BIOL 190

Introduction to Chemistry: Physical, Mathematical and Dimensional Perspectives.

Chemistry is the study of the portion of nature that deals with substances, their compositions and structures and their abilities to be changed into other substances.

Chemistry is the root science for understanding and applying medicine, dentistry, chiropractic medicine, botany, physiology, nutrition, pharmacology, nursing, microbiology, dental hygiene health sciences and biochemistry.

Biophysiological Chemistry and Biophysics

Properties

- A property is any characteristic of something that we can use to identify and recognize it when we see it, again. A chemical property is a property that causes a substance to change into another substance.

- A chemical reaction is the change of one substance into another that is observable.

  - Physical properties include things like color, height, weight – something that can be observed without changing an object into something different.

  - Physical quantities are properties to which a numerical value and a unit is assigned, e.g., height -- 5.75 feet. The numerical value is 5.75; the unit is feet. The UNIT in a physical quantity is just as important as the number -- the physical quantity is a number TIMES a unit.

  - A measurement is an operation by which an unknown physical quantity is compared with one that is known.

Matter

- Matter is anything that occupies spaces and has mass. There are three kinds of matter we'll explore: Solids, Liquids and Gases.

- There are three states of matter:

States of Matter		
Solid	Liquid	Gas
Has definite shape. Has own definite volume.	Shape conforms to the container occupied by a liquid. Has definite volume -- may be its own or conform to the container occupied.	Shape conforms to container occupied. Volume is the same as the container.

- Mass is a measurement of the amount of matter in an object.
- Weight is a measurement of the gravitational force acting on an object.
- Inertia is the inherent resistance to any kind of change in motion.
- Mass, weight and inertia are related through Newton's second law: force is equal to the product of mass and acceleration.
- A large mass has a large inertia.
- A large mass, though, does NOT necessarily mean having a large weight, e.g., your weight on earth is 6 times that on the moon.
- Your mass hasn't changed, though.

Matter, Mass and Conservation

- Matter may be subdivided into several categories.
- In Mixtures, proportions of the components may vary.
  - Properties vary with the composition.
  - Mixtures may be separated physically into 2 or more pure substances.
- Pure substances have a constant composition.
  - They have a fixed set of properties and can not be separated into simpler substances.
  - Pure substances may be elements (e.g., carbon, oxygen, hydrogen, nitrogen, neon, argon) or compounds (water, sugar, salt, plaster of Paris, phenol).

- Homogeneous matter is matter that has the same properties throughout the sample.

- Heterogeneous matter is matter with properties that are not the same throughout the sample, e.g., fruit salad, pizza, wood and lasagna.

- Solutions are homogeneous mixtures of 2 or more substances, e.g., sugar water, gasoline, gold alloy and salt water.

- Elements are pure substances made up of **HOMO**atomic molecules.

- Compounds are those made up of **HETERO**atomic molecules.

Elements	Compounds	Mixtures
These are substances that can not be broken down into anything simpler, yet are stable.	Compounds are products of chemical subdivisions and produce either elements or simpler compounds.	These occur by blending two or more compounds or elements in any relative amounts.

The table, below, illustrates these
latter two definitions:

Element (HOMOatomic)	Compound (HETEROatomic)	Compound (HETEROatomic)
X-X O-O $= O_2 =$ Oxygen	X-O-X H-O-H $= H_2O =$ Water	X-O-Z-Q C-H-H-H-H-N-N-O $= CH_4N_2O =$ Urea

Monoatomic molecules are molecules that contain only a single atom. Homoatomic molecules are molecules that contain only one kind of atom. Heteroatomic molecules are molecules that contain 2 or more kinds of atoms. Polyatomic molecules are molecules that contain 2 or more atoms. The table, below, graphically illustrates these new terms:

Monoatomic	Homoatomic	Heteroatomic
	Polyatomic, also	Polyatomic, also
X Ca = Calcium	X-X-X-X-X-X-X O-O-O = O_3 = Ozone	X-O-Q NH_4OH = ammonium hydroxide

All matter gives rise to the Law of Definite Proportion: the elements in specific compounds are combined in the same proportion by mass, e.g.:

Water (H_2O) at the simplest:	Methanol (CH_3OH) at the simplest:	Glucose ($C_6H_{12}O_6$) at the simplest:
1.0 g hydrogen and 8 g oxygen = 9.0 g water	3 g carbon, 1 g hydrogen and 4 g oxygen = 8 g methanol	6 g carbon, 1 g hydrogen and 8 g oxygen = 15 g glucose

When mixtures are blended, this is a physical change.
A physical change is defined any change without a chemical reaction.
A chemical reaction is an event in which substances change into other substances:

Reactants	→	Products
$H_2O_2 + Fe^{3+}$	→	$H_2O + O_2$
$Na + H_2O$	→	$NaOH + H_2$
$C + S + KNO_3$	→	BOOM!
$H_2 + O_2 + spark$	→	H_2O*
Urea + H_2O	→	"ice pack"#

*This is an exothermic reaction (a reaction that generates and gives off heat).

#This is an endothermic reaction (a reaction that absorbs heat and feels cold).

All chemical reactions follow the Law of Conservation of Mass.
This Law says that mass is neither gained nor lost in a chemical
reaction, i.e., mass is conserved.
Staying with our earlier examples from the Law of Definite
Proportions:

Reactants	$\rightarrow$	Products
$1.01 \text{ g H} + 8 \text{ g O}$	$\rightarrow$	$9.01 \text{ g H}_2\text{O}$
$3 \text{ g C} + 1 \text{ g H} + 4 \text{ g O}$	$\rightarrow$	$8 \text{ g CH}_3\text{OH}$
$6 \text{ g C} + 1 \text{ g H} + 8 \text{ g O}$	$\rightarrow$	$15 \text{ g C}_6\text{H}_{12}\text{O}_6$
$6 \text{ g C} + 1 \text{ g H} + 8 \text{ g O}$	$\rightarrow$	$15 \text{ g HC}_2\text{H}_3\text{O}_2$ (HOAc is slang)

The Atom: Modern Atomic Theory

- Atoms of the same element have the same average mass.

- Those of different elements have different average masses.

- Atom comes from "atomos" which means "not cuttable".

- Atoms consist of protons, neutrons and electrons:

Atoms		
Protons	Neutrons	Electrons
Positively charged; located in the nucleus of an atom; we write it as either p or p$^+$	Have no charge; found in the nucleus; written as n	Negatively charged; in the energy shells/orbitals around the nucleus; written as e$^-$
In an element, the number of protons = the number of electrons; the number of protons is also equal to the atomic number of that element.	Effects atomic mass.	Has no effect on atomic mass; in elements, the number of electrons equals the number of protons.
The number of protons + the number of neutrons = the atomic mass		

- When we talk about atoms, the Bohr model, aka the solar system model, is the easiest with which to work. It is set up like our solar system with the "sun" being the nucleus and the "planets' orbits" the orbitals for the electrons.
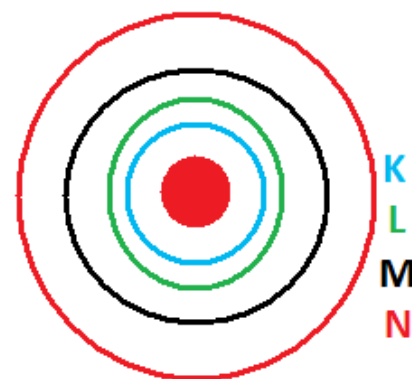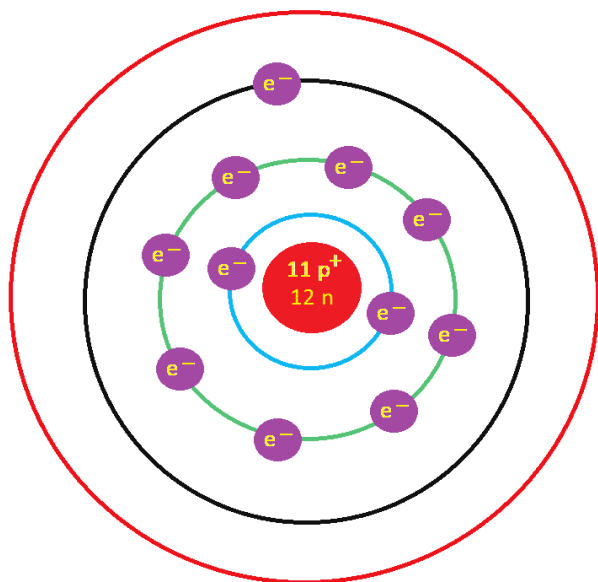
Nucleus		K	L	M	N
H	$1p^+$	$1e^-$			
He	$2p^+$ $2n$	$2e^-$			
Li	$3p^+$ $4n$	$2e^-$	$1e^-$		
Na	$11p^+$ $12n$	$2e^-$	$8e^-$	$1e^-$	
Sc	$21p^+$ $24n$	$2e^-$	$8e^-$	$9e^-$	$2e^-$

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Chemical Formulas and Symbols

- Figure, below, illustrates how to read a simple element from the periodic table. In short, the atomic number is always a non-decimal, whole, number and the atomic mass represents an average mass of each atom. In this example, we are looking at hydrogen.

1

H

1.00797

1.00797

H

1

1 = Atomic Number; 1.00797 = Atomic mass; H = hydrogen

Elemental symbols [is] are [a] symbols assigned to an element based on the name of the element.
These symbols are represented by either one capital letter or one capital letter followed by a lower case letter:

One capital letter		One capital letter and one lower case letter	
B = boron	O = oxygen	Ag = silver	He = helium
C = carbon	P = phosphorus	Au = gold	Ne = neon
F = fluorine	S = sulfur	Pt = platinum	Ar = argon
H = hydrogen	U = uranium	Hg = mercury	Tc = technetium
I = iodine	V = vanadium	Mg = magnesium	Fe = iron
K = potassium	W = tungsten	Ca = calcium	Co = cobalt
N = nitrogen	Y = yttrium	Be = beryllium	Mn = manganese

Compound formulas are symbols for the molecule of compounds, consisting of the symbols of the atoms found in the molecule. Atoms present in numbers greater than one have a number indicated by a subscript (number behind and below that atom):

$HCl =$ hydrochloric acid	$H_2SO_4 =$ sulfuric acid	$HNO_3 =$ nitric acid	$H_3PO_4 =$ phosphoric acid
$NaOH =$ sodium hydroxide	$KOH =$ potassium hydroxide	$CaCO_3 =$ calcium carbonate	$Li_2CO_3 =$ lithium carbonate
$HC_2H_3O_2 =$ acetic acid	$Al(OH)_3 =$ aluminum hydroxide	$C_6H_{12}O_6 =$ glucose	$CH_4N_2O =$ urea
$Na_3PO_4 =$ sodium phosphate	$Al_2S_3 =$ aluminum sulfide		$CaC_2O_4 =$ calcium oxalate

In General

- Elements on the periodic table below and to the left of the metalloids are metals.

- Elements on the periodic table above and to the right of the metalloids are non-metals.

Periodic Table -- Metals

- Most of the elements are metals
- They have high thermal conductivity (they conduct heat readily).
- Metals have high electrical conductivity (they transmit electricity readily).
- The metals are ductile (they can be drawn into wires) and malleable (they can be pounded/hammered into thin sheets).
- They also have a metallic luster (a characteristic "metallic" appearance).

Periodic Table -- Metalloids

Seven elements (depending on the author) are metalloids:

B	Si	Ge	As
Sb	Te		At

The properties of metalloids range between those of the metals and the non-metals.

Periodic Table – Non-Metals

- About 20 elements are non-metals.
- Their properties are typically the opposite that of the metals.
- They occur as brittle, powdery solids or as gases.

Composition of the Atmosphere

- This topic, I believe is of importance as our atmosphere does contain noble gases.

- The table, following slide, summarizes the composition of our atmosphere.

- Keep in mind that as altitude increases, the per cent composition does not vary - the PRESSURE does, e.g.,

  – at sea level, atmospheric pressure is 760 mm Hg;

  – at 15000 feet, 400 mm Hg;

  – at 10 miles, 40 mm Hg and

  – at 30 miles, 0.1 mm Hg.

N_2	78%
O_2	20.99%
Ar ←	0.94%
CO_2	0.035-0.04%
H_2	0.01%
Ne ←	0.0012%
He ←	0.0005%
Kr ←	0.0001%
O_3	0.00006%
Xe ←	0.000009%

← All noble gases

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Elements and Isotopes

- Every element consists of a mixture of its isotopes.

- Isotopes are atoms which are identical in atomic number and electronic configuration, but different in atomic mass.

- The difference between the two is in the number of neutrons.

```
┌─────────────────┐
│        1        │
│        H        │
│     1.00797     │
└─────────────────┘

┌─────────────────┐
│     1.00797     │
│        H        │
│        1        │
└─────────────────┘
```

1 = Atomic Number; 1.00797 = Atomic mass; H = hydrogen

One example of an isotope is Cl.
It has an atomic number of 17.
There are two isotopes of chlorine:

Isotope	Number of Neutrons
^{35}Cl	18
^{37}Cl	20

The atomic mass of an element reflects the abundance of all isotopes of that element.
There are three times as much ^{35}Cl as ^{37}Cl.
We can determine the average atomic mass of chlorine in the following manner:

Again, note that the difference is in neutron number.

$$3 \times 35 = 105 \; for \; 35Cl$$
$$1 \times 37 = \;\; 37 \; for \; 37Cl$$
$$4 \qquad = 142$$

$$Avg \, atomic \, mass = \frac{142}{4} = 35.5$$

Since there are 3 parts ^{35}Cl and 1 part ^{37}Cl,
simply multiply each isotope's mass by the ratio observed in nature.
Add up both the parts (4) and the total masses due to those parts (142).
Divide the total mass (142) by the total parts (4) and
the average atomic mass is obtained (35.5).

We can do the same thing with ^{79}Br and ^{81}Br.
Both are present in nature in equal parts.
The average atomic mass is determined as follows:

$$1 \times 79 = 79$$
$$1 \times 81 = 81$$
$$2 \quad = 160$$

$$Avgmass = \frac{160}{2} = 80$$

The operation is carried out just as before with the chlorine.

Ionization

- Before discussing Mass Spectroscopy, we need to discuss ionization

- In order for most metals and non-metals to be reactive, they must find a way to be charged, i.e., they must either lose electrons (and be positively charged) or gain electrons (to be negatively charged).

- When this occurs, they are said to ionize. Ions are charged particles.

- **Cations are positively charged ions.**

- **Anions are negatively charged ions.**

CATIONS

- Elements in Groups I, II and III have less than 4 electrons in their outer shells (specifically, they have 1, 2 and 3 electrons, respectively).

- In order for these elements to be most stable when they ionize, i.e., to attain the electronic configuration of the previous noble gas, they must lose 1,2 and 3 electrons, respectively.

- This will yield charges of +1, +2 and +3, respectively.

- The positive charges are due to the excess of protons left in the nucleus after the electrons are removed

ANIONS

- Elements in Groups V, VI and VII have more than 4 electrons in their outer shells (specifically, the have 5, 6 and 7 electrons, respectively).

- In order for these elements to be most stable when they ionize, i.e., to attain the electronic configuration of the following noble gas, the must gain 3, 2 and 1 electrons, respectively.

- In other words, the outer shell, unlike that of the cations, must fill up with electrons to make a total of 8 electrons in the outer shell.

- When this happens, the charges obtained are -3, -2 and -1, respectively.

- The negative charges are due to the accumulation of electrons which out number the protons in the nucleus.

Electrolytes

- Cations and anions are collectively known as electrolytes: charged particles that conduct an electrical current in aqueous solution.

- Biological Application???

- When looking at the periodic table and remembering the electron shells from discussions, the periodic table tells you very valuable information about how those elements in the representative group will ionize.

- We first have to accept that when an element's **outer most shells** are **filled or are empty** is when that element is **most stable**.

Group IV Elements

- One issue that was not discussed in earlier discussion was that of what happens when the atom is in Group IV?

- Elements in this group will gain or lose electrons depending on the reaction conditions.

Chemical Bonds

- Chemical bonds are strong forces of attraction between reorganized atoms.
- Oppositely charged particles (ions) attract each other on ionic compounds.
- Remember that ions form from metal and non-metal atoms.

