ar]4s<sup>2</sup>3d<sup>10</sup>4p<sup>1</sup>

Gallium has 3 valence electrons, 2 in the 4*s* and 1 in the 4*p*. Let me do a few more for you.

# $Kr...[Ar]4s^23d^{10}4p^6$

 $Tc...[Kr]5s^24d^5$ 

 $Cs...[Xe]6s^1$ 

#### **INTERACTIVE 4.4** Electron Configurations

# What is the electron configuration of lanthanum?



After lanthanum, you go down down to the *f* sublevel which are the inner transition metals. These metals are also known as the rare earth metals because of their scarcity in nature. In fact, almost half of them are man-made. The periods in which they live are the 6th and 7th, and the energy levels are the 4th and 5th, respectively. Cerium is the beginning of the 4f sublevel. Its electron configuration is [Xe]6s<sup>2</sup>5d<sup>1</sup>4f<sup>1</sup>. One electron is placed into the 5*d* and then the last electron is placed in the 4*f*. You will continue to fill the 4*f* until you reach lutetium whose configuration is [Xe]6s<sup>2</sup>5d<sup>1</sup>4f<sup>14</sup>.

After lutetium, you go back into the 5*d* with hafnium, [Xe]6s<sup>2</sup>4f<sup>14</sup>5d<sup>2</sup>, combining like terms with the 5*d*.

#### **Exceptional Electron Configurations**

There are four elements who have exceptional electron configurations. They will take advantage of the concept that the most stable that a sublevel can be is when it is filled with its maximum number of electrons. The next most stable is when it is half-filled, and the next most stable is when it is empty. So, we expect the electron configuration of chromium to be [Ar]4s<sup>2</sup>3d<sup>4</sup>. However, its actual electron configuration is [Ar]4s<sup>1</sup>3d<sup>5</sup>. It uses ambient energy to boost a 4*s* electron into the 3*d* sublevel. In doing so, it leaves both the 4*s* and the 3d half-filled which is more stable than the original.

The other three elements that have exceptional electron configurations are copper, molybdenum, and silver. Write their expected configurations, and then look ahead for their corrected ones.

Cu... [Ar]4s<sup>1</sup>3d<sup>10</sup>

```
Mo... [Ar]5s<sup>1</sup>4d<sup>5</sup>
```

```
Ag... [Ar]5s^{1}4d^{10}
```

Why would tungsten, gold, seborgium, and roentgenium not do the moving around of the *s* electron?


# SECTION 3 Orbital Diagrams

## THE PLAN

- 1. The Template
- 2. Examples

# The Template

You know how to write electron configurations, and now you will learn how to write orbital diagrams for elements. If you look at the beginning of this chapter (p. 25), you will see an orbital digram. The information that you get from it is the energy level, the sublevel, and the spin. Thus, Aufbau, Pauli's Exclusion, and Hund's Rule are all obeyed and visible in an orbital diagram. Up and down arrows are used to represent electrons and their spins. Here is a template for an orbital diagram.



All that you need to have available is an electron configuration, and then you translate it into the orbital diagram. The only real difference is the application of Hund's Rule. This rule states that when you fill orbitals of equal energy, you fill parallel-spinning electrons before putting in oppositely spinning electrons. Click below to see a little video of drawing orbital diagrams. *They are too hard for me to type in this book*.

# Examples

# **Orbital Diagrams**

CHAPTER 5

# Periodicity

In this chapter, I will share the fathers of the periodic table's stories with you and go over different regions of the table. You will also learn about periodic trends.





First ionization energy (kJ/mol)

ncreasing



Magnitude of electron affinity (kJ/mol)



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### SECTION 1

# The Fathers

#### THE PLAN

- 1. Mendeleev
- 2. Meyer
- 3. Moseley

#### Mendeleev

Dimitri Mendeleev is often considered to be the one and only father of the periodic table. I believe that he is one of the fathers. He was a Russian chemist and inventor who organized



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a periodic table of the elements according to atomic weights, valences, and properties. He published this table March, 6 1869, unaware that others had organized tables of the like earlier in the 1860s. His table is shown below.

	TABELLE II								
REIHEN	GRUPPE 1.  R <sup>2</sup> O	GRUPPE II.  RO	RUPPE III. R2O3	GRUPPE IV. RH4 RO2	GRUPPE V. RH <sup>3</sup> R <sup>2</sup> 05	GRUPPE VI. RH <sup>2</sup> RO <sup>3</sup>	GRUPPE VII. RH R <sup>2</sup> 07	GRUPPE VIII. RO4	
1	H=1 Li=7	Be = 9,4	B = 11	C=12	N=14	0=16	F=19		
3	Na = 23	Mg = 24	A1 = 27,3	Si = 28	P = 31	\$=32	CI = 35,5		
4	K=39	Ca = 40	-= 44	Tí = 48	V= 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.	
5	(Cu=63)	Zn = 65	-= 68	-= 72	As = 75	Se = 78	Br = 80		
6	RЬ = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	-=100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.	
7	(Ag = 108)	Cd = 112	In=113	\$n=118	Sb=122	Te=125	J=127		
8	CS = 133	Ba = 137	?Di= 138	?C8 = 140	-	-	-		
9	()	-	-	-	-	-			
10	-	-	?Er = 178	?La ≈180	Ta = 182	W=184	-	0s = 195, Ir = 197, Pt = 198, Au = 199	
11	(Au=199)	Hg = 200	TI = 204	Pb=207	8; = 208	-	-		
12	-	-	-	Th = 231	-	U=240	-		

**Figure 2.5** Dmitri Mendeleev's 1872 periodic table. The spaces marked with blank lines represent elements that Mendeleev deduced existed but were unknown at the time, so he left places for them in the table. The symbols at the top of the columns (e.g., R<sup>2</sup>O and RH<sup>4</sup>) are molecular formulas written in the style of the 19th century.

#### Meyer

Just a few months after Mendeleev published his periodic table, a German chemist named Lothar Meyer published a similar periodic table based upon the atomic volumes of the elements. Both he and Mendeleev worked with Robert Bunsen (as in the burner), by the by.



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#### Julius Lothar Meyer (1830-1895)

Table from Annalen der Chemie, Supplementband 7, 354 (1870).

		Pete	odic table acc	cording to	Lothar Mey	vr. 1870		
L	11.	III	IV.	V.	VL	VIL	VIII.	IX.
	B=11.0	Al=27.3				7in=113,4	TI=000 7	
			-		-			
	C=11.97	St=28				Sa=117.8		Pb=206,4
			Tin48		Zi=89,7		-	
	N=14,01	P=30.9		As=749		Sb=122.1		Bi=207,5
			V=51.2		Nb=93.7		Ta=182.2	
	O=15,96	31,98		Se=78		Te=1187		÷.
			Ch-52.4		Mo-95.6		W=183.5	
++	F=19.1	CI=3538		Br=79.75		J=126.5		
			Mn=54.8		Ru=103.5		Os=198.6 7	
			Fe=35.9		Rh=104.1		b=196.7	
			Cn=Ni=58.6		Pd=106.2		P=1957	
Li=7.01	Na=22.99	K=39.04		Rb=85.2		Ct=132.7		
		2000	Cu=63.3		As=107.66		An=196.2	
7Re-03	Men23.9	Cai:10.0	20022	Sru\$7.0		Rent16.8	N	
	010-000	2006	Zz=64,9		Cd+111,6		Hg=199.8	



### Moseley

aprendelahistoriadelatabla.blogspot.com

The periodic table as we know it today was crafted by a young man by the name of Henry Gwyn Jeffreys Moseley. He was a physicist who helped to prove the Bohr model of the atom to be a feasible model. He based his periodic table on nuclear charge, which we also call atomic number. He was killed by a sniper at the Battle of Gallipoli in Turkey during WWI. It is thought by many that his death was one of the most significant losses to mankind. He was only 27 years old when he died, and he is responsible for the periodic table as we use it today. Just think of what else this young man could have contributed.

#### SECTION 2

# The Regions

### THE PLAN

- 1. Hydrogen
- 2. Alkali Metals
- 3. Alkaline Earth Metals
- 4. Groups 13-16
- 5. Halogens
- 6. Noble Gases
- 7. Transition Metals
- 8. Inner Transition Metals

H <sup>1</sup>	Periodic Table of the Elements © www.elementsdatabase.com											2 He					
Li 3	Be		hydro alkali	ogen i meta	ls	le.	■ p ■ n	oor me onmet	etals als			5 B	C 6	7 N	08	۶ F	10 Ne
11 Na	12 Mg		trans	ition n	netals	15	<ul> <li>noble gases</li> <li>rare earth metals</li> </ul>				13 Al	14 Si	15 P	16 <mark>S</mark>	17 Cl	18 Ar	
19 K	Ca <sup>20</sup>	21 Sc	22 Ti	V <sup>23</sup>	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53	54 Xe
Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

Ce	59 Pr	60 Nd	Pm	62 Sm	Eu Eu	64 Gd	<sup>65</sup> Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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## Hydrogen

The most abundant element in the universe, hydrogen is in a group of its own. Though it lives in Group 1, it has very little in common with the remaining elements in that group. It is a nonmetal; it has one valence electron. Recall that it is also diatomic when in nature by itself.

# Alkali Metals

The rest of the elements in Group 1 are the alkali metals. The word, "alkali," refers to the formation of basic mixtures. The elements in this group are from lithium down to cesium, and they are solids at room temperature, 25°C, that are so soft they can be cut with a dull knife. They love to react with water, and they do make basic solutions in water. Electricity is

well-conducted through these metals, and they all have one valence electron just like hydrogen does.

# **Alkaline Earth Metals**

As per the name, these Group 2 elements also make basic solutions, yet they are harder than Alkali Metals and not as reactive. These metals are found in compounds and substances with structural strength. Some examples are emeralds that contain beryllium, aircraft skins that can contain magnesium, and marble that contains calcium. From their electron configurations, you can determine that these metals have two valence electrons.

# **Groups 13-16**

The elements from aluminum over to oxygen and down to thallium over to polonium, are a conglomeration of properties. All three phases, solid, liquid, and gas, are represented by these elements as are metals, metalloids, and nonmetals. They have 3, 4, 5, and 6 valence electrons for the respective groups of 13-16. In other words, they're all over the place.

# Halogens

Group 17 constitutes the halogens, or "salt formers." These nonmetals represent all three phases...F and Cl are gases, Br is a liquid, and I and At are solids. All of them are diatomic when by themselves. They have seven valence electrons and are highly reactive.

# **Noble Gases**

Ah, the royalty of the periodic table present themselves in Group 18. These gases are also known as inert gases because they do not readily react with any other elements. They are so inactive because their outermost energy levels are satisfied. Helium has two valence electrons, and the 1*s* orbital is filled. The remainder of the gases beneath helium have eight valence electrons and make their respective energy levels' happy with filled *s* and *p* sublevels. Every one on the periodic table is striving to look like a noble gas.

# **Transition Metals**

These metals are the *d* sublevel elements. Their electrons configurations end in the *d* sublevel. They are all solids except one, mecury; and these solids are harder than Groups 1 and 2 elements. The metals in this group have varying properties, but most are good conductors of both heat and electricity. All of them are naturally occurring except technetium.

## **Inner Transition Metals**

These elements whose electron configurations end in the *f* sublevel are also known as the rare earth elements. In fact almost half of them are synthetic. The Lanthanides are those that follow lanthanum and end their configuration in 4*f*. These metals tend to be shiny and reactive. The Actinides are the 5*f* metals and all of them have at least one radioactive isotope. In fact, those elements past uranium are all synthetic and every isotope is radioactive.

# SECTION 3

# Trends

# THE PLAN

- 1. Atomic Radius
- 2. Ionization Energy
- 3. Electron Affinity
- 4. Electronegativity

# **Atomic Radius**

The atomic radii of each element are determined experimentally by making homonuclear, diatomic molecules and measuring from nucleus to nucleus. That is two atoms of the same type are made into a molecule and the distance from the nucleus of one to the nucleus of the other is measured and divided by two. The unit of measurement is typically nm.



In order to discuss atomic radius and its trends, we need to know a bit about the shielding effect. The shielding effect occurs when valence electrons' attractions to the nucleus are blocked by the electrons that are not valence electrons, core electrons. These core electrons provide a shield that exists between the nucleus and the outermost electrons. This means that the more core electrons there are, the less attraction to the nucleus the valence electrons feel. As you move across a period from left to right, the electrons will successively enter the same energy level for the *s* and *p* sublevel elements. This means that the valence electron number increases across a period, while the core number of electrons remains the same. So, the nucleus does not increase its shielding effect when going across a period. Rather the nucleus pulls the valence electrons in closer and closer as we move across the period. This means that the atomic radius gets a bit smaller and smaller as we traverse the period.

Conversely, as we move down a group, the number of core electrons increases, while the number of valence electrons remains the same. This means that the shielding effect increases as we go down the group, and the atoms become bigger since the nucleus cannot pull as hard on the electrons.

Observe the trend below in the mock periodic table layout.



### **Ionization Energy**

The energy required to remove an electron from an atom or an ion is known as ionization energy. The values are measured in kilojoules per mole (kJ/mol). Picture yourself as an atom. Someone walks up to you and wants to take one of your electrons. You will not just give up the electron; the person must pay for the electron. That payment is ionization energy.



As we move across a period, the size gets smaller thus the electrons are held more tightly by the nucleus. That means that it will require more energy to remove an electron as we move across a period. As we move down a group the electrons are farther away from the nucleus and are not held as tightly; thus, the ionization energy decreases as we move down a group. The first ionization energy is the energy required to remove the first electron from an atom. The second ionization energy is the energy required to remove a second electron, and so on. The second ionization energy is always greater than the first, and the third greater than the second, etc.

# **Electron Affinity**

Picture yourself as an atom like fluorine. You have seven valence electrons, and you are only one electron away from having a full sublevel of eight. You really want to look like neon, and you really want to gain one more electron. As you can imagine, it will cost you. You must pay to get another electron. The energy that is paid is electron affinity also measured in kJ/mol. Electron affinities tend to be negative, indicating that energy is lost by the atom in order to gain an electron.

The trend is to increase (get more negative) the energy paid or lost as we move across a period and to decrease (pay less) as we move down a group. Think about poor francium, it has



only one valence electron. Its nucleus does not care about it since it is in the seventh energy level, and it is not willing to shell out any energy in order to get another electron that it would not attract.

# Electronegativity

While electron affinity is an energy measurement of the willingness of an atom to attract an electron to itself, electronegativity is a measurement that is unitless of the ability of an atom in a molecule to attract electrons to itself. Linus Pauling came up with the concept and arbitrarily assigned fluorine to



have an electronegativity of 4.0. The other atoms' electronegativity values are relative to that of fluorine. The trend is to increase going across and decrease going down for the same reasons as were mentioned in ionization energy and electron affinity.

#### INTERACTIVE 5.1 Atomic Size

Arrange the following elements in order of increasing atomic size: chlorine, oxygen, fluorine, polonium

A. F<O<Cl<Po</li>
 B. F>O>Cl>Po
 C. Po<Cl<O<F</li>
 D. They are equal

INTERACTIVE 5.2 Lorem Ipsum dolor amet, consectetur

Arrange the following elements in order of increasing ionization energy: boron, helium, lithium, nitrogen A. Li>B>N>He **B.** He<N<B<Li **C.** Li<B<N<He **D.** They are equal **Check Answer** 

**Check Answer** 

INTERACTIVE 5.3 Lorem Ipsum dolor amet, consectetur

Arrange the following elements in order of increasing electron affinity: cesium, potassium, rubidium, sodium

A. Na<K<Rb<Cs</li>
B. Cs<Rb<K<Na</li>
C. Cs>Rb>K>Na
D. They are equal

**Check Answer** 

INTERACTIVE 5.4 Lorem Ipsum dolor amet, consectetur

Arrange the following elements in order of decreasing electronegativity: carbon, fluorine, francium, lithium



**B.** F<C<Li<Fr

 $\bigcirc$  C. Fr<Li<C<F

**D.** They are equal

**Check Answer** 

# The Mole & Its Friends



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I will share with you the magic of the mole much more in this chapter. Representative particles, smaller bits, molar masses will all be covered, as well as calculations of such.

# Section 1

# The Mole

## THE PLAN

- 1. What is a Mole?
- 2. Avogadro's Number
- 3. Representative Particles
- 4. Molar Mass
- 5. Isotopes
- 6. Mole Problems

# What is a Mole?

I imagine that you have heard of a mole in a few contexts...a burrowing critter (pictured on the cover of this chapter), or a skin pigmentation. Neither of those is what we reference in chemistry as a mole. In chemistry a mole is a word that represents a number just as a dozen represents 12 of something.

### Avogadro's Number

A mole of a pure substance means 6.02 x 10<sup>23</sup> representative particles of that substance . That gargantuan number is known as Avogadro's number. You need to know what pure substances can be and what representative particles are.

## **Representative Particles**

Kind of like it reads, a representative particle (rp) is the smallest part that is still indicative of the pure substance. Examples of pure substances are atoms, molecular compounds, or ionic compounds.

Elements are those on the periodic table that are not diatomic. That means that the BrINClHOF substances are not considered to be elements, rather they are molecules. So, Fe, S, Al, P, U are all elements. The simplest part of an element is the atom. That means that the smallest part of Fe that is still Fe is its atom. Even one atom of Fe still has the 55 protons, thus it is Fe.

Recall from Chapter 2 that molecular compounds involve the bonding of two or more nonmetals. Once again, nonmetals in-

clude H and those elements to the right of the metalloids. H<sub>2</sub>O is an example of a molecular compound. The smallest part of water that is still water is the water molecule. Get it? *Molecular* compounds have the *molecule* as their representative particles. The water molecule is actually made up of atoms, in particular, two H atoms and one O atom.

You should also remember that ionic compounds are made of a metal bonded to a nonmetal. You know what the nonmetals and metalloids are, so the rest of the periodic table is made of metals. An example of an ionic compound is CaCl<sub>2</sub>. The smallest part of calcium chloride that is still calcium chloride is the formula unit. That means that the formula unit is the representative particle of an ionic compound. The formula unit is made of smaller bits called ions. The calcium chloride formula has one calcium ion and two chloride ions.

In summary...

SUBSTANCE	REPRESENTATIVE PARTICLES	SMALLER BITS
Element	atoms	
Molecular Compound	molecules	atoms
Ionic Compound	formula units	ions

From the preceding information the following should make sense:

- + 1 mol of Fe contains 6.02 x  $10^{23}$  atoms of Fe
- + 1 mol of Br<sub>2</sub> contains 6.02 x 10<sup>23</sup> molecules (molec) of Br<sub>2</sub>
- + 1 mol of NaCl contains 6.02 x 10 $^{23}$  formula units (fu) of NaCl
- + 1 mol of SO3 contains 6.02 x 10<sup>23</sup> molec of SO3
- + 1 mol of Na<sub>2</sub>O contains 6.02 x  $10^{23}$  fu of Na<sub>2</sub>O

Transferring this information that is more useful in chemistry work, leads to...

<u>1 mol Fe</u>	or	<u>6.02 x 10<sup>23</sup> atoms Fe</u>
6.02 x 10 <sup>23</sup> atoms Fe		1 mol Fe

<u>1 mol Br<sub>2</sub></u>	or	6.02 x 10 <sup>23</sup> molec Br <sub>2</sub>
6.02 x 10 <sup>23</sup> molec Br <sub>2</sub>		$1 \text{ mol } Br_2$

<u>1 mol NaCl</u> 6.02 x 10<sup>23</sup> fu NaCl or <u>6.02 x 10<sup>23</sup> fu NaCl</u> 1 mol NaCl

#### and so on...

The smaller bits that make up molecules and formula units are determined by looking at the subscripts of each element that makes up the compound. For example...

<u>1 molec <math>SO_3</math></u>	or	<u>1 molec <math>SO_3</math></u>
1 atom S		3 atoms O

or

<u>1 atom S</u>	or	<u>3 atoms O</u>
1 molec SO <sub>3</sub>		1 molec SO <sub>3</sub>

#### **Molar Mass**

One more piece of this puzzle that I am building is molar mass. The mass of one mole of a substance is the definition of molar mass. Use average atomic masses from the periodic table and round their masses to the hundredths place for consistency with the way that I work problems throughout this book. The unit of measurement is gram per mol. For an element it is as simple as looking at the periodic table and getting the mass of that element.

1 mol Fe = 55.85 g Fe or 55.85 g Fe = 1 mol Fe

1 mol Feor55.85 g Fe55.85 g Fe1 mol Fe

For a compound, the molar mass must be calculated...Molar Mass of  $\mathrm{Br}_2$ 

Br---2 x 79.90 = 159.80 g/mol

 $\begin{array}{cccc} \underline{1 \ mol \ Br_2} & \text{or} & \underline{159.80 \ g \ Br_2} \\ 159.80 \ g \ Br_2 & 1 \ mol \ Br_2 \end{array}$ 

For a compound with different elements, you will do the following...Molar Mass of SO<sub>3</sub>

S---1 x 32.06 = 32.06 O---3 x 16.00 = <u>48.00</u> 80.06 g/mol

When you have a compound with parentheses, you must distribute the subscript outside of the parentheses through to each element inside the parentheses....Molar Mass of  $Mg(C_2H_3O_2)_2$ 

 $\frac{1 \text{ mol } Mg(C_2H_3O_2)_2}{142.37 \text{ g } Mg(C_2H_3O_2)_2} \text{ or } \frac{142.37 \text{ g } Mg(C_2H_3O_2)_2}{1 \text{ mol } Mg(C_2H_3O_2)_2}$ 

#### Isotopes

So, where do those molar masses come from? They come from the average atomic masses that you find on the periodic table. The average is determined by considering all isotopes that exist for each element. For example, carbon has two naturally occurring isotopes, C-12 and C13. Carbon-12's mass is exactly 12.00 g/mol or atomic mass unit (amu), and C-13's mass is close to 13 amu. The amu is only used in isotope problems, by the by. Carbon's average atomic mass is 12.01 g/mol. You should be able to reason that more C-12 exists in nature than C-13 since the average atomic mass is so close to that of C-12.

The two factors that contribute to average atomic mass are the mass of the isotope and the abundance (percentage of time found in nature) of the isotope.

The formula to solve isotope problems is as follows:

 $avg mass = (Mass_A x Abundance_A) + (Mass_B x Abundance_B)...$ 

• Carbon consists of carbon-12, whose mass is 12.0000 amu and whose abundance is 98.89%. What are the abundance and mass of the other isotope, carbon-13?

Since there are only two isotopes, and you know the percent of one of them, just subtract the known percentage from 100% to get the missing abundance.

100% - 98.89% = 1.11% is the abundance of C-13

Now plug into the formula that is above. Remember that when you use percentages in calculations, you need to convert them to decimal form.

 $12.01 = (12.0000 \times 0.9889) + (Mass<sub>C-13</sub> \times 0.0111)$ 

Mass<sub>C-13</sub> = 12.9009 amu

• Chlorine has two naturally occurring isotopes. Cl-35 has a mass of 34.96885 amu, and Cl-37 has a mass of 36.93513 amu. What is the abundance of each isotope?

You know each isotope's mass, but neither abundance. You know that the abundances will add together to give you 100% or 1. Thus, let one abundance equal x and the other abundance will be (1-x).

35.45 = (34.96885 x) + (36.93513 (1-x))

35.45 = 34.96885x + 36.93513 - 36.93513x

-1.48513 = -1.96628x

x = 0.7553

1 - x = 0.2447

Cl-35, 75.53% and Cl-37, 24.47%

#### **Mole Problems**

Here is another handy schematic to help you travel through the process of the problems we are about to work.



From this schematic you should be able to see that we can go from moles to representative particles or to grams. We can go from grams to moles to representative particles to smaller bits if you need to do so. And then you can go the opposite direction. Let's get started with some problem solving.

• How many atoms of helium are in 4.50 mol of helium?