Chemical Bonding & Reactions
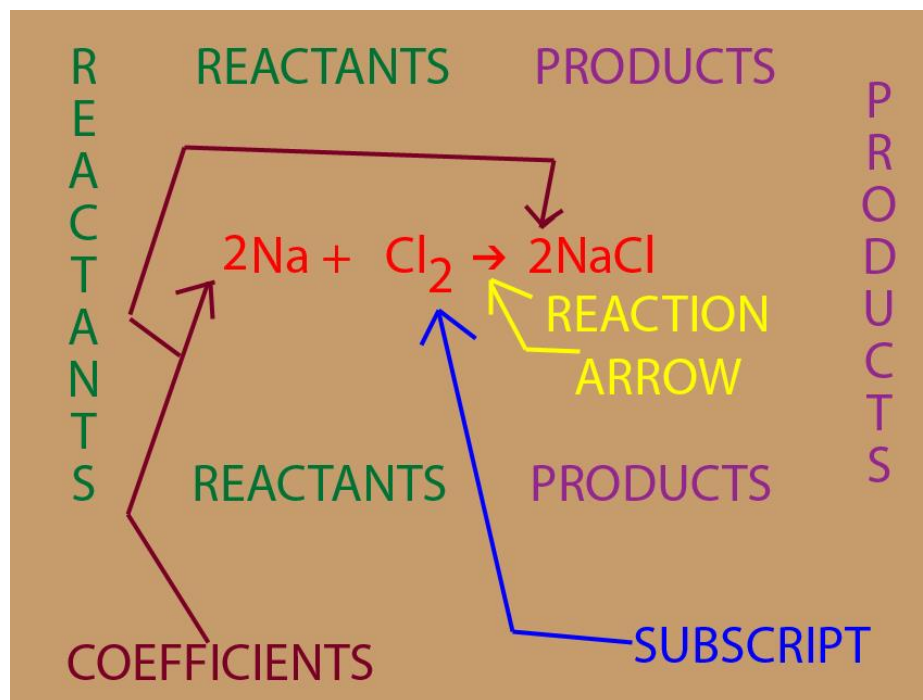
Covalent Compounds and/or Ions
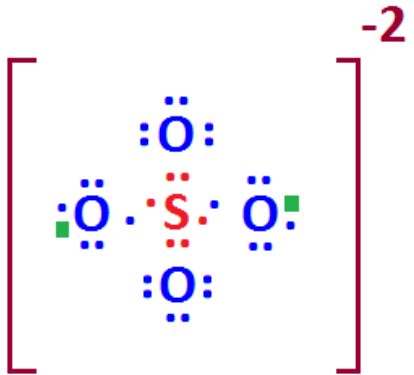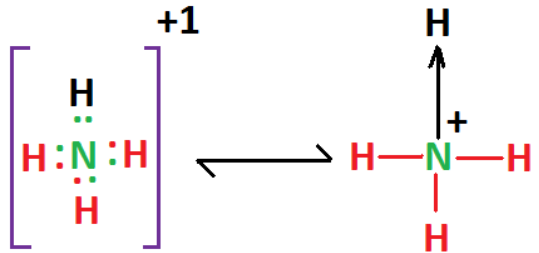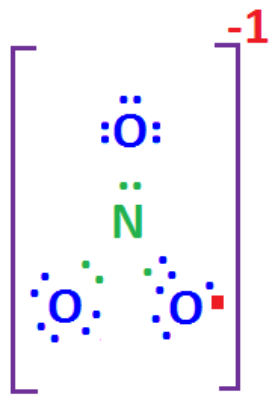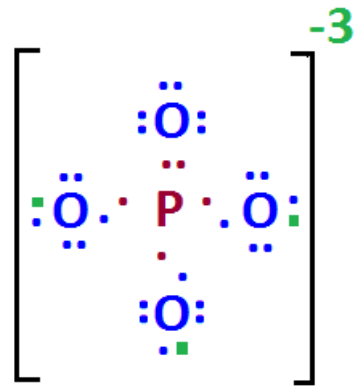
When discussing covalent molecules, there are several terms
one must know in order to fully appreciate the diversity of these molecules.
These terms are summarized in the table, below:

|	
Nonpolar covalent bond	**A covalent bond in which the bonding pair of electrons is shared equally by the bonded atoms.**
Polar covalent bond	**A covalent bond that shows bond polarization (bonding electrons are not shared equally).**
Bond polarization	**The attraction of the shared electrons to the more electronegative atom of a bonded pair of atoms.**
Electronegativity	**The tendency of an atom to attract shared electrons of a covalent bond.**
Dipolar force	**The attractive force that exists between the positive end of one polar molecule and the negative end of the same molecule.**
Polar molecule	**A molecule with polarized bonds which results in asymmetrical distribution of charge.**
Nonpolar molecule	**Molecules with nonpolarized bonds which results in symmetrical distribution of charge.**

- Binary compounds are pretty simple.
- Not all covalent substances are as simple.
- Polyatomic ions are ions that are bound covalently to each other with a net charge.
- Most polyatomic ions are negatively charged.

Examples of polyatomic ions are tabulated, below:

Name	Formula	Name	Formula
SO_4^{2-}		NH_4^+
Sulfite	SO_3^{2-}	Bicarbonate	HCO_3^-
	NO_3^-		PO_4^{3-}
Nitrite	NO_2^-	Arsenate	AsO_4^{3-}
Carbonate		CO_3^{2-}	

- The ammonium ion is a bit different from the other polyatomic ions -- besides being the only cation mentioned.
- It also contains a coordinate covalent bond.
- A coordinate covalent bond is a bond between 2 atoms in which one atom donates the 2 electrons (both electrons) to make the bond.
- In the case of the ammonium ion, the coordinate covalent bond occurs between the unbonded pair of electrons in nitrogen and the extra hydrogen ion (proton) to make the polyatomic cation.
- A coordinate covalent bond is drawn as an arrow going from the two electrons' source to the electron acceptor.
- Remember that ammonia is neutral; the ammonium ion has the extra charge due to an extra proton and no electron to balance it out.

Chemical Reaction Types

Centerfire

Powder

Primer

Powder

Primer

Rimfire
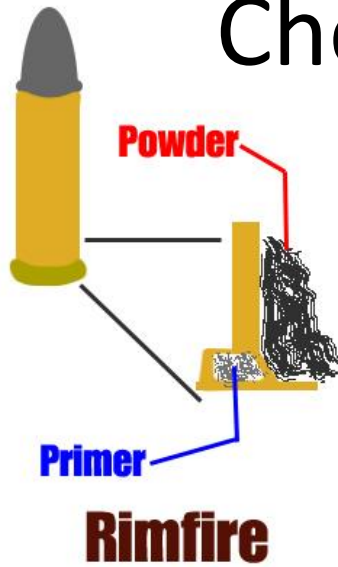
- Just mixing chemicals together is a physical change.
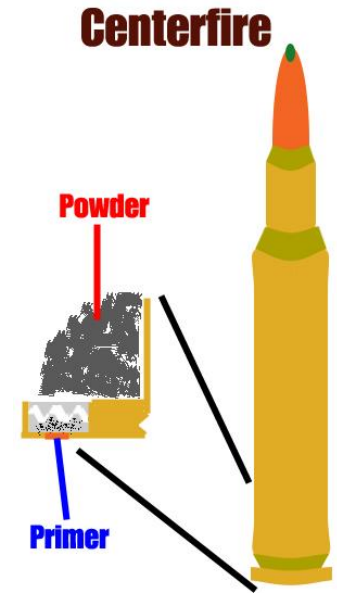
- Adding energy that drives a reaction is a chemical change.
  - Firing pin
  - Match
  - Spark
  - Heat
  - Force

- Ionic compounds form when electrons shift between atoms, Figure, right.
- In this example, elemental sodium reacts with elemental chlorine to form sodium chloride.
- The movement of electrons is that the sodium loses its single outer electron and chlorine gains it.
- Note the final Lewis Structure of sodium chloride.
- This occurs only when the sodium chloride is solid.
- Otherwise, when this is in water, table salt (sodium chloride) exists as two distinctly separate ions.
- Indeed, one does not actually taste NaCl, rather, when NaCl hits the mouth and mixes with the saliva, it dissolves and separates (dissociates) into its two ionic components.
- Each ion is detected by different portions of taste buds.
- The detected presence is converted into an electrical signal that is sent to our brains for interpretation.
- The message we receive following interpretation is that we have "tasted" salt.
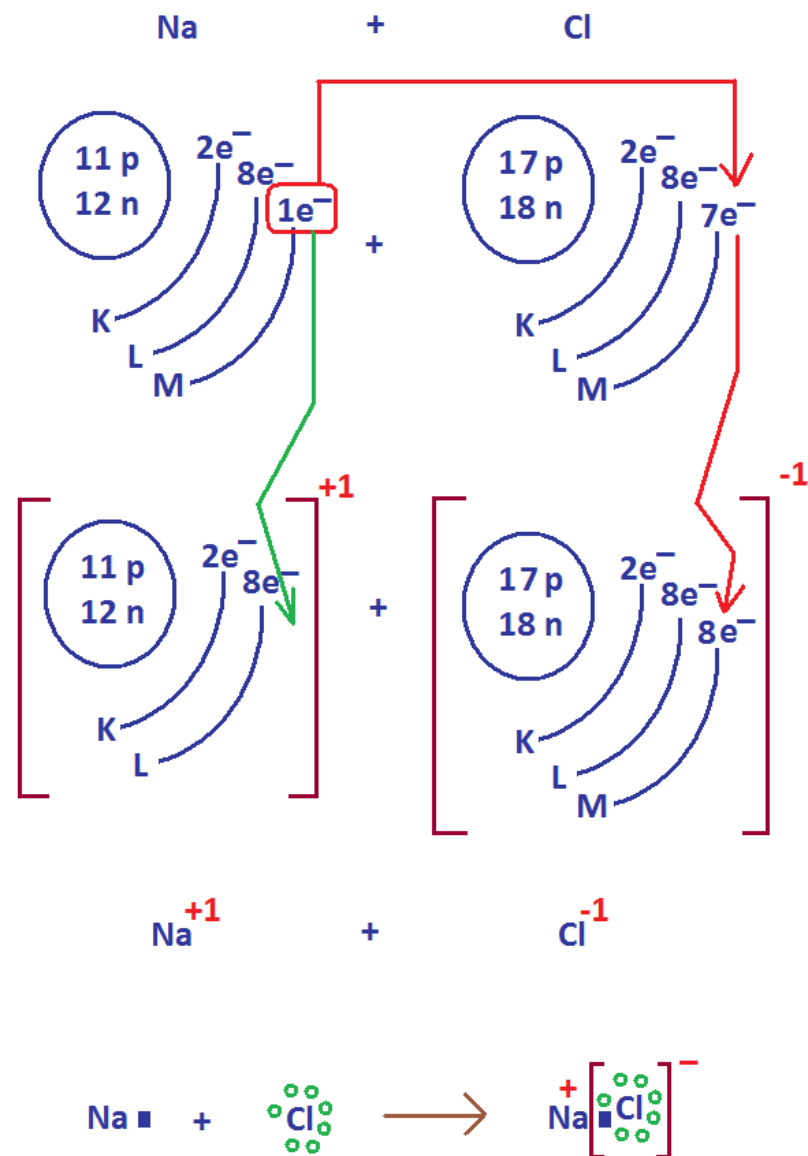
- The reactions between magnesium and fluorine and potassium and sulfur, below, respectively, form magnesium fluoride and potassium sulfide.
- To name these binary compounds (compounds which contain only two kinds of atoms), put the metal's name first, add the non-metal stem and add "ide".
- The non-metal stem for fluorine and sulfur are "fluor" and "sulf".
- These two examples also bring up something else we need to discuss: balancing chemical formulas.

$$Mg : + 2 \cdot \ddot{F} : \longrightarrow : \ddot{F} : Mg : \ddot{F} :$$

$$2K \cdot + \cdot \dot{S} \cdot \longrightarrow K : \ddot{S} : K$$

- Balancing chemical formulas is not difficult.
- All of us can balance checkbooks, hence, we can all balance formulas.
- There are a number of methods by which to do this.
- Probably the simplest is to remember that for neutral compounds the sums of the charges for ALL of the ions involved must equal zero.

- Looking at magnesium fluoride, for example, below, note that it took 2 fluorides to balance the single magnesium.
- This is because the magnesium ionized to a +2 charge while the fluorine ionized to the -1 charged fluoride ion.
- Since +2 -1 is +1, it follows that there has to be 2 fluorides to give a total of -2 for the negative charges, i.e. +2-2 = 0 for a neutral compound.
- The same thing applies to the potassium in potassium sulfide.
- In this case, two potassiums are required to balance out the -2 charge on the sulfide ion.
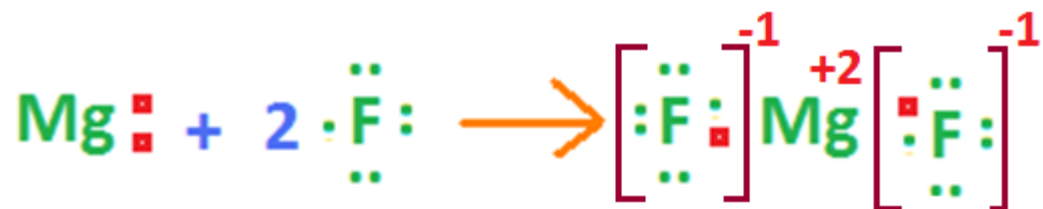
Thus far, these two specific reactions are examples of what are called "redox" reactions.

Redox reactions are oxidation (a reactant loses electrons) and reduction (a reactant gains electrons) reactions.

If there is reduction, there MUST be oxidation -- i.e., ya can't have one without the other.

Each part of a redox reaction may be written separately as a half reaction.

When the oxidation half reaction and the reduction half reaction are added up and adjusted (balanced) for electron exchange, the complete redox reaction is obtained.

Note that when the electrons are not equal between each half reaction that they must be made equal -- this includes multiplying the whole half reaction by the exact same number you multiply the electrons by.

$$Fe \rightarrow Fe^{3+} + 3e^- \quad Oxidation$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad \mathrm{Re}\,duction$$

$$3(Cu^{2+} + 2e^- \rightarrow Cu)$$
$$2(Fe \rightarrow Fe^{3+} + 3e^-)$$

$$TOTAL: 3\,Cu^{2+} + 2\,Fe \rightarrow 3\,Cu + 2Fe^{3+}$$
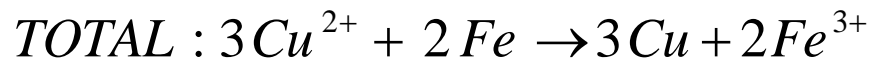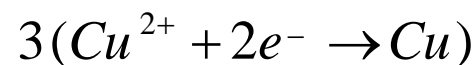
Now that we've gone through some elementary bonding and reaction concepts,
it's time to get down to some nitty-gritty with reactions.
Chemical reactions may be subdivided into main categories: non-redox and redox.
Each of these two categories may be further sub-divided into three more categories, apiece.
The categories of reactions are illustrated, below:

Chemical Reactions					
Non-Redox			Redox		
Combination	Double Replacement (Metathesis)	Decomposition	Combination	Single Replacement (Substitution)	Decomposition

- Since both main categories of reactions contain specifically combination and decomposition reactions, we'll examine each of those headings by comparing the redox version against the non-redox version, first.

Decomposition Reactions	
In this kind of reaction, a single substance is broken down to form 2 or more simpler substances	
$X \rightarrow Y + Z$	
Redox Examples	Non-Redox Examples
$2MgO \rightarrow 2Mg + O_2$ $2Ag_2O \rightarrow 4Ag + O_2$ $ZrI_4 \rightarrow Zr + 2I_2$ $KClO_3 \rightarrow KCl + O_2$	$MgCO_3 \rightarrow MgO + CO_2$ $H_2CO_3 \rightarrow CO_2 + H_2O$ $PbCO_3 \rightarrow PbO + CO_2$

- The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not.
- If an element is used or formed, it's probably a redox.
- If there's no charge change, it's probably a non-redox.
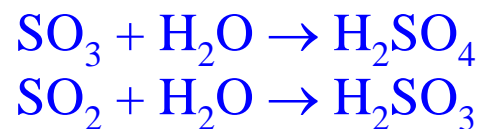
Combination Reactions	
These reactions are also known as (aka) addition or synthesis reactions. In this type of reaction, 2 or more substances react to form a single substance	
$D + E \rightarrow F$	
Redox Examples	Non-redox Examples
$2Ca + O_2 \rightarrow 2CaO$ $H_2 + Cl_2 \rightarrow 2HCl$ $4Al + 3O_2 \rightarrow 2Al_2O_3$ $Zr + 2I_2 \rightarrow ZrI_4$ $N_2 + 3H_2 \rightarrow 2NH_3$	$SO_3 + H_2O \rightarrow H_2SO_4$ $SO_2 + H_2O \rightarrow H_2SO_3$
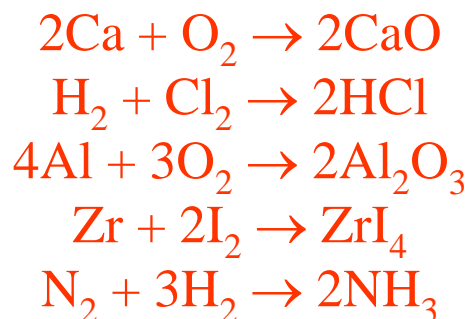
- The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not.
- If an element is used or formed, it's probably a redox.
- If there's no charge change, it's probably a non-redox.

Replacement Reactions	
Single Replacement	Double Replacement
Always redox; 1 element reacts with a compound and displaces another element from the compound.	aka Metathesis or neutralization reaction; **not redox**; "partner swapping"; tends to occur in aqueous solution.
$A + CX \rightarrow C + AX$	$CX + DY \rightarrow CY + DX$
Iron stripped from ore with C: $3C + 2Fe_2O_3 \rightarrow 4Fe + 3CO_2$	$KOH + HNO_3 \rightarrow KNO_3 + H_2O$

Redox Reactions

- Reduction ALWAYS occurs with oxidation -- you can not have one without the other.

- One substance is oxidized and the other is reduced.

- Whenever you work with redox reactions, there are 4 things to remember:
    - 1) the oxidizing agent is always reduced;
    - 2) the reducing agent is always oxidized;
    - 3) the oxidizing agent gains electrons;
    - 4) the reducing agent loses electrons.

The table, below, summarizes some basic information about reduced and oxidized forms of matter:

Reduced Forms of Matter	Oxidized Forms of Matter
High energy	Low energy
Sugar Coal Gas	Carbon dioxide Water

- In a classic sense, redox reactions require some discussion about oxygen and hydrogen.

Three Definitions of Oxidation

- 1) A substance is oxidized when it GAINS oxygen atoms, e.g.:
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 \uparrow + 6H_2O$
- 2) A substance is oxidized when it LOSES hydrogen atoms, e.g.:
- Methanol (CH_3OH) $\rightarrow$ formaldehyde (CH_2O) + $H_2\uparrow$
- 3) A substance is oxidized when it LOSES electrons, e.g.:
- $Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$ (equivalent to $MgCl_2$ -- Mg has to undergo electron loss, first)

Three Definitions of Reduction

- 1) A substance is reduced when it LOSES oxygen atoms, e.g.:
- $2\ KClO_3 + heat \rightarrow 2KCl + 3O_2\uparrow$
- 2) A substance is reduced when it GAINS hydrogen atoms, e.g.:
- $CO + 2H_2 + Pt, Pd\ or\ Ni\ catalyst \rightarrow CH_3OH$ (methanol)
- 3) A substance is reduced when it GAINS electrons, e.g.:
- $Cu^{2+} + 2e^- \rightarrow Cu$

Summary Thus Far

The table, below, summarizes oxidation
and reduction definitions:

Oxidation	Substance/Particle Involved	Reduction
Gains	O_2	Loses
Loses	H_2	Gains
Loses	e^-	Gains

Redox Reactions -- More Terms

- When a redox reaction occurs, one substance is reduced and another oxidized.
  - The substance that is reduced is the OXIDIZING AGENT.
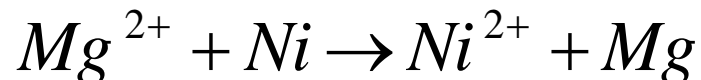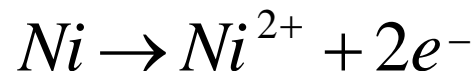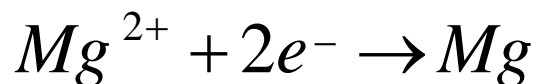 - The substance that is oxidized is the REDUCING AGENT, e.g.:
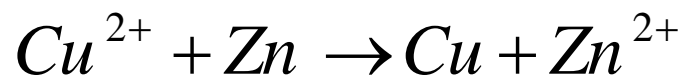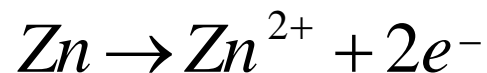
$$CuO + H_2 \rightarrow Cu + H_2O$$
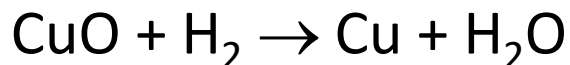
- The **CuO is the oxidizing agent** as the Cu in the CuO is reduced from the +2 state on the left side of the arrow to the elemental state on the right side of the arrow.
- The **H_2 is the reducing agent** as the H_2 goes from the elemental state on the left side of the arrow to a +1 state on the right side of the arrow.
- This reaction also demonstrates another way in which to remember reduction.
- Reduction of something occurs when its charge is further reduced.
- This means that if Cu is in a +2 state that it is reduced to Cu in a +1 state in the appropriate reaction.
- Likewise, Br in the elemental state (I'm using atomic -- not molecular Br_2) may be reduced to Br in the -1 state.
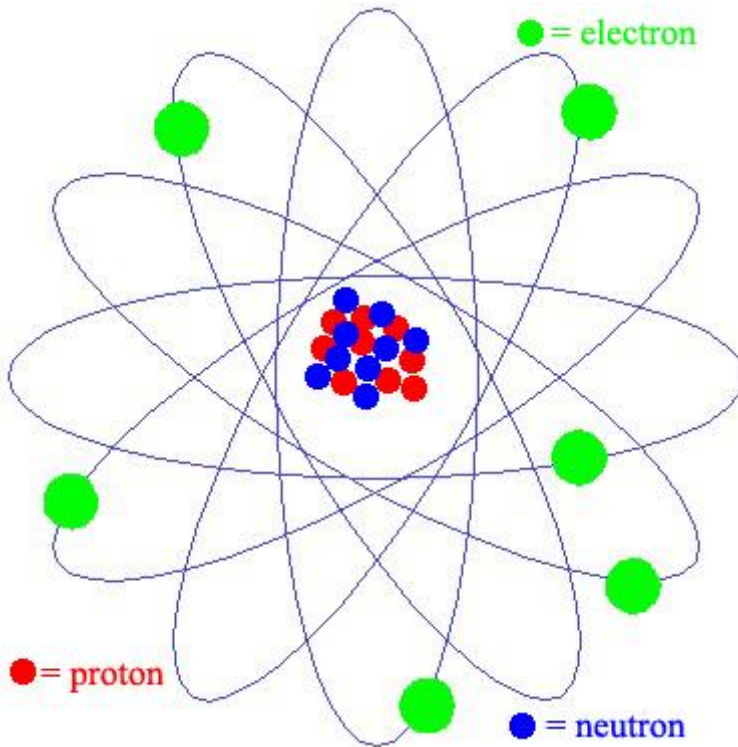- As long as electrons may be GAINED, the substance will be reduced in its charge.

- The following three examples further illustrate the idea of oxidizing and reducing agents (NOTE: I've color coded them for you per the previous statement):

$$2C + O_2 \rightarrow 2CO$$

$$SnO + H_2 \rightarrow Sn + H_2O$$

$$Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$$
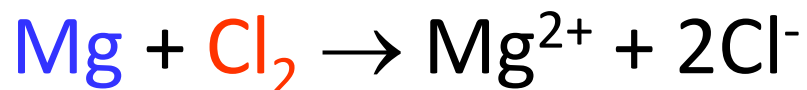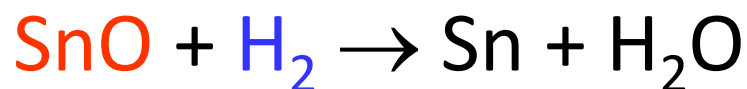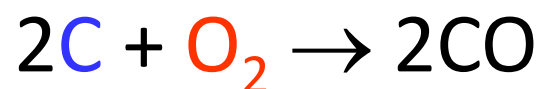
Additional Redox Examples

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

$$Mg^{2+} + 2e^- \rightarrow Mg$$

$$Ni \rightarrow Ni^{2+} + 2e^-$$

$$Mg^{2+} + Ni \rightarrow Ni^{2+} + Mg$$

Electricity and The Atomic Nature of "Things"

= electron

= proton

= neutron

- Electrostatics = study of fixed or stationary, electric charges.
- Static electricity is the most common form we encounter.
- Electric charges = $\pm$
- Smallest units = electrons (-) and protons (+)
- Have equal magnitude with opposite signs

Remember

- Static electricity is an excess of electric charge trapped on the surface of an object. The charge remains until it is allowed to escape to an object with a weaker or opposite electrical charge, such as the ground, by means of an electric current or electrical discharge.

- Static electricity is named in contrast with current electricity, which flows through wires or other conductors and transmits energy.
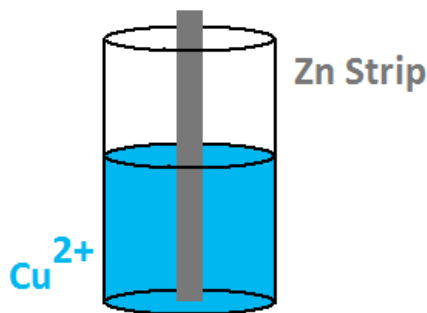
Electrons

- May travel from atom to atom
- Protons don't
- Discussions of electricity, then, revolve around negative charges
- An object is electrified if it has excess or missing electrons

- How lose or gain electrons?
- Touch
- Sock feet on carpet
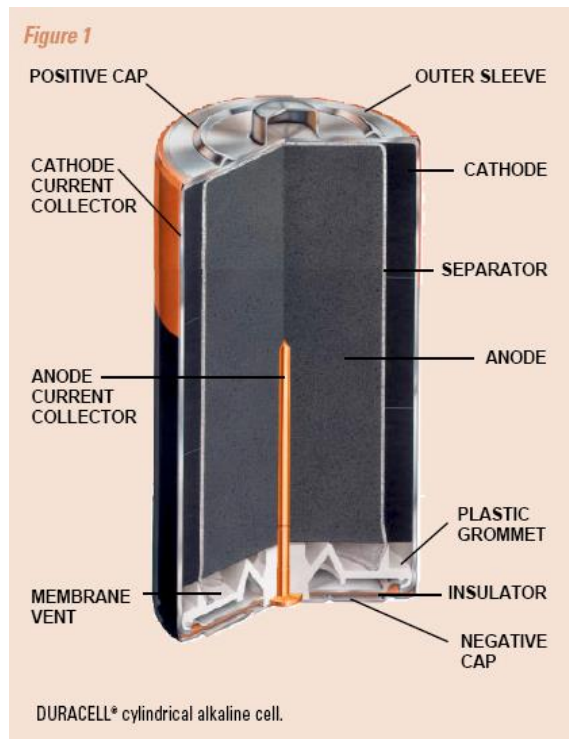- Using a magnet to induce an electrical current.

Electrodynamics

- We recognize electrodynamic phenomena as electricity.

  - The flow of electrons along a wire is the electric current.

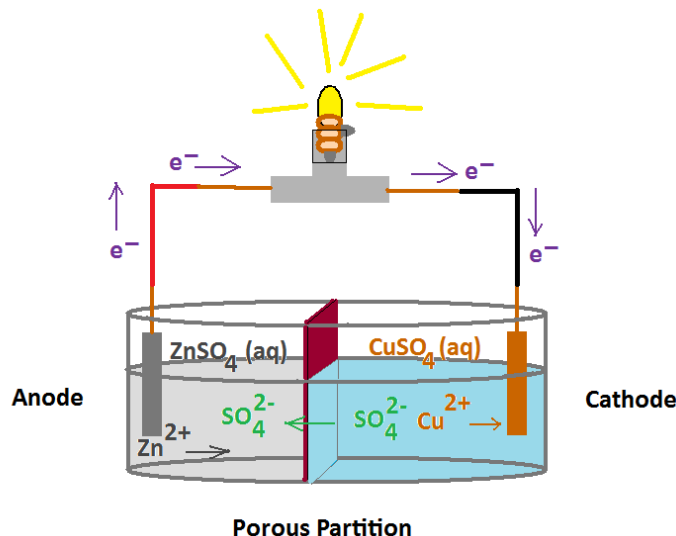- Any material through which electrons easily flow is called a conductor.

Batteries

- A very simple battery may be constructed by simply placing a zinc strip in an aqueous solution of copper (II) sulfate.

- Over time, the zinc strip disappears and elemental copper precipitates.

- The reaction is:

- Zn: + $Cu^{2+} \rightarrow Zn^{2+}$ + Cu:

- where the ":" represent the two electrons that were removed from the Zn by the Cu^{2+}.

Figure 1

POSITIVE CAP
OUTER SLEEVE
CATHODE CURRENT COLLECTOR
CATHODE
SEPARATOR
ANODE
ANODE CURRENT COLLECTOR
PLASTIC GROMMET
MEMBRANE VENT
INSULATOR
NEGATIVE CAP

DURACELL® cylindrical alkaline cell.

- Used with permission from Duracell
- Anode = Zinc (Zn)
- Cathode = manganese dioxide (MnO_2)
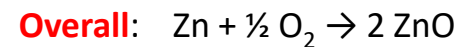- Electrolyte = potassium hydroxide (KOH)

Zn Strip

Cu^{2+}

Anode   ZnSO$_4$ (aq)   CuSO$_4$ (aq)   Cathode

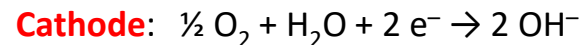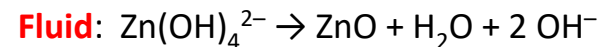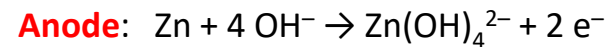SO$_4^{2-}$ SO$_4^{2-}$ Cu^{2+}
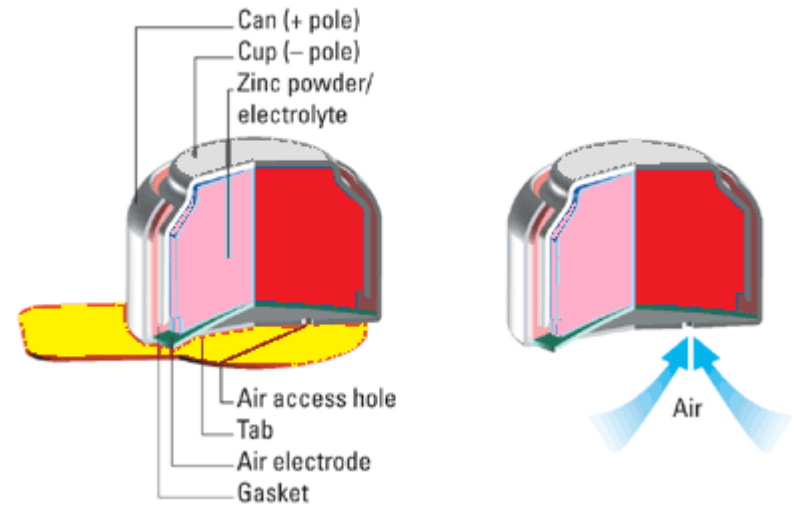
Zn^{2+}

Porous Partition

- The following graphic is an example of a fairly simple battery set up with a light in the circuit.
- Note the flow of electrons from the elemental zinc strip to the copper (II) side.
- The side of a battery that gives up electrons is the ANODE (I use the mnemonic "anoxia" -- "an" = anode and "ox" = oxidation), i.e., oxidation occurs on the anode of the battery.
- That means then, that the other side of the battery will be reduced.
- This side is the CATHODE, i.e., reduction occurs on the cathode side of the battery.
- The porous portion allows for anions to flow from one side of the battery to the other to maintain the negative charge balance lost and gained from the anode and cathode, respectively.
- The same net ionic reaction occurs in this simple battery as we saw with the Zn strip stuck in the aqueous copper (II) sulfate solution.
- The battery we have been describing (above) is called an electrochemical cell.

- A car battery is a series of 6 cells wired in series. On discharge (when you start the engine), the following reaction occurs:

- $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

- And on recharge (when your car is running and the generator or alternator is recharging it), the following reaction occurs:

- $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

Negative Grill; Spongy Pb

Positive Plates; Grill filled with PbO_2
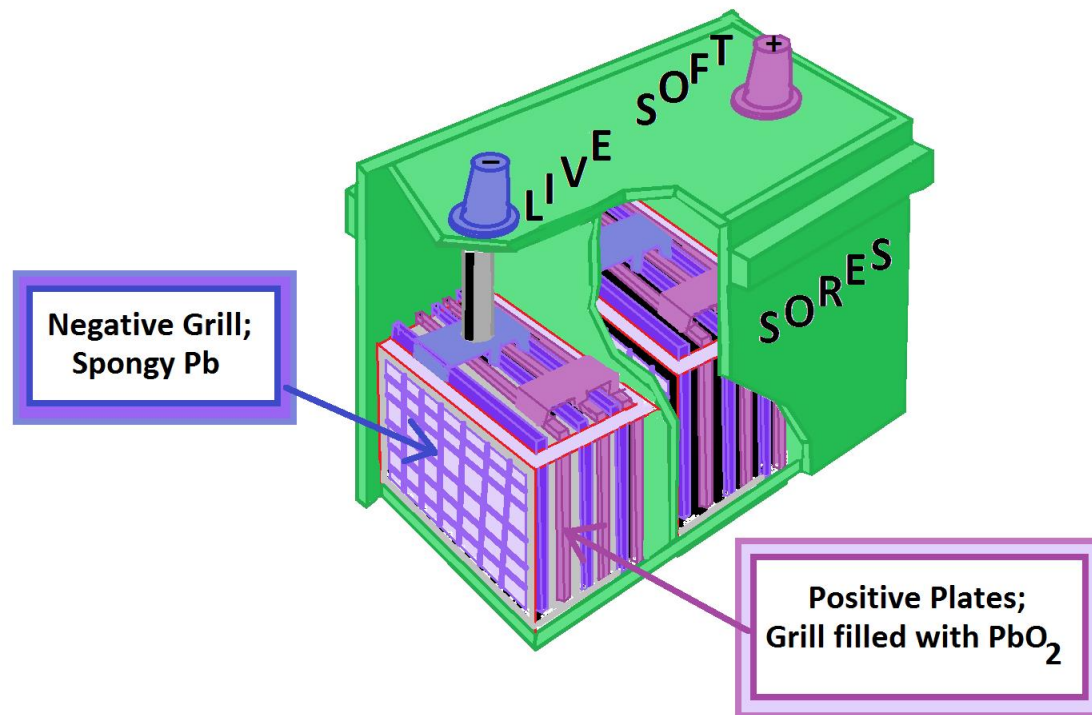
Zinc-Air Batteries

- Left: Inactivated (tab in place)

- Right: Activated (tab removed)

- Research is exploring battery development to run off of a person's blood sugar – ramifications: pacer's/defib's

Can (+ pole)
Cup (– pole)
Zinc powder/ electrolyte
Air access hole
Tab
Air electrode
Gasket
Air

Anode: $Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$

Fluid: $Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2\ OH^-$

Cathode: $\frac{1}{2}\ O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-$

Overall: $Zn + \frac{1}{2}\ O_2 \rightarrow 2\ ZnO$

ca 1.60 V produced theoretically

Batteries and Electrical Circuits

- Electrons flow along the outer wire surface.

- The wire can be modified to resist the flow in certain regions.

- When resistance (Ω) is controlled and conductor is in a closed path, you've got an electric circuit.
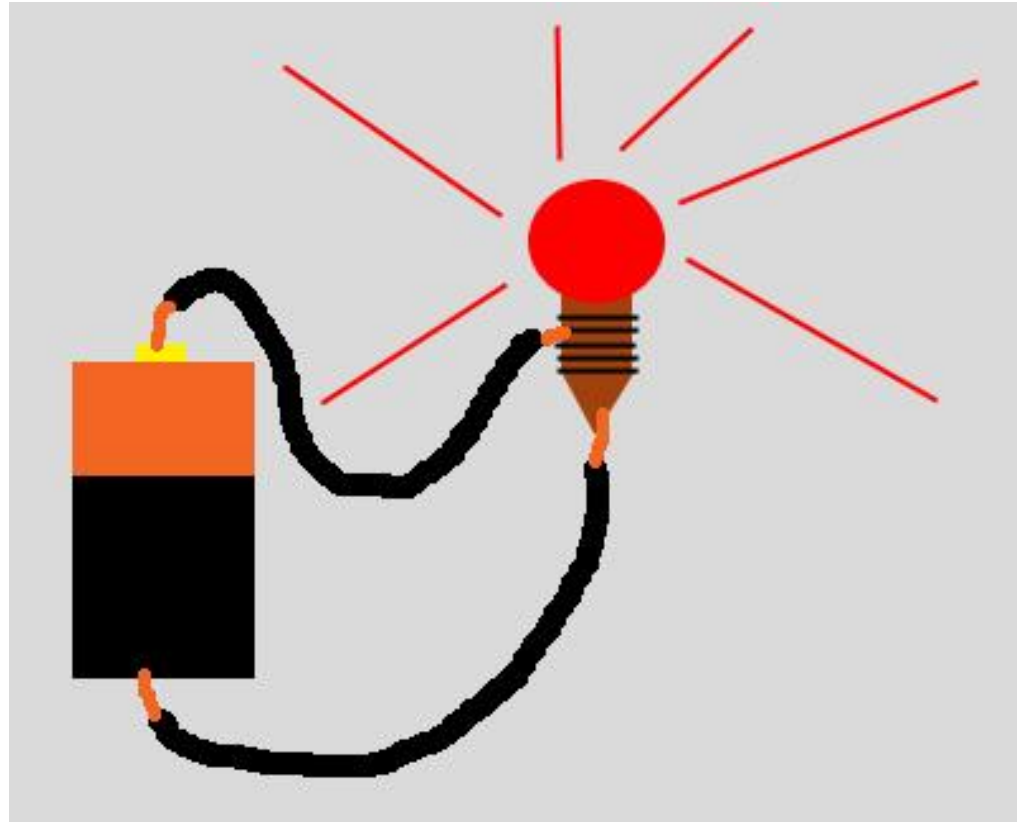
- Current is measured in amperes (amps; I in equations)
- The electrical potential is measured in volts (V)
- Resistance is measured in ohms (Ω; R in equations)

  - Ohm's Law
    - V = I R

Electric Power

  - $P = I\,V = I^2\,R$

  - 1 kW = 1000 Watts

  - 1kWh = 1000 watts used in one hour

Solar Batteries

- Since I developed this part of the lecture, solar power has gone through numerous changes.