Ask yourself the following questions. *Is helium an element, molecular compound, or ionic compound? What is its representative particle?* 

Use your given information to begin your dimensional analysis or unit conversion...always write a number, unit, and substance.

4.50 mol He x <u> $6.02 \times 10^{23}$  atoms He</u> = 2.71 x  $10^{24}$  atoms He 1 mol He

 If a sample of chlorine gas contains 2.97 x 10<sup>24</sup> atoms of Cl, how many moles of chlorine gas are there? Remember BrINClHOF.

Is chlorine gas an element, molecular compound, or ionic compound? What is its representative particle?

 $2.97 \times 10^{24} \text{ atoms Cl x } \underline{1 \text{ molec Cl}_2} \qquad \text{x } \underline{1 \text{ mol Cl}_2} = \\ 2 \text{ atoms Cl} \qquad 6.02 \times 10^{23} \text{ molec Cl}_2$ 

- How many sulfide ions are present in 10.0 g of ferric sulfide, Fe $_2S_3$ ?

Is ferric sulfide an element, molecular compound, or ionic compound? What is its representative particle?

If mass is mentioned in problem, you will need to calculate molar mass, so I recommend doing that first.

Fe---2 x 55.85 = 111.70 S---3 x 32.06 = <u>96.18</u> 207.88 g/mol

 $10.0 \text{ g Fe}_2\text{S}_3 \times \underline{1 \text{ mol Fe}_2\text{S}_3} \times \underline{6.02 \times 10^{23} \text{ fu Fe}_2\text{S}_3} \times \underline{3 \text{ S ions}} = \\ 207.98 \text{ g Fe}_2\text{S}_3 \quad 1 \text{ mol Fe}_2\text{S}_3 \quad 1 \text{ fu Fe}_2\text{S}_3?$ 

8.69 x 10<sup>22</sup> ions S

Isotopes, Moles, etc Practice #1 Isotopes, Moles, etc Practice #2 Work for #2

 $2.47\,mol\,Cl_2$ 

CHAPTER 7

# Writing Formulas & Naming Compounds

In this chapter, you will learn why atoms form compounds and how they form those compounds. You will need to commit ions' names and formulas to memory so that you can name and write formulas for ionic compounds. You will then learn how to name and write formulas of acids. Finally, you will learn about molecular compounds' formulas and names.



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## Section 1

# Ionic Compounds

### THE PLAN

1. Stability

2. Ions

3. Making Ionic Compounds

# Stability

Every element's dream is to look like a noble gas. They will strive to move their electrons around so as to have a pseudonoble gas electron configuration. That is, they will lose or gain electrons in order to do so.

Some elements will follow the duet rule, which means that they will strive to have two electrons in the outermost energy level. The elements that try to obey the duet rule are the first five elements on the periodic table: H, He, Li, Be, B.

The remainder of the elements do their very best to obey the octet rule. I hope you guessed that the octet rule means they want to have eight in their outermost energy level.

Ionic compounds, also called salts, are made when electrons are lost or gained. Molecular compounds are made when electrons are shared. Either way, stability is the goal.

#### Ions

Ionic bonds are made by transferring electrons, losing them or gaining them. Remember the electrons are negatively charged. If an electron is gained, then an atom becomes negatively charged. If an electron is lost then an atom becomes positively charged since it lost negative charge. Which elements lose and which elements gain electrons?

Hydrogen is in its own little world. Because it has only one electron, it can gain one, become negatively charged, and look like helium's electron configuration. However, hydrogen can also lose its one electron, become positively charged, and have no electron configuration.

The other nonmetals on the periodic table lie closer to the noble gases than do the metals. Thus, the nonmetals will gain electrons in order to look like the noble gas that comes after them. These nonmetals form negatively charged ions called anions.

The metals will lose electrons in order to look like the noble gas that precedes them. These positively charged ions are called cations.



Everyone in group 1 on the periodic table has one valence electron and need only lose one electron to have a full valence level. So, every element in group 1 has a charge of 1+. Charges are written with the number first and then the sign and as superscripts to the right of the symbol. Cations' names are simply the name of the element. Na<sup>1+</sup> is just called sodium ion. Group 2 elements have two valence electrons and will elect to lose two electrons to look like a noble gas. Be down to Ra will have charges of 2+.

Group 13 elements, from B down to Tl will have to lose three valence electrons and have a charge of 3+.

Group 14 is wishy washy. Since they are half-way to stability with 4 valence electrons, some of them do not like to lose or gain electrons. Rather, they prefer to share them in covalent bonds as opposed to ionic bonds. While some of the elements in Group 14 like to lose either two or four electrons.

Group 15 elements have five valence electrons and find it easier to gain three electrons rather than lose five in order to look like a noble gas. They will have charges of 3-. The names of these anions are different from the names of the elements. They will take on an "ide" ending. Sb and Bi do not gain electrons since they are a metalloid and a metal, respectively.

Group 16 elements have six valence electrons and will gain two electrons to look like noble gases. Their charges are 2-. Po does not gain electrons.

Finally, everyone in group 17, the halogens, has seven valence electrons and need only gain one electron to be stable. Their charges will be 1-.

The chart that follows is a synopsis of the nonmetals' anion formulas and names.

ELEMENT	ANION FORMULA	ANION NAME
nitrogen	N <sup>3-</sup>	nitride
phosphorus	Р3-	phosphide
arsenic	As <sup>3-</sup>	arsenide
oxygen	O <sup>2-</sup>	oxide
sulfur	S <sup>2-</sup>	sulfide
selenium	Se <sup>2-</sup>	selenide
tellurium	Te <sup>2-</sup>	telluride
fluorine	F <sup>1-</sup>	fluoride
chlorine	Cl1-	chloride
bromine	Br <sup>1-</sup>	bromide
iodine	I1-	iodide
astatine	At <sup>1-</sup>	astatide

Did you notice that I skipped the transition metals? They are weird, so I have selected the more common ones to have you know. They are in the following table with both stock names and classic names, know both:

CATION	STOCK NAME	CLASSIC NAME
Cr <sup>2+</sup>	chromium (II)	chromous
Cr <sup>3+</sup>	chromium (III)	chromic
Mn <sup>2+</sup>	manganese (II)	manganous
Mn <sup>3+</sup>	manganese (III)	manganic
Fe <sup>2+</sup>	iron (II)	ferrous
Fe <sup>3+</sup>	iron (III)	ferric
C0 <sup>2+</sup>	cobalt (II)	cobaltous
Co <sup>3+</sup>	cobalt (III)	cobaltic
Ni <sup>2+</sup>	nickel (II)	nickelous
Ni <sup>3+</sup>	nickel (III)	nickelic
Cu <sup>1+</sup>	copper (I)	cuprous
Cu <sup>2+</sup>	copper (II)	cupric
Sn <sup>2+</sup>	tin (II)	stannous
Sn <sup>4+</sup>	tin (IV)	stannic
Pb <sup>2+</sup>	lead (II)	plumbous
Pb <sup>4+</sup>	lead (IV)	plumbic

There are three common transition metals that do not have variable charge; therefore, they do not have stock or classic names. They are just like the other metals and have their normal names.

Ag<sup>1+</sup>...silver

Zn<sup>2+</sup>...zinc

Cd<sup>2+</sup>...cadmium

And then there is mercury. It is almost as weird as is hydrogen. There are two ions of mercury, but both have a charge of 2+. The difference is that one of them is monatomic and the other is diatomic.

Hg<sub>2</sub><sup>2+</sup>...mercury (I) or mercurous

Hg<sup>2+</sup>...mercury (II) or mercuric

You are almost finished with being exposed to all of the ions I want you to know. The final straw is the **polyatomic ions**. Click on the hyperlink to find those that you need to know.

I highly recommend making flash cards for these ions' formulas and names. I mean old-style flash cards where you write the information on one side and then flip it to write it on the other side. Something like Quizlet is nice, but you learn it better if you write it.

# **Making Ionic Compounds**

The objective of making a compound is to bring the sum of ion charges to zero. If you have a cation with a charge of 1+ and an anion with a charge of 3-, you will need three of the cations to balance the charge of the anion.

An easy way to do this is to use a criss-cross method. This means that the charge of the cation is brought down as a subscript of the anion (without its sign), and the charge of the anion is brought down as a subscript of the cation.

Cations are always written first and are followed by anions. To name the compound, simply name the ions in order from left to right.

 $Ca_1^{2+}Cl_2^{1-}$ ...The 2 has been brought down as a subscript of the Cl, and the 1 has been brought down as a subscript of the Ca. Cleaned up this formula is  $CaCl_2$ , and the name of the compound is calcium chloride.

Always reduce subscripts of ionic compounds.

 $Mg^{2+}$  O<sup>2-</sup>...You would like to write  $Mg_2O_2$ , but you must reduce the subscripts to be MgO. The name is magnesium oxide.

Apply subscripts to polyatomic ions by placing them outside of parentheses if the subscript if not an understood one. Pb<sup>4+</sup> OH<sup>1-</sup>...The correct formula is Pb(OH)<sub>4</sub> , and the name is either lead (IV) hydroxide or plumbic hydroxide.

Never reduce or change the subscripts of a polyatomic ion.

Al<sup>3+</sup> NO<sub>3</sub><sup>1-</sup>...The correct formula is Al(NO<sub>3</sub>)<sub>3</sub> , and the name is aluminum nitrate.

Always reduce subscripts that you apply but never those within the parentheses.

 $Sn^{4+} C_2O_4^{2-}...The$  formula is  $Sn(C_2O_4)_2$ . Notice that the subscripts within the parentheses are unscathed, but those outside of the parentheses are reduced. The name of the compound is tin (IV) oxalate or stannic oxalate.

# **Ionic Compounds Practice**

# SECTION 2

# Acids

# THE PLAN

1. Acids in General

2. "-ide"

3. "-ite"

4. "-ate"

# Acids in General

Acids are a prevalent part of general chemistry, organic chemistry, and biochemistry. They can be defined in numerous ways, but one way for now is to understand that the following section will teach you how to name acids that have hydrogen ion as their cations. The only variant then, is the anion. Anions have three types of suffixes: -ide, -ite, and -ate. Thus, the way to name acids is to use these suffixes.

# "-ide"

When the anion of a compound with H<sup>1+</sup> as the cation ends in "-ide," you will drop the "-ide" ending and be left with the root word of the anion.

 $H_2S$ ...anion name is sulfide...drop the suffix and you are left with "sulf"

Normally, you would then just add "hydro-" as a prefix and "ic" as a suffix with "acid" as a separate word. However, S and P are weird in that their root words change a bit to accommodate the prefix and suffix. "Sulf" becomes "sulfur" with the accent on the second syllable and a long "u" sound on that second "u."

# H<sub>2</sub>S...is named hydrosulfuric acid

If you are given a name like hydrochloric acid, you deduce that the anion was chloride because of the obvious prefix of "hydro-" and suffix of "-ic" that have been added to "chlor."

## hydrochloric acid...formula is HCl



### "-ite"

When the anion of an acid ends in "-ite," you will drop the "-ite" ending and be left with the root word of the anion. Then just add "-ous" as a suffix with "acid" as a separate word.

 $H_2PO_3$ ...anion name is phosphite...drop the suffix and you are left with "phosph"

Again S and P are weird. "Phosph" becomes "phosphor" with the accent on the second syllable.

H<sub>2</sub>PO<sub>3</sub>...is named phosphorous acid

If you are given a name like iodous acid, you deduce that the anion was iodite because of the obvious suffix of "-ous" that has been added to "iod."

iodous acid...formula is HIO<sub>2</sub>



"-ate"

When the anion of an acid ends in "-ate," you will drop the "-ate" ending and be left with the root word of the anion. Then just add "-ic" as a suffix with "acid" as a separate word. Do not confuse with with adding "hydro-" <u>and</u> "-ic."

 $H_2CO_3$ ...anion name is carbonate...drop the suffix and you are left with "carbon"



# SECTION 3

# Molecular Compounds

# THE PLAN

- 1. Recognizing a Molecular Compound
- 2. Prefixes
- 3. Applying the Prefixes

# **Recognizing a Molecular Compound**

Again, molecular compounds are made of two or more nonmetals. Recall that the nonmetals consist of those elements to the right of the metalloids as well as hydrogen. Do not ever reduce the subscripts on molecular compounds and always reduce subscripts on ionic compounds. We will focus on binary molecular compounds, that is compounds with only two elements.

## Prefixes

In order to indicate the number of nonmetal atoms present in a molecular compound, we must first learn prefixes that are applied to the atoms' names. These prefixes represent numbers 1-10, and are as follows respectively:

mono	hexa
di	hepta
tri	octa
tetra	nona
penta	deca

These prefixes are only applied to molecular compounds and never to ionic compounds.

# **Applying the Prefixes**

The prefixes are always applied to the second element in the compound. However, the first element only gets a prefix if the subscript is something other than "one." That means that a molecular compound's name will not begin with "mono."

Let us begin with CO. There is only one carbon, and it is the first element. So, the first part of the name does not get a prefix. It is just "carbon." As a separate word, the second element gets a prefix indicating that there is one oxygen. The second element always ends in "-ide." When oxygen is the second element, it will end in "oxide." In the case of CO, the prefix that goes on "oxide" is "mono." Someone in chemistry land decided that having two "o's" consecutively looked and sounded silly. So, when you apply any prefix other than "di" or "tri" to "oxide," you will drop the last "o" or "a" of the prefix. The name of CO is therefore carbon monoxide.

If we go the other way, and I give you a name, you should be able to write a formula from that name. A compound's name is dinitrogen tetroxide. You understand that to mean that there are two nitrogens and four oxygens. So, the formula is  $N_2O_4$ .

**INTERACTIVE 7.4** Molecular Compounds

# What is the name of P<sub>5</sub>O<sub>10</sub>? A. pentapotassium decaoxide **B.** pentaphosphorus decoxide **C.** phosphorus dioxide **D.** phosphorus oxide **Check Answer**



# Acids and Molecular Compounds Practice

# Percent Composition

Now that you know how to write formulas and name compounds, you can begin to do some calculations with that information. Percent composition is one such computation that is used practically to identify unknown substances.



edia.org/wiki/File:Percent\_18e.svg

Percent is shortened from the Latin phrase, "*per centum*," which means "by the hundred." You know from your prior experience that percent means that a number has been multiplied by 100. You know that you are dealing with part of a whole. If there are 10 people in a room and 4 of them have blue eyes, what percentage of people have blue eyes? That is easy, right?

In order to work with percent composition, you need to know how to calculate molar mass and write chemical formulas. You now know how to do both.

In general, a percent composition problem consists of writing a formula, determining a molar mass, and then finding the percentage of the part in question. There is some variation in the problem-solving, but the same ideas are still there.

Determine the percent composition of water.

First, write the formula of water:  $H_2O$ 

Next, calculate the molar mass of water:

H---2 x 1.01 = 2.02 O---1 x 16.00 = <u>16.00</u>

18.02 g/mol

Now, find the percent of each element in the compound by taking the total mass of the element at hand and dividing by the molar mass of the compound. Then, multiply by 100.

H----<u>2.02</u> x 100 = 11.2% 18.02 O---<u>16.00</u> x 100 = 88.8% 18.02

A compound contains only copper and chloride ions. It is found to be 47.3% copper. Determine the formula of the compound.

First, determine the possible formulas: copper can have charges of 1+ or 2+. So, your choices are: CuCl and  $CuCl_2$ 

Next, calculate both molar masses

Cu—1 x 63.55 = 63.55 Cl—1 x 35.45 = <u>35.45</u> 99.00 g/mol

Cu—1 x 63.55 = 63.55 Cl—2 x 35.45 = <u>70.90</u> 134.45 g/mol

Then, determine the percentage of copper in each.

Cu—1 x 63.55 = <u>63.55</u> x 100 = 64.2% Cu 99.00

Cu—1 x 63.55 = <u>63.55</u> x 100 = 47.3% Cu 134.45

So, the answer is CuCl<sub>2</sub>

INTERACTIVE 8.1 Percent Composition	
A compound is known to contain 41.7% magnesium. Determine if the compound is magnesium fluoride, magnesium hydrox- ide, or magnesium oxide.	
• A. magnesium fluoride	
🕜 <b>B.</b> magnesium hydroxide	
<b>C.</b> magnesium oxide	
<b>D.</b> none of the above	
Check Answer	

Percent Composition Practice Answers page 1 Answers page 2

# Electron Dot Structures

You know how to write formulas of compounds now, and you know how to do a little math with those formulas. Now, it is time to draw what those formulas look like. Gilbert Lewis came up with electron dot structures that show us what compounds and ions kind of look like.



lauras-science-blog.blogspot.com

## SECTION 1

# **Electron Dot Structure**

## THE PLAN

- 1. The Dots
- 2. The Rules
- 3. Illustration
- 4. The Kelter Method
- 5. Illustration

# The Dots

The dots will represent valence electrons. So, you need to know how many valence electrons atoms have by looking at the periodic table. Recall that those elements in group 1 have 1 valence electron, group 2 have 2 valence electrons, group 13, have 3 valence electrons, etc.



www.chemicalelements.com

Dots will be placed around an element's symbol to indicate the number of valence electrons, with a maximum of eight dots. The placement of the dots is as follows:



# The Rules

There are two rules that you must understand in order to properly draw electron dot structures.

The duet rule states that there are five elements that will do what they can in order to have two valence electrons around them. These five elements are hydrogen, helium, lithium, beryllium, and boron...the first five elements.

The octet rule states that the remainder of the elements will do what they can in order to have eight valence electrons around them.

You will need to be able to answer whether the duet or octet rule should be obeyed.

## Illustration of placing dots on atoms and compounds.

# The Kelter Method

Rather than guessing how the compounds and ions will form their dot structures, I teach a method that is impressive with its logic. Paul Kelter is a professor at Northern Illinois Universtiy, and he proposed a method to ease the illustration of electron dot structures. I will provide the details of the method and then show you a video that will illustrate his method. This method does the following:

- saves a lot of grief
- enables the successful drawing of electron dot structures without the hassle of figuring out whose electrons go where
- has exceptions, but they are logical

Here is the step by step method:

- Determine the number of happy valence e<sup>-</sup> in the entire molecule or ion.
  - Happy electron number depends upon whether the atom obeys the duet or octet rule
- Determine the number of owned valence e<sup>-</sup> in the entire molecule or ion.
  - Owned electron number depends upon the number of valence electrons that the atom has
- Subtract the number of owned e<sup>-</sup> from the number of happy e<sup>-</sup> and divide that difference by two...this will equal the number of bonds in the molecule or ion.
- Place the appropriate number of bonds around the central atom.
  - Central atom is the one that occurs one time in the molecule or ion. It is usually carbon if carbon is present.
- Attach the perimeter atoms and make them all happy (obey the appropriate rule) by placing electron dots around them.
- Account for all of the owned e-that you originally indicated, and add any leftovers to the central atom.
- If you are dealing with a polyatomic ion, place brackets around the formula and put the charge outside of the brackets.
- Multiple bonds will be blatantly indicated by the Kelter Method.
  - If the Kelter Method tells you that you need more bonds than you think you can possibly have in the molecule or ion, then there will be at least one multiple (double or triple) bond in the molecule or ion.
- Exceptions to the method will be exceptions to the duet or octet rule...that is, holding more than 2 or more than 8 earound a central atom.
  - If the Kelter Method tells you that you need fewer bonds than you know you can have in the molecule or ion, then it will be an exceptional situation.

#### Illustration of the Kelter Method

Electron Dot Structure Practice Answers page 1 Answers page 2

#### Chapter 10

# VSEPR Theory

Now that you know how to draw electron dot structures, or Lewis structures, you are ready to understand the geometry of those molecules and ions.



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#### SECTION 1

## **VSEPR** Theory

#### THE PLAN

- 1. The Theory
- 2. The Table of Information
- 3. Video

#### The Theory

The idea behind the geometry of molecules or ions is that electrons want to be as far away from each other as they can get. VSEPR is an acronym of Valence Shell Electron Pair Repulsion. Those lines that you drew for electron dot structures' bonding electrons will move away from each other to maximize the bond angle. Any lone pairs will push harder to get away from everyone.

You need to know that an effective pair of electrons is any bonding pair or any lone pair. As you look at a dot structure, you need to be able to determine the number of effective pairs around an atom. Of that number, the lone pair number is important.

For example, water's oxygen atom has four effective pairs around it, and two of those pairs are lone pairs. Knowing this allows you to predict that the shape is called bent and the bond angle is  $104.5^{\circ}$ .

#### The Table of Information

To determine the shape of a molecule or ion, you first need to draw the electron dot structure. Then you will determine the number of effective pairs and of those how many are lone. Next, use the chart on the next page to guide you in the shape names and bond angles.

EFF PRS	LONE PRS	SHAPE	BOND ANGLES
2	0	linear	180°
3	0	trigonal planar	120 <sup>0</sup>
4	0	tetrahedral	109.5°
4	1	pyramidal	107.3°
4	2	bent	$104.5^{\circ}$
5	0	trigonal bipyramidal	90°, 120°, 180°
5	2	t-shaped	90°, 180°
5	3	linear	180°
6	0	octahedral	90°, 180°
6	2	square planar	90°, 180°

#### VSEPR Video

VSEPR Practice Answers

# Empirical and Molecular Formulas

You know that you always reduce subscripts in ionic compounds, but with molecular compounds you do not reduce subscripts. Well, now we will look at what the reduced form of molecular compounds is all about. You will learn how to determine both the empirical and molecular formulas of unknowns.



#### Section 1

## EF and MF

#### THE PLAN

- 1. What are EF and MF?
- 2. Example

#### What are the EF and MF?

The empirical formula (EF) of a compound is the simplest whole number ratio of elements that can exist for a particular compound. Whereas, the molecular formula (MF) is some whole number multiple of the EF, including but not limited to one.

For example,  $C_6H_{12}O_6$ , is the MF of glucose. If the substance is indeed glucose, it must have 6 C atoms, 12 H atoms, and 6 O atoms bonded to each other. The EF of glucose is the reduced form of those subscripts,  $CH_2O$ . Notice that the MF is six times the EF.

#### Example

A compound contains only carbon, hydrogen, and chlorine. A sample is known to contain 49.67%C, 1.39%H, and 48.92%Cl. The molecular weight of the compound is 289.90 g/mol. What are the EF and MF of the compound?

First assume that you have 100 g of the compound. This enables you to turn your percentages into grams.

Convert each of those grams into moles using the element's molar mass...

C	49.67 g x <u>1 mol</u> = 4.14 mol C
	12.01 g
Η	$1.39 \text{ g x } \underline{1 \text{ mol}} = 1.38 \text{ mol H}$ 1.01 g
Cl	48.92 g x <u>1 mol</u> = 1.38 mol Cl
	35.45 g

Now divide each of those moles by the smallest number of moles. After doing this you will have no unit.

C <u>4.14 mol C</u> = 3 1.38 mol

H <u>1.38 mol H</u> = 1 1.38 mol

Cl <u>1.38 mol Cl</u> = 1 1.38 mol

At this point, if you have numbers that are roundable to whole numbers, you then have your ratio that makes up the empirical formula. If not, you must do some more work. These problems have goofy rounding rules; rules I have only seen in use with EF and MF problems. These rounding rules are that if the number you get upon dividing your moles by moles is something 0.2 or less, then you can round down. That is if we had gotten 3.18 rather than 3, you would have rounded that value to 3.00. If you get a value that is 0.8 or higher, you can round up. So, if you had gotten 2.83, you would have rounded that to 3.00.

If you get a value between 0.2 and 0.8, you must multiply the value by some whole number that will allow all of the values to be roundable. So, assume that rather than 3, 1, and 1, you got 2.3, 1, and 1. You would have to multiply the 2.3 by some whole number to a roundable point. That number is 3. When you multiply 2.3 by 3, you get 6.9 which is roundable to 7. So, now that 3 works for the 2.3, you must make it work for the 1's. Therefore, you ratio would be 7, 3, and 3.

You did not need to do any fancy footwork to get your ratio in the problem at hand. You know that it is 3:1:1 for C:H:Cl. So, your EF is C<sub>3</sub>HCl.

Now, find the molar mass of the EF (known as the empirical weight EW), so that you can find the MF.

C...3 x 12.01 = 36.03 H...1 x 1.0= 1.01 Cl...1 x 35.45= <u>35.45</u> 72.49 g/mol Next, take the MW that was given in the problem, and divide the MW by the EW (empricial formula's molar mass)

 $\frac{289.90 \text{ g/mol}}{72.49 \text{ g/mol}} = 4$ 

You now know that the MF is 4 times the EF. So, the MF is  $C_{12}H_4Cl_4$ . Congrats, you have worked through an EF/MF problem.

INTERACTIVE 11.1 Empirical and Molecular Formulas A compound consists of 43.6%P and 56.4%O and has a molecular weight of 283.88g/mol. What is its MF?



**Empirical and Molecular Formulas Practice Answers** 

# Reaction Types

We will now learn to balance chemical equations and predict products when reactants are presented to us. There are five classes of reactions and a total of 13 types that we will cover.



#### Section 1

## **Reaction Types**

#### THE PLAN

- 1. Composition
- 2. Decomposition
- 3. Single Replacement
- 4. Double Replacement
- 5. Combustion

You will learn to balance chemical equations as you write the equations. Reactants always yield products, R --> P. So, we will begin with the first reaction type.

#### Composition

In a composition reaction, two substances react to make one substance.

 $A + X \rightarrow AX$ 

So, if you are told that aluminum metal reacts with oxygen gas, you should be able to write an equation for the reaction and balance it.

 $Al(s) + O_2(g) \longrightarrow Al_2O_3(s)$  unbalanced

Notice that the aluminum is by itself in nature, and the oxygen exists as a diatomic molecule when by itself in nature. The charge of the aluminum ion in the product is 3+, and the charge of the oxide ion in the product is 2-. Now, you need to balance the equation. You will do so with coefficients that are written to the left of the substances. These coefficients represent the number of moles that react and are produced. Always reduce coefficients, if possible.

Since there is one Al on the left, and there are two Al on the right, I can start by putting a 2 in front of the Al on the left. Alas, I will notice that when I go to fix the O's, there are 2 on the left and 3 on the right. In order to fix the O's, there needs to be a 2 in front of the  $Al_2O_3$  on the right. When I do that the coefficient in front of Al needs to change to a 4, and the coefficient in front of  $O_{2}$  needs to be a 3. Thus, the balanced equation is

 $4Al(s) + 3O_2(g) -> 2Al_2O_3(s)$ 

Always check to make sure that the coefficients cannot be reduced to smaller numbers.

INTERACTIVE 12.1 Reaction Types--Composition

What is the correctly balanced equation for the reaction of solid sodium and solid sulfur?

**A.** S(s) + S(s) --> 2S(s)

**B.** Na(s) + S(s) --> NaS(s)

**C.**  $Na(s) + S(s) --> Na_2S(s)$ 

**D.** 
$$2Na(s) + S(s) --> Na_2S(s)$$

**Check Answer** 

#### Decomposition

Whereas, a composition reaction involves the coming together of two substances, a decomposition involves the breaking up of one substance.

 $AX \dashrightarrow A + X$ 

There are six types of decomposition reactions that we will cover. Each of them has a catalyst that is written over the yield sign (-->).

#### Metallic Carbonate

When a metallic carbonate is heated, a solid metallic oxide and carbon dioxide gas are produced.

 $MCO_3(s)^{heat} = MO(s) + CO_2(g)$ 

M represents any metal from the periodic table. So, write the reaction of ferric carbonate's being heated.

 $Fe_{2}(CO_{3})_{3}(s) \xrightarrow{\text{heat}} Fe_{2}O_{3}(s) + CO_{2}(g) \qquad \text{unbalanced}$ 

Think about balancing the reaction. Notice that the O's are in two locations on the product side. Start by balancing the Fe's. There are 2 on the left, and there are 2 on the right. Now there are 3C's on the left, and only 1 on the right. Place a coefficient of 3 in front of the CO<sub>2</sub>. Surprise, it is now balanced.

 $\operatorname{Fe}_2(\operatorname{CO}_3)_3(s) \xrightarrow{\text{heat}} \operatorname{Fe}_2\operatorname{O}_3(s) + 3\operatorname{CO}_2(g)$ 



#### Metallic Chlorate

When a metallic chlorate is heated, a solid metallic chloride and oxygen gas are produced.

 $\overset{heat}{\text{MClO}_3(s) \dashrightarrow \text{MCl}(s) + O_2(g)}$ 

We will write the reaction of solid calcium chlorate's being heated.

 $Ca(ClO_3)_2(s) \xrightarrow{heat} CaCl_2(s) + O_2(g)$  unbalanced

Now balance the equation by looking at the calciums, and then at the chlorides. They are both already balanced. It is the oxygens that are not balanced. There are six oxygens on the left and only two on the right. Place a 3 as a coefficient in front of the oxygen gas.

 $\operatorname{Ca}(\operatorname{ClO}_3)_2(s) \xrightarrow{\text{heat}} \operatorname{Ca}(cl) + 3O_2(g)$ 

INTERACTIVE 12.3 Reaction Types--Decomposition

What is the properly balanced reaction for the heating of solid cesium chlorate?

**Check Answer** 

#### Metallic Hydroxide

When a metallic hydroxide is heated, a solid metallic oxide and steam are produced.

 $MOH(s) \xrightarrow{\text{heat}} MO(s) + H_2O(g)$ 

We will write the reaction of solid zinc hydroxide's being heated.

 $Zn(OH)_2(s) \xrightarrow{\text{heat}} ZnO(s) + H_2O(g)$ 

Now balance the equation by looking at the zincs, the oxygens, and the hydrogens. You should see that all three are already balanced, so the equation is balanced.

INTERACTIVE 12.4 Reaction Types--Decomposition

Identify the properly balanced equation that represents the heating of solid lithium hydroxide.

#### Metallic Oxide

There are not many metallic oxides that decompose upon heating, but there are two worth noting. One is the heating of solid plumbic oxide. It forms solid plumbous oxide and oxygen gas.

 $PbO_2(s) \xrightarrow{heat} PbO(s) + O_2(g)$  unbalanced

Notice that the reaction is unbalanced. Balance it properly.

The other decomposition of a metallic oxide that you should know is the heating of solid mercuric oxide yields liquid mercury and oxygen gas.

$$HgO(s)^{heat}$$
  $Hg(l) + O_2(g)$  unbalanced

Now balance the reaction.

#### <u>Electrolysis</u>

There are two substances that you need to know that decompose upon exposure to electricity. First, solid sodium chloride can decompose into solid sodium and gaseous chlorine upon being electrified.

 $NaCl(s) \xrightarrow{elec} Na(s) + Cl_2(g)$  unbalanced

A second substance that will decompose when electric current is passed through it is water.

 $H_2O(l) \xrightarrow{elec} H_2(g) + O_2(g)$  unbalanced

#### Acids

Some acids decompose upon heating. I tend to keep these reactions rather simple. That is each heating of an acid will yield steam. The other product will simply be what remains when two hydrogens and one oxygen are removed from the acid. These simple forms of acid decomposition are always already balanced.

If I tell you that sulfurous acid is heated. You should predict that the products are steam and sulfur dioxide gas.

 $\underset{H_2SO_3(aq) \longrightarrow}{\text{heat}} H_2O(g) + SO_2(g)$ 

INTERACTIVE 12.5 Reaction Types--Decomposition

Which is the correctly balanced reaction for the heating of carbonic acid?

#### **Single Replacement**

Think of a single replacement reaction as having a couple dancing, and someone comes to cut in on one of the partners. The substance that is cutting in must be stronger that the substance it is replacing. There is no catalyst such as heat or electricity required for single replacement reactions.

In chemistry we determine strength of a substance for single replacement reactions by using an activity series. Below you will find the activity series of metals and the activity series of nonmetals.

Two Activity Series				
Metals	Decreasing Activity	Halogens		
lithium potassium calcium	heat heat	fluorine chlorine bromine		
sodium magnesium aluminum	heat	iodine		
zinc chromium iron pickol	heat			
tin lead				
HYDROGEN* copper mercury				
silver platinum gold				

**Check Answer** 

There are two generic formulas because the cutting in substance can be either a metal or a nonmetal.

 $AX + B \longrightarrow BX + A$ 

 $AX + Y \rightarrow AY + X$ 

In each of these cases, B is stronger than A, and Y is stronger than X.

There are four types of single replacement reactions.

#### Highly Active Metal Replaces Hydrogen in Water

A highly active metal is considered to be an alkali metal, those metals that are in Group 1 of the periodic table. If one of these metals is added to water, an alkali metal hydroxide and hydrogen gas are generated. If a metal that is not one of these alkali metals is added to water, nothing happens.

 $Na(s) + H_2O(l) -> NaOH(aq) + H_2(g)$  unbalanced

Balance the equation.

Cu(s) + H<sub>2</sub>O(l) --> no rxn..yeah for plumbing pipes!

INTERACTIVE 12.6 Reaction Types--Single Replacement

Which represents the balanced equation for the reaction of solid potassium and water?

#### More Active Metal Replaces Less Active Metal

Upon consulting the activity series of metals, you will find that the higher the metal is on the list, the more active it is. A metal that is higher than another metal can kick the weaker metal out of a compound and take its place. For example, solid magnesium can kick silver out of aqueous silver sulfate.

 $Mg(s) + Ag_2SO_4(aq) -> MgSO_4(aq) + Ag(s)$  unbalanced

Balance the equation.

If silver were to be added to a solution of chromic nitrate, then the silver would not be strong enough to kick chromium out of the compound. There would be no reaction, written as:

 $Ag(s) + Cr(NO_3)_3(aq) \rightarrow no rxn$ 

INTERACTIVE 12.7 Reaction Types--Single Replacement

Identify the correctly balanced equation for the mixing of solid lithium and aqueous lead (II) nitrate.

- A.  $4Li(s) + Pb(NO_3)_4(aq) --> 4LiNO_3(aq) + Pb(s)$
- **B.**  $2\text{Li}(s) + Pb(NO_3)_2(aq) -> 2\text{LiNO}_3(aq) + 2Pb(s)$
- **C.**  $2\text{Li}(s) + Pb(NO_3)_2(aq) --> 2\text{LiNO}_3(aq) + Pb(s)$
- **D.**  $2Li(s) + Pb(NO_2)_2(aq) --> 2LiNO_2(aq) + Pb(s)$

**Check Answer** 

#### Active Metal Replaces Hydrogen in Acid

Those metals that are above hydrogen on the activity series are active enough to replace hydrogen in an acid but not in water. So, solid zinc can react with hydrochloric acid, but nothing will happen if you place gold metal into hydrochloric acid. When these types of single replacement reactions take place, the hydrogen is kicked out of the acid and must exist in nature on its own. Recall that hydrogen does so diatomicly.

 $Zn(s) + HCl(aq) -> ZnCl_2(aq) + H_2(g)$ 

Au(s) + HCl(aq) --> no rxn

Balance the reaction.



#### More Active Nonmetal Replaces Less Active Nonmetal

The activity series of nonmetals indicates that the most active nonmetal is fluorine, and the least active is iodine. The remainder of the nonmetals are not listed on such a chart.

When fluorine is by itself in nature, it is diatomic. Even in its diatomic state, it desires to bond with another element. So,

we rarely find fluorine in nature by itself. It is able to kick any other halogen out of a compound and take its place.

When fluorine gas reacts with chromic chloride solution...

 $F_2(g) + CrCl_3(aq) \longrightarrow CrF_3(aq) + Cl_2(g)$  unbalanced

Balance the equation.

If solid iodine is placed in a solution of sodium bromide, nothing happens.

 $I_2(s) + NaBr(aq) --> no rxn$ 

INTERACTIVE 12.9 Reaction Types--Single Replacement

Which is the correct equation for the reaction of liquid bromine with aqueous calcium fluoride?

 $\bigcirc$  **A.** Br(l) + CaF(aq) --> CaBr(aq) + F

- **B.**  $Br_2(l) + CaF_2(aq) --> CaBr_2(aq) + F_2(g)$
- **C.**  $Br_2(l) + CaF_2(aq) --> BrF_2(aq) + Ca(s)$

D. Br<sub>2</sub>(l) + CaF<sub>2</sub>(aq) --> no rxn

**Check Answer** 

#### **Double Replacement**

When two ionic compounds react with each other the cations switch places. It is like switching dance partners. There is no activity series to consult, that is only with single replacement reactions. Double replacement reactions just happen.

When sodium chloride solution is mixed with silver nitrate solution, there is a phase change. I do not expect you to know how to predict those phase changes at this point in chemistry.

 $NaCl(aq) + AgNO_3(aq) -> NaNO_3(aq) + AgCl(s)$ 

INTERACTIVE 12.10 Reaction Types--Double Replacement

Determine the correctly balanced equation for the reaction of aqueous barium nitrite and aqueous potassium sulfate.

- A.  $Ba(NO_3)_2(aq) + KSO_4(aq) --> BaSO_4(s) + KNO_3(aq)$
- **B.**  $Ba(NO_3)_2(aq) + K_2SO_4(aq) --> BaSO_4(s) + 2KNO_3(aq)$
- C.  $Ba(NO_2)_2(aq) + KSO_4(aq) --> BaSO_4(s) + KNO_2(aq)$
- **D.**  $Ba(NO_2)_2(aq) + K_2SO_4(aq) --> BaSO_4(s) + 2KNO_2(aq)$

#### Combustion

The final type of reactions that we will cover is the combustion reaction. In combustion reactions, we will keep it simple and assume that a hydrocarbon will react with oxygen gas to produce carbon dioxide gas and steam. Hydrocarbons are compounds that consist of solely carbon and hydrogen. The simplest hydrocarbon is methane,  $CH_4$ . Methane is also called natural gas. Its combustion is as follows:

 $CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$  unbalanced

Balance the equation. A tip that I give for balancing combustion reactions is to start with a coefficient of 2 in front of the hydrocarbon. That tends to make the rest of the balancing a bit easier. Always make sure that you reduce coefficients to the simplest whole number ratios.



#### **Reaction Types Practice**

- Answers page 1
- Answers page 2
- Answers page 3

CHAPTER 13

## Stoichiometry

You will now take those balanced equations and do calculations with them. You will find out how much product you can get from a certain amount of reactant. You will determine the amount of reactant needed to get a certain amount of product, and you will calculate percent yield to see how effective a reaction is.



### SECTION 1 Stoichiometry

#### THE PLAN

- 1. Sandwiches
- 2. Balanced Equations
- 3. Making Stoichiometry Work

#### Sandwiches

Yep, you read that correctly. We are going to talk about sandwiches for a bit.

Here is the recipe for a sandwich:

2 pieces of bread 4 pieces of meat 1 piece of cheese

Unless you have all of those ingredients, you cannot make a sandwich. So, if you have 4 pieces of bread, 8 pieces of meat, and 2 pieces of cheese, you could make 2 sandwiches, right? What if you had 4 pieces of bread, 4 pieces of meat, and 2 pieces of cheese? You could only make 1 sandwich. Which substance would you run out of? Yep, the meat is the correct answer.

I introduce stoichiometry by talking about making sandwiches because the quantities are easy to understand for most folks. Easier than the quantities we will use for elements and compounds, that is.

#### **Balanced Equations**

If I were writing an equation for the production of a sandwich, it would look like this:

2 bread + 4 meat + 1 cheese --> 1 sandwich

The numbers represent pieces. Pieces is the unit in the preceding equation. We will consider that equation to be balanced. Reactants are on the left of the yields sign (-->), and the products are on the right side.

When we get into real chemical equations, we will have numbers that represent <u>moles</u>, not pieces. We will have <u>symbols</u> that represent elements and compounds.

If you feel that you need a little more practice on balancing equations, click here.

#### **Making Stoichiometry Work**

The word "stoichiometry" comes from the Greek for "element" and "the process of measuring." It is a quantitative analysis of reactants and products. We will be able to determine how much reactant is required to make a specific amount of product, or how much product can be made from a specific amount of reactant.

You will use the following concepts in order to make stoichiometry work for you: molar masses, mole ratios, and balanced equations, and dimensional analysis. You already know how to calculate molar masses and convert from mass to moles and back. You also already know how to balance chemical equations. The parts of the puzzle are here awaiting your skillful hands to piece it all together.

Consider the following balanced reaction:

 $2H_2 + O_2 -> 2H_2O$ 

Recall that the coefficients = moles. So, 2 moles of hydrogen react with 1 mole of oxygen to produce 2 moles of water. What if you only had 1 mole of hydrogen? How much oxygen would you need? If you answered 0.5 of a mole, you are on target. How much water could you produce if you only had 1 mole of  $H_2$ ? Yep, 1 mole of water is correct.

What if you had 10 moles of both hydrogen and oxygen? You could use the 10 moles of  $H_2$ , but you would only need to use 5 moles of  $O_2$ . Thus, you will run out of hydrogen before you will run out of oxygen. You could also only produce 10 moles of water from these quantities. There would be 5 moles of oxygen just hanging out without any more hydrogen around.

What if you needed to make 5 moles of water? Well, that would require 5 moles of hydrogen and 2.5 moles of oxygen. Hopefully, this is making some sense to you.

Convert each of the moles in the previous equation to grams.

 $2 \mod H_2 \ge 2.02 \ \text{g} \ \text{H}_2}{1 \ \text{mol} \ \text{H}_2} = 4.04 \ \text{g} \ \text{H}_2$ 

 $1 \mod O_2 \ge 32.00 \ge O_2 = 32.00 \ge O_2$  $1 \mod O_2$ 

 $2 \text{ mol } H_2\text{O x } \underline{18.02 \text{ g } H_2\text{O}} = 36.04 \text{ g } H_2\text{O} \\ 1 \text{ mol } H_2\text{O}$ 

Add the reactants' masses together. Compare to the product's mass. Be in awe! The total mass of the reactants equals the total mass of the products...always. This is known as the Law of Conservation of Mass.

Consider mole ratios...an equation must be balanced in order to obtain mole ratios. These ratios allow you to relate reactants to each other, products to each other, or reactants to products

Think about molar masses...if mass is mentioned, find that substance's molar mass. It is as simple as that. You will need that molar mass as you work through the problem.

Now ponder dimensional analysis...converting one thing into another. You will use this concept throughout stoichiometry. Remember to always have a number, unit, and substance for each numerator and denominator in your dimensional analysis.

Let's get started with a simple stoichiometry problem.

When 2.50 g of hydrogen gas are mixed with an excess of oxygen gas, how many grams of water should be produced? We will work this problem in steps.

Write a balanced equation.

 $2H_2 + O_2 --> 2H_2O$ 

Begin with your given information and make a plan of conversions.

grams of hydrogen-->moles of hydrogen-->moles of water-->grams of water

Write the plan as dimensional analysis.

 $\begin{array}{c} g \ H_2 \ x \ \underline{mol} \ H_2 \ x \ \underline{mol} \ H_2 O \\ g \ H_2 & mol \ H_2 \end{array} \\ x \ \underline{mol} \ H_2 \\ mol \ H_2 \end{array} = g \ H_2 O \\ \end{array}$ 

Fill in your numbers.

 $\begin{array}{c} \textbf{2.50 g } H_2 \, x \, \underline{1 \ mol \ H_2} \, x \, \underline{2 \ mol \ H_2O} \, x \, \underline{18.02 \ g \ H_2O} = g \ H_2O \\ \textbf{2.02g } H_2 \quad \textbf{2 \ mol \ H_2} \quad \textbf{1 \ mol \ H_2O} \end{array}$ 

Cross out what divides out.

 $\begin{array}{c} 2.50 \ \underline{g} \ \underline{H}_2 \ x \ \underline{1 \ mol \ H_2} \ x \ \underline{2 \ mol \ H_2O} \ x \ \underline{18.02 \ g \ H_2O} = g \ H_2O \\ \\ 2.02 \ \underline{g} \ \underline{H}_2 \ 2 \ \underline{mol \ H_2O} \ 1 \ \underline{mol \ H_2O} \end{array}$ 

Calculate your answer.

 $22.3 \text{ g} \text{H}_2\text{O}$ 

How many grams of oxygen gas would be required to obtain 22.3 g of water? You can use the Law of Conservation of Mass to determine the answer:  $22.3 \text{ g} - 2.50 \text{ g} = 19.8 \text{ g} \text{ O}_2$ . But, you really should use dimensional analysis to answer the question. If you had gotten the first problem incorrect, it would automatically make the second problem incorrect. Your dimensional analysis would look like this:

## $\begin{array}{c} 2.50 \ \underline{g} \ \underline{H_2} \ x \ \underline{1 \ mol \ H_2} \ x \ \underline{1 \ mol \ O_2} \ x \ \underline{32.00 \ g \ O_2} = g \ O_2 \\ \\ 2.02 \ \underline{g \ H_2} \ 2 \ \underline{mol \ H_2} \ 1 \ \underline{mol \ O_2} \end{array}$

Watch the thermite reaction which involves the reaction of aluminum with ferric oxide. Now, let's assume that 0.010 g of aluminum reacted with excess ferric oxide. What mass of aluminum oxide should be produced? Go through your steps and you should have the following:

 $2Al + Fe_2O_3 --> Al_2O_3 + 2Fe$ 

 $\begin{array}{c} g \ Al \ x \ \underline{mol \ Al} \ x \ \underline{mol \ Al_2O_3} \ x \ \underline{g \ Al_2O_3} = g \ Al_2O_3 \\ g \ Al \quad mol \ Al \quad mol \ Al_2O_3 \end{array} = g \ Al_2O_3$ 

 $0.010 \text{ g Al x } \underline{1 \text{ mol Al}} \text{ x } \underline{1 \text{ mol Al}_2 O_3} \text{-x } \underline{101.96 \text{ g Al}_2 O_3} = 26.98 \text{ g Al } 2 \text{ mol Al } 1 \text{ mol Al}_2 O_3$ 

 $0.0189 \text{ g Al}_2\text{O}_3$  should be produced.

So, What if only 0.0150 g of  $Al_2O_3$  were actually produced in the previous problem? What is the percent yield?

Percent yield is a means of determining how efficient the reaction is. It is calculated by:

% yield =  $\frac{\text{actual amount}}{\text{theoretical amount}}$  x 100

The theoretical amount is the amount that should be produced.

Ideally, the perfect amount of each reactant is present such that each reactant is completely used in the reaction process. However, often one reactant limits how much product can be formed. This substance is known as a limiting reagent (LR). The LR is like whatever you ran out of in making the aforementioned sandwich. The other reactant(s) is(are) often excess reagents (ER). When you are given a problem with two or more quantities of reactants, you must determine which substance is the LR. It is the LR, after all, that determines how much product can be made. So, here is a problem that requires determination of the LR before the problem can be solved:

0.500 g of silver nitrate in solution reacts with 0.750 g of tin (IV) chloride in solution. If 0.400 g of solid silver chloride are retrieved, what is the percent yield?

Write a balanced equation.

4AgNO<sub>3</sub> + SnCl<sub>4</sub> --> 4AgCl + Sn(NO<sub>3</sub>)<sub>4</sub>

Ask yourself, when I have 0.500 g of  $AgNO_3$ , how many grams of  $SnCl_4$  do I really need? This will determine the LR. Set up the plan

 $\begin{array}{l} g \ AgNO_3 \ x \ \underline{mol} \ AgNO_3 \ x \ \underline{mol} \ SnCl_4 \ x \ g \ SnCl_4 = g \ SnCl_4 \\ g \ AgNO_3 \ \ mol \ AgNO_3 \ \ mol \ SnCl_4 \end{array} = g \ SnCl_4 \\ \end{array}$ 

Plug in the numbers.