- I have given up trying to keep up with these changes, as they tend to be very rapid, i.e., by the time I get it updated, it's already changed, again.

- Hence, this is a very generic, low-key description to give you the idea behind solar batteries.

- In general, a solar battery is made up of two "wafers" of material: an electron donor wafer and an electron acceptor wafer.

e⁻ donor

(-)

(+)
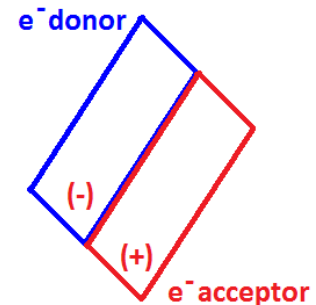
e⁻ acceptor

The table, below, summarizes the characteristics of the donor and acceptor wafers:

Donor	Acceptor
Has 1 extra electron in its repeating structure, therefore, its partially negative.	**Has 1 less electron in its repeating structure, therefore, its partially positive.**
Si is the base and is "doped" with As to give the 5th electron (the extra electron pointed out, below).	**Si is the base and is "doped" with B to give three electrons (lacks the 4th electron pointed out, below; makes an electron "hole" in the repeating sequence).**

- By itself, electrons flow from the electron donor plate to the electron acceptor plate. **Sunlight, though, reverses the "natural process" and electrons are driven through the circuit via the donor layer to the acceptor layer**. This closes the circuit and runs electric appliances and toys (TV, stereos, ad nauseum).

Normal

Sunlight reverses the flow of e⁻ and drives the e⁻ through the circuit.
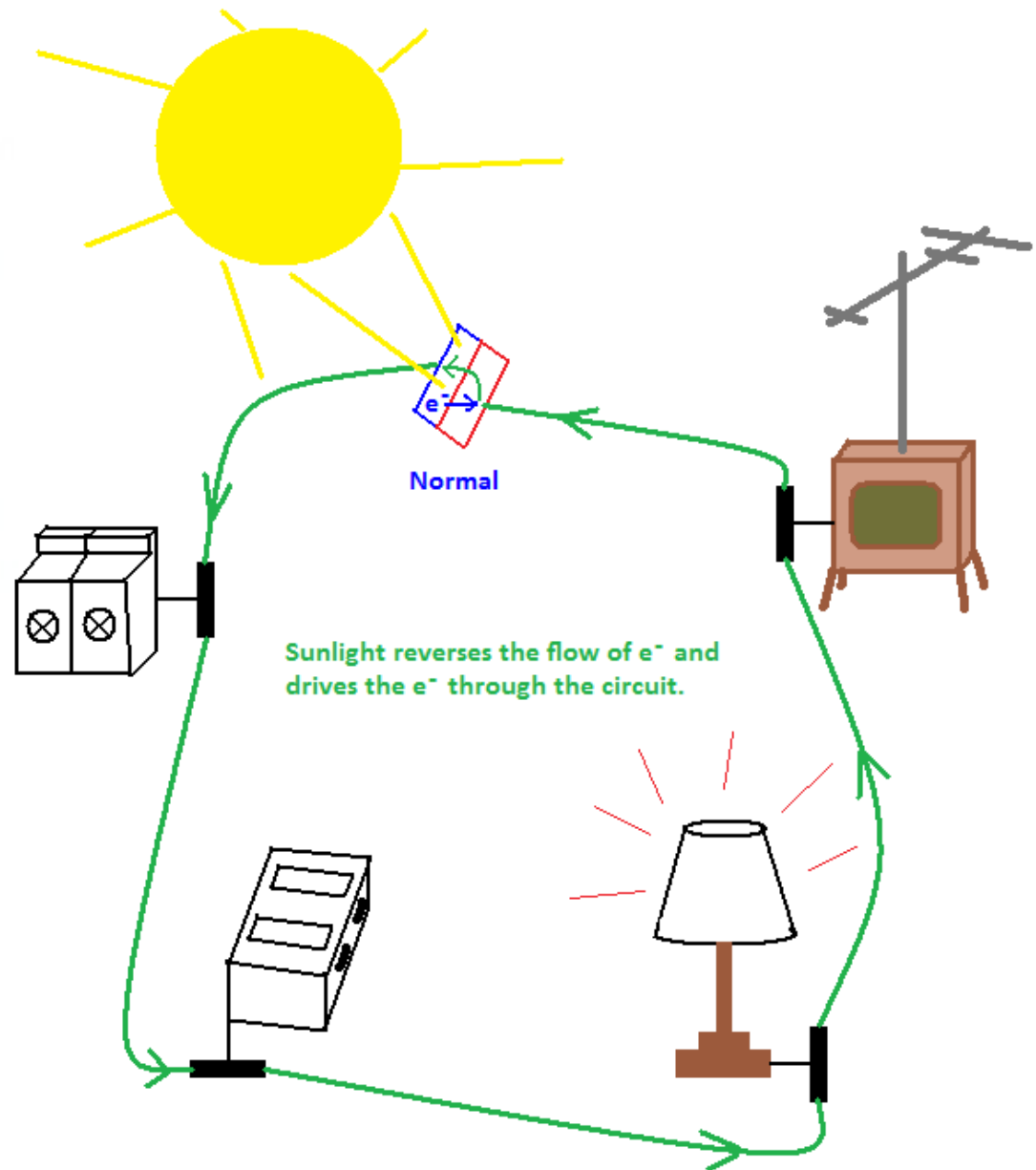
✓ At the time I put this together, solar cells were only about 10% efficient in energy conversion.

✓ Efficiencies, now, range from 8-20% depending on the technology and manufacturer

✓ What the 10% meant was that to operate one 100W bulb would require a series of solar cells 1m by 1m.

✓ At that time, 5000 acres of solar cells would produce the energy equivalent to one nuclear power plant.

✓ To give you some perspective on this, one section of land is 640 acres and is one mile by one mile.

✓ This means that it would take (at old efficiency rates) a piece of ground that is 8 sections or 8 square miles in area (equivalent to a strip of land 4 miles long and 2 miles wide).

Piezo Electric Effect et How It Works

- Piezoelectricity = pressure electricity.
- We know it from BBQ grills with the propane "starter".
- 1st discovered in quartz and tourmaline
- Found in tendon, dentin, aorta, trachea, elastin and BONE!
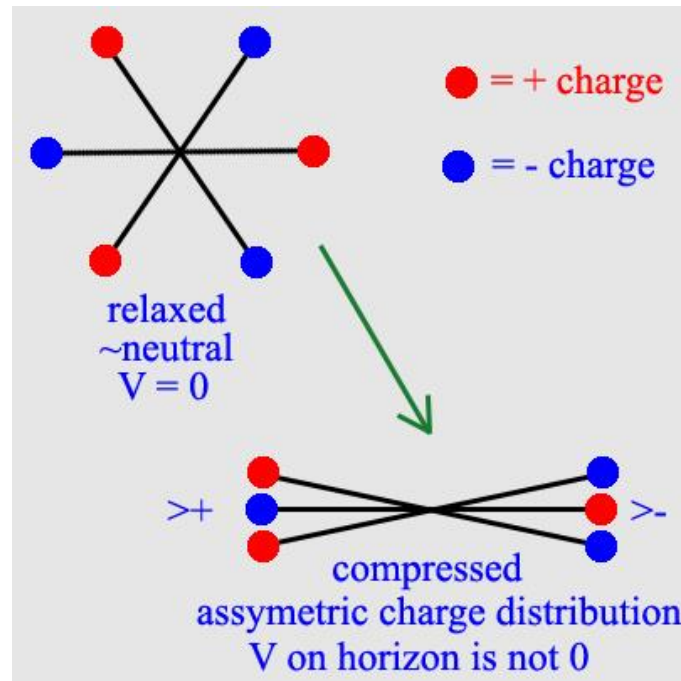
- The effect is the ability of a mineral or crystal to acquire opposing electrical charges on opposing surfaces when bending, stretching or compression is applied to the crystal.
- Is caused by displacing ionic charges within a crystal structure – the magnitude of the charge is usually proportional to the amount of stress applied.

Electrical Circuits
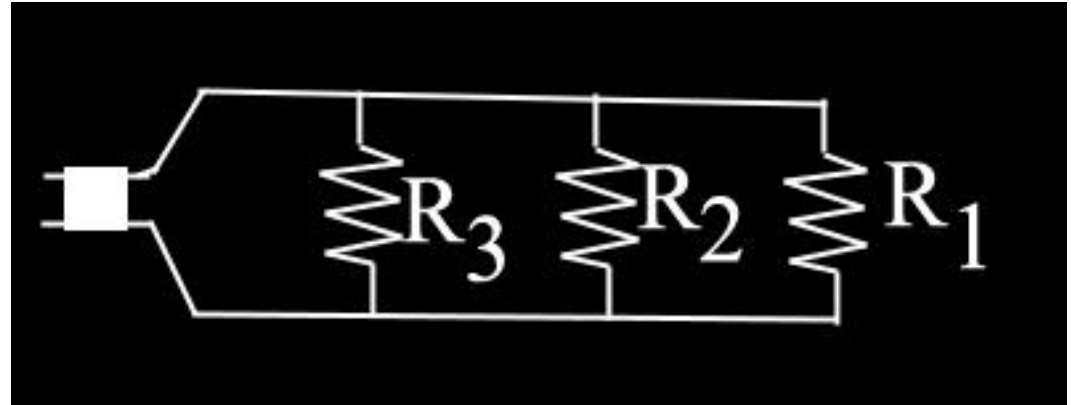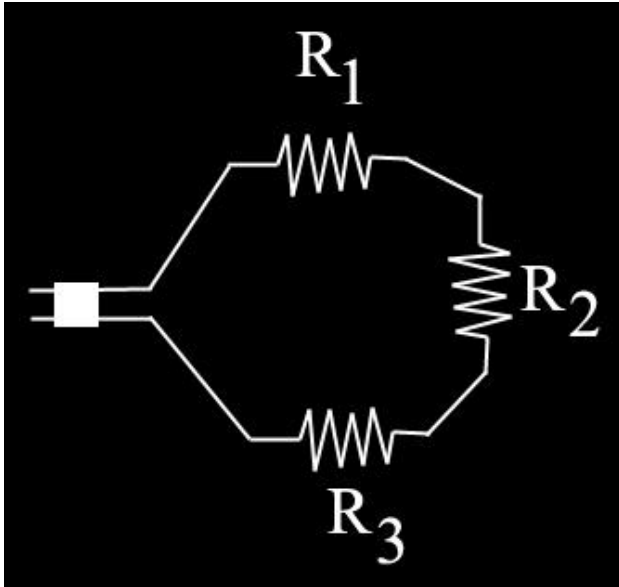
- Series (left) – set up like X-mas lights: one goes out, they all go out – Greatest Ω, least electron flow
  - Parallel (right) – one goes out, the rest stay on – Least Ω, greatest electron flow (conductance)

Blood Vessels

- In parallel, have least resistance to flow, hence, greatest flow

- In series, have greatest resistance to flow, hence, least flow

- Is why circulatory system is set up in parallel – most flow with least amount of resistance

Resistance of Vessels or Tubes

- The resistance to flow of a fluid, like blood, through a vessel is critical:
  - too little and the fluid flows easily;
  - too much and the fluid doesn't flow.

Vessels in series.
This sort of arrangement has the least amount of flow
and the most resistance to flow.
The total resistance to flow in this model is
equal to the sums of the individual resistances:

$$R_T = R_1 + R_2 + R_3 + \ldots + R_n$$

5 RU   **20 RU**   **40 RU**   **80 RU**   **120 RU**

**Vessels in parallel.
This sort of arrangement has the
least resistance
and the most flow.
This is the layout in the circulatory
system of the human body.
The total resistance to flow in this
model is equal to the –
be careful, here -- reciprocal of the
sums of the reciprocals
(conductances) of the individual
resistances:**

$$R_T = (\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \ldots + \frac{1}{R_n})^{-1}$$

In other words, the
conductances are
calculated FIRST.

5 RU
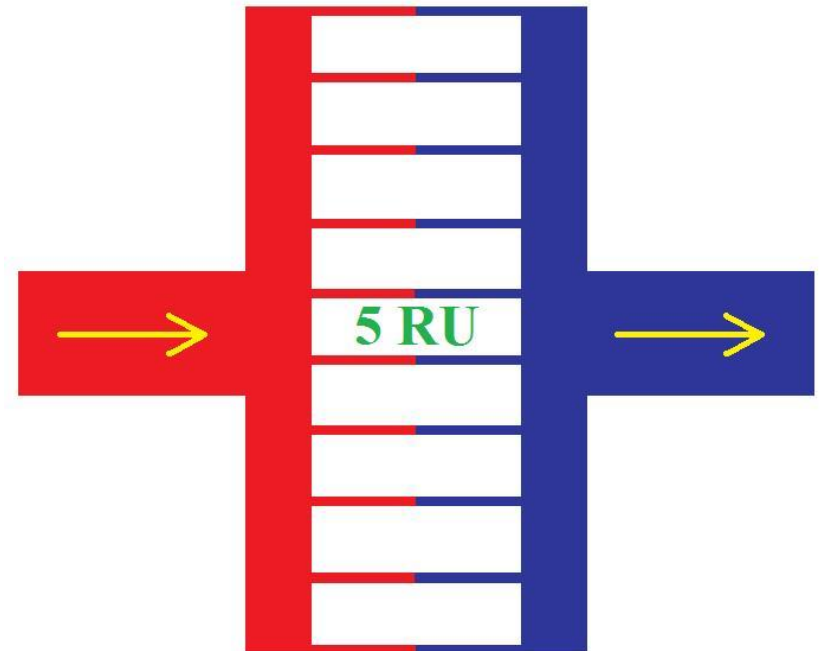
- Example: Determine the resistance to flow for a system in series and in parallel if the following resistances are given: R_1 = 5 resistance units, R_2 = 10 resistance units, R_3 = 15 resistance units and R_4 = 20 resistance units.

- Solution:

- In series: add 'em up! 50 resistance units

In parallel: take the reciprocal of the sum of the conductances:

$$(\frac{1}{5} + \frac{1}{10} + \frac{1}{15} + \frac{1}{20})^{-1} = (0.2 + 0.1 + 0.067 + 0.05)^{-1} = 2.4\,units$$

This means that at the same pressure gradients,
the flow in series is much less and the flow in parallel is much more.

With substitution and re-writing, Poisueille's Law becomes:

$$\Delta P = Q\ R$$

This equation is useful in thinking about fluid pressures, including blood pressure regulation.
The table, below, summarizes the effects of altering one or two parts of Poisueille's Equation and their effects on fluid pressure in a vessel or tube:

Flow	Resistance	→	Pressure Gradient
Q	R	→	ΔP
Up	No change	→	Up
No change	Up	→	Up
Up	Down	→	No change
Down	Up	→	No change
Down	No change	→	Down
No change	Down	→	Down
Up	Up	→	Up
Down	Down	→	Down

The Mole

- When you go to the bakery to buy 12 rolls, you are also buying a dozen rolls.
- When you go to the feed store and buy a ton of corn, you are also buying 2000 pounds of corn.
- When you buy a lot that measures about 44,000 square feet, you are also buying an acre.
- All of these are just another way of saying the same thing.

- Chemists and biologists do the same thing: when speaking about the number of particles contained in a sample of element or compound with its atomic or molecular mass expressed in grams, they are also speaking about a mole of that substance.

- For example, if you look at sulfur on the periodic table, you see that it has a mass of 32.1.

- Since we've discussed the mole, we can now put units on it that are better than atomic mass units: grams per mol (g/mol).

- That means that one mole of sulfur has a mass of 32.1 grams.

- If we were to look at chlorine on the periodic table, we now know that it has a mass of 35.5 grams per mole.

- That means that if we have 35.5 grams of chlorine, we have one mole of chlorine -- just another way of saying something in another way.

Let's look at some numerical examples.

Example 1:

Determine the mass in grams of 1.35 mol S.
Solution:

$$(1.35\,mol\,S)\frac{(32.1\,g\,S)}{1\,mol\,S} = 43.34\,g\,S$$

Example 2:
Determine the mass in grams of 1.5 mol Cu.
Solution:

$$(1.5\,mol\,Cu)\frac{(63.55\,g\,Cu)}{1\,mol\,Cu} = 95.33\,g\,Cu$$

Example 3:
Determine the mass in grams of 0.5 mol Ca.
Solution:

$$(0.5\,mol\,Ca)\frac{(40.1\,g\,Ca)}{1\,mol\,Ca} = 20.05\,g\,Ca$$

Example 4:

Determine the mass in grams of 0.10 mol HCl.

Solution: This one is slightly different: it involves a compound instead of just an element. Go to the periodic table and look up the atomic masses of H and Cl. Add them up (1 + 35.5 = 36.5 g/mol). NOW it's just like the other problems:

$$(0.1\,mol\,HCl)\frac{(36.5\,g\,HCl)}{1\,mol\,HCl} = 3.65\,g\,HCl$$

Example 5:

Determine the mass in grams of 0.4 mol acetic acid ($HC_2H_3O_2$).