 $0.500g \operatorname{AgNO}_{3} \ge 1 \operatorname{\underline{mol}} \operatorname{AgNO}_{3} \ge 1 \operatorname{\underline{mol}} \operatorname{SnCl}_{4} \ge 260.50 \operatorname{g} \operatorname{SnCl}_{4} = 169.88 \operatorname{g} \operatorname{AgNO}_{3} 4 \operatorname{mol} \operatorname{AgNO}_{3} 1 \operatorname{mol} \operatorname{SnCl}_{4}$ 

0.192 g SnCl<sub>4</sub> are needed to react completely with 0.500 g AgNO<sub>3</sub>. Well, you have 0.750 g of the SnCl<sub>4</sub> available, and you only need 0.192 g of it. Therefore, you have an excess of the SnCl<sub>4</sub>. So, if you have an excess of SnCl<sub>4</sub>, then you will run out of the AgNO<sub>3</sub> first. Thus, the AgNO<sub>3</sub> is the LR.

Once you determine the identity of the LR, you need to use the *given* amount of the LR to solve the original problem, determining the percent yield of the reaction.

Set up your plan.

 $g \operatorname{AgNO}_{3} x \operatorname{\underline{mol}} \operatorname{AgNO}_{3} x \operatorname{\underline{mol}} \operatorname{AgCl} x g \operatorname{AgCl} = g \operatorname{AgCl} \\ g \operatorname{AgNO}_{3} \operatorname{mol} \operatorname{AgNO}_{3} \operatorname{mol} \operatorname{AgCl}$ 

Plug in your numbers.

0.500 g  $AgNO_3$  x  $\underline{1 \text{ mol } AgNO_3}$  x  $\underline{4 \text{ mol } AgCl}$  x  $\underline{143.32 \text{ g } AgCl} = 169.88 \text{ g } AgNO_3 4 \text{ mol } AgNO_3 1 \text{ mol } AgCl$ 

0.422 g AgCl should be formed. Only 0.400 g of AgCl were actually formed according to the original problem. So, now you can determine the percent yield.

<u>0.400 g AgCl</u> x 100 = 94.8% yield 0.422 g AgCl Now sit down with some bread, meat, and cheese and have fun with these practice problems.

Stoichiometry Practice Answers Page 1 Answers Page 2 Answers Page 3

## Thermodyna mics



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We will look at the energy associated with chemical processes. You will learn about specific heat capacity, Hess's Law, enthalpy, entropy, and free energy.

#### Section 1

### Heat Energy

#### THE PLAN

- 1. Heat v. Temperature
- 2. Heating Curve
- 3. Specific Heat Capacity
- 4. Calorimetry

#### Heat versus Temperature

Energy is defined as the capacity to do work, and it is often measured as heat. Think about a tub of water at 35°C and a cup at the same temperature. If you dip the cup into the tub of water, does the water in the tub have the same temperature as the water in the cup? Yes, is the answer.

The two samples of water, however, have differing amounts of heat, that is energy. Because, there is more water in the tub than in the cup, the tub contains more heat than the cup. So, two substances may have the same temperature but have different amounts of heat energy.

Temperature is a measurement of the average kinetic energy of a substance. Kinetic energy is the energy of motion. Thus, a substance must have motion of its particles in order for it to have a temperature above absolute zero, oK.

Heat is the measure of the total energy transferred from an object with a higher temperature to an object with a lower temperature. Two units of measurement of heat are the Joule (J) and the calorie (cal). A J is considered to be a metric unit, while a cal is an English unit. One calorie is defined as the amount of heat energy required to raise one gram of water by one degree Celsius. 1 cal = 4.18 J

Do not confuse Calorie with calorie. On food labels in the U.S., you will see something like 240 Cal. That capitalized calorie is really a kcal. Yep, so when you think you are getting 240 calories, you are really getting 240000 calories!

#### **Heating Curve**

Heat is also known as enthalpy (H). You will use H as you work problems regarding heat throughout this chapter.

A heating curve illustrates the effect that heat energy has on temperature. Below is a heating curve.



Note that the phase changes are the horizontal lines, or plateaus. The temperature is constant during a phase change. If the amount of heat is being added, then you are moving from left to right. A solid gains enough heat to begin melting, and once melted the liquid can gain enough heat to begin boiling. Once boiling is complete, a gas can continue to gain heat. The amount of heat gained is gleaned by looking at the length of the plateau.

If you go the opposite direction on the graph, then heat is being removed. When enough heat is removed from a gas, it reaches its condensation point and begins turning into a liquid. Upon liquifying, more heat can be lost until the freezing point is reached. Once all of the liquid turns into solid, the solid can continue to lose heat. The amount of heat lost is again determined by looking at the length of the plateau. The amount of heat absorbed by a solid to turn in to a liquid is equal to the amount of heat released by a liquid to turn into a solid. The heating curve for water is below. Please notice that



the heat is quantified at 4 kJ per square. It requires much more heat to be absorbed for water to turn into steam than for ice to turn into water.

#### **Specific Heat Capacity**

Specific Heat Capacity (C) is the amount of heat required to raise one gram of a substance one degree Celsius. Sound familiar? Yes, the C of water is 1 cal/g°C or 4.18 J/g°C. When a substance's C is greater than another substance's C, more heat is required to make that first substance equal in temperature to the second substance with a lesser C. Think about a silicon oven mitt. Compare the amount of heat that the mitt takes to get hot to the amount of heat that an iron pan takes to get hot. Which has the greater C? Silicon does. It requires more energy to get that silicon mitt to 100°C than it does the iron pan. Do you not imagine that an egg will cook faster on an iron pan than on a silicon mitt?

Here is a handy formula for working with heat, mass, temperature, and C:  $\Delta H = (m)(\Delta T)(C)$ 

 $\Delta$  means change. Heat's unit is J or cal. The mass unit is g. T is Celsius. C is J/g°C or cal/g°C.

Find the mass of water that can have 500. J of heat applied to it to have the temperature go from 20.0°C to 100.°C.

You can simply plug into the formula, or you can use dimensional analysis to solve the problem. I will show you both methods. You know the C of water, and you should use  $4.18 \text{ kJ/g}^{\circ}\text{C}$  since you have been given J in the problem.

500. J = (m)(100.°C-20.0°C)(4.18J)  
$$g^{\circ}C$$

m = 1.50 g water

OR

Knowing that I want to end up with g, I flip the C and put my g in the numerator and proceed to cross out units.

<u> $g^{\Theta}C$ </u> x <u>500. J</u> x <u>1</u> = 1.50 g 4.18 J <u>1</u> 80.0<sup> $\Theta$ </sup>C

Neither method is easier than the other. The dimensional analysis technique shows that you know how to manipulate units, whereas, the plug-in method only shows that you can plug into a formula.

#### Calorimetry

The science of measuring heat changes is called calorimetry. A calorimeter is a device that measure heat changes. There are two types of calorimeters: coffee-cup and bomb. A coffeecup calorimeter is usually made of a few styrofoam cups nested in each other with another smaller cup forming a lid. A small hole is made in the lid to allow for the insertion of a thermometer. A coffee-cup calorimeter is useful for reactions that do not involve combustion and is also known as a constant pressure calorimeter. A bomb calorimeter is used for combustion reactions, and it is a sealed metal cylinder that will hold the volume constant and allow the pressure to increase.



#### SECTION 2

## Enthalpy

#### THE PLAN

- 1. Hess's Law
- 2. Standard Heats of Formation

#### Hess's Law

Enthalpy is a fancy word for heat. It is represented by H and is typically referenced as a change in enthalpy,  $\Delta$ H. There are several ways to determine  $\Delta$ H, and two of those methods will be discussed in this section. The  $\Delta$ H of a process will always be the same regardless of how it is calculated.

Hess's Law tells us that  $\Delta H$  is independent of pathway. It does not matter how you get there, the  $\Delta H$  will always be the same for a particular process. You need to understand that most reactions do not necessarily occur in a single step as we have heretofore represented.

That is, there are elementary steps that add together to give an overall reaction. Reactants are added to reactants, and products are added to products. Like terms can be cancelled. Each reaction has its own  $\Delta$ H, and the  $\Delta$ H's are also additive. Here is an example of a Hess's Law problem:

Find the  $\Delta$ H of N<sub>2</sub>(g) + 2O<sub>2</sub>(g) --> 2NO<sub>2</sub>(g)

Plausible elementary steps:

a. $N_2(g) + O_2(g)> 2NO(g)$	$\Delta H = 180.6 \text{ kJ}$
b. $2NO(g) + O_2(g) -> 2NO_2(g)$	$\Delta H$ = -114.2 kJ

You have two choices of how to manipulate the elementary steps in order for them to add to give you the overall reaction. You may flip a reaction, in which case, the sign of the  $\Delta$ H is reversed. You may also multiply the reaction by some factor, in which case you multiply the  $\Delta H$  by the same factor. You may not need to manipulate a reaction, however.

In this particular problem, you need not manipulate the elementary steps. You can add them together to get the overall reaction without changing the elementary steps at all.

In order to work a Hess's Law problem, take one substance in the overall reaction and look for it in an elementary step. You will want to have the same number of that substance on the same side as in the overall reaction.

So, I first look for 1 mole of  $N_2(g)$  on the left side of an elementary step. I find that step "a" has 1 mole of  $N_2(g)$  on the left side. I then write elementary step "a" as is...

 $N_2(g) + O_2(g) --> 2NO(g)$   $\Delta H = 180.6 \text{ kJ}$ 

Because  $O_2(g)$  is in both elementary steps, I will next look for 2 moles of  $NO_2(g)$  on the right side of an elementary step. I write elementary step "b" just beneath elementary step "a," lining up the yields signs.

$N_2(g) + O_2(g)> 2NO(g)$	$\Delta H = 180.6 \text{ kJ}$
$2NO(g) + O_2(g) -> 2NO_2(g)$	$\Delta H = -114.2 \text{ kJ}$

Since I have now used both elementary steps, I add them together, combining like terms on the same side and canceling like terms on opposite sides, to see if I can get the overall reaction. I also add the  $\Delta H$  values.

$N_2(g) + O_2(g)> 2NO(g)$	$\Delta H = 180.6 \text{ kJ}$
$2NO(g) + O_2(g) -> 2NO_2(g)$	$\Delta H = -114.2 \text{ kJ}$
$N_2(g) + 2O_2(g) + 2NO(g)>2NO(g) +$	$2NO_2(g) \Delta H = 66.4 \text{ kJ}$

Since the  $\Delta$ H is +66.4kJ, the reaction is endothermic and must absorb 66.4 kJ of heat to proceed. Had the value been negative, then it would have been an exothermic process that would have released 66.4 kJ.

Here is another Hess's Law problem in which an elementary step will need to be manipulated:

 $C_{(graphite)}(s) \longrightarrow C_{(diamond)}(s) \qquad \Delta H = ?$ 

The elementary steps are: a.  $C_{(graphite)}(s) + O_2(g) \longrightarrow CO_2(g)$   $\Delta H = -393.5 kJ$ b.  $C_{(diamond)}(s) + O_2(g) \longrightarrow CO_2(g)$   $\Delta H = -395.4 kJ$ 

I will write step "a" as is since 1 mole of graphite is on th

I will write step "a" as is since 1 mole of graphite is on the left side where it is in the overall reaction.

a.  $C_{(graphite)}(s) + O_2(g) --> CO_2(g)$   $\Delta H = -393.5 kJ$ 

However, I will flip step "b" in order to get 1 mole of diamond on the right side. Because I will flip the reaction, the sign of the  $\Delta$ H will change.

$$\begin{array}{ll} C_{(\text{graphite})}(s) + O_2(g) & -> CO_2(g) & \Delta H = -393.5 \text{kJ} \\ \underline{CO_2(g) --> C_{(\text{diamond})}(s) + O_2(g)} & \Delta H = 395.4 \text{kJ} \\ C_{(\text{graphite})}(s) + O_2(g) + CO_2(g) --> CO_2(g) + C_{(\text{diamond})}(s) + O_2(g) \end{array}$$

 $C_{(graphite)}(s) \longrightarrow C_{(diamond)}(s) \qquad \Delta H = 1.9 \text{ kJ}$ 

#### **Standard Heats of Formation**

Another method of determining  $\Delta H$  for a process is to use standard heats of formation,  $\Delta H^{o}_{f}$ . These values are the enthalpy changes associated with the formation of the substance referenced. All elements in their natural states have  $\Delta H^{o}_{f}$  values of zero. That includes the BrINClHOF elements that are diatomic in nature. In order to use  $\Delta H^{o}_{f}$  values, you must use the following formula:

 $\Delta H^{o} = \Sigma \Delta H^{o}{}_{f\,products} - \Sigma \Delta H^{o}{}_{f\,reactants}$ 

Where  $\Sigma$  represents "sum of." You use a table of thermodynamic data to look up  $\Delta H^{o}{}_{f}$  values and make sure that you pay attention to the number of moles of each substance, as that is part of your calculation.

We will now find the  $\Delta H^{\circ}$  of a familiar reaction using  $\Delta H^{\circ}_{f}$  values from the linked table:  $N_{2}(g) + 2O_{2}(g) -> 2NO_{2}(g)$ 

ΔH°=[2 mol NO<sub>2</sub> x <u>33.2 kJ</u>] -1 mol NO<sub>2</sub>

 $[(1 \text{ mol } N_2 \times \underline{0 \text{ } kJ}) + (2 \text{ mol } O_2 \times \underline{0 \text{ } kJ})] = 66.4 \text{ } kJ$   $1 \text{ mol } N_2 \qquad 1 \text{ mol } O_2$ 

Notice that the  $\Delta H^{\circ}$  is the same as it was using Hess's Law. It does not matter how you get there, the  $\Delta H$  of a particular process will not differ.

INTERACTIVE 14.2 Enthalpy change via heats of formation

Determine the  $\Delta H^o$  of the following reaction using heats of formation from the thermodynamics table link:  $C_{(graphite)}(s) \rightarrow C_{(diamond)}(s)$ 



## Entropy & Free Energy

#### THE PLAN

1. Entropy

2. Free Energy

#### Entropy

Entropy, S, is another thermodynamic term that means chaos or disorder. It is part of the 2nd Law of Thermodynamics which states that the entropy of the universe is increasing. As many times as you clean your room, it always gets messy does it not? That process of becoming messy is increasing entropy, or a positive  $\Delta S$ .

In general, a process is increasing its  $\Delta S$  if it goes from fewer moles to more moles, or if it goes from solid to liquid, liquid to gas, or solid to gas. So, you can predict the sign of the  $\Delta S$  by looking from reactants to products. You can calculate the  $\Delta S$ by using a familiar looking formula:

 $\Delta S^{o} = \Sigma S^{o}_{products} - \Sigma S^{o}_{reactants}$ 

You look up S<sup>o</sup> values on a thermodynamics data chart just as you did the standard heats of formation. Notice that the units of S<sup>o</sup> are J/mol K. Thus the units of  $\Delta$ S<sup>o</sup> will be J/K.

We will now find the  $\Delta S^{\circ}$  of a familiar reaction using  $S^{\circ}$  values from the linked chart:  $N_2(g) + 2O_2(g) -> 2NO_2(g)$ 

 $\Delta H^{0} = [2 \text{ mol NO}_{2} \times 240.1 \text{ J}] - 1 \text{ K mol NO}_{2}$ 

 $[(1 \text{ mol } N_2 \text{ x} \underline{191.6 \text{ J}}) + (2 \text{ mol } O_2 \text{ x} \underline{205.1 \text{ J}})] = -121.6 \text{ J/K}$ 1 K mol N<sub>2</sub> 1 K mol O<sub>2</sub>

The negative value of  $\Delta S^{\circ}$  indicates that the process involves increased order, or less chaos. The rationale for this is that

there are a total of three moles of gas on the reactants side and only two moles of gas on the products side. Thus, the products are more organized than the reactants.

**INTERACTIVE 14.3** Entropy change via standard entropies

#### Determine the $\Delta S^o$ of the following reaction using standard entropy values from the thermodynamics table link:

 $C_{(graphite)}(s) \rightarrow C_{(diamond)}(s)$ 



**Check Answer** 

#### **Free Energy**

A third piece of the thermodynamics puzzle is free energy, G. The change in free energy enables us to determine if a process is spontaneous or nonspontaneous. Spontaneous means that a process will happen without outside intervention, no extra energy is needed, but no reference to rate of reaction is indicated. A nonspontaneous process will not occur without outside intervention, extra energy, regardless of the amount of time allotted.

If  $\Delta G^{\circ}$  is negative, then a process is spontaneous or exergonic. If  $\Delta G^{\circ}$  is positive, then a process is nonspontaneous or endergonic.  $\Delta G^{\circ}$  is calculated by using the  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and the Kelvin T in the formula:

 $\Delta G^{o} = \Delta H^{o} - T \Delta S^{o}$ 

You can reason mathematically that if a reaction is exothermic  $(\Delta H^{\circ} \text{ is negative})$  and entropy increases ( $\Delta S^{\circ}$  is positive), then regardless of T, the process will be spontaneous ( $\Delta G^{\circ}$  is negative).

You can also reason that if a reaction is endothermic and entropy decreases, then regardless of T, the process will be nonspontaneous. Think about the signs.

In order to determine the  $\Delta G^{\circ}$  of  $N_2(g) + 2O_2(g) --> 2NO_2(g)$  at 298 K, we need to use the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  that have been previously calculated. Note that you must

have like units in order to subtract. I recommend converting the J/K to kJ/K.

 $\Delta G^{o} = 66.4 \text{ kJ} - (298 \text{ K}) \text{ x} (-0.1216 \text{ kJ}) = 102.6 \text{ kJ}$ K

Since the value of  $\Delta G^{\circ}$  is positive, the process is nonspontaneous at 298 K. In fact, regardless of temperature, this process is endergonic.

#### **INTERACTIVE 14.4** Free Energy

Determine the value of  $\Delta G^{\circ}$  for the  $C_{(graphite)}(s) \longrightarrow C_{(diamond)}(s)$  process at 1 K using the previously determined enthalpy and entropy change values.

A. -1.9 kJ
B. -3.3 kJ
C. -1.4 kJ
D. 1.9 kJ

Now take some time to practice all of this energy stuff using the following sheets that mimic a quiz format:

Energy Practice Answers page 1 Answers page 2
# Gases

You will learn about properties of gases, units of pressure, how four variables of gases rely upon each other for their values, and how the mass of a gas impacts its movement.



impactingkids.org

# Properties

# THE PLAN

1. Volume

2. Temperature

3. Moles

4. Pressure

# Volume (V)

By this time in your chemistry careers, you probably already know that gasses occupy the total volume offered to them. That is, a gas will not hunker down in the bottom of a flask and leave the remainder of the flask as a vacuum. Rather, the gas takes up all available space. That amount of available space can be altered by temperature, moles, and pressure.

# **Temperature (T)**

The gaseous phase of a substance is at a higher temperature than its liquid or solid phases. Alas, that does not always mean that gases are going to have high temperatures. For example, the boiling point of hydrogen gas is about 20 K. That's pretty chilly according to most folks. All gas problems must use Kelvin temperatures. Like the volume of a gas, the temperature can be affected by the gas's volume, moles, and pressure.

# Moles (n)

The number of moles of a gas is indicative of the amount of gas present. The more gas particles, the more moles there will be. Changing the number of moles of a gas can change the volume, temperature, and pressure of that gas. The number of moles may change by adding or removing gas particles.

# Pressure (P)

So, pressure has been mentioned, but has yet to be defined. It is defined as the property due to the number of collisions of gas particles with the walls of their container. The greater the number of collisions, the greater the pressure, and *vice versa*. Pressure is measured in a variety of units. Several of these units are below and are related to a common pressure unit, the atmosphere (atm). 1 atm is what normal atmospheric pressure is near at sea level on Earth.

1 atm= 101.3 kPa= 760 mmHg= 760 torr= 29.9 inHg= 14.7 psi

kPa is read as a kiloPascal; mmHg is read as millimeter of mercury; torr is read as is and is named for the inventor of the barometer, a device that measures atmospheric pressure, Torricelli; inHg is read as inches of mercury; and psi is read as pounds per square inch.

One other pressure unit used commonly in meteorology is the millibar (mbar). There are 1013 mbar for every 1 atm. Hurricane Katrina in 2005, had a pressure of 920 mbar. That low pressure indicates the strength of the storm. The lower the pressure the stronger the storm.

Pressure can also be affected by volume, temperature, and moles.

#### SECTION 2

# Five Guys

#### THE PLAN

- 1. Dalton
- 2. Boyle
- 3. Charles
- 4. Gay-Lussac
- 5. Avogadro

#### **Dalton's Law of Partial Pressures**



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John Dalton (1776-1844) was an English chemist, meterologist, and physicist. You have previously encountered him while learning his Atomic Theory. He is also known for his work with gases. His Law of Partial Pressures states that the total pressure of a mixture of gases equals the sum of the partial pressures of those gases. An example of a mixture of gases is air. The four principal components of dry air are nitrogen, oxygen, argon, and carbon dioxide. Those four gases each have their own pressures. The sum of their pressures gives us atmospheric pressure. At normal atmospheric pressure the partial pressures are as follows:

 $P_{N2} = 0.781 \text{ atm}$ 

 $P_{O_2} = 0.201 atm$ 

 $P_{Ar} = 0.0093 \text{ atm}$ 

#### $P_{CO_2} = 0.0087$ atm

The sum of those partial pressures is 1 atm. That is the normal atmospheric pressure at sea level.

Often in a laboratory, gases are collected by water displacement. Thus, there exists a combination of gases within the container, water vapor and the gas that was collected. Dalton's Law of Partial Pressures is used in such problems to determine properties of the collected gas. In such problems the pressure of the water vapor must be subtracted from the total pressure in order to find the partial pressure of the collected gas. You will have a practice problem with such a scenario.

#### INTERACTIVE 15.1 Dalton's Law

At sea level and 0°C, the partial pressure of the nitrogen in clean, dry air is 601 torr when the atmospheric pressure is 760 torr. If oxygen is the only other gas what is its partial pressure?



#### **Boyle's Law**



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Robert Boyle (1627-1691) was an Anglo-Irish chemist, philosopher, and inventor. He is most well-known for his law that holds that when temperature and number of moles are held constant, there will be an indirect relationship between pressure and volume of a gas. It is commonly stated mathematically in a manner that compares an initial and a final condition, represented as 1 and 2, respectively.

 $V_1P_1=V_2P_2$ 

There are no specific units, but the units for volume must be the same on each side as must the units of pressure. If volume increases, pressure decreases, and *vice versa*. Think about squeezing a balloon. When you squeeze it, you can sense that the volume is getting smaller while the pressure is getting larger. In fact, you can make the volume so small as to exceed the capacity of the balloon to hold such a high pressure. When the balloon pops, the volume increases im-

#### **Check Answer**

mensely, and the pressure comes down to stabilize at the atmospheric pressure.

#### **INTERACTIVE 15.2** Boyle's Law

A given mass of oxygen occupies 500 mL at 760 mmHg and 20°C in a sealed vessel. At what pressure (in mmHg) will it occupy 450 mL at the same temperature?



# **Charles's Law**



Jacques Charles (1746-1823) was a French inventor, mathematician, and balloonist. His gas law was actually formulated by Gay-Lussac (forthcoming guy) and credited to Charles for the work that Charles did. Charles's Law states that there is a direct relationship between the volume and temperature of a gas, if the pressure and number of moles remain constant.

 $V_1 = V_2$  $T_1 = T_2$ 

The volume units are not specific, but must be the same in each scenario. The temperature units must be Kelvin. You can again think of a balloon, but you must have willing suspension of disbelief in that you must believe that the pressure remains the same. If you place a balloon in a freezer, you will notice that the volume of the balloon is less. If you leave the

balloon in a hot car, the volume of the balloon will increase. Again, the pressure is not really kept constant in that example, but imagine that it is for ease of understanding.

#### INTERACTIVE 15.3 Charles's Law

Some of the total anesthetics used in surgery are gases at 37°C. If 1.50L of a gas is obtained at 20.0°C, to what volume (in L) does the gas change when the temperature becomes 37.0°C at the same pressure?



# Gay-Lussac's Law



Joseph Louis Gay-Lussac (1778-1850) was a French chemist and physicist who is most well known for indicating that the pressure and temperature of a gas vary directly when volume and number of moles are held constant. This is known as Gay-Lussac's Law. Again the temperature must be in Kelvin, and the pressure units must simply be the same.

```
\frac{\underline{P}_1}{\underline{T}_1} = \underline{\underline{P}_2}\underline{T}_1 = \underline{T}_2
```

Think about a pressure cooker. It is able to work as well as it does because of Gay-Lussac's Law. The pressure in the vessel is increased, and the temperature increases proportionally. This enables food to be cooked at a higher temperature than is typical in a pot on a stove.

#### INTERACTIVE 15.4 Gay-Lussac's Law

So, you're working at a fast food joint and you're told to move a CO<sub>2</sub> canister to storage. You inadvertently move the cylinder from its cozy 27.0°C to the chilly cold storage temp of -10.0°C. If the pressure inside the cylinder was originally 2.25 atm, what will the pressure (in atm) be once it stabilizes in cold storage?



#### Avogadro's Law



www.thefamouspeople.com

Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e di Cerreto (1776-1856) was an Italian scientist who is most wellknown for the number named in his honor. His work actually focused upon proving that equal volumes of gases at 273 K and 1 atm contained equal number of moles. That is that 1 mole of a gas at this standard temperature and pressure (STP) occupies a volume of 22.4 L. This is known as molar volume and will come in handy a bit later.

Avogadro's Law states that there is a direct relationship between the volume of a gas and the number of moles of a gas at constant temperature and pressure.

 $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ 

Again, envision a balloon. Imagine that its temperature and pressure are constant. If you blow more air into the balloon

(add more moles of gas), then the volume of the balloon will also increase. If you let air out of the balloon, the balloon's volume decreases.

You must use moles in Avogadro's Law problems, not grams. The volume units must simply be the same.

INTERACTIVE 15.5 Avogadro's Law

10.0 g of helium are in a pliable balloon with a volume of 2.50 L at 1 atm and 25°C. If the balloon has a slow leak and the volume is arrested at 1.10 L, what mass of helium will be left in the balloon?



# Section 3

# More Gas Laws

#### THE PLAN

- 1. Combined Gas Law
- 2. Ideal Gas Law

#### **Combined Gas Law**

There is no known founder of the combined gas law, it is an amalgamation of Boyle's, Charles's, Gay-Lussac's, and Avogadro's laws. It exists to make the laws more applicable to real world occurrences. Recall that in each of the four guys' laws, two of the four variables were held constant? Well, in real life, that is not always what occurs. So, we use the combined form to apply to situations that do not hold two variables constant. The law reads:

 $\frac{V_1P_1}{T_1n_1} = \frac{V_2P_2}{T_2n_2}$ 

A balloon is filled with 3.47 g of He that occupies 4.25 L at  $24.0^{\circ}\text{C}$  and 762 mmHg. You put the balloon in a freezer at  $-23.3^{\circ}\text{C}$ , and you let it sit for an hour. When you come back, you find that the atmospheric pressure inside the freezer has dropped to 755 mmHg, and you only have 3.00 g of the He left in the balloon. What is the volume of the balloon after the hour spent in the freezer?

In order to work this problem, align each variable with its partners on each side. You will find that there is one variable whose value is unknown. Remember that you must convert the grams to moles.

 $\frac{(4.25 \text{ L})(762 \text{ mmHg})}{(297 \text{ K})(0.8675 \text{ mol})} = (\underline{V_2})(755 \text{ mmHg})}$  (249.7 K)(0.750 mol)

 $V_2 = 3.12 L$ 

Here is a more complicated problem that involves stoichiometry and gas laws:

How many mL of oxygen gas at STP (recall that means 273 K and 1 atm) will be produced when 5.25 g of potassium chlorate are heated and the temperature stabilizes at  $27.5^{\circ}$ C while the atmospheric pressure is 14.6 psi? Assume none of the oxygen is lost.

The first thing that you must realize is that you have been given a reaction that produces this oxygen. Write the balanced equation as your first task.

 $2\text{KClO}_3 \xrightarrow{\Delta} 2\text{KCl} + 3\text{O}_2$ 

Now, use the given amount of  $KClO_3$  to determine the number of L of  $O_2$  that should be produced at STP. Recall that Avogadro told us that every 1 mole of a gas at STP occupied 22.4 L.

 $5.25 \text{ g KClO}_3 \text{ x } 1 \text{ mol} \text{-} \text{KClO}_3 \text{ x } 3 \text{ mol} \text{-} \text{O}_2 \text{ x } 22.4 \text{ L } \text{O}_2 =$ 122.55 g KClO<sub>3</sub> 2 mol KClO<sub>3</sub> 1 mol O<sub>2</sub>

1.44 L  $O_2$  should be produced at STP.

We now ask ourselves what that volume will be under the laboratory conditions indicated in the problem.

The fact that none of the oxygen is lost means that the number of moles remains constant. Thus  $n_1$  and  $n_2$  are the same and do not need to be represented in the equation. So, plugging into the combined gas law gives us:

 $\frac{(1.44 \text{ L})(14.7 \text{ psi})}{(273 \text{ K})} = (\underline{V}_2)(14.6 \text{ psi})$  (300.5 K)

 $V_2 = 1.60 L O_2$ 

Now convert the volume to mL as the problem requested. So, your final answer should be 1600 mL O<sub>2</sub>.

## Ideal Gas Law

There are times when there are not initial and final variables, and you only have one set of data. In such cases, the combined gas law is converted into the ideal gas law. The ideal gas law considers that one side of the combined gas law has data that is ideal. The given data then is placed into the other side of the formula.

So, what are ideal conditions? Here is a list of the four variables and their ideal values:

V = 22.4 L P = 1 atm T = 273 Kn = 1 mol

If I plug these values into one side of the combined gas law, it looks like this:

```
(22.4 \text{ L})(1 \text{ atm}) = \underline{VP}
(273 K)(1 mol) Tn
```

or

- $0.0821 \underline{\text{Latm}} = \underline{\text{VP}} = R$ Kmol Tn
- R = 0.0821 <u>Latm</u> and is known as the ideal gas law constant. Kmol

Again, the clue to your needing to use the ideal gas law is that you will be given one set of data. The units are quite specific for the ideal gas law. V must be in L. P must have atm. T is in K, as always. n must be mol. Here is a familiar problem.

How many mL of oxygen gas will be produced when 5.25 g of potassium chlorate are heated and the temperature stabilizes at  $27.5^{\circ}$ C while the atmospheric pressure is 14.6 psi? Assume none of the oxygen is lost.

Just as with the previous problem, the first thing you need to do is write the balanced equation as your first task.

2KClO $_3$  --> 2KCl + 3O $_2$ 

Now, use the given amount of  $KClO_3$  to determine the number of mol of  $O_2$  that should be produced.

 $5.25 \frac{\text{g KClO}_3 \text{x}}{1 \text{ mol KClO}_3} \frac{1 \text{ mol KClO}_3}{2 \text{ mol KClO}_3} \frac{1 \text{ mol KClO}_2}{2 \text{ mol KClO}_3} = 0.0643 \text{ mol O}_2$ 

Now that you know the number of mol  $O_2$ , you can use the given information and plug into the ideal gas law. Notice that I have converted my pressure into atm.

 $0.0821 \underline{\text{Latm}} = \underline{V(0.993 \text{ atm})}$ Kmol (300.5 K)(0.0643 mol)

V = 1.60 L = 1600 mL

INTERACTIVE 15.6 Ideal Gas Law Problem

If 20.0 L of CO<sub>2</sub> are retrieved from the combustion of propane, C<sub>3</sub>H<sub>8</sub>, at 150.°C and 764.1 ;mmHg, how many grams of propane were combusted?



# Effusion and Graham's Law

# GAS MOVEMENT

- 1. Effusion
- 2. Graham's Law

# Effusion

You may have heard of diffusion in a biology class, as in diffusion across a semi-permeable membrane. If you know what I am talking about, then you probably recall that aqueous solutions diffuse from higher concentration to lower concentration.

Well, effusion is a very similar concept, except it deals with the movement of gases from higher concentration to lower concentration rather than aqueous solutions.

## Graham's Law

The rate at which gases effuse is the focus of Graham's Law. In order to understand the law, it is necessary to understand rate.

Rate is something divided by time. In the case of effusion, it is the amount of gas (usually a volume) that moves through the gradient per unit time.

Graham's Law states that the rate of effusion of a gas is indirectly related to the square root of the molar mass (molecular weight) of that gas. The greater the molar mass of a substance that slower the rate of effusion.

Remember that when something is raised to the 0.5 power, it is the same thing as taking the square root of that something. When comparing two different gases, the formula used is:

 $(MW_1^{0.5})(rate_1) = MW_2^{0.5})(rate_2)$ 

This formula can be rearranged to by:

 $\frac{(MW_1^{0.5})}{(MW_2^{0.5})} = \frac{(rate_2)}{(rate_1)}$ 

If equal amounts of helium and argon are placed in a porous container and allowed to escape, which gas will escape faster and how much faster?

He's molar mass is 4.00 g/mol and Ar's is 39.95 g/mol. Thus, the He will escape faster. To answer the question of how much faster, we must rely upon the aforementioned formula and compare the rate of He to the rate of Ar. Let rate<sub>2</sub> be that of He, and rate<sub>1</sub> be that of Ar. Plug in their respective molar masses and solve for the ratio of the rate of He to the rate of Ar.

 $\frac{(39.95 \text{ g/mol})^{0.5}}{(4.00 \text{ g/mol})^{0.5}} = \frac{(\text{rate}_{\text{He}})}{(\text{rate}_{\text{Ar}})} = 3.16$ 

That means that the He will effuse 3.16 times faster than the Ar. In other words, 3.16 mL of He could effuse in 1 min, while only 1 mL of Ar could effuse in 1 min. Notice that the rate is described as a volume unit per time unit.

Here is another more challenging problem involving effusion:

Two porous containers are filled with hydrogen and neon respectively. Under identical conditions, 2/3 of the hydrogen escapes in 6 hours. How long will it take for half of the neon to escape? You will approach the problem using the same formula as you did in the previous problem. Recall that hydrogen gas is diatomic.

The molar mass of  $H_2$  is 2.02 g/mol, and the molar mass of Ne is 20.18 g/mol. The volume of gas effusing in either case is unknown, but you may assume a volume and work with it. I will assume that 0.667 mL of  $H_2$  escapes in 6 h. The question then is how many hours will it take for 0.500 mL of Ne to effuse. So, plugging in, we have:

 $(2.02 \text{ g/mol})^{0.5} = (0.500 \text{mL}/x)$ (20.18 g/mol)<sup>0.5</sup> (0.667 mL/6 h)

Be careful with this, the x is in the denominator of the numerator expression.

x = 14.2 h

# **Gas Laws Practice**

# Solutions

You should recall that a solution is another name for a homogeneous mixture of two or more pure substances. We will be looking at various properties and ways to describe solutions. There are plenty of practice problems in this chapter and on the practice link at the end.



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# SECTION 1

# Solutions

#### THE PLAN

- 1. Parts of a Solution
- 2. Factors Affecting Solution Formation Rate
- 3. Henry's Law
- 4. Concentrated vs. Dilute
- 5. Molarity
- 6. Mass Percent
- 7. Mass/Volume Percent
- 8. Volume/Volume Percent
- 9. Mole Fraction
- 10. Molality
- 11. Dilutions

## Parts of a Solution

Solutions may be solid, liquid, gaseous, or aqueous phases. An example of a solid solution is steel. Steel is a homogeneous mixture of carbon atoms surrounded by iron atoms.

An example of a liquid solution is isopropyl alcohol, which is isopropyl alcohol molecules surrounding water molecules.

Air is a homogeneous mixture of nitrogen molecules surrounding oxygen molecules, argon atoms, and carbon dioxide molecules.

The substance doing the surrounding is the solvent, and the substance present in the lesser amount is the solute.

Aqueous means that a substance is dissolved in water. The substance being dissolved is the solute. The substance doing the dissolving is the solvent. Water his known as the "universal solvent." That is a bit misleading in that there are substances that do not dissolve in water.

#### **Factors Affecting Solution Formation Rate**

The time that it takes for a solution to form is known as the solution formation rate. There are three factors that affect how fast a solution will form: temperature, agitation, and particle size.

Increased temperature generally decreases the time that it takes for a solution to form. Notice the word *generally*. There are exceptions. However, think about dissolving sugar in tea. You can dissolve the sugar faster in hot tea rather than in cold tea.

Agitation is another word for shaking or stirring. Again think about tea and sugar. You usually stir your mixture rather than staring at it and willing it to become a solution.

The smaller the particle size the faster the solution will form. A final thought on sugar and tea. You use granulated sugar rather than a stick of sugar cane!

## Henry's Law



English chemist William Henry

(1774-1836) developed a law that states that the solubility (C) of a gas in a liquid is directly proportional to the gas's pressure above that liquid.

 $\frac{\underline{C}_1}{\underline{P}_1} = \frac{\underline{C}_2}{\underline{P}_2}$ 

Think about carbonated beverages. Before you open a carbonated drink, the pressure of the gas above the liquid solution is higher than atmospheric pressure. Therefore there is a great deal of carbon dioxide dissolved in the solution prior to the opening of the beverage. Upon opening the drink, the pressure above the liquid quickly becomes equal to the lesser atmospheric pressure, and the  $CO_2$  is less soluble at that lower pressure. It is made evident to the person opening the drink as the  $CO_2$  comes out of solution surrounding by some of the beverage. The bubbles of  $CO_2$  and surrounding beverage are what create the foam layer.

Henry's Law is also quite applicable in scuba diving. The greater the depth of the dive, the greater the pressure will be. At greater pressure, surrounding gases become more soluble in blood, the solution of importance. Nitrogen, in particular, is of concern. At depth, too much nitrogen (since it makes of 78% of air) can easily be dissolved in the blood, causing nitrogen narcosis. Upon rising to the surface too quickly, the nitrogen can come out of the blood too quickly, causing decompression sickness. The trick is to rise to the surface slowly to allow the nitrogen bubbles to exit via the lungs.

#### Concentrated vs. Dilute

You have probably heard of these terms in reference to orange juice. Concentrated orange juice is the frozen stuff that does not have much water in it. In order to dilute the orange juice, you would add water. What you should gather from that is that concentrated is a qualitative term used to describe a solution with a relatively small amount of solvent. Likewise, a dilute solution is one that has a relatively large amount of solvent. Neither of these terms is used to describe a quantitive measurement. We have several ways to quantitatively describe solutions that follow.

# Molarity

Represented by M, the molarity of a solution (soln) is determined by dividing the moles of solute by the liters of solution.

M = <u>#mol solute</u> #L soln

The units of molarity are mol/L, but it is often just written as something like 6 M. This translates into 6 molar, or 6 moles per liter. Molarity is one of the most commonly used quantitative measurements.



# **Mass Percent**

As the name implies, the mass percent is determined by dividing the mass of solute by the mass of solution and multiplying that quotient by 100.

The units of mass must be the same for the solute and the solution, such that the resulting mass % is unitless. The notation used to indicate that mass percent is provided is (m/m)%





How many grams of water are present in a 5.00% (m/m) solution containing 0.875 g of calcium acetate?



#### **Mass/Volume Percent**

Usually written as some number followed by (m/v)%, mass/ volume percent is determined by dividing the grams of solute by the milliliters of solution and multiplying that quotient by 100. The units are quite specific. (m/v)% = <u>#g solute</u> x 100 #mL soln



#### **Volume/Volume Percent**

The last of the percent calculations for determining the quantitative concentration of a solution, volume/volume percent is the volume of the solute divided by the volume of the solution. The quotient is then multiplied by 100. The shorthand notation is usually written as (v/v)%. Units are not specific, but they must be the same.

 $(v/v)\% = \frac{\#mL \text{ solute}}{\#mL \text{ soln}} x 100$ 



#### **Mole Fraction**

The mole fraction of both the solute and the solvent may be determined. As the name implies, a part over a whole is the idea here. Mole fraction is represented by the Greek letter chi,  $\chi$ .

 $\chi_{solute} = \frac{\#mol \ solute}{\#mol \ soln}$  $\chi_{solvent} = \frac{\#mol \ solvent}{\#mol \ soln}$ 

Both of the mole fractions of solute and solvent should add to be 1. Notice this is not a percent. Do not multiply by 100.



# Molality

A quantitative measurement that is typically only used to solve colligative properties (next chapter) problems is molality, represented by a lowercase m. It is unlike the other measurements in that the solution is not part of the calculation. Molality is determined by dividing the number of moles of solute by the number of kilograms of solvent. It is very unit specific.

m = <u>#mol solute</u> #kg solvent

INTERACTIVE 16.6 Molality

10.0 g of calcium acetate is added to 100. g of water. What is the molality of this solution?



# Dilutions

I do not store every possible concentration of solutions that I used in labs. Rather, I store the most concentrated form of these solutions, and then I dilute them to the concentration needed for a particular situation. To do so, I use a dilution equation:

 $(M_1)(V_1) = (M_2)(V_2)$ 

If I know that I have 12 M HCl, and I wish to make 500 mL of a 2 M HCl solution, then I employ the equation:

(12 M)(V1) = (2 M)(500 mL)

V1 = 83.3 mL

That means that I will measure 83.3 mL of 12 M HCl and add it to the complementary amount of water, 416.7 mL. The rule of thumb is to always add acid to water, as it will be the water that splashes. I would then cork the vessel and agitate it to mix the solution.

# **Solutions Practice**

Check Answer

CHAPTER 17

# Colligative Properties

You will investigate the effect on freezing points and boiling points that solution formation has.





(a) Sea water

(D) Fulle water

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# **Colligative Properties**

# THE PLAN

- 1. What is a colligative property?
- 2. Freezing Point Depression
- 3. Boiling Point Elevation

# What is a Colligative Property?

Properties that depend upon the number of solute particles in solution are known as colligative properties. Among the colligative properties are freezing point, boiling point, vapor pressure and osmotic pressure. I will focus upon the previous two in this chapter.

# **Freezing Point Depression**

When a solute particle is surrounded by solvent particles, the solvent particles are busy. They are not inclined to behave as they would if they were by themselves. In order for freezing of a substance to occur, energy must be lost and organization must increase. When a solute is present in a solvent, the freezing point of the solution is lower than the freezing point of the pure solvent. The freezing point is depressed. That is the reason for salting roads in the winter. If water freezes at 0°C, then water with NaCl in it will freeze at a lower temperature, perhaps preventing ice from forming on roads.

In order to determine by how much the freezing point is lowered, three pieces of information must be known: freezing point constant for the solvent ( $k_f$ ), molality(m), and van't Hoff factor (*i*).

Freezing point constants are known for all possible solvents. The identity of the solvent determines the freezing point constant. For example, water, the most common solvent, has a freezing point constant of 1.86°Ckg/mol. The unit is read as degrees Celsius kilogram per mole. The molality you recall is the number of moles of solute divided by the number of kilograms of solvent.

The van't Hoff factor is a number that represents the number of particles that the solute yields per representative particle. For example, NaCl is an ionic compound that dissociates in water to yield one Na<sup>+</sup> and one Cl<sup>-</sup>. Because it yields those two ions, its *i* is 2. A molecular compound does not break into its individual atoms in solution, so it will have an *i* of 1. Recall that molecular compounds are made of two or more nonmetals. Other ionic compounds may yield more than two ions,



such as AlCl<sub>3</sub>. There are 1 Al<sup>3+</sup> and 3 Cl<sup>-</sup> ions that dissolve for each formula uinit. So, its *i* is 4.

When you put all three of these pieces together, you can formulate the equation to determine the change in freezing point for a particular solution.

 $\Delta T_{\rm f} = (k_{\rm f})(m)(i)$ 

Once you know the  $\Delta T_f$ , you can then find the new freezing point of the solution by subtracting the change from the normal freezing point. The normal freezing point of water is 0°C. For other solvents, you would have to be given both the  $k_f$  and the normal freezing point.

 $T_{fsoln} = T_{fsolvent} - \Delta T_f$ 

What is the freezing point of a solution made by adding 15.0 g of ammonium sulfate to 100. g of water?

First realize that the solvent is water, so the  $k_f$  is 1.86°Ckg/mol.

Now, calculate the molality.

 $15.0 \text{ g} (\text{NH}_4)_2 \text{SO}_4 \text{ x} \underbrace{1 \text{ mol } (\text{NH}_4)_2 \text{SO}_4}_{132.17 \text{ g} (\text{NH}_4)_2 \text{SO}_4} = 0.113 \text{ mol}(\text{NH}_4)_2 \text{SO}_4$ 

 $0.113 \text{ mol } (\text{NH}_4)_2 \text{SO}_4 = 1.13 \text{ mol/kg}$ 0.100 kg H<sub>2</sub>O

You know the van't Hoff factor from the previous problem. It is 3. Now plug into the  $\Delta T_f$  equation.

 $\Delta T_{\rm f} = (\underbrace{1.86^{\circ}\text{Ckg}}_{\text{mol}})(\underbrace{1.13 \text{ mol}}_{\text{kg}})(3) = 6.33^{\circ}\text{C}$ 

You may now subtract the  $\Delta T_f$  from the normal freezing point of the solvent to get the freezing point of the solution.

 $T_{fsoln} = 0^{o}C - 6.33^{o}C = -6.33^{o}C$ 

# **Boiling Point Elevation**

When a substance boils, its vapor pressure (the pressure of gas particles sitting above the substance) equals the atmospheric pressure. At sea level that atmospheric pressure is 1 atm. At a high altitude, the atmospheric pressure is lower. That means that a substance boils at a lower temperature at a higher altitude than it does at a lower altitude. Look at the directions for baking a cake. They usually include some reference to cooking at higher altitudes.

In order for boiling to occur in a solution, the solvent particles must release their hold on the solute particles. To encourage that release, more energy is required to be gained by the solution. That translates into an elevation, or raising, of the boiling point of a solution when compared to the boiling point of its pure solvent. Water's normal boiling point is 100°C. If a solute is mixed with water, then the boiling point will be above 100°C.

The necessary information for determining the change in boiling point is similar to the information needed for freezing point change.

The boiling point constant  $(k_b)$  is required for the solvent. The  $k_b$  of water is 0.512°Ckg/mol. Any other solvent's  $k_b$  value will be provided for you.

You also need to know the molality and the van't Hoff factor of the solute. Piecing that together gives you:

 $\Delta T_{\rm b} = (k_{\rm b})(m)(i)$ 

Once you know the  $\Delta T_b$ , you will then *add* the  $\Delta T_b$  to the normal boiling point of the pure solvent to determine the boiling point of the solution.

 $T_{bsoln} = T_{bsolvent} + \Delta T_b$ 

Now, we will find the boiling point of the same mixture from the previous problem.

The solvent is water so the  $k_b$  is 0.512°Ckg/mol.

The molality is the same as it was in the previous problem, 1.13 mol/kg.

The van't Hoff factor is the same as in the previous problem, 3.

 $\Delta T_{b} = (\underbrace{0.512^{\circ}\text{Ckg}}_{\text{mol}})(\underbrace{1.13 \text{ mol}}_{\text{kg}})(3) = 1.74^{\circ}\text{C}$ 

You now add the  $\Delta T_{\rm b}$  to the normal boiling point of water.

 $T_{\rm bsoln} = 100^{\rm o}{\rm C} + 1.74^{\rm o}{\rm C} = 101.74^{\rm o}{\rm C}$ 

# **Colligative Properties Practice**

# Equilibrium

Equilibrium processes are prevalent in chemical reactions, and are a major component in the study of general chemistry. You will learn about equilibrium constants, and you will learn how to solve complex equilibrium problems.