Solution: Do just like the previous example. Go to the periodic table and look up the atomic masses for H, C and O (1, 12 and 16 g/mol). Multiply the mass of H by 4, C by 2 and O by 2 – there are 4-H, 2-C and 2-O. Add the totals up (4 + 24 + 32 = 60 g/mol). Do it just like the previous problem:

$$(0.4\,mol\,HC_2H_3O_2)\left(\frac{60\,g\,acetic\,acid}{1\,mol\,acetic\,acid}\right) = 24\,g\,acetic\,acid$$

Chemical Reactions and Molarity

By definition, molarity (M) is the number of moles of solute (the substance[s] in lesser amounts) per liter of solution.

Example 1:

36.5 g HCl are dissolved in enough water to make 1 liter of solution.

What is the molarity of the solution?

$$M = \frac{mol\ HCl}{L} = \frac{(36.5\,g\,HCl)\dfrac{1\,mol\,HCl}{36.5\,g\,HCl}}{1L} = 1M$$

Example 2: 18.25 g HCl are dissolved in
enough water to make 250 mL of solution.
What is the molarity of the solution?
Solution:

$$M = \frac{mol\,HCl}{L} = \frac{(18.25\,g\,HCl)\dfrac{1\,mol\,HCl}{36.5\,g\,HCl}}{(250\,mL)\dfrac{1\,L}{1000\,mL}} = \frac{0.5\,mol}{0.25\,L} = 2\,M$$
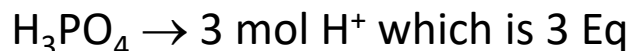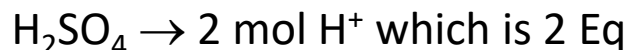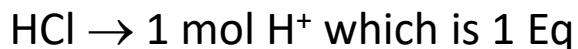
Normality

In reactions, thus far, we've looked at grams and moles. Sometimes, though, we need to express units in terms of protons, hydroxide ions or charges.

When we do this we use a unit called EQUIVALENTS.

By definition, an equivalent (Eq) of base is that amount of base that contributes or provides 1 mol of hydroxide ion (OH^-):

$NaOH \rightarrow$ 1 mol OH^- which is 1 Eq

$Ba(OH)_2 \rightarrow$ 2 mol OH^- which is 2 Eq

$Al(OH)_3 \rightarrow$ 3 mol OH^- which is 3 Eq

By definition, an equivalent (Eq) of acid is that amount of acid that contributes or provides 1 mol of hydronium (H_3O^+) or hydrogen (H^+) ion:

$HCl \rightarrow$ 1 mol H^+ which is 1 Eq

$H_2SO_4 \rightarrow$ 2 mol H^+ which is 2 Eq

$H_3PO_4 \rightarrow$ 3 mol H^+ which is 3 Eq

By definition, an equivalent (Eq) of salt is that amount of salt that will contribute or provide 1 mol of positive (OR negative) charges when dissolved or dissociated:

$KCl \rightarrow K^+ + Cl^-$ which gives 1 Eq

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$ which gives 2 Eq

$AlCl_3 \rightarrow Al^{3+} + 3Cl^-$ which gives 3 Eq

Remember that we can calculate Molecular Weight by dividing the mass of X mol of substance (in grams) by the number of mols ("X") to get molecular weight in g/mol.
Using equivalents, we can calculate EQUIVALENT WEIGHT, as well:
Let's calculate the equivalent weight of $AlCl_3$ -- this has a molecular weight of 133.5 g/mol

$$\frac{133.5\,g}{mol} * \frac{1\,mol\,AlCl_3}{3\,Eq} = \frac{44.5\,g}{Eq}$$

Notice that we used the total number of positive charges (OR negative charges: 3 * 1 = 3) for our equivalents.

Let's calculate the equivalent weight of sulfuric acid:

$$\frac{98\,g\,H_2SO_4}{mol} * \frac{1\,mol\,H_2SO_4}{2\,Eq} = \frac{49\,g}{Eq}$$

Let's calculate the equivalent weight of LiCl:

$$\frac{42.5\,g\,LiCl}{mol} * \frac{1\,mol\,LiCl}{1\,Eq} = \frac{42.5\,g}{Eq}$$

Let's calculate the equivalent weight (Eq Wt) of $Mg(OH)_2$

$$\frac{58.3\,g\,Mg(OH)_2}{mol} * \frac{1\,mol\,Mg(OH)_2}{2\,Eq} = \frac{29.15\,g}{Eq}$$

Clinically, the unit milli-equivalent is used (mEq) when measuring serum concentrations of electrolytes, e.g., sodium and potassium ions.

When we first learned about the mole, we extended our knowledge by studying a concentration term called molarity (M = Molar). This is a unit that expresses how many mols of a substance are dissolved in one liter of solution.
We can use equivalents to do a similar concentration term: normality (N = Normal). Normality is defined as the number of equivalents of a substance that is dissolved in one liter of solution (Eq/L).
Let's begin by calculating the normality of a solution that has 40 g NaOH dissolved in 1 L of water:

$$(40\ g\ NaOH) * \frac{1\ mol}{40\ g\ NaOH} * \frac{1\ Eq}{1\ mol} * \frac{1}{1\ liter} = 1\ N = 1\frac{Eq}{L}$$

Notice how the units cancel out.
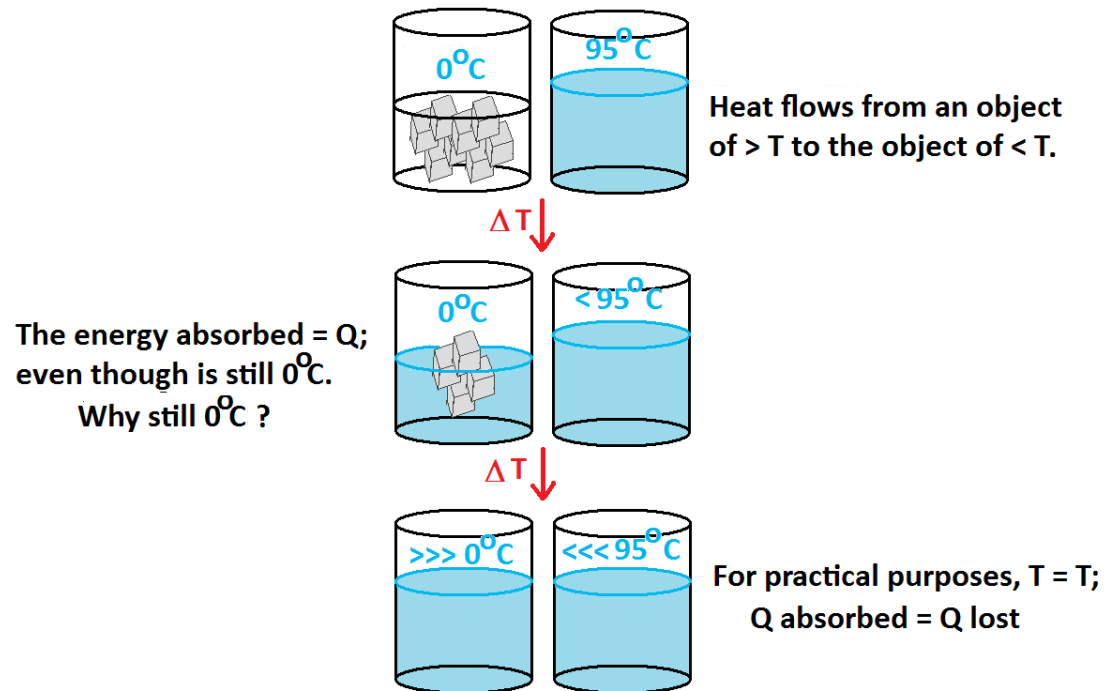Let's calculate the normality of a solution of 29.15 g $Mg(OH)_2$ that is dissolved in 500 mL of water.

$$(29.15\ g\ Mg(OH)_2 * \frac{1\ mol}{58.3\ g\ Mg(OH)_2} * \frac{2\ Eq}{1\ mol} * \frac{1}{0.5\ L} = 2\ N = 2\frac{Eq}{L}$$

Elements of Thermal Chemistry

- Thermodynamics is the study of the change of energy from one form to another.
- Energy is the ability to do work.
- Work is the change in kinetic energy of the object.
- Kinetic energy is the energy of motion.

Heat

- Heat flows from an object of hotter temperature to an object of cooler temperature. The absorbed energy we represent by "Q".

0°C   95°C

Heat flows from an object of > T to the object of < T.

The energy absorbed = Q; even though is still 0°C. Why still 0°C ?

0°C   < 95°C

ΔT

>>> 0°C   <<< 95°C

For practical purposes, T = T; Q absorbed = Q lost

When talking about heat, it would be helpful to have some terms defined that will allow us to quantitatively determine just how much heat has been transferred between objects or between systems.

The first term for discussion is heat capacity (C). Heat capacity is defined as the amount of energy transferred per change in absolute temperature or:

$$C = \frac{Q}{\Delta T}$$

C is in units of Joules per mole per Kelvin.

- This term (heat capacity) is all fine and dandy -- it doesn't, though, give us a measure in terms of mass and/or amount.
- To that end we use the term specific heat capacity (c).
- Specific heat capacity is equal to the heat capacity divided by the molecular weight and is in units of joules per Kelvin per gram.
- Joules aren't as widely known as are calories.
- One calorie is equal to 4.184 Joules.
- One calorie (cal) is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1° C -- a little less than a perfect definition, yet close enough for our purposes.
- One Calorie (Cal or kcal) is 1000 calories or 1 kilocalorie (kcal).
- The kcal is the unit we use for "food calories".

How could we use this information to determine the amount of heat, Q, that has been transferred between two objects? We use a simple equation:

$$Q = mc\Delta T$$

Where Q = the amount of heat in calories or Joules,
m = the mass in grams,
c = the specific heat in joules per Kelvin per gram OR calories per Kelvin per gram, and
ΔT = the change in temperature in Kelvins (also in °C, since the difference is numerically equivalent -- remember, though, to keep your units straight).

The table, below, summarizes the
specific heat capacity of some representative substances:

Substance	Specific Heat Capacity (J/K/g)
Water	4.169
Al	0.898
Diamond	0.518
Fe	0.443
Pb	0.130
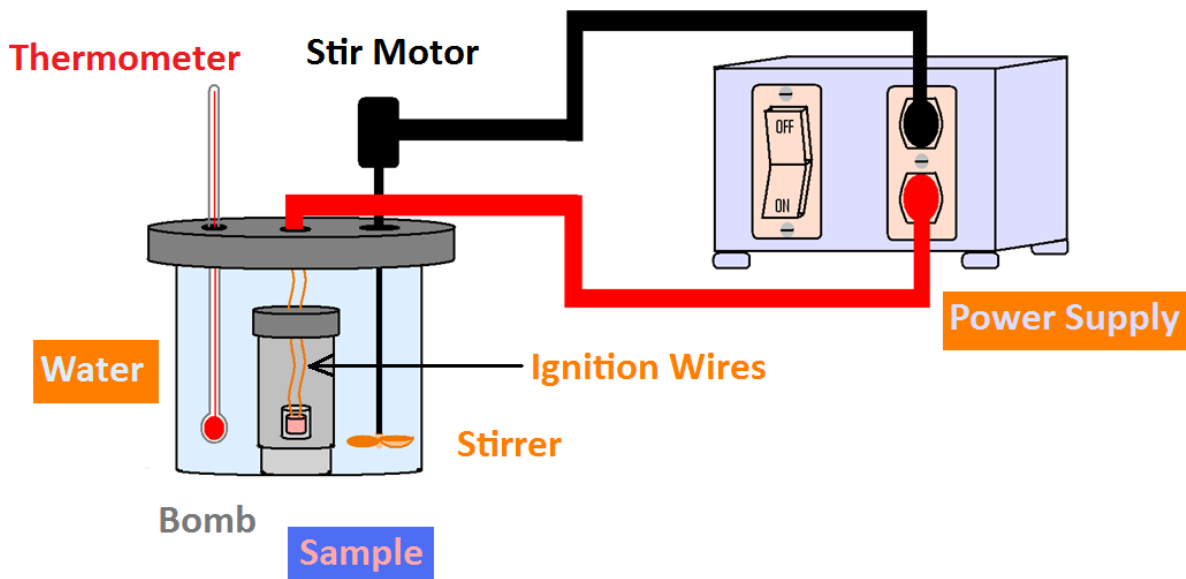
- Specific heat capacities are measured in a "bomb calorimeter":
- The way this works is that sample is placed in the sample holder in the "bomb" and two wires are set in the substance through the water-tight lid.
- The lid is sealed, the wires are attached to a power supply, water is poured around the bomb and the stirrer rotates to mix the water.
- When the temperature of the water is equilibrated, the power is turned on, the sample is ignited and the temperature increase from the sample combustion is measured by an increased water temperature.

Flow of Heat

- When discussing heat, it's important to actually comprehend how heat flows.

- Among other reasons to comprehend heat flows, we can eventually fold a discussion on the flow of heat into a discussion of how gases traverse membranes in the body to provide oxygen to the cells and CO_2 transport out of the body.

- To begin the discussion, let's examine Fick's Law.

- Fick's Law says that **the rate of diffusion of heat per unit area through a cylinder in a direction perpendicular to the area is proportional to the heat gradient through the cylinder in that direction**

90
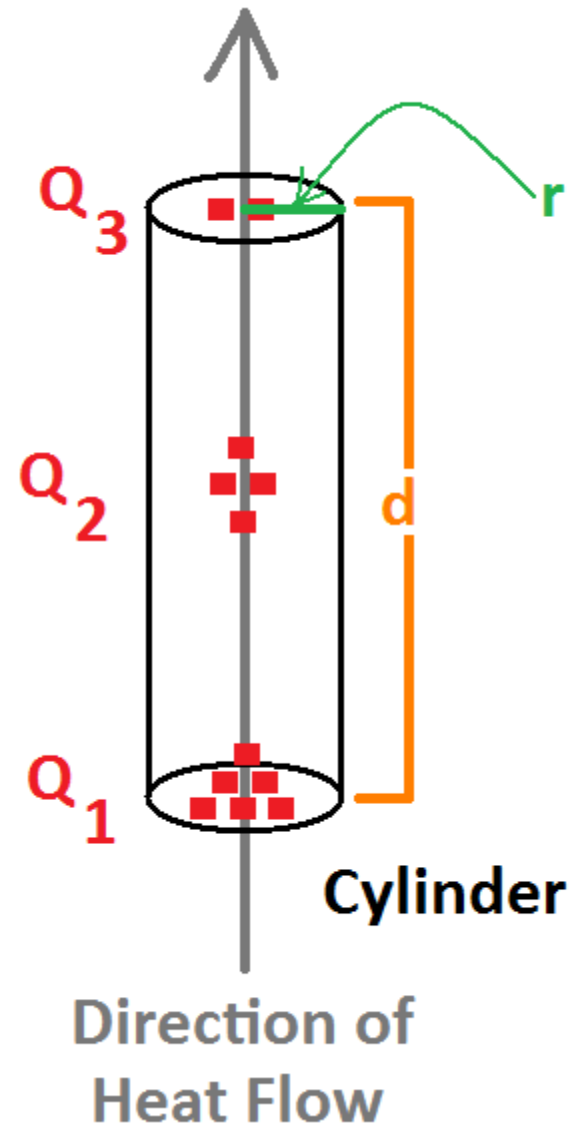
The heat gradient is defined as:

$$\frac{\Delta Q}{volume \times d} \Leftrightarrow \frac{H}{d}$$

And the area of the face of the cylinder is $\underline{\pi\, r^2}$.
If we combine these two equations with one more:

$$\frac{Q}{t} = Flow\ of\ heat$$

We get the following:

$$\frac{Q}{t} = D\, A\, \frac{H}{d}$$

Where Q is the amount of heat,
t is time,
D is a constant,
A = $\pi\, r^2$,
H is the heat per unit volume
d is distance or thickness of the cylinder.

This cylinder for heat diffusion may be likened to a semipermeable membrane, therefore, the heat flow is analogous to diffusion of a solute. The rate of diffusion of a solute per unit area in a direction perpendicular to the area is proportional to the concentration gradient in that direction. By substituting mass (m) for amount of heat (Q) and concentration gradient (Δ [C]) for H, then, the mass of solute diffusing per unit time may be expressed as below:

$$\frac{m}{t} = D\, A\, \frac{\Delta[\,C\,]}{d}$$

Again, "m" is mass diffusing,
"t" is the time in which diffusion is occurring,
and Δ [C] is the concentration gradient.
The remainder of the terms are as defined before.

Diffusion is analagous to the flow of gas through semipermeable membranes:

$$\frac{\Delta d}{\Delta t} \propto \frac{A \Delta P}{d}$$

$$or$$

$$\frac{\Delta d}{\Delta t} = D \frac{A \Delta P}{d}$$

**Where Δ d is the difference in thickness of the membrane,
Δ t is the time it takes to cross the membrane (time difference) and
Δ P is the pressure gradient or pressure difference across the membrane.**

- This last equation tells us that the speed of a gas through a semi-permeable membrane is directly proportional to the cross sectional area of that membrane and the pressure gradient ($P_1 - P_2 = \Delta P$) between the two sides of the membrane.

- It also tells us that flow is inversely proportional to the thickness (d) of the membrane.

- This is illustrated at right where a semi-permeable membrane is placed in a tube with gas flowing in one direction through the membrane.