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# Section 1

# Equilibrium

## THE PLAN

- 1. What is Equilibrium?
- 2. Equilibrium Constant
- 3. Small K Problem
- 4. Large K Problem

# What is Equilibrium?

Many chemical reactions do not occur in the typical reactants yield products with a right-pointing arrow. In fact, many reversible reactions occur in which reactants yield products until enough products are made to turn around and make more reactant. The process continues until the rate at which products are made equals the rate at which reactants are made. When the forward and reverse rates equal, equilibrium is reached. There is no limiting reagent, so you do not run out of any substance. Though equilibrium is a dynamic situation, one that changes, the concentrations of reactants and products are static at equilibrium.

Consider the reaction known as the dimerization of nitrogen dioxide:

 $2NO_2(g) \rightleftharpoons N_2O_4(g)$ 

Here is an illustration of this reaction:



Notice that at time point a, no  $N_2O_4(g)$  has formed; you only have  $NO_2(g)$  molecules. At point b, one molecule of  $N_2O_4(g)$ has formed. At point c, three molecules of  $N_2O_4(g)$  have formed. And at point d, three molecules of  $N_2O_4(g)$  have formed. Though the atoms used to make the three molecules of  $N_2O_4(g)$  changed from point c to point d, the system reached equilibrium at point c. This is because no net change in the concentration of the molecules changed from c to d.

Here is a picture of this reaction.



On the left you have an ice water bath that shows the predominance of a lighter color gas,  $N_2O_4(g)$ . In the middle you have a slightly darker color flask at room temperature (25°C) that shows both  $N_2O_4(g)$  and  $N_2O_4(g)$ , though the color is still relatively light. On the right, you have a darker color in a hot water bath that shows the predominance of  $N_2O_4(g)$ , the darker gas. What you can gather from this is that at cold temperatures and at room temperature,  $N_2O_4(g)$  is more prevalent than  $N_2O_4(g)$ ; whereas at warm temperatures, the  $N_2O_4(g)$  is present in higher concentration than is the  $N_2O_4(g)$ . We will revisit this scenario once we get into equilibrium constant concepts.

# **Equilibrium Constant**

The equilibrium constant (K) is a value that indicates the preferred direction of reaction. Consider the following reaction where the uppercase letters represent the reactants and products, and the lowercase letters represent the number of moles of each reactant and product, respectively.

 $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ 

K is determined by using the law of mass action:

 $K = [\underline{C}]^{c}[\underline{D}]^{d}$  $[A]^{a}[B]^{b}$ 

It is important that you note several things from this equation, known as an equilibrium expression or K expression. One is that the products are in the numerator, and the reactants area in the denominator. That will always be the case, just as reactants are always written on the left side of the arrows, and products are written on the right side of the arrows. You should note that there are brackets around each reactant and product. The [] always mean concentration in the unit of molarity (M), so you will not see the M next to the number in brackets. It is understood. A third point to make is that the products' and reactants' concentrations are raised to the power of their coefficients (moles) from the balanced equation. Finally, the only phases that may be represented in a K expression are gaseous and aqueous. If a solid or a liquid is a reactant or a product, the number 1 is simply substituted for its concentration.

K is classified as being small or large. If K <1, it is a small K. The reason for noting this, is that there are different methods of solving problems depending on what a K value is. A small K value means that the denominator is larger than the numerator. In turn, this means that the reactants prefer to be made rather than the products. Conversely, a large value of K is greater than 1 and means that product formation is favored.

In writing the K expression for the dimerization of nitrogen dioxide, you would have

 $K = [N_2O_4]$  $[NO_2]^2$ 

At 25°C, the equilibrium concentrations of  $NO_2$  and  $N_2O_4$  are 0.0370 M and 0.2315 M, respectively. What is the value of K at this T?

All that you need to do at this point, is plug into the K expression. Treat the K expression as your formula in these problems.

K = [0.2315] = 169 L/mol\*[0.0370]<sup>2</sup>

Since the value of K is 169, this is a large K. This reaction prefers to make product. The product happens to be  $N_2O_4$ . Look back at the pictures of the reactant and product. Recall that the lighter color prevails at room temperature. The lighter color is indeed  $N_2O_4$ . What we gather from this knowledge is that the K value verifies that this reaction likes to make product at room temperature. If we were to increase the temperature, we could drive the reaction to have a smaller value of K and thus make more  $NO_2$ .

Try another problem using the following reaction for the synthesis of ammonia,  $NH_3$ :

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 

Determine the value of K given the equilibrium concentrations at 300°C:

 $[N_2]_{eq} = 2.59$  $[H_2]_{eq} = 2.77$  $[NH_3]_{eq} = 1.82$ 

\*Do not worry about the units of K at this point in your chemistry career.

First write your K expression.

 $K = [NH_3]^2$  $[N_2][H_2]^3$ 

Next substitute into the K expression the equilibrium concentrations of the reactants and product and solve for K.

$$K = [1.82]^2 = 0.0602 L^2/mol^{2*}$$
$$[2.59][2.77]^3$$

Since this value of K is small, this reaction prefers to make reactants at  $300^{\circ}$ C

If a reaction is reversed then the reciprocal of its K value becomes the new K value. That means that a large K would become a small K, and *vice versa*.

#### **Small K Problem**

Consider the decomposition of dinitrogen tetroxide at room temperature rather than the dimerization of nitrogen dioxide:

 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ 

In reversing the reaction, what was reactant is now product and what was product is now reactant. So, the value of K will be the reciprocal of 169 L/mol, or 0.00592 mol/L. Now the value of K is small, and still the reaction prefers to make  $N_2O_4$ .

In a typical equilibrium problem, you will not be asked to

	$[N_2O_4]$	[NO <sub>2</sub> ]
initial		
change		
equil.		

solve for the value of K. Instead, you will be asked to solve for the equilibrium concentrations of the reactants and/or prod-ucts.

At 25°C K is 0.00592 mol/L and the initial concentration of  $N_2O_4$  is 0.750 M. What are the equilibrium concentrations of both species (reactants and products) at this temperature?

Your first step is to notice that the K value is small.

The next step is to write the K expression.

 $K = [NO_2]^2$  $[N_2O_4]$ 

Now, you will make an equilibrium chart that will have all reactants and products in the order originally indicated as well as initial [], change in [], and equilibrium []. Your empty chart will look like this:

As you begin to fill the chart in, you will eventually see that you will have equilibrium concentrations to plug into your K expression. So, start plugging in with information that is given.

You know that you initially have  $0.750 \text{ M N}_2\text{O}_4$ , and nothing is mentioned about the product. That means that no product has been formed initially; it will be zero.

	$[N_2O_4]$	[NO <sub>2</sub> ]
initial	0.750	0
change		
equil.		

Any substance whose initial concentration is zero must increase its concentration. This is because neither the numerator nor the denominator may be zero in a K expression. If the product is zero, as is the case in this problem, then it will increase its concentration, and the reactant will decrease its concentration. We do not know by how much they will change, so we work in terms of x. The mole to mole ratio from the balanced equation must be reflected in the change line.

	$[N_2O_4]$	[NO <sub>2</sub> ]
initial	0.750	0
change	- <i>x</i>	+2x
equil.		

Notice that the 1:2 mol ratio is reflected in the amounts of *x* that are subtracted and added.

The next step is to complete the last line of the chart, the equilibrium line. To achieve this, you simply add the initial and change lines for each respective substance.

	$[N_2O_4]$	[NO <sub>2</sub> ]
initial	0.750	0
change	- <i>x</i>	+2x
equil.	0.750 - <i>x</i>	2 <i>x</i>

Now you are ready to plug into your K expression. You

know the value of K, and you know the value of the equilibrium concentrations of both substances in terms of *x*.

$$0.00592 = [2x]^2$$
$$[0.750 - x]$$

In solving for *x*, you have two choices, you may use the quadratic formula since you have a second order polynomial; or you may test the 5% rule.

The 5% rule allows you to remove any amount of x that has been added to or subtracted from an initial value that is not zero. In doing so the math becomes much easier. Take a look at when I remove the -x from 0.750:

$$0.00592 = [2x]^2$$
  
[0.750]

*x* = 0.0333

If you use the 5% rule, you must test it upon getting your value of x. To do so, take that which you removed (in this case x) and divide by that from which you pulled it and multiply by 100. If the value that you obtain is less than 5%, then the assumption you made in removing what was removed is a good assumption, and you have an acceptable value of x. If it is greater than 5%, then you must replace what was removed and solve using the quadratic.

Testing the 5% rule:

<u>0.0333</u> x 100 = 4.44%...your assumption is good 0.750

You may now look back at the equilibrium line of the chart and solve for the equilibrium concentrations now knowing what *x* is.

 $[\mathrm{N}_2\mathrm{O}_4] = 0.0750 - 0.0333 = 0.717$ 

 $[NO_2] = 2(0.0333) = 0.0666$ 

You may check you answers by plugging them back into the K expression to see if you get a value of K close to that which you know it to be.

 $[0.0666]^2 = 0.00619$ [0.0717]

In fact, it is about 4.44% off:)

#### Large K Problem

Go back to the dimerization of nitrogen monoxide and its large K value. The reaction was:

 $2NO_2(g) \le N_2O_4(g)$ 

The K value was 169 L/mol. Since this is a large K value and the reaction favors making product, we have a slightly different method of solving such a problem.

At 25°C, the initial concentration of NO<sub>2</sub> is 0.500 M. What are the equilibrium concentrations of both species at this temperature? K = 169 L/mol

You first notice the large K value, and this tells you to set the problem up differently from a small K problem.

Write your K expression.

 $K = [N_2O_4]$  $[NO_2]^2$ 

Now, you will make a *stoichiometry* chart that will have all reactants and products in the order originally indicated as well as initial [], change in [], and final []. Your empty chart will look like this:

	$[NO_2]$	$[N_2O_4]$
initial		
change		
final		

In a stoichiometry chart the final line replaces the equilibrium line. This is because the reaction proceeds far to the right (that is, it makes lots of product) before it turns around to make a little bit of reactant. Remember that no substance can have a concentration of zero at equilibrium. So, the initial line still comes from the initial information that is given.

	[NO <sub>2</sub> ]	$[N_2O_4]$
initial	0.500	0
change		
final		

Any substance whose initial concentration is zero must increase its concentration. This time the change line will have numbers, not *x*'s. This is because the reactants are going to act like a limiting reagent exists for the time being. The mole to mole ratio must still be reflected in the change line.

	[NO <sub>2</sub> ]	$[N_2O_4]$
initial	0.500	0
change	-0.500	+0.250
final		

Notice that the 2:1 mol ratio is reflected in the numbers that are on the change line. Now to obtain the final line, you will add the initial and change lines for each substance.

	$[NO_2]$	$[N_2O_4]$
initial	0.500	0
change	-0.500	+0.250
final	0	0.250

You now have a zero for the  $[NO_2]$ . That is a no-no. The next step is to correct that no-no by making an equilibrium chart which starts from the final position of the stoichiometry chart. In other words the initial line of the equilibrium chart is the same as the final line of the stoichiometry chart.

	$[NO_2]$	$[N_2O_4]$
initial	0	0.250
change		
equil.		

From this point you do the same as you did for the small K problem. You fill in your change line with *x*'s.

	$[NO_2]$	$[N_2O_4]$
initial	0	0.250
change	+2x	- <i>x</i>
equil.		

And again, your equilibrium line is the sum of your initial and change lines for each substance.

	[NO <sub>2</sub> ]	$[N_2O_4]$
initial	0	0.250
change	+2x	- <i>X</i>
equil.	2 <i>x</i>	0.250 - <i>x</i>

Now you are ready to plug into your K expression. You know the value of K, and you know the value of the equilibrium concentrations of both substances in terms of *x*.

169 = [0.250 - x] $[2x]^2$ 

Remove any amount of *x* that has been added to or sub-tracted from an initial value that is not zero. And you have:

169 = [0.250] $[2x]^2$ 

x = 0.0192

Testing the 5% rule:

<u>0.0192</u> x 100 = 7.69%...your assumption is bad! 0.250

Since your assumption is not good, you must now replace that which you pulled out and use the quadratic equation to solve for *x*.

$$169 = [0.250 - x]$$
  
 $[2x]^2$ 

Set you equation equal to zero in order to utilize the quadratic equation's format:  $ax^2 + bx + c = 0$ .

 $676x^2 + x - 0.25 = 0$ 

Here's the formula for the quadratic just in case you have forgotten:

$$x = -b \pm (b^2 - 4ac)^{0.5}$$
  
2a

You will get two values of *x*. If both are positive, then you will always select the smaller one. If one is positive and the other negative, you will select the positive one.

Plugging in with our a, b, and c values, we will have:

 $x = \frac{-1 \pm (1^2 - 4(676)(-0.25))^{0.5}}{2(-0.25)}$ 

x = 0.0185 or -0.0200

Accept the positive one: 0.0185.

You may now look back at the equilibrium line of the chart and solve for the equilibrium concentrations now knowing what *x* is.

 $[NO_2] = 2(0.0185) = 0.0370$ 

 $[N_2O_4] = 0.0250 - 0.0185 = 0.231$ 

You may check you answers by plugging them back into the K expression to see if you get a value of K close to that which you know it to be. This time it should be spot on, since you have the most accurate value of *x*.

```
K = [0.231] = 169 L/mol
[0.0370]^2
```

You now know how to work small and large K problems, and you have learned about one of the key concepts in chemistry.

Equilibrium Practice Answers
CHAPTER 19

# Le Chatelier & K<sub>sp</sub>

Continuing with the concept of equilibrium, you will learn about how an equilibrium system deals with stress applied to it, and you will learn about equilibrium reached by ionic compounds.



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# Le Chatelier's Principle

# THE PLAN

- 1. What is the Principle?
- 2. Concentration
- 3. Pressure
- 4. Temperature
- 5. Problem

# What is the Principle?

Henri Louis LeChatelier (1850-1936) was a French chemist who explained what a system at equilibrium will do to relieve stress. The principle states that when a stress is applied to a system at equilibrium, the system will respond in a manner that attempts to bring the system back to equilibrium. Stresses are concentration, pressure, and temperature.

## Concentration

A system at equilibrium may become stressed if more reactant or product is added or if reactant or product is removed. The response to such a stress is to shift the reaction either right or left. Recall that equilibrium reactions are reversible. So, if a reaction shifts to the right, then more product is made. If a reaction shifts to the left, then more reactant is made.

So, if you add more reactant, then...

the reaction will shift to the right to use the excess reactant.

If you add more product, then...

the reaction will shift to the left to use the excess product.

If you remove reactant, then...

the reaction will shift to the left to replenish the lost reactant. If you remove product, then...

the reaction will shift to the right to replenish the lost product.

#### Pressure

There are two means of affecting the pressure of a gaseous system at equilibrium: changing concentration of gases and changing the volume of the container.

Changing the concentration of gases in a system at equilibrium has the same effect as changing the concentration did in the previous examples.

Changing the volume of a container changes the number of collisions that the gaseous particles have with the walls of their container. Think about Boyle's Law.

If you decrease the volume of the container, then the pressure will increase and the system will adjust by...

shifting to the side with the fewer number of moles in an effort to bring the pressure back down to what it was at equilibrium.

If you increase the volume of the container, then the pressure will decrease and the system will adjust by...

shifting to the side with the greater number of moles in an effort to bring the pressure back up to what it was at equilibrium. If you increase or decrease the volume of the container for a reaction that has equal number of moles on reactant and product side, then...

the system cannot make the appropriate changes and the reaction will not be able to reach equilibrium.

If you add an inert gas (noble gas) to a system at equilibrium, then...

there will be no shift because the inert gas only increases the total pressure of the system (think Dalton's Law) and has no effect on the partial pressures of the reactants or products. The system is not truly stressed by the addition of an inert gas.

#### Temperature

The effect that changing temperature has on a system at equilibrium depends on whether the system is endothermic or exothermic.

An endothermic process absorbs heat energy, thus the energy appears as a reactant or the change in enthalpy is positive.

If you add more heat to an endothermic reaction, then...

the reaction will shift to the right to use the excess heat. (think of the heat as a reactant).

If you remove heat from an endothermic process, then...

the rxn will shift to the left to replenish the missing heat that is treated like a reactant.

Whereas an exothermic reaction releases heat energy, thus the energy appears as a product or the change in enthalpy is negative.

In an exothermic process if you add more heat, then...

the reaction will shift to the left to use the excess heat. (think of the heat as a product).

If you remove heat from an exothermic reaction, then...

the reaction will shift to the right to replenish the missing heat that acts like a product.

# Problem

Consider the following reaction:

 $N_2(g) + 2O_2(g) + 66.4 \text{ kJ} \rightleftharpoons 2NO_2(g)$ 

If the following changes are applied, then the direction of shift will be indicated below.

a. The system is heated.

b.Its container is squeezed.

c. Nitrogen dioxide is added to the system.

d.Neon is added to the system.

a. The reaction will shift to the right to use the excess heat that is a reactant since this reaction is endothermic.

b. The volume of the container will decrease as it is squeezed, therefore the pressure will increase. The reaction will shift to the right because there are only 2 moles of gas on the right, while there are 3 moles of gas on the left. Shifting to the side with the fewer number of moles will bring the pressure back down.

c. Since nitrogen dioxide is a product, the reaction will shift to the left to use the excess product.

d. Neon is an inert gas. It will not change the partial pressure of the reactants and products, it will only change the total pressure of the system. There will be no shift.

# SECTION 2

# $K_{sp}$

# THE PLAN

- 1. Solubility Product Constant
- 2. Solving for Ion Concentration
- 3. Solving for Solubility
- 4. Solving for K<sub>sp</sub>

# Solubility Product Constant (K<sub>sp</sub>)

Unlike NaCl, not all salts dissolve completely in aqueous solutions. The level to which a salt dissolves is expressed as its solubility product constant and is represented by  $K_{sp}$ .(same concept as K)

Remember that only gaseous and aqueous substance can be represented in K expressions. In a salt's dissociation, only the products are in aqueous phase. The reacting salt is always a solid in these problems.

Consider the salt silver hydroxide, AgOH. Its dissociation in water is written as

 $AgOH(s) \rightleftharpoons Ag^{1+}(aq) + OH^{1-}(aq)$ 

While paying attention to the phases, a K expression for this reaction would look like:

 $K = [Ag^{1+}][OH^{1-}]$ 

Notice that the AgOH is not present in the K expression because it is a solid. The ions' concentrations are raised to the first power because there is only one mole of each one. This is just like the equilibrium constant from the previous chapter. The only change is that the K is known as a K<sub>sp</sub>, so:

 $K_{sp} = [Ag^{_{1+}}][OH^{_{1-}}]$ 

This expression allows you to work three types of problems: determining the concentrations of ions that have dissolved, determining the solubility of the salt (it will always equal x in your equilibrium chart), and determining the  $K_{sp}$  of a salt.

# **Solving for Ion Concentration**

Determine the concentration of each ion if the  $K_{\rm sp}$  of calcium fluoride is 4.0 x 10  $^{-11}$  .

The first step is to write the dissociation of the salt.

 $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{1-}(aq)$ 

Notice that there are 2 fluoride ions because of the subscript of fluoride in the formula  $CaF_2$ .

Write an equilibrium expression.

 $K_{sp} = [Ca^{2+}][F^{1-}]^2$ 

Now make an equilibrium chart using only gaseous or aqueous substances. The solid substance may appear in the chart, but it will have no values.

	[CaF <sub>2</sub> ]	[Ca <sup>2+</sup> ]	[F <sup>1-</sup> ]
initial		0	0
change			
equil.			

Recall that any substance that is zero initially, must increase its concentration by an amount that reflects the mole to mole ratio. So, the change line will look like:

	[CaF <sub>2</sub> ]	[Ca <sup>2+</sup> ]	[F <sup>1-</sup> ]
initial		0	0
change		+X	+2x
equil.			

The equilibrium line is the combination of the initial and change lines.

	[CaF <sub>2</sub> ]	[Ca <sup>2+</sup> ] +	[F <sup>1-</sup> ]
initial		0	0
change		+X	+2x
equil.		x	2 <i>x</i>

You may now plug into your  $K_{\mbox{\scriptsize sp}}$  expression and solve for

*x*.

4.0 X 10<sup>-11</sup> =  $[x][2x]^2$ 

 $x = 2.15 \ge 10^{-4}$ 

Looking back at the equilibrium line of the chart, you may now solve for the equilibrium concentrations of each ion.

 $[Ca^{2+}] = 2.15 \times 10^{-4}$ 

 $[F^{1-}] = 2(2.15 \times 10^{-4}) = 4.30 \times 10^{-4}$ 

#### Solving for Solubility

Determine the solubility of calcium fluoride from your work in the previous problem.

You have already done all of the work for this problem. Since the mol:mol:mol for the salt to its ions is 1:1:2, the solubility of the salt in this case is equal to the concentration of the calcium ion. In fact, the moles of the salt will always be 1 in these problems. So, just remember that the solubility of the salt will always equal x.

The solubility of the CaF<sub>2</sub> is  $2.15 \times 10^{-4}$  M. That means that  $2.15 \times 10^{-4}$  moles of CaF<sub>2</sub> can dissolve in 1 L of solution. You can convert that value to a more practical g/L by using the molar mass of CaF<sub>2</sub>.

 $\frac{2.15 \text{ x } 10^{-4} \text{ mol } \text{CaF}_2 \text{ x } 77.98 \text{ g } \text{CaF}_2}{1 \text{ L soln}} = \frac{1 \text{ mol } \text{CaF}_2}{1 \text{ mol } \text{CaF}_2}$ 

0.0168 g CaF<sub>2</sub> may dissolve in 1 L of solution. If you try to put more than that amount into the solution, a precipitate will form at the bottom of the vessel.

# Solving for K<sub>sp</sub>

Determine the value of the solubility product constant of bismuth sulfide which has a solubility of  $1.0 \times 10^{-15}$  M.

Write the dissociation of salt and the  $K_{sp}$  expression.

 $Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$ 

 $K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3$ 

Since you know the solubility (or *x*) of the salt, you can deduce the concentrations of the ions from the mol:mol of the ions. Therefore, [Bi<sup>3+</sup>] will be two times the solubility, and [S<sup>2-</sup>] will be three times the solubility.

If you make an equilibrium chart, it will look like

	$Bi_2S_3$	Bi <sup>3+</sup>	S <sup>2-</sup>
initial		0	0
change		+2x	+3 <i>x</i>
equil.		2x	3 <i>x</i>

Plugging into the K<sub>sp</sub> expression, gives you

 $K_{sp} = [2x]^2 [3x]^3$ 

You know what *x* is, so just substitute 1.0 x  $10^{-15}$  for *x* and solve for K<sub>sp</sub>.

$$K_{sp} = [2(1.0 \text{ x } 10^{-15})]^2 [3(1.0 \text{ x } 10^{-15})]^3$$

 $K_{sp} = 1.08 \text{ x } 10^{-73}$ 

You now know how to solve solubility product constant problems, and you have more K practice along with Le Chatelier and  $K_{\rm sp}$ .

K, Le Chatelier, Ksp Work

#### CHAPTER 20

# Acids & Bases

Taking equilibrium concepts one more step further, brings us to acids and bases. You will learn about typical properties, indicators, how to determine pH, strong, and weak acids and bases.



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# **Properties & Classification**

# THE PLAN

- 1. Properties of Acids & Bases
- 2. Arrhenius Acids & Bases
- 3. Bronsted-Lowry Acids & Bases
- 4. Lewis Acids & Bases
- 5. Water
- 6. pH & pOH

# **Properties of Acids and Bases**

Acids have the following general properties

- Taste sour
- Contain H<sup>1+</sup> ion
- pH less than 7 (dependent upon T)
- React with bases to form a salt and water
- React with some metals to produce hydrogen gas
- Turn litmus paper red
- Phenolphthalein is colorless in the presence of an acid
- Bromothymol blue is yellow in the presence of an acid
- Found in citrus fruits in the form of citric acid
- Found in soured milk and in sore muscles in the form of lactic acid
- Found in vitamin C in the form of ascorbic acid
- Found in carbonated beverages in the form of carbonic acid...that is also what you exhale

Bases have the following general properties

• Taste bitter

- Contain OH<sup>1-</sup> ion
- pH greater than 7 (dependent upon T)
- React with acids to form a salt and water
- React with organic material
- Feel slippery because they immediately begin to react with the outer layer of skin tissue
- Turn litmus paper blue
- Phenolphthalein is fuchsia in the presence of a base
- Bromothymol blue is blue in the presence of a base
- Found in drain cleaners usually in the form of sodium hydroxide
- Found in ammonia-based cleaners like Windex
- Lye (NaOH) is used to make soaps

# Arrhenius Acids and Bases

Svante Arrhenius (1859-1927) was a Swedish chap who put forth his definitions of acids and bases in 1884 at the age of 25. He worked with our buddy van't Hoff of the van't Hoff factor fame, and Arrhenius received the 1903 Nobel Chemistry Prize for electrolytic dissociation discoveries.