P_2 Gas Flow

Semi-permeable Membrane

r

d

P_1 Gas Flow
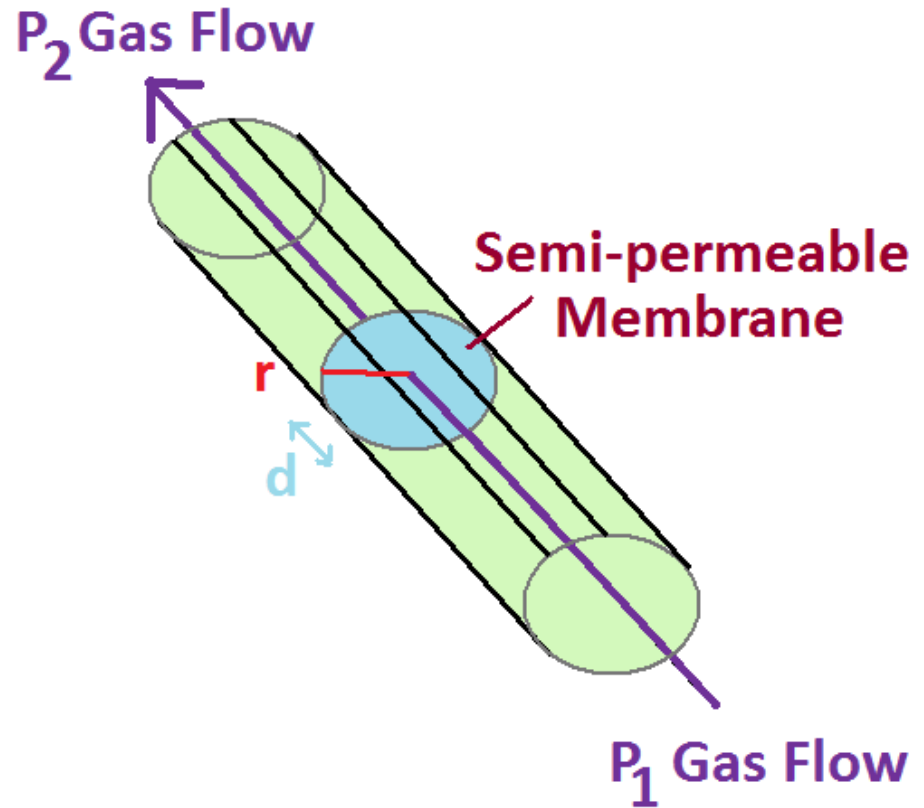
From our previous equation, note that that the distance difference per time difference is simply velocity. We can re-write the equation, now, as follows:

$$\frac{\Delta d}{\Delta t} = v = D\frac{A\,\Delta P}{d}$$

Where the only new variable is "v": velocity (or speed). We may, thus, write the equation as follows:

$$v = D\frac{A\,\Delta P}{d}$$

If d reduces by half, v increases by two-fold. If d increases its thickness by 3 fold, then v reduces to one third its original value. Hence, the thicker the membrane, the slower the diffusion of the gas. Can we apply this in a clinical perspective? Yes, we can.

Normal Gas Exchange Across Alveolar Membranes
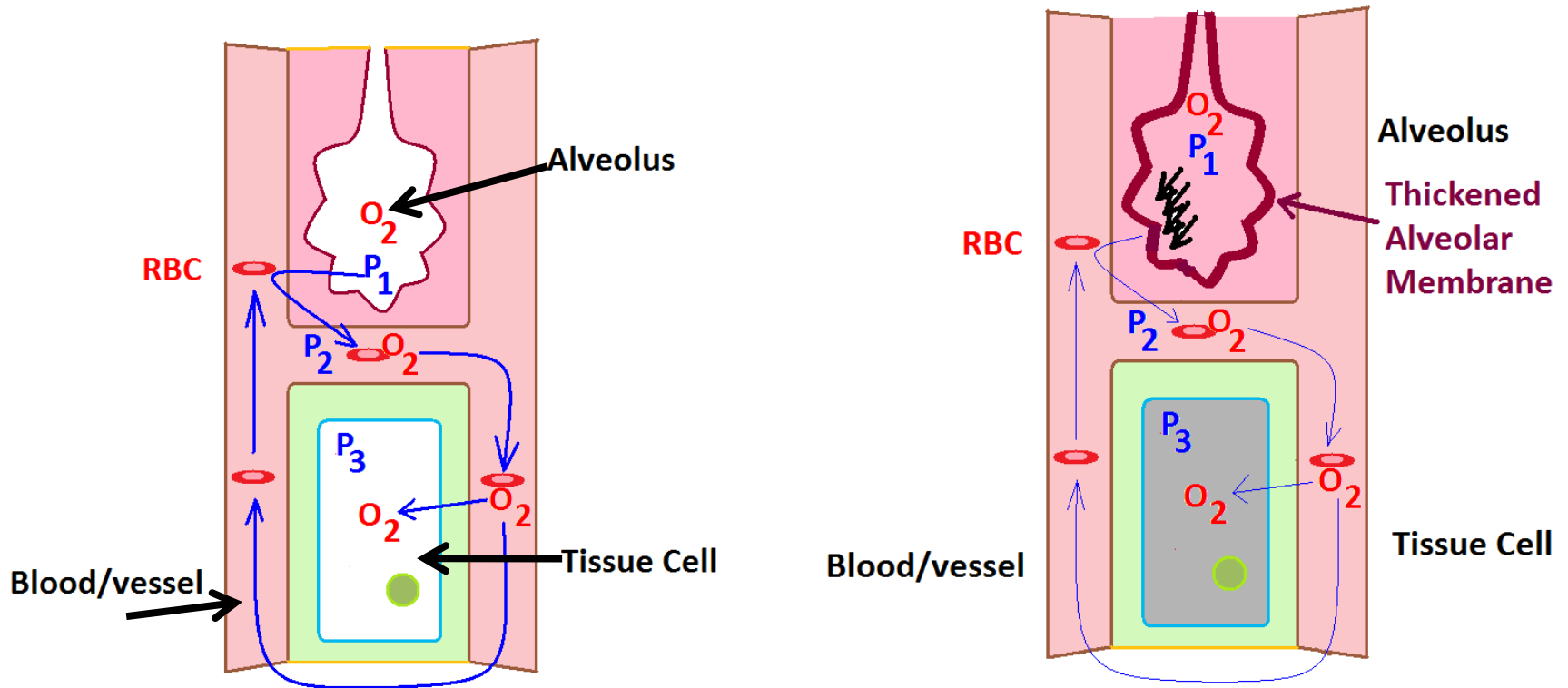
Normal Gas Flow, left; Reduced Gas Flow, right.

- If, though, one develops pulmonary edema through heart failure, chemical inhalation, mountain sickness or pulmonary frostbite, then the alveolar membranes thicken as in the figure, right, that makes it very difficult to get gases across the membranes and cause the cells to begin to consider the possibility of their death without treatment as long as the body can function (have you seen "Vertical Limit"?) .

- **REFERENCE**: MacDonald, S. and Burns, D. : Physics for Life and Health Sciences. (Addison-Wesley: London) © 1975.

Gas Laws

- The gas laws give us arithmetic relationships which tell us about the gases when
  - they are mixed (Dalton's Law),
  - the temperature is altered (Charles' Law), when
  - the pressure is changed (Boyle's Law),
  - they diffuse (Graham's Law) and
  - they are under pressure over a liquid (Henry's Law).

- Before we get into the specific laws, let's remember that a standard atmosphere of pressure is 1 atmosphere.
- This is also equal to
  - 760 mm Hg,
  - 29.92 inches Hg and
  - 14.7 psi.
- This standard atmosphere is the pressure needed to support a 760 mm column of mercury in a barometer tube.
- Pressure, remember, is the force exerted upon a substance per unit area.

- Example: Express 1600 psi as
  - a) atm,
  - b) torr,
  - c) mm Hg and
  - d) inches Hg.
- Solution: 1 Torr = 1 mm Hg. The Torr was named for the developer of the barometer, Torricelli.

$$(1600\,psi)*\frac{1\,atm}{14.7\,psi}=108.8\,atm$$

$$108.8\,atm*\frac{760\,torr}{1\,atm}=82721\,torr \Leftrightarrow 82721\,mm\,Hg$$

$$(82721\,mm\,Hg)*\frac{1\,inch}{25.4\,mm\,Hg}=256.7\,inches\,Hg$$

Boyle's Law

- The first gas law we'll examine is Boyle's Law.
- Boyle's Law says that the product of the pressure (P_1) and volume (V_1) of a gas under a first set of conditions is equal to the product of the pressure (P_2) and volume (V_2) it occupies under a second set of conditions:

$$P_1 V_1 = P_2 V_2$$

In order for Boyle's Law to work,
the temperature must remain a constant.

- **When the pressure is increased on a gas in a cylinder fitted with a frictionless piston, the volume is proportionately reduced.**
- **The converse is equally as true.**
- **Note that if P_1 = 1 atm and V_1 = 1 whatever volume label that the product is 1.**
- **The same holds true for a P_2 of 2 atm and a V_2 of 0.5 whatever volume label.**
- **Even in this day and age of new math, 1 still equals 1.**
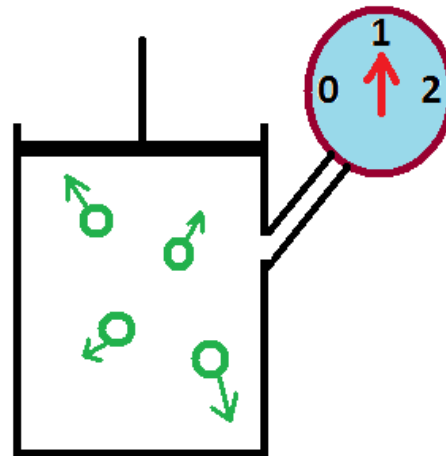
P_1 = 1 atm
V_1 = 1 whatever
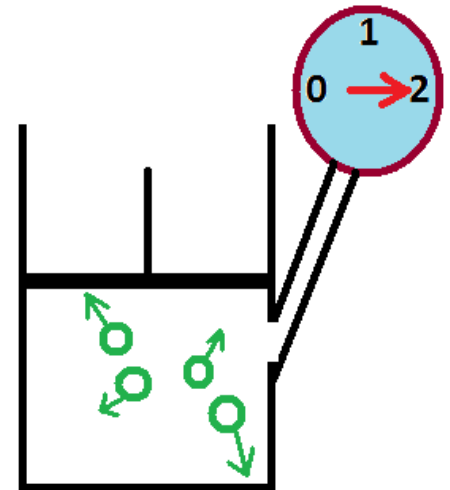
P = 2 atm
V = 0.5 whatever

1 x 1 = 2 x 0.5

- Boyle's Law is applicable to breathing.
- Note that just before inspiration that the atmospheric, intrapleural (in between the two membranes around the lungs) and intrapulmonic (in the lungs) pressures are all equal: 760 mm Hg.
- During inspiration, when the diaphragm contracts, the intrapleural and intrapulmonic pressures decrease (a vacuum has been created) and the air rushes in to fill the space.
- Once our lungs are full, and the diaphragm relaxes, the intrapleural and intrapulmonic pressures increase to the point to of being greater than atmospheric pressure and the air is forced out of the lungs.

760 mm Hg

758

756

Inspiration

760 mm Hg

763

Expiration
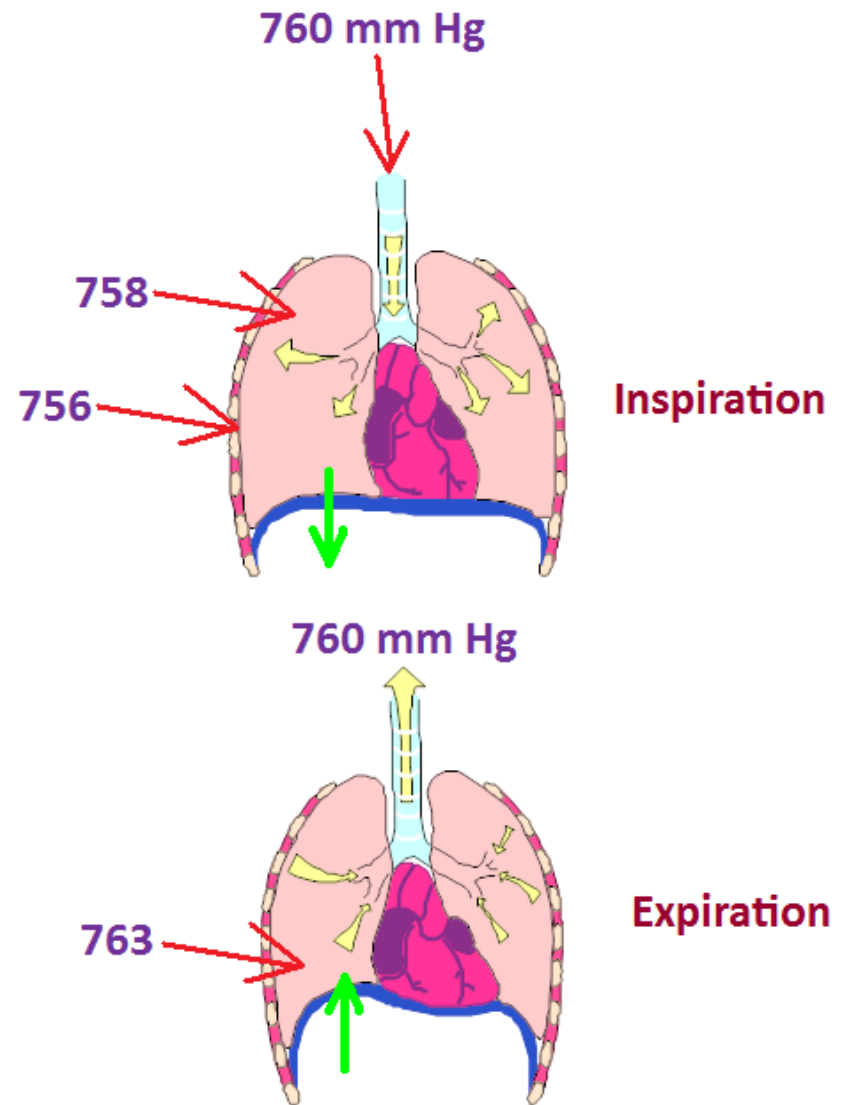
Charles' Law

Charles' Law says that the volume of a gas is
directly proportional to the absolute temperature of that gas
while the pressure is held constant.
You've all seen this when you watch a hot air balloon
fill with air.
Arithmetically, Charles' Law may be expressed in a
manner similar to that of Boyle's Law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

**Where the first volume of a gas divided by a first absolute temperature
of that gas is equal to the second volume of the gas
divided by its second absolute temperature.**

- Note that the pressure never changes when a gas in a cylinder kept at constant pressure is heated and its volume expands.
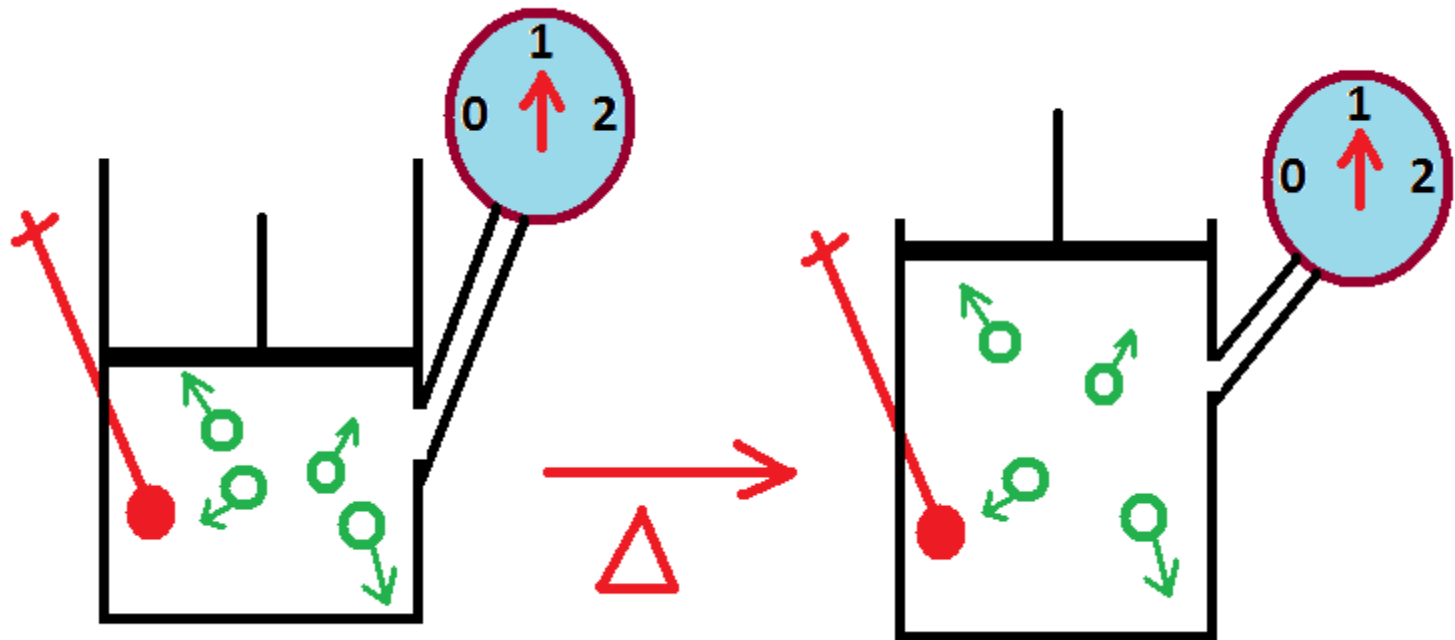
- Charles' Law also is applicable to breathing.
- Given that the temperature of the air outside the body is generally cooler than the air inside the body, this pretty much makes sense,
- i.e., as we inhale cooler air, when it heats up, it takes up more space causing our lungs to fill with the heated air and increase their volumes from completely exhaled to completely inspired.