He classified acids as substances that dissociate (come apart) in water to yield the H<sup>1+</sup> ion. He would classify HCl as an acid because of the following reaction:

 $HCl (g)^{H_2O} \to H^{_1+}(aq) + Cl^{_1-}(aq)$ 

While he classified bases as substances that will dissociate in water to yield OH<sup>1-</sup> ion.

NaOH (s) 
$$\xrightarrow{H_2O}$$
 Na<sup>1+</sup>(aq) + OH<sup>1-</sup> (aq)

1

He would classify NaOH as being a base because of the previous reaction.

His method works well for many simple acid and base concepts, but it is lacking in others. Thus, there are other methods of classifying acids and bases.

# **Brønsted-Lowry Acids and Bases**

Danishman Johannes Brønsted (1879-1947) and Englishman Martin Lowry(1874-1936) share the idea of classifying acids and bases in a new way that not only identifies acids and bases but also their conjugates. They defined an acid as a reactant that donates a proton in a chemical reaction. The proton is actually the hydrogen ion...s-ince a hydrogen atom has 1 proton and 1 electron and the ion with a 1+ charge indicates that it has lost an electron and is just a proton.

A base under Brønsted-Lowry definitions is a reactant that accepts a proton in a chemical reaction.

They went further and classified the products of these reactions as conjugate acids or conjugate bases.

A conjugate acid may be defined in two ways. The product that is what the base becomes when it has gained its proton is a conjugate acid. Additionally, since these reactions reach equilibrium and are therefore reversible, another definition of a conjugate acid is that in the reverse direction, the product that gives up a proton is the conjugate acid.

Conversely, the conjugate base is the product that remains when the acid has lost a proton, or it is the product in the reverse direction that accepts a proton.

 $HCl (aq) + H_2O (l) \rightleftharpoons H_3O^{1+}(aq) + Cl^{1-}(aq)$ 

HCl is a Brønsted-Lowry acid because from left to right, it loses a H<sup>1+</sup>. H<sub>2</sub>O is a base because from left to right, it gains a H<sup>1+</sup>.

The conjugate acid is  $H_3O^{1+}$  because it is what is formed when the base,  $H_2O$ , accepts a proton. Another reason that  $H_3O^{1+}$  is

the conjugate acid is that in the reverse direction, from right to left, the  $H_3O^{1+}$  loses a  $H^{1+}$ .

The conjugate base is Cl<sup>1-</sup> because it is what is formed when the acid, HCl, loses a proton. Another reason that Cl<sup>1-</sup> is the conjugate acid is that in the reverse direction, from right to left, the Cl<sup>1-</sup> gains a H<sup>1+</sup>.

 $NH_{3}(g) + H_{2}O(l) \rightleftharpoons NH_{4^{1+}}(aq) + OH^{1-}(aq)$ 

 $\rm H_2O$  is a Brønsted-Lowry acid because from left to right, it loses a  $\rm H^{1+}$ .  $\rm NH_3$  is a base because from left to right, it gains a  $\rm H^{1+}$ .

The conjugate acid is  $NH_4^{1+}$  because it is what is formed when the base,  $NH_3$ , accepts a proton. Another reason that  $NH_4^{1+}$  is the conjugate acid is that in the reverse direction, from right to left, the  $NH_4^{1+}$  loses a  $H^{1+}$ .

The conjugate base is  $OH^{1-}$  because it is what is formed when the acid,  $H_2O$ , loses a proton. Another reason that  $OH^{1-}$  is the conjugate acid is that in the reverse direction, from right to left, the  $OH^{1-}$  gains a  $H^{1+}$ .

# Lewis Acids and Bases

Gilbert Lewis (1875-1946) is the same chap who came up with Lewis dot structures. He liked electrons! His method is a broader method that encompasses much more than either of the previous two methods does. This method is used in later chemistry classes more than the other two. Lewis defined an acid as a reactant that accepts an electron pair. It helps to draw electron dot structures to see what he is talking about. He defined a base as a reactant that donates an electron pair. Look at the video below to see what this classification looks like.

## Lewis video

## Water

Did you happen to notice that water acted as a base in one of the reactions and as an acid in another? Substances that can be both acid and base are known as amphoteric or amphiprotic. Water is one among many substances that can be so classified.

Every acid and base that you use in this text will be dissociating in water, including water. Yes, it dissociates in itself.

 $2H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + OH^{1-}(aq)$ 

The reaction is often abbreviated to be:

 $H_2O(l) \rightleftharpoons H^{1+}(aq) + OH^{1-}(aq)$ 

Since the reaction reaches equilibrium, a K expression can be written for the reaction. This expression is known as the Kw, or equilibrium constant for water, expression

 $K_w = [H^{1+}][OH^{1-}]$ 

Notice that there is no denominator because the reactant is liquid phase. Recall that only aqueous and gaseous phase reactants and products are included in K expressions. Each product is raised to the first power, because each has a coefficient of one in the balanced equation.

The value of  $K_w$  at 298K is 1.0 x 10<sup>-14</sup>. If temperature changes, so too does the value of  $K_w$ . This is a small K value because it is less than 1. Small K values tell us that reactant formation is favored over product formation. Because this reaction reaches equilibrium, you can make an equilibrium chart for the reaction. Again the water is liquid, so no values will be placed in the chart to represent water's concentration.

	[H <sub>2</sub> O]	[H <sup>1+</sup> ]	[OH1-]
initial		0	0
change			
equil.			

Both product initial concentrations are zero since the reaction has yet to begin. Recall that anything with a concentration of zero initially must increase its concentration. Equilibrium charts have *x*'s in them that reflect the mole to mole ratio.

	[H <sub>2</sub> O]	[H <sup>1+</sup> ]	[OH1-]
initial		0	0
change		+x	+x
equil.			

Just as you did for a normal small K problem, you will combine your initial and change lines to get your equilibrium line of the chart.

	[H <sub>2</sub> O]	[H <sup>1+</sup> ]	[OH1-]
initial		0	0
change		+ <i>x</i>	+x
equil.		x	x

From this information, you can substitute into the  $K_{\rm w}$  expression the known information.

 $1.0 \ge 10^{-14} = [x][x]$ 

1.0 x 10<sup>-7</sup> = [x]

Remember that *x* represents both  $[H^{1+}]$  and  $[OH^{1-}]$ . So, their concentrations are equal. The truest definition of neutrality in acid-base chemistry is that the  $[H^{1+}] = [OH^{1-}]$ . We, thus, classify water at 298K to be a neutral substance.

If  $[H^{1+}]>[OH^{1-}]$ , then the substance is an acid. If  $[H^{1+}]<[OH^{1-}]$ , then the substance is a base. Since every acid or base dissociation we will entertain occurs in water, then the  $K_w$  expression is applicable to any of these dissociations.

The relationship of  $[H^{1+}]$  and  $[OH^{1-}]$  can then be known for any acid of base. If you know the  $[H^{1+}]$  of a solution, you can determine the [OH<sup>1-</sup>]. And, if you know the [OH<sup>1-</sup>] of a solution, you can determine the [H<sup>1+</sup>].

# pH and pOH

pH is an abbreviation of the "power of hydrogen," and is calculated by taking the opposite logarithm of the hydrogen ion concentration in molarity.

 $-\log[H^{1+}] = pH$ 

pH is a common method of determining acidity or alkalinity of a substance. You have probably been taught that if a substance has a pH of 7, it is neutral. If the pH is less than 7, it is acidic; and if the pH is greater than 7, it is basic. Those statements are true at 298K, but not necessarily at other temperatures. For our purposes, we will assume a temperature of 298K for all acid/base work.

Thus, we know from our previous work that the [H<sup>1+</sup>] of water is 1.0 x 10<sup>-7</sup>; so we can calculate the pH to be 7.00 by taking -log[H<sup>1+</sup>]. That works with what we previously thought about water; it is neutral.

The less often used complement to pH is pOH. You guessed it... "power of hydroxide." Also temperature dependent, pOH works kind of the opposite of pH. A pOH of 7 means a neutral substance. Yet, a pOH less than 7, translates into a basic substance; and a pOH greater than 7 means an acidic substance. So, the pOH of water is also 7.00. The sum of pH and pOH will always equal 14 at 298K. So, if you know a pH, you now have a very easy means of finding the pOH.

If you know the pH and you wish to know the [H<sup>1+</sup>], you will take the inverse log of the opposite pH. That is,

 $10^{-pH} = [H^{1+}]$ 

For water  $10^{-7}$  is the [H<sup>1+</sup>], but it should be written with the mantissa (the number that is not the 10 or superscript) as  $1.0 \times 10^{-7}$  M.

Likewise, the [OH<sup>1-</sup>] can be found by

 $10^{-pOH} = [OH^{1-}]$ 

or

That means that the  $[OH^{1-}]$  for water is also 1.0 x 10<sup>-7</sup> M. Remember that when  $[H^{1+}] = [OH^{1-}]$ , we have a neutral solution.

You now have a plethora of formulae to help you work acid/ base problems. Here is an example problem:

Find the pH, pOH, and [OH-] and state whether the solution is acidic, neutral or basic if the hydrogen ion concentration is  $3.48 \times 10^{-4}$  M.

pH = -log [3.48 x 10<sup>-4</sup>] = 3.458, so solution is acidic pOH = 14-3.458 = 10.542 [OH-] = 10<sup>-10.542</sup> = 2.87 x 10<sup>-11</sup> M  $[OH-] = \underline{1.0 \times 10^{-14}} = 2.87 \times 10^{-11} M$  $3.48 \times 10^{-4}$ 

INTERACTIVE 20.1 Acids & Bases

# Determine the pH when the pOH is 12.70



**Check Answer** 

#### INTERACTIVE 20.2 Acids & Bases





**B.** neutral

**C.** basic

**D.** cannot be determined

INTERACTIVE 20.3 Acids & Bases



**Check Answer** 





# Strong and Weak

## THE PLAN

- 1. Strong Acids & Bases
- 2. Weak Acids
- 3. Weak Bases
- 4. Polyprotic Acids

# **Strong Acids & Bases**

A solution that ionizes or dissociates completely into ions in water is classified as being a strong electrolyte. That means that that solution will conduct electricity. Those solutions that have acidic or basic properties and dissociate completely are classified as strong acids or strong bases.

Recall that the level of dissociation is represented by a substance's K value. If K>1, then the substance prefers to make reactants at equilibrium and does not dissociate completely. A large K value (>100) means that the reaction prefers to make product at equilibrium, and thus likes to dissociate. The larger the K value, the more dissociated the solution is.

The strong acids are as follows: HCl, HBr, HI, HClO<sub>4</sub>, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. All other acids are weak and do not dissociate completely in water. If a strong acid has a K<sub>a</sub> value, it is a very large value. All weak acids have "small" K<sub>a</sub> values.

Strong bases will dissociate completely in water, as well. The strong bases are as follows: LiOH, NaOH, KOH, RbOH, CsOH. Some sources also include the Group II metal hydroxides as strong bases, though they have small K<sub>b</sub> values. Strong bases have very large K<sub>b</sub> values.

When given the concentration of a strong acid, the assumption is made that the acids completely dissociates into the hydrogen ion and the remaining anion.

 $HCl (aq) -> H^{1+} (aq) + Cl^{1-} (aq)$ 

Please notice that the arrow indicates the reaction goes to completion and does not reach equilibrium. If we are given a concentration of HCl of 12 M (the maximum concentration for HCl...other acids will have their own maxima), then we know that there is not really any HCl present. There are only H<sup>1+</sup> and Cl<sup>1-</sup> ions. The mole to mole ratio tells us that the concentrations of both ions will be 12 M. A stoichiometry chart showing this process follows:

	[HCl]	[H <sup>1+</sup> ]	[Cl1-]
initial	12	0	0
change	-12	+12	+12
final.	0	12	12

Since equilibrium is not reached, and the [H<sup>1+</sup>] is 12 M, you can easily determine the pH. You do not need to make a chart since it is understood that the strong acids dissociates completely into its ions. You can just take the concentration of the strong acid, and use that value to determine the pH by the following:

-log[12] = -1.08...yes, you can have negative pH

If we consider the diprotic acid,  $H_2SO_4$ , we see that it has two ionizable hydrogen ions, hence the name diprotic. It only dissociates one hydrogen ion at a time. Therefore it goes through two dissociation reactions that look like this:

 $H_2SO_4(aq) -> H^{1+}(aq) + HSO_4^{1-}(aq)$ 

and then,

 $HSO_{4^{1-}}(aq) \rightleftharpoons H^{1+}(aq) + SO_{4^{2-}}(aq)$ 

The first dissociation is complete as is indicated by the oneway arrow. The second dissociation reaches equilibrium as is indicated by the reversible arrows. In the case of a strong diprotic acid, the first dissociation prevails; and the second dissociation contributes very little relative hydrogen ion to the solution.

So, given that the maximum concentration of  $H_2SO_4$  is 18 M, you know that the first dissociation yields 18 M H<sup>1+</sup> and  $HSO_4^{1-}$ . Relative to 18 M, the second dissociation yields very little H<sup>1+</sup>. The pH is thus determined by

-log[18] = -1.26

A strong base such as NaOH will dissociate completely in water and no NaOH will be present, only Na<sup>1+</sup> and OH<sup>1-</sup> ions will be present. Given a maximum molarity of NaOH of 19.1 M, the pOH is determined as follows:

-log[19.1] = -1.281

and the pH is then calculated using:

14 - (-1.281) = 15.281

You see now that the pH can be greater than 14.

Strong acids and bases make determining pH or pOH quite easy, Weak acids and bases reach equilibrium and therefore need all of the accompanying equilibrium information in order to solve for pH or pOH.

# Weak Acids

Any acid that was not on the aforementioned list of strong acids is considered to be weak. Weak acids reach equilibrium, and they will have  $K_a$  values that are less than 1. We will work weak acids problems just like we worked small K problems.

Determine the pH of a 17.4 M (maximum concentration) of acetic acid,  $HC_2H_3O_2$ .  $K_a$  of acetic acid is 1.8 x 10<sup>-5</sup>.

Your first step is the write the dissociation of the acid. Though acetic acid has four hydrogen ions in it, there is only one hydrogen ion that is dissociable. It is a monoprotic acid.

 $HC_{2}H_{3}O_{2}$  (aq)  $\rightleftharpoons$   $H^{1+}$  (aq) +  $C_{2}H_{3}O_{2}^{1-}$  (aq)

Next write a K expression from the reaction.

 $K_{a} = \underline{[H^{1+}][C_{2}H_{3}O_{2}^{1-}]}$  $[HC_{2}H_{3}O_{2}]$ 

An equilibrium chart needs to be made in order to determine what will be placed into the  $K_a$  expression.

	$[HC_2H_3O_2]$	[H <sup>1+</sup> ]	$[C_2H_3O_2^{1-}]$
initial	17.4	0	0
change	- <i>x</i>	+X	+x
equil.	17.4 - <i>x</i>	x	x

Now plug your information into the  $K_a$  expression, and solve for x.

$$1.8 \ge 10^{-5} = [x][x]$$
  
[17.4 - x]

[x] = 0.018...test the 5% rule, and it works

Therefore the  $[H^{1+}]$  is 0.018. You may now find the pH, since you know the  $[H^{1+}]$ .

-log[0.018] = 1.75

## Weak Bases

Any base that was not on the aforementioned list of strong bases, is a weak base. Weak bases reach equilibrium, too. They will have  $K_b$  values that are less than 1. Again, you will work a weak base problem just as you worked small K problems.

Determine the pH of a 15.3 M solution of ammonia,  $\rm NH_3.$  The  $K_b$  is also 1.8 x 10^-5.

Again, the first step is the write the dissociation of the base. Since this is a base, it will dissociate in water to yield hydroxide ion rather than hydrogen ion. It is easier to see the origin of the OH<sup>1-</sup> when you show the base's dissolving in water.

 $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^{1+}(aq) + OH^{1-}(aq)$ 

Remember that you only include aqueous and gaseous phase substances in a K expression. So, you will leave water out of the  $K_b$  expression

 $K_b = [NH_4^{1+}][OH^{1-}]$ [NH<sub>3</sub>]

The equilibrium chart is the next step.

	$[NH_3]$	[NH4 <sup>1+</sup> ]	[OH1-]
initial	15.3	0	0
change	- <i>X</i>	+ <i>x</i>	+x
equil.	15.3 - <i>x</i>	x	x

Plug the information into the expression.

 $1.8 \ge 10^{-5} = [x][x]$ [15.3 - x] [x] = 0.017...test the 5% rule, and it works

So, the [OH<sup>1-</sup>] is 0.017. You were asked to find the pH. You have your choice of how to do so, either finding pOH and then subtracting, or finding [H<sup>1+</sup>] and then taking the opposite log.

pOH = -log[0.017] = 1.78

pH = 14 - 1.78 = 12.22

# **Polyprotic Acids**

You have already seen a polyprotic acid,  $H_2SO_4$ . Polyprotic means that there is more than one dissociable hydrogen ion, and reaction must be written for each dissociation. Each dissociation of a polyprotic weak acid reaches its own equilibrium, and each has a K<sub>a</sub> expression.

Determine the pH of a 0.333 M solution of tartaric acid,  $H_2C_4H_4O_6$ .  $K_{a1}$  is 9.20 x 10<sup>-4</sup> and  $K_{a2}$  is 4.31 x 10<sup>-5</sup>.

Once again the first step is to write the dissociations of tartaric acid.

 $H_2C_4H_4O_6$  (aq)  $\rightleftharpoons$   $H^{1+}$  (aq) +  $HC_4H_4O_6^{1-}$  (aq)

 $HC_4H_4O_6^{1-}(aq) \rightleftharpoons H^{1+}(aq) + C_4H_4O_6^{2-}(aq)$ 

You will have two  $K_a$  expressions. The first dissociation has the  $K_{a1}$  value, and the second dissociation has the  $K_{a2}$  value.

$$K_{a1} = \underline{[H^{1+}][HC_4H_4O_6^{1-}]}$$
$$[H_2C_4H_4O_6]$$

and

 $K_{a2} = \underline{[H^{1+}][C_4H_4O_6^{2-}]}$  $[HC_4H_4O_6^{1-}]$ 

You will make successive equilibrium charts for the reactions. This is the chart for the first dissociation.

	$[H_2C_4H_4O_6]$	[H <sup>1+</sup> ]	[HC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> <sup>1-</sup> ]
initial	0.333	0	0
change	- <i>x</i>	+X	+x
equil.	0.333 - <i>x</i>	x	X

Plug into the first K<sub>a</sub> expression.

9.20 x 10<sup>-4</sup> = [x][x][0.333 - x]

[x] = 0.0175...test the 5% rule, and it does not work.

Solve for *x* using the quadratic equation. Remember you will get two values of *x*. If both are positive, accept the smaller. If one is positive and one is negative, accept the positive.

After the quadratic, [x] = 0.0170. *x* represents the equilibrium concentration of both the H<sup>1+</sup> and the HC<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>1-</sup> ions at the end of the first dissociation.

The beginning of the second dissociation is the end of the first dissociation. This chart is for the second dissociation. Note that values obtained from the first dissociation are present initially.

	[HC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> <sup>1-</sup> ]	[H <sup>1+</sup> ]	$[C_4H_4O_6^{2-}]$
initial	0.0170	0.0170	0
change	- <i>x</i>	+x	+x
equil.	0.0170 - <i>x</i>	0.0170 + <i>x</i>	x

Plug the appropriate values into the second  $K_{\rm a}$  expression.

$$4.31 \times 10^{-5} = \underline{[0.0170 + x][x]}$$
$$[0.0170 - x]$$

 $[x] = 4.31 \times 10^{-5}$ ...test the 5% rule, and it does work.

Since we are trying to find the pH, we must consider all of the hydrogen ions that have dissociated. The equilibrium line of the second dissociation, shows the concentration of hydrogen ions at the end of the second dissociation to be 0.0170 + x. Therefore,

 $[H^{1+}] = 0.0170 + 4.31 \times 10^{-5} = 0.0170431$ 

The additional hydrogen ions that came out of the second dissociation did not make a noticeable difference in the concentration of hydrogen ion from the first dissociation. Find the pH using the total amount of hydrogen ion that dissociated.

pH = -log[0.0170] = 1.770

Now practice using the following documents, and learn to love acid/base chemistry.

Acid/Base Practice #1 Acid Base Practice #2 with my work CHAPTER 21

# Kinetics

Kinetics is also known as reaction rates. We will look at methods of describing rate of reaction, factors affecting reaction rate, rate laws, activation energy, catalysts, and intermediates.



# Kinetics

# THE PLAN

- 1. Rate
- 2. Necessities of Reaction
- 3. Factors that Affect Rate
- 4. Rate Law
- 5. Reaction Mechanism

# Rate

We have discussed reactions and how they get to completion or reach equilibrium, but we have not entertained the idea of how fast reactions occur. The speed at which a reaction occurs is known as its rate.

Rate refers to the amount of reactant that reacts divided by the time it takes to react.

Rate =  $-\Delta$ amount reactant  $\Delta$ time

Notice the there is a negative sign in front of the change in amount. This is because that change is determined by taking the final amount and subtracting the initial amount. Since the amount of reactant decreases as time progresses, this difference is a negative difference. It is conventional to have positive rates, so the negative difference is negated, and the rate, in turn, is positive. Rates are studied from the viewpoint of the reactant(s).

The reaction rate of a one-way reaction, one that goes to completion, will decrease as time progresses because there is progressively less and less reactant. The amount of reactant will eventually be zero, as will the rate.

When looking at a reaction that reaches equilibrium, the rate decreases as time progresses; but the rate eventually levels off at the point of equilibrium. Remember that an equilibrium reaction does not stop, it goes back and forth at equal rates. The graph at the beginning of this chapter graphically depicts what happens in the following reaction:

 $2\mathrm{HI}\left(g\right) \rightleftharpoons \mathrm{H}_{2}\left(g\right) + \mathrm{I}_{2}\left(g\right)$ 

The HI begins with a high concentration, while the products' initial concentrations are zero. Though the graph does not show it, the lines will eventually be parallel to each other. The point at which they are parallel is when equilibrium is reached.

## **Necessities of Reaction**

Proper orientation and sufficient energy are the two necessities of chemical reaction.

Proper orientation means that the particles that are reacting are facing each other in such a way as to promote reaction. Each set of reactants has its own preferred spacial arrangement. For example, when ethene,  $C_2H_4$ , reacts with HCl, the H of the Cl must be near the double bond. If that is not the case, then reaction will not occur. Let the following image help explain this.



http://chemwiki.ucdavis.edu/

The other necessity of chemical reaction is sufficient energy. This means that reactants must gain enough activation energy in order to reach the transition state. Once in the transition state, the products can then be formed. Once again, an image helps to understand this. In this illustration, the two molecules of BrNO are the reactant. These molecules gain enough energy, activation energy ( $E_a$ ), to turn into the transition state. The transition state then loses energy to turn into the products, two moles of NO and one mole of Br<sub>2</sub>.



#### **Factors that Affect Rate**

While proper orientation and sufficient energy are necessities of reaction, the rate may be affected by several conditions.

Concentration of reactants can affect how fast a reaction occurs, but it is not always the case. For example, paper will burn faster in a 100% oxygen environment rather than the typical 21% oxygen environment of air. When analyzing whether proper orientation or sufficient energy is affected, we should see that the greater concentration provides more particles with the opportunity to collide with proper orientation.

Temperature is another factor that can affect reaction rate. Temperature can slow down a reaction or speed up a reaction. What happens is dependent upon the reaction's endothermicity or exothermicty. The oxidation of the phenols in an apple are what eventually make the apple meat turn brown. This oxidation reaction can be slowed by placing the apple in a refrigerator. While the reaction rate can be increased if the apple remains at a higher temperature. The browning of an apple must therefore be an endothermic reaction.

Decreased particle size will accelerate the rate of reaction. Think about burning a block of wood or sawdust. Which one burns faster? Of course, the sawdust does. Again making the particles smaller provides more surface area and a greater chance for proper orientation.

The presence of a catalyst increases the rate of reaction. A catalyst is a substance that enters a chemical reaction as a reactant, lowers the activation energy, and then exits the chemical reaction, unscathed, as a product. The catalyst is not actually a reactant or product.  $MnO_2$ , commonly called manganese dioxide, increases the rate of the decomposition reaction of hydrogen peroxide,  $H_2O_2$ , to water and oxygen gas. The  $MnO_2$  can be retrieved and used again and again.

A final determinant of reaction rate is the aptly-termed rate determining step. This will be the slowest step in a series of reactions known as the reaction mechanism. This is reminiscent of Hess's Law, in that we will add the elementary steps together to get an overall reaction. Here is a reaction mechanism: with the first step as the rate determining step:

a.	$2NO_{2}(g) \rightarrow NO(g) + NO_{3}(g)$	slow
b.	$NO_{3}(g) + CO(g) -> NO_{2}(g) + CO_{2}(g)$	fast

#### **Rate Law**

A rate law relates the rate as a function of the reactant(s). The units of rate are typically a concentration unit over a time unit. mol/L-s are common units for describing rate. These units indicate how molarity of reactant(s) change as the reaction progresses.

There are two types of rate laws: differential and integrated. We will focus upon differential rate laws for now.

In the hypothetical reaction, A --> B, the differential rate law is written as:

rate =  $k[A]^x$ 

k is the rate law constant, and x is the order of reactant. [A] as you should remember from equilibrium problems means the molarity of reactant A. k's units are dependent upon the order. The order indicates how the rate changes with respect to the concentration of the reactant. The order can be any value, negative, fractional, zero, positive. The three most commonly evaluated orders are zero, first, and second order.

If a reactant is deemed zero order, then its rate law is written as:

rate =  $k[A]^{o}$ 

Mathematically, you should be able to see that if I double the concentration, it has no effect on the rate, because anything raised to the zero power is one. Thus, in a zero order reaction

with only only reactant, the rate always equals the rate law constant, k.

For a first order reactant, the rate changes in the same way as the concentration. That is, if the concentration is doubled, the rate doubles. If the molarity is tripled, the rate triples. The rate law is written as follows:

rate =  $k[A]^1$ 

Again, you should be able to see what happens mathematically.

When a reactant is determined to be second order, the rate will change in a way that reflects the square of the change. So, if the concentration is doubled, then the rate will be quadrupled ( $2^2$  is 4). If the concentration is tripled, then the rate will be nonupled ( $3^2$  is 9). A second order reactant's rate law is as follows:

rate =  $k[A]^3$ 

The order must be determined experimentally. We cannot look at the coefficients to determine order <u>unless</u> we are looking at the rate-determining step. So from this reaction mechanism,

a. 
$$2NO_2(g) \rightarrow NO(g) + NO_3(g)$$
 slow  
b.  $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$  fast

the rate law is rate =  $k[NO_2]^2$ 

The overall order of reaction is calculated by simply adding the individual orders of the reactants. This over all order allows an easy way to determine the units of k.

If we have another hypothetical reaction,  $A + B \rightarrow C$ , and the rate law is determined to be rate =  $k[A]^1[B]^2$ , then the overall order is 3. This overall order tells us that the units of k will be the overall order - 1 for the exponents of the reciprocal molarity units. That means the the units of k for this hypothetical reaction will be  $L^2/mol^2$ -s.

Here is a problem. For the rxn:

 $I^{1-} + OCl^{1-} - -> IO^{1-} + Cl^{1-}$ 

The following data were collected:

TRIAL	RATE (MOL/L-S)	[I1-]	[OCL <sup>1-</sup> ]
1	0.0791	0.120	0.180
2	0.0395	0.060	0.180
3	0.00988	0.030	0.090
4	0.0791	0.240	0.090
5	0.030	0.030	0.00329

a. Determine the differential rate law.

b. Determine the overall order of reaction.

c. Determine the rate law constant with its units.

We begin by solving for the order of each reactant individually using the given data. We analyze only one reactant at a time. Therefore, we must look for two trials where one reactant's concentration is held constant. In trials 1 and 2, OCl<sup>1-'</sup>s concentration is a constant 0.180 M. From a mathematical approach, the way to work this is to set up to rate law expressions as so:

 $\frac{\text{rate}_{1} = k[I^{1-}]^{x}[[OCl^{1}]^{y}}{\text{rate}_{2} = k[I^{1-}]^{x}[[OCl^{1}]^{y}}$ and plugging in the given... rate<sub>2</sub> = k[I^{1-}]^{x}[[OCl^{1}]^{y}  $\frac{0.0791 \text{ mol/L-s} = k[0.120]^{x}[[0.180]^{y}}{0.0395 \text{ mol/L-s}} = k[0.060]^{x}[[0.180]^{y}$ 2.00 = 2.0<sup>x</sup>  $\log 2.00 = x(\log 2.0)$  $\frac{\log 2.00}{\log 2.0} = x$  $\log 2.0$ 1.0 = x

So, the I<sup>1-</sup> is first order. Now, we could have just looked at the changes and deduced this one. When the concentration of the I<sup>1-</sup> was halved, the rate was also halved. From the definitions of order, this means that I<sup>1-</sup> is first order.

We now must find the order of the OCl<sup>1-</sup> by looking at two trials that hold the I<sup>1-</sup> concentration constant. Those two

trials are trials 3 and 5. You may work the problem mathematically as previously illustrated, or you may reason it. If you reason you way through it, then you will see that the concentration in trial 5 is approximately 1/3 of the concentration in trial 3. The rate in trial 5 is also about 1/3 of the rate in trial 3. Because the rate did the same thing as the concentration, the OCl<sup>1-</sup> is also first order.

We are now ready to write the rate law for the reaction:

rate =  $k[I^{1-}]^{1}[OCl^{1-}]^{1}$ 

The next step is to determine the overall order of reaction. Simply add the individual orders, and you get 2.

Finally we will determine the value of k along with its units. To do so, you just select one of the trials and plug in the given information. The only thing you will not know will be k.

 $0.0791 \text{ mol/L-s} = k[0.120]^{1}[0.180]^{1}$ 

k = 3.66 L/mol-s

## **Reaction Mechanisms**

As previously indicated, the reaction mechanism is a series of elementary steps that add together to give a summative reaction. One of the steps in the mechanism is slower than any other step and is therefore the rate determining step. When asked to write a rate law from a given reaction mechanism, look at the rate determining step and use the moles of reactants to indicate the order of each. Some reactions have intermediate substances. These are substances that are produced in one step and then consumed (act as a reactant) in a later step. Intermediates are not part of rate laws.

Catalysts are also found in some reaction mechanisms. A catalyst is a reactant in one step and a product in some subsequent step. Catalysts are also not part of a rate law.

If it appears that an intermediate or a catalyst needs to be part of a rate law, then substitutions must be made.

Here is an example of a simple reaction mechanism:

a.	$2NO_{2}(g) -> NO(g) + NO_{3}(g)$	slow
b.	$NO_{3}(g) + CO(g) -> NO_{2}(g) + CO_{2}(g)$	fast

The overall reaction is the sum of the two steps cancelling out any intermediates and/or catalysts:

 $NO_2(g) + CO(g) -> NO(g) + CO_2(g)$ 

One mole of the  $NO_2$  is used as a catalyst in that it is a reactant in step a and a product in step b. Thus, it does not appear in the overall reaction. One mole of  $NO_3$  is an intermediate as it is a product in step a and a reactant in step b. It, too, does not appear in the overall reaction.

The rate law for this overall reaction is determined by step a, since it is the slow step. The order of the reactant is equal to the number of moles of the reactant. This is known as using the reaction's molecularity. Thus the rate law is rate =  $k[NO_2]^2$ 

Here is an example of a more complex reaction mechanism problem.

Find the overall reaction, the intermediates and catalysts, and the rate law for the following mechanism.

a. 
$$2NO(g) \stackrel{k_1}{\underset{k_{-1}}{\leftarrow}} H_2O_2(g)$$
 fast  
b.  $H_2O_2(g) + H_2(g) \stackrel{k_2}{\underset{k_{-2}}{\leftarrow}} N_2O(g) + H_2O(g)$  slow  
c.  $N_2O(g) + H_2(g) \stackrel{k_3}{\underset{k_{-2}}{\leftarrow}} N_2(g) + H_2O(g)$  fast

In order to find the overall reaction, we just add all of the reactants to each other and all of the products to each other and then cross out the intermediates and/or catalysts that are present. The result is

 $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ 

The  $H_2O_2$  and the  $N_2O$  are both intermediates as they are produced in on step and consumed in a subsequent step. There are no catalysts in this reaction mechanism.

The rate law appears to be written as

rate =  $k_2[H_2O_2]^1[H_2]^1$ 

However, it is improper to have an intermediate as a part of the rate law. So, we look at the source of the  $H_2O_2$ . It comes from the fast reaction a. The  $H_2O_2$  came from the decomposi-

tion of 2 moles of NO. So, a substitution is made for the  $H_2O_2$  by using the 2NO.

The correct rate law is thus

rate =  $k[NO]^2[H_2]^1$ 

#### CHAPTER 22

# Redox

In this chapter you will learn about reduction and oxidation reactions, chemical reactions that involve the transference of electrons. Half-reaction technique of balancing redox reactions will be addressed.



# Redox

# THE PLAN

- 1. The Basics
- 2. Oxidation Numbers
- 3. Half-Reaction Method of Balancing

# The Basics

Redox is a contraction of reduction and oxidation. All redox reactions involve the exchange of electrons. One substance loses electrons and one substance gains electrons. One reactant experiences oxidation, and one reactant experiences reduction. The same substance can be both oxidized and reduced, by the by.

Reduction means that there is a gain of electrons, and there can be a gain of hydrogen while there is the loss of oxygen. We will see a decrease in oxidation number for the substance being reduced from reactant to product. The substance being reduced is known as the oxidizing agent.

Oxidation is just the opposite of reduction. There is a loss of electrons, and there can be a loss of hydrogen while there is a gain of oxygen. The oxidation number of the substance being oxidized will increase from left to right side of the reaction. The substance being oxidized is known as the reducing agent.

There is a silly mnemonic device used to remember what goes on in each type of reaction. It is LEO the lion goes GER. LEO represents "lose electrons oxidation," while GER is "gain electrons reduction."

# **Oxidation Numbers**

Oxidation numbers are also called oxidation states. They are numbers that are written directly above a substance's symbols, and they represent the charge of the substance even if it appears to have no charge. Oxidation numbers are written with the sign and then the number, unlike charges. There are several rules for assigning oxidation numbers, and it is important to be able to assign oxidation numbers before you can use the half-reaction to balance redox reactions.

Rule 1: The oxidation state of an atom of an element in its natural state is zero.

This includes the BrINClHOF elements that must be diatomic when by themselves in nature.

0	0	0	0
$O_2$	Fe	Na	$F_2$

Rule 2: The oxidation state of a monatomic ion is equal to its charge.

+1	+1 -1	+3	+3-2
Na <sup>1+</sup>	NaCl	Fe <sup>3+</sup>	Fe <sub>2</sub> O <sub>2</sub>
1.100	11401	10	1020,

Rule 3: Oxygen is assigned an oxidation number of -2 in compounds; an exception is found in the peroxide ion,  $O_2^{2-}$ , where each of the two oxygens is assigned an oxidation number of -1.

 ${}^{+1}_{Na_2O}$   ${}^{+1}_{Na_2O_2}$   ${}^{+1}_{MgO}$   ${}^{+2}_{MgO}$ 

Rule 4: Hydrogen is assigned an oxidation number of +1 in its covalent compounds with nonmetals. In compounds with metals, the oxidation number of hydrogen is -1.

+1-2	+1 -1	+1-1
H <sub>2</sub> O	NaH	HCl

Rule 5: The sum of the oxidation states in a compound must be zero, as a compound's charge is zero. Multiply every oxidation number by its subscript and add that to every other oxidation number multiplied by its subscript. Check the previous compounds in Rules 2-4.

Rule 6: The sum of the oxidation states in a polyatomic ion must be equal to that ion's charge.

+4-2 +1+5-2 +2+7-2 SO<sub>3</sub>2- HNO<sub>3</sub> Mg(ClO<sub>4</sub>)<sub>2</sub>





## Half-Reaction Method of Balancing Redox Reactions

Many redox reactions are very long and complex, so there are techniques for balancing such equations. There will be a video link at the end of these steps that elucidates this method step by step.

Step 1: Assign oxidation numbers to every atom in the reaction.

Step 2: Identify what is oxidized and what is reduced. Anything whose oxidation number does not change is a spectator.

Step 3: Write a <sup>1</sup>/<sub>2</sub> reaction (rxn) for the oxidation reaction without the spectators.

Step 4: If an atom being reduced is part of a solid, a polyatomic ion, or a molecular compound, you will keep that ion or cpd together when you bring it down for the ½ rxn.

Step 5: Balance the  $\frac{1}{2}$  rxn by first balancing the non-H, non-O atoms.

Step 6: Then balance the H's and O's using the following guide:

- Use H<sup>1+</sup> and H<sub>2</sub>O if the rxn occurs in an acidic medium.
- Use OH1- and H2O if the rxn occurs in a basic medium.

Step 7: Balance the  $\frac{1}{2}$  rxn electrically (charge-wise) by adding electrons (e<sup>-</sup>) to the right side since an oxidation rxn is LEO.

Step 8: Repeat steps 3-6 for the reduction 1/2 reaction.

Step 9: Balance the 1/2 rxn electrically by adding electrons to the left side since a reduction rxn goes GER.

Step 10: Normalize the electrons in each ½ rxn by finding the least common multiple of the two numbers of electrons and distributing the multipliers through each entire ½ rxn.

Step 11: Add the two ½ rxns and cancel any like atoms, ions, or compounds that appear on both sides.

Step 12: Add the spectators back into the rxn and balance the rest by inspection.

# Half Reaction Video

**Redox Practice**-- ignore the oxidation states method
CHAPTER 23

# Electrochemistry

You will learn to put redox reactions to work in this chapter. Electrochemistry allows us to harness those electrons that are being transferred and make them do work for us in the form of a battery. We can also make the reaction go backwards and recharge a battery.



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#### Section 1

# Electrochemistry

## THE PLAN

- 1. Electrochemical Cells
- 2. Making a Galvanic Cell
- 3. Measuring the Output of an Electrochemical Cell
- 4. Line Notations
- 5. Concentration Cells

# **Electrochemical Cells**

Electrochemical cells are made of two half-cells based upon two half-reactions. Electrons travel between the two halfcells. Recall that in an oxidation half-reaction, the electrons are lost; while in the reduction half-reaction, the electrons are gained. Redox reactions are the crux of all electrochemical cells.

An electrochemical cell is either spontaneous or nonspontaneous. That is it either happens without outside intervention, or it does not happen without outside intervention.

Spontaneous cells are all galvanic or voltaic cells. The chemical energy is converted into electrical energy that can then power devices. This is the concept behind a typical calculator battery.

Nonspontaneous cells are known as electrolytic cells. The electrical energy is converted into chemical energy. When your cell phone's battery is being charged, it is acting as an electrolytic cell. When you are using the phone without its being plugged into an electrical socket, then the battery in the phone is acting as a galvanic cell.

## Making a Galvanic Cell

We will write the reaction and half-reactions for solid magnesium placed in a copper (II) sulfate solution. We will then illustrate the electrochemical cell that this reaction represents.

 $Mg(s) + CuSO_4(aq) \longrightarrow Cu(s) + MgSO_4(aq)$ 

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-1}$$

 $Cu^{2+}(aq) + 2e^{-} --> Cu(s)$ 

Each of these half-reactions represents a half-cell in an electrochemical cell. The reaction is balanced as written because the same number of electrons lost and gained is the same. Here is an illustration of the electrochemical cell made by this reaction:



In this illustration, the Mg oxidation reaction occurs in the left beaker, while the Cu<sup>2+</sup> reduction reaction occurs in the right beaker. An electrode is a point at which electrons are transferred, either lost or gained. There are two types of electrodes, anodes and cathodes. The anode is made of Mg (s) in this particular cell, and it is where electrons are lost by the Mg (s). The cathode is made of Cu (s), and electrons are gained by this electrode.

The illustration indicates that each electrode is attached to a voltmeter. The voltmeter is not a necessary component of the cell, but it enables us to determine the work output of the cell.

The  $SO_4^{2-}$  (aq) ion is originally with the  $Cu^{2+}$  (aq) ion. As the  $Cu^{2+}$  (aq) gains electrons and Cu (s) is formed, the  $SO_4^{2-}$  (aq) ion is no longer needed in the right beaker. It is thus, transferred to the left beaker to hang out with the  $Mg^{2+}$  (aq) ion that is forming as the Mg (s) loses its electrons. The  $SO_4^{2-}$  (aq) travels through a salt bridge in order to make the jump from beaker to beaker. The salt bridge consists of an ionic compound paste that allows the ion to flow smoothly through the glass tube bridge.

The mass of the anode (Mg) will decrease as time progresses because the Mg (s) is becoming  $Mg^{2+}$  (aq). The  $Mg^{2+}$  (aq) ions will float around with the transferred  $SO_4^{2-}$  (aq).

The mass of the cathode will increase as  $Cu^{2+}$  (aq) gains electrons and Cu (s) is formed. The  $Cu^{2+}$  (aq) forms a blue colored solution. As the  $Cu^{2+}$  (aq) ions convert to Cu (s), the blue color fades. That fading is another indicator of chemical reaction.

#### Measuring the Output of an Electrochemical Cell

The voltmeter measures the output of energy that an electrochemical cell is capable of producing. A Joule/Coulomb (J/C) is the unit of energy output, and it is usually known as a volt (V). The output is more commonly known as cell potential, represented by  $\mathcal{E}$ . Standard cell potentials are determined under normal laboratory conditions with 1 M solutions. Thus, the potential is standardized and written as  $\mathcal{E}^{\circ}$ . The determine the  $\mathcal{E}^{\circ}$ , we need to look at the half-reactions and the voltages associated with each reaction.

A reduction potential table is used to do so.

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions				
Half-reaction	$\mathfrak{C}^{\circ}(V)$	Half-reaction	$\mathfrak{C}$ (V)	
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40	
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34	
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27	
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22	
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20	
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16	
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00	
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036	
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13	
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$\operatorname{Sn}^{2+} + 2e^- \rightarrow \operatorname{Sn}$	-0.14	
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23	
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35	
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40	
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44	
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50	
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73	
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76	
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83	
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18	
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66	
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23	
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37	
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37	
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71	
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76	
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90	
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92	
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05	
$Cu^+ + e^- \rightarrow Cu$	0.52			

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This table represents most reduction half-reactions that are commonly used. You will find only reduction half-reactions, no oxidation half-reactions. So, in order to calculate the  $\mathcal{E}^{\circ}$ , you will look up the reverse of the oxidation half-reaction, find its voltage, and reverse the sign of it since you found the reverse of the reaction. You then find the reduction reaction on the table, and note its voltage without changing the sign. You apply these voltages to the half-reactions, and add them just as you do the half-reactions.

$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-1}$	$\mathcal{E}^{0}_{0X}$ = +2.37	v V
$Cu^{2+}(aq) + 2e^{-}> Cu(s)$	$\mathcal{E}^{o}_{red}$ = +0.34	<u>V</u>
$Mg(s) + Cu^{2+}(aq) -> Mg^{2+}$	(aq) + Cu (s)	$\mathcal{E}^{o}_{cell}$ = +2.71 V

The illustrated electrochemical cell produces 2.71 V and is a spontaneous cell. Positive potentials are spontaneous, and negative potentials are nonspontaneous. Nonspontaneous cells are electrolytic cells, while spontaneous cells are galvanic cells.

#### **Line Notations**

A shorthand notation is used in electrochemistry to indicate the two half-reactions at hand. They are known as line notations. The line notation for the magnesium and copper reaction is as follows:

 $Mg|Mg^{2+}(1 M)||Cu^{2+}(1 M)|Cu|$ 

To decipher a line notation, not the following rules:

•A single vertical line indicates a change in state or phase.

•Within a half-cell, the reactants are listed before the products.

•Concentrations of aqueous solutions are written in parentheses after the symbol for the ion or molecule.

•A double vertical line is used to indicate the junction between the half-cells.

•The line notation for the anode (oxidation) is written before the line notation for the cathode (reduction).

Given the following line notation, you should be able to determine the two half-reactions, their potentials, the overall reaction, and its cell potential.

 ${\rm Al}|{\rm Al}^{_{3^+}}\,(1~{\rm M})|\,|{\rm Ag}^{_{1^+}}\,(1~{\rm M})|{\rm Ag}$ 

The oxidation half-reaction involves the conversion of Al (s) to  $Al^{3+}$  (aq). The reduction half-reaction is the  $Ag^{1+}$  (aq) becoming Ag (s). While writing those two half-reactions, and gazing upon the reduction potentials table, you can come up with the following: *(the multipliers are not applied to the V)* 

 $1(Al (s) --> Al^{3+} (aq) + 3e^{-}) \qquad \mathcal{E}^{o}_{ox} = +1.66 V$   $\underline{3(Ag^{1+} (aq) + 1e^{--->} Ag (s))} \qquad \mathcal{E}^{o}_{red} = +0.80 V$   $Al (s) + 3Ag^{1+} (aq) --> Al^{3+} (aq) + 3Ag (s) \qquad \mathcal{E}^{o}_{cell} = +2.46 V$ 

**INTERACTIVE 23.1** Electrochemical Cells



#### **Concentration Cells**

Did you notice that the concentrations of any aqueous solutions in the previous problems were 1 M? When the concentrations are not 1 M, then you must do further calculations in order to determine the cell potential. You will use the Nernst equation to make your calculation.

 $\mathcal{E}_{cell} = \mathcal{E}^{o}_{cell} - [(\underline{0.0592})(\log Q)]$ n

n is the number of normalized electrons from the balanced equation. It is the least common multiple from the redox halfreaction process. Q is the same as K, but with initial concentrations. That is, products' concentrations raised to the power of their coefficients divided by reactants' concentrations raised to the power of their coefficients.

Since you have done the bulk of the work for a previous problem, I will give you a slight amendment to a previous problem:

 $Al|Al^{3+}$  (0.001 M)||Ag^{1+} (0.500 M)|Ag

You have already written the overall reaction and determined the  $\mathcal{E}^{o}_{cell}$  of the reaction. You must simply make a few amend-ments to determine the nonstandard  $\mathcal{E}_{cell}$ .

Al (s) +  $3Ag^{1+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$   $\mathcal{E}^{o}_{cell} = +2.46 \text{ V}$ 

 $\mathcal{E}_{cell} = +2.46 \text{ V} - [(0.0592)(log[0.001]^1]$ 3 [0.500]<sup>3</sup>

$$\mathcal{E}_{cell}$$
 = +2.50 V

Concentration cells are used to tweak voltages to be exactly appropriate for a particular setting. For example, if a battery needs to be 1.5 V, then the concentrations of the solutions in a

particular reaction can be changed in order to give the desired voltage.

#### Electrochemistry Practice

Thank you for reading this book; I hope it has assisted you in the learning of chemistry.