298 K

304 K

310 K
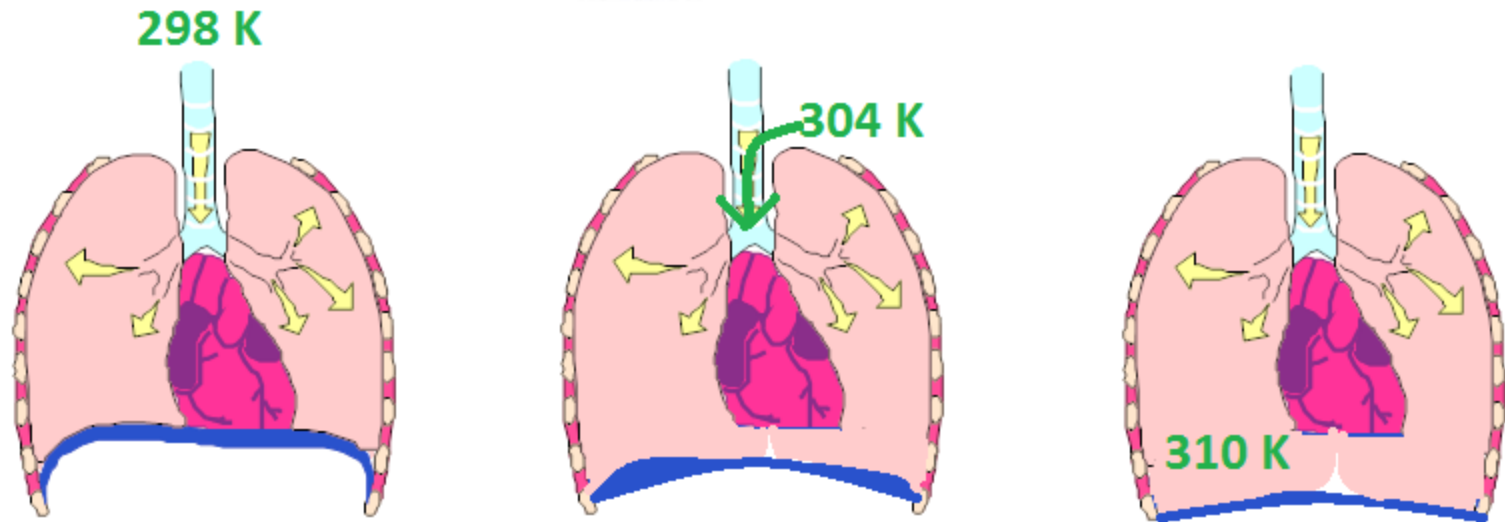
Gay-Lussac's Law

- If volume is held to a constant,
- Then pressure and absolute temperature vary directly

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

The Combined Gas Law

The combined gas law is just that: combined.
It is Boyle's, Charles' and Gay-Lussac's Laws combined:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Remember, too, that the temperature
MUST be the absolute temperature.
Note the Boyle's part and the Charles' part
and the Gay-Lussac's part of this law.

Dalton's Law

- Dalton's Law is defined as "the pressure of a mixture of gases is equal to the sum of the pressure of each individual gas (partial pressure)", i.e., $P_T = P_1 + P_2 + P_3 + P_4 + \ldots + P_n$,
  - where P_T is the total pressure of the gaseous mixture,
  - P_1 is the partial pressure of gas 1,
  - P_2 is the partial pressure of gas 2,
  - P_3 is the partial pressure of gas 3, ad nauseum.

- Example: A sample of air is collected at a pressure of 745 mm Hg. The partial pressure of nitrogen (pN_2) is 600 mm Hg and the pO_2 is 50 mm Hg. If water vapor is the only other gas present, what is the pH_2O vapor?

- $P_T = P_1 + P_2 + P_3$;
  - P_T is 745 mm Hg,
  - P_1 is 600 mm Hg,
  - P_2 is 50 mm Hg and
  - P_3 is to be determined:

- $745 = (600 + 50) + P_3$

- $P_3 = 745 - 650 = 95$ mm Hg $= pH_2O$

Graham's Law

Graham's Law says that the rate of diffusion or effusion of 2 gases is inversely proportional to the square root of the molecular masses of the gases:

$$\frac{Rate\ of\ A}{Rate\ of\ B} = \sqrt{\frac{MW_B}{MW_A}}$$

Effusion is defined as gas
"leaking" out of a container through a small hole.
Diffusion is defined as gases
mixing on their own when brought together.

Example: Compare the rate of diffusion of
molecular chlorine with molecular hydrogen:

$$\frac{Rate\ of\ H_2}{Rate\ of\ Cl_2} = \sqrt{\frac{MW_{Cl_2}}{MW_{H_2}}} = \sqrt{\frac{71}{2}} \approx 6$$

Therefore H_2 diffuses 6 times faster than does Cl_2.

Example: Compare the rate of diffusion of
molecular oxygen with molecular iodine:

$$\frac{Rate\ of\ O_2}{Rate\ of\ I_2} = \sqrt{\frac{MW_{I_2}}{MW_{O_2}}} = \sqrt{\frac{254}{32}} \approx 3$$

O_2 diffuses 3 times faster than iodine.

Example: Compare the rate of diffusion of molecular nitrogen with molecular oxygen:

$$\frac{Rate\ of\ N_2}{Rate\ of\ O_2} = \sqrt{\frac{MW_{O_2}}{MW_{N_2}}} = \sqrt{\frac{32}{28}} \approx 1.07$$

Nitrogen and oxygen diffuse at about the same rate.

LaPlace's Law

- LaPlace's Law says that a pressure gradient across a closed ELASTIC membrane or liquid film is related to the membrane/film tension -- sort of makes you think of Ficke's Law, doesn't it?!

- The closed sphere shows the pressure inside the balloon (P_i) and the pressure outside the balloon (P_o).
- The difference between the two pressures (P_i - P_o) is the pressure gradient (ΔP).
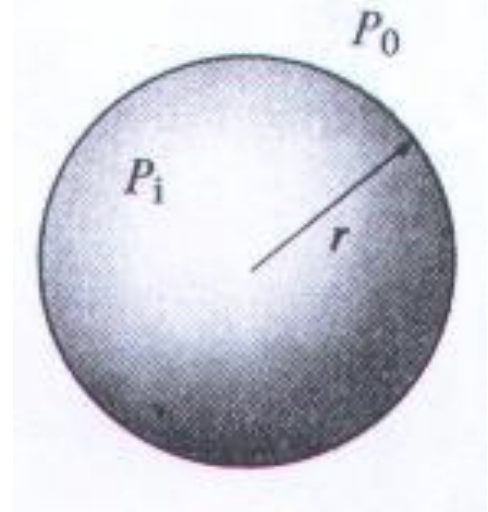
- Why would we even want to study something like LaPlace's Law?

- Let's answer that by asking 2 questions:

- The first question is: you have two balloons inflated at different pressures, joined together by a piece of tubing that has a pinch clamp between the two. Which way will the air move when the pinch clamp is opened? From the largest one into the smallest? From the smallest into the largest?

- The second question is physiologically oriented: why is it that we can breathe without our alveoli either collapsing or exploding?

- LaPlace's Law answers these questions. Let's start examining this law.

- When a sphere is placed in front of a screen and a light is shown onto the sphere in such a manner that the shadow on the screen is a circle, the circular shadow is the projected area of the sphere and the first force (F_1) we want to examine is due to the wall tension. This is arithmetically equal to:
- $2 \pi r \gamma = F_1$
- where γ = the wall tension.
- This force is represented by the arrows pointing anti-parallel to the direction of the light beam.

- The second force (F_2) is the force due to the pressure gradient (or pressure differential, if you prefer). This is arithmetically equal to:

- $(P_i - P_o) \pi r^2 = F_2 = \Delta P \pi r^2$

- This force is represented by the arrows pointing away from the body of the sphere.
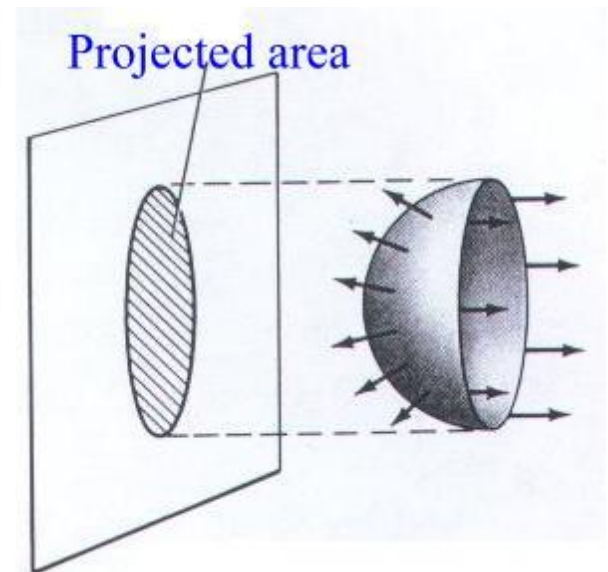
Projected area

In physics, equal but opposite forces occur in nature,
hence the two forces must be equal to each other:
$$F_1 = F_2,$$
or
$$2 \pi r \gamma = \Delta P \pi r^2$$
Since πr is common to both sides of the equation, the equations reduce to:
$$2 \gamma = \Delta P \, r,$$
where r = the radius of the projected circle.
This equation is the equation for a spherical membrane with one (1) surface.
A baseball seems to be the most adequate example of this sort of phenomenon.

Soap bubbles have 2 surfaces
(one on the outside and one on the inside),
hence, for a soap bubble, the equation is:
$$4 \gamma = \Delta P \, r$$

Arithmetic Example #1:
A balloon is blown up to 12" in diameter. The pressure inside the balloon is 5 atmospheres (73.5 psi) and the pressure outside the balloon is 1 atmosphere (14.7 psi). What is the wall tension of the balloon?

This is a sphere question, hence, we use:
$2 \gamma = \Delta P r$.
With rearranging:
$\gamma = (\Delta P r)/2$
and
$\gamma = (73.5-14.7) * 3 = 176.4$ psi

Arithmetic Example #2

A balloon is blown up to 18" in diameter. The pressure inside the balloon is 8 atmospheres (117.6 psi). The pressure outside the balloon is 1 atmosphere (14.7 psi). What is the wall tension in the balloon?

This is a sphere question, hence:

$2 \gamma = \Delta P r$.

With rearranging:

$\gamma = (\Delta P r)/2$

$\gamma = (117.6 - 14.7) * 4.5 = 463.05$ psi

NOTE: With increasing radius comes increasing wall tension.

Arithmetic Example #3
A balloon is blown up to 12 inches in diameter. The wall tension is 240 psi.
What is the pressure gradient?
This is another sphere question, hence, we use
$2 \gamma = \Delta P\, r$,
and we need to solve for ΔP:

$2 \gamma /r = \Delta P = \{(2) * (240)\}/6 = 80$ psi

Arithmetic Example #4
A balloon is blown up to 16 inches in diameter. The wall tension is 120 psi.
What is the pressure gradient?
This is yet another sphere question, hence, we use
$2 \gamma = \Delta P r$,
and we need to solve for ΔP:

$2 \gamma / r = \Delta P = \{(2) * (120)\}/8 = 30$ psi

NOTE: a greater pressure gradient is required to maintain a smaller sphere.

- This answers our first question.

- Have you figured it out?

- The air will flow FROM the SMALLER balloon INTO the larger balloon.

- Now to get a handle on our second question.

Application of LaPlace's Law to Lungs and Breathing

- Observe an alveolus with internal pressure, P_i, outer pressure, P_o, and radius, r.

- The biggest question we need an answer to is: does an alveolus fit the equation for a sphere, i.e., $2\gamma = \Delta P\, r$?

Terminal bronchiole

P_i

P_o

Alveolus
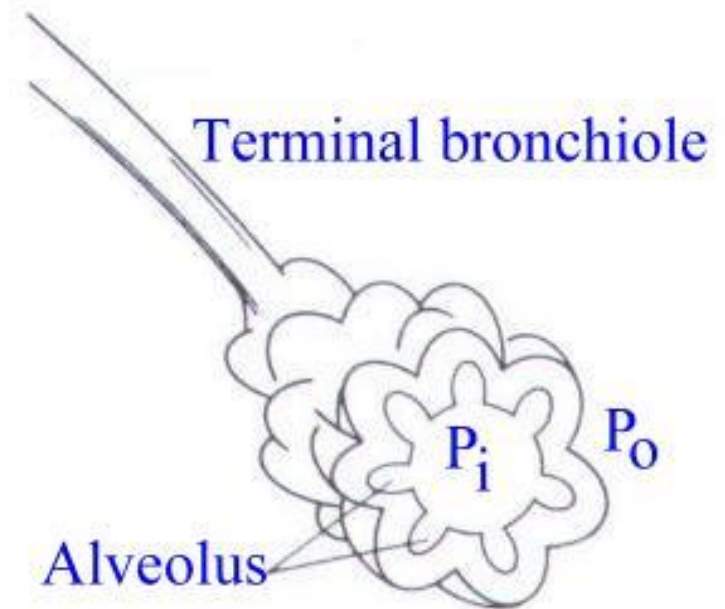
There are some problems with this, see Table below:

At expiration	At inspiration
P_o increases and r decreases	P_o decreases and r increases
At expiration, the pressure gradient goes down	At inspiration, the pressure gradient goes up

Since 2 γ = Δ P r, it suggests that at expiration,
if the wall tension is constant, the alveoli will COLLAPSE and,
at inspiration, if the wall tension is constant,
the alveoli will RUPTURE.
Why doesn't this happen in our lungs?

•The answer to this last question is because of something called surfactant.

•Surfactant, as we've discussed before, destroys the surface tension of a liquid -- in this case an aqueous based fluid.

•This allows O_2 and CO_2 to freely diffuse across the alveolar membranes for uptake and exhaust, respectively.

•Surfactant changes the wall tension to MAINTAIN the relationship between the two forces,

    - i.e., to maintain $2\gamma = \Delta$ Pr, by making the alveolar walls more elastic.

•This makes the alveoli unable to rupture or collapse during eupnea and the alveolar patency is maintained with/for gas exchange.

In short, **with surfactant**, as the wall tension increases,
so does the pressure gradient.
Without surfactant, the alveoli are collapsed until they reach a pressure
gradient threshold point, at which point the wall tension increases until the
alveoli rupture.
Note that $2\gamma = \Delta P\, r$ may be re-written as:
$$\gamma = (\Delta P)\,(r/2) + 0$$
which is in the form of a straight line. **WITH surfactant**, this relationship is
maintained completely. **WITHOUT surfactant**, this relationship is conditional.
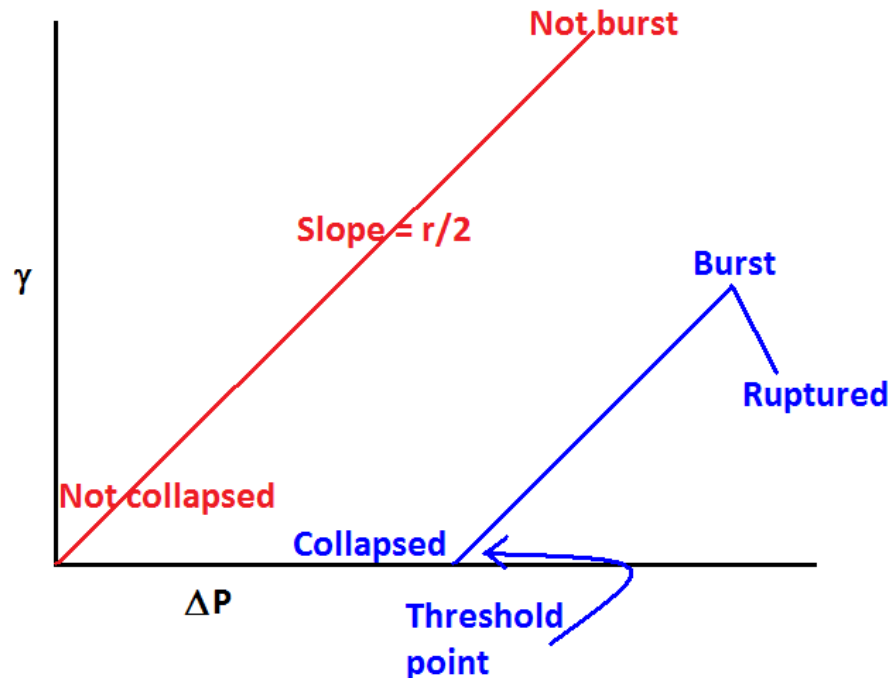
Arithmetic Example

At exhalation, the radius of a "standard" alveolus is 0.002 inches. The pressure in the alveolus is -0.058 psi and the pressure outside the alveolus is -0.077 psi. What is the wall tension of this alveolus? Compare your answer to that of an alveolus without surfactant, $4.42*10^{-5}$ psi.

$\gamma = (\triangle\,P)\,(r/2) = (-0.058 - (-0.077)) * (0.002/2) = 1.9*10^{-5}$ psi WITH surfactant.

The difference between the two conditions is:
$\{(1.9*10^{-5})/(4.42*10^{-5})\}*100 = 42.99\%$

Hence, there is a 57% DEcrease in the wall tension due to the presence of surfactant.

Gases are Soluble in Water

**As mentioned shortly,
Henry's Law says that the greater the pressure of a gas over a solution,
the greater the amount of gas dissolved in the solution.
The table, below summarizes the solubilities of 3 gases in water:**

Gas	Solubility per 100 g water at 20° C
O_2	4.3 mg
CO_2	169 mg
NH_3	10.6 **grams**

**effervescence -- loss of gas
bubbles from the liquid**

SODY POP → SODY POP

**pressurized
with CO$_2$**   **depressurized
with loss of CO$_2$**
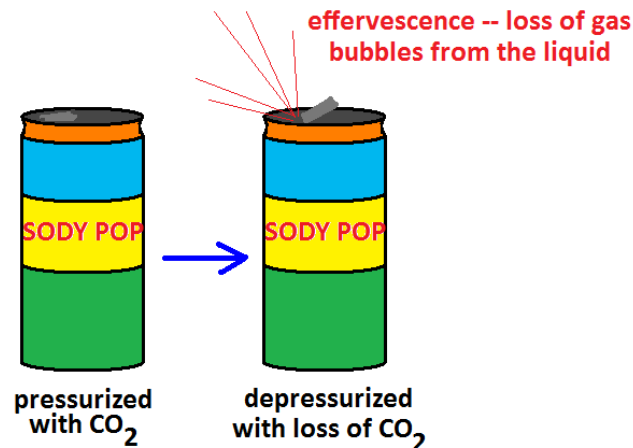
- Henry's Law is also responsible for people getting the "bends".
- When people dive deeply using compressed air, they MUST slowly come back up so that the nitrogen bubbles that are driven into tissues at deep levels (and, hence, with high pressures) may slowly be released and breathed out.
- If the person comes up too rapidly, these bubbles expand and can cause death as they compress tissues.
- Helium is less soluble than nitrogen and is used when deep diving is expected and a bit more rapid ascent is expected and reduces the instances of getting the bends.

Gas	Solubility Coefficient
CO_2	0.57
O_2	0.024
N_2	0.012
He	0.005±

- He, also has no triple point, unlike water.

- He is used in arc welding, to fill weather balloons, to fill blimps/dirigibles (it's non-flammable).

- He is also used in deep-sea diving:

- In general, He is much less soluble in water than are either oxygen or nitrogen.

- At the high pressures of deep sea diving, LOTS of nitrogen (N_2) dissolves in water, blood and cerebrospinal fluid.

- If decompression is attained appropriately, there is no problem.

- If, however, decompression is too rapid, the person develops the bends.

- In this part of the country, this is usually fatal as there is no decompression chamber at Tahoe, any more and the closest one is at Davis, I believe.

- OTOH, if He is substituted for the N_2, even rapid decompression is not as deadly as it is for nitrogen-containing gas mixtures.

- This means that for long term deep-sea diving, the likelihood of developing the bends is greatly reduced.

N_2 He

sea level

ca 120' under water

DECOMPRESSION

slowly   fast   slowly   fast

ok   ok   NOT bends or worse

BENDS or WORSE
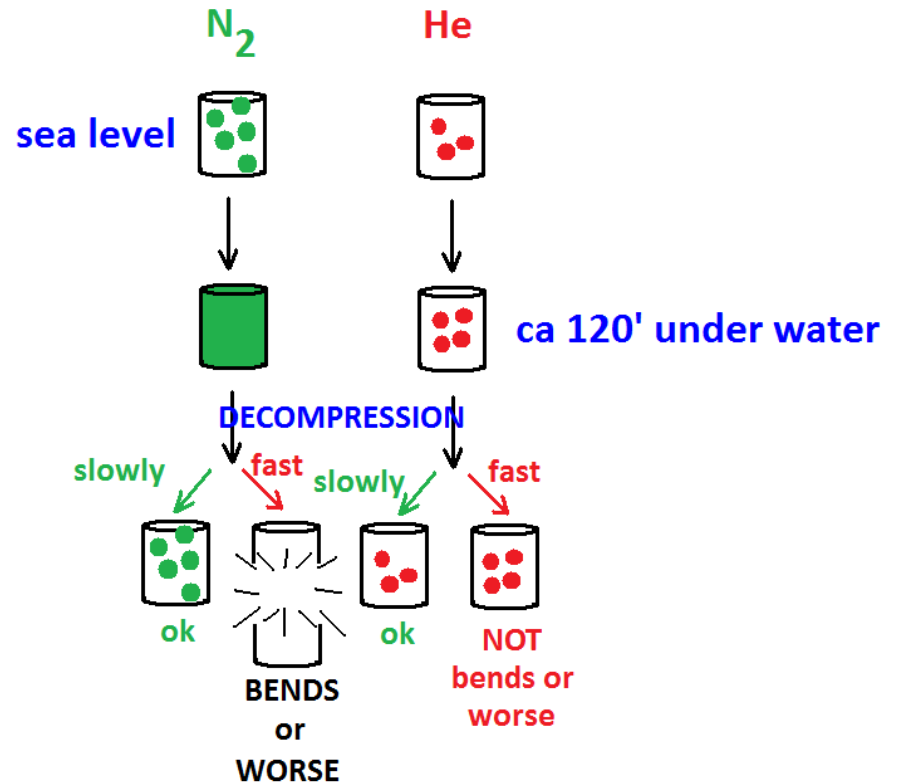
- Note that oxygen, relatively speaking, isn't very soluble in aqueous systems while carbon dioxide is.

- As a general rule, the greater the temperature, the lower the solubility, which explains why warm soda goes "flat" faster than does cold soda.

Liquid Laws, Pressures and Fluid Flow

- Whether it be in topical product development or in health care, knowledge of how fluids function (flow) is critical.

- To understand fluids, a number of laws must be examined.

Pascal's Law

- Pascal's Law says that when a pressure is applied to a confined liquid, the pressure is spread out over the liquid.

- Three really good examples of this are illustrated in the Figure.

- These examples are amniotic fluid, fluid in the eye and cerebrospinal fluid.

- Keep in mind that these fluids are wonderful shock absorbers at low pressure, but that at high pressure, they become a "weapon", i.e., these fluids are double edged swords.

132
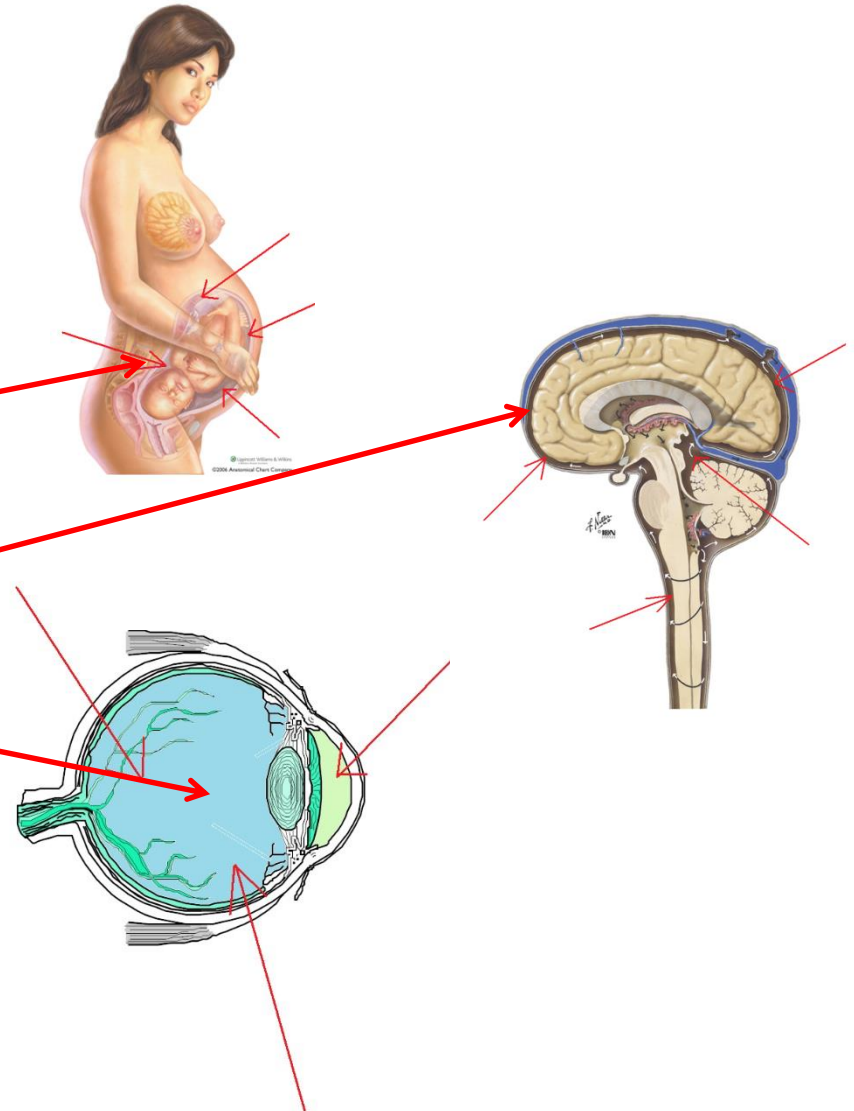
Bernoulli's Law

- Bernoulli's Law says that the faster a liquid flows through a tube, the less pressure that liquid exerts on the sides of the tube :

Slow Flow
↑**Pressure**

Fast Flow
↓**Pressure**
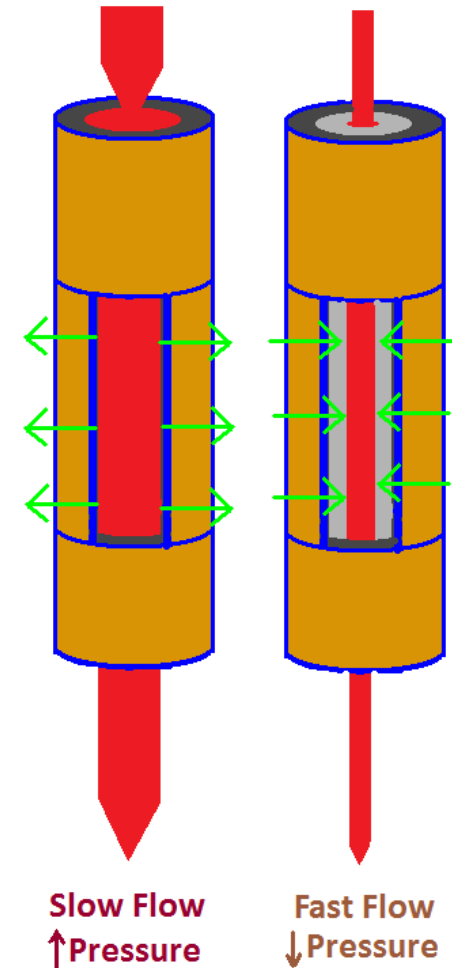
- It is this concept by which aspirator "pumps" work on sink faucets, Figure, right.

- Note that in the aspirator that with rapid flow, the pressure on the sides of the tube are reduced (a vacuum) and air rushes into the aspirator to make a suction.

- A modification on this law is the Venturi effect for gases and liquids.
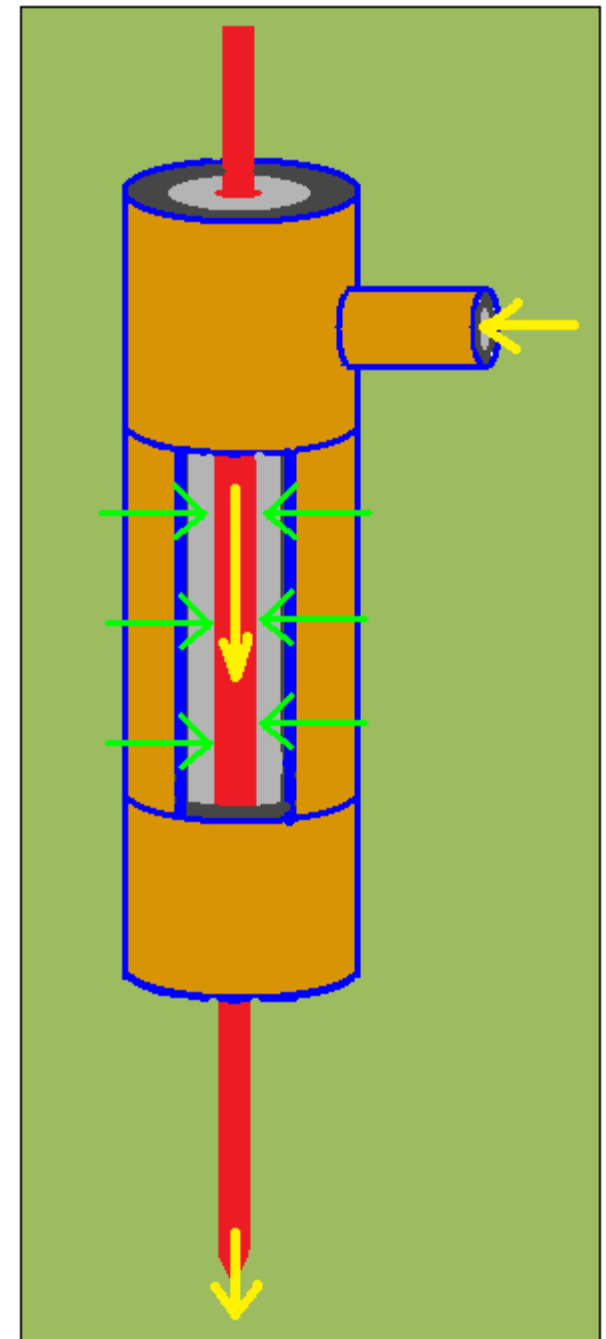
The Flow of Fluids

- Although my personal fluid preference is blood, this next section pertains to most fluids, specifically, those water based. Fluids tend to flow in one of two manner: laminar flow or turbulent flow. In laminar flow, a fluid, or fluids, flows in streamlines and in concentric layers through a tube.

- In the graphic, note that there are two obvious portions of the fluid flowing through the tube: the leading edge that has the least resistance to flow and the trailing edge that has the most resistance to flow and, hence, sort of "sticks" more to the sides of the tube.

↑ Ω

Trailing Edge

Leading Edge

↓ Ω
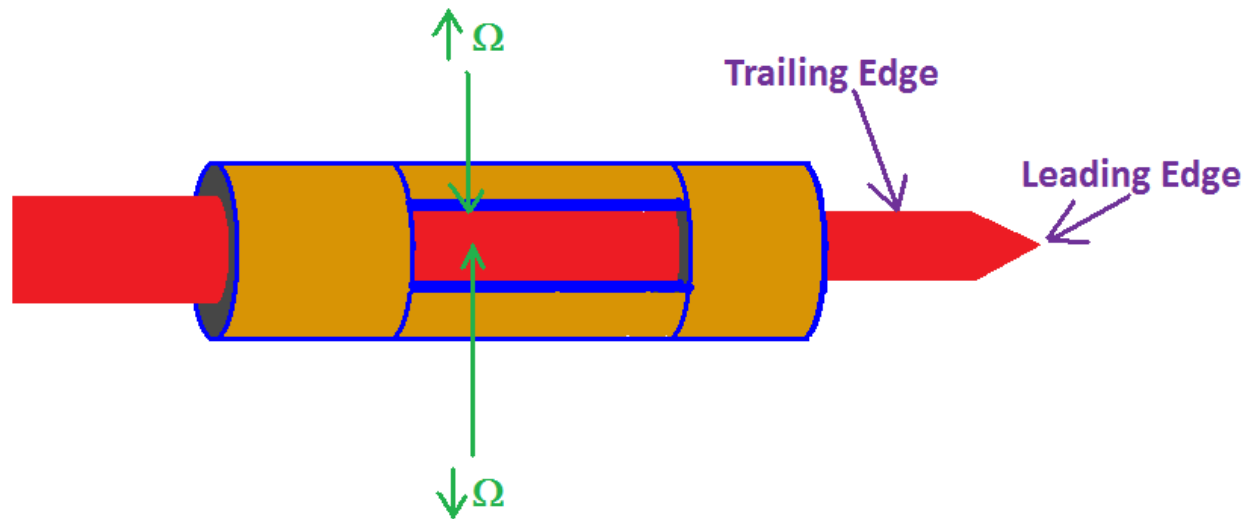
- If you looked down the barrel of the tube, you would see the fluid coming out of the tube at you with a sort of "bullet" shape.

Turbulent flow occurs when the fluid, or fluids, is flowing in all directions and continuously mixing in a crosswise flow pattern.

The whorls observed in the figure are called Eddy currents and are very much like what one sees in rivers at blockages or obstructions.
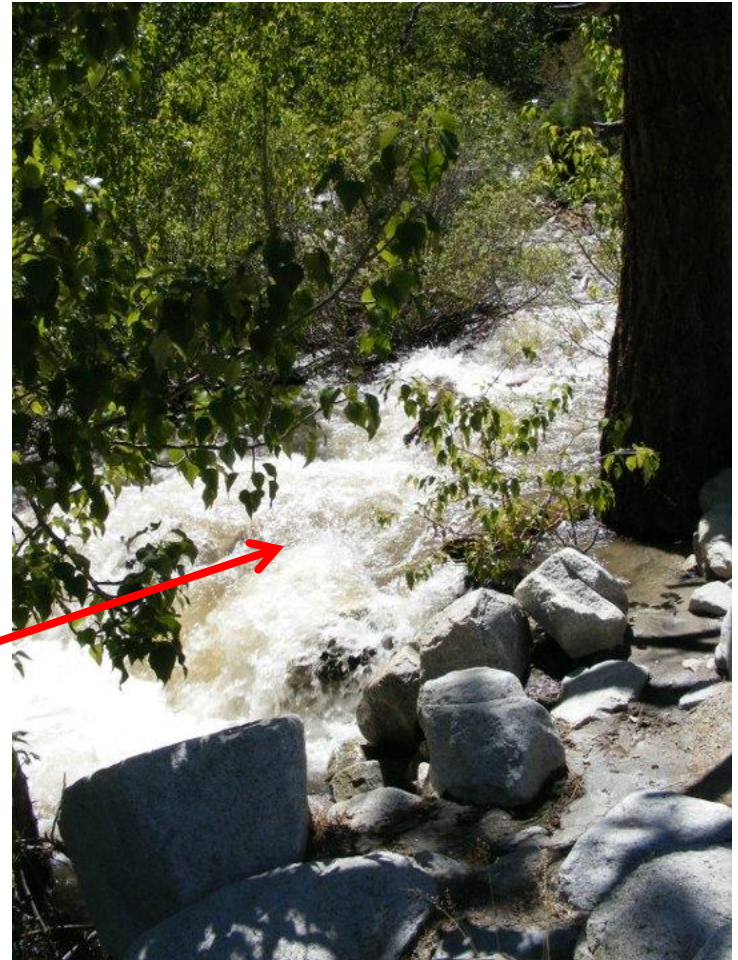
The tendency to turbulent flow may be measured in terms of a number

called the Reynold's number (R_e). This number is used for the prediction of turbulent flow.

The R_e may be determined as below:

$$R_e = \frac{v\,d\,\rho}{\eta}$$

Where R_e is the Reynold's number,
v is the velocity of the fluid flow,
d is the diameter of the vessel and
η is the viscosity of the fluid, whether it be blood, fuel, or perfume.

- A Reynold's number between about 200-400 indicates that turbulent flow occurs at branches of vessels (tubes) but NOT along the length of the vessels or tubes.
  - In the human body this tends to be in the large arteries where they branch off.
- A Reynold's number greater than 2000 indicates that turbulent flow occurs even in straight, smooth lengths of vessels or tubes.
  - In the human body this would occur in ventricles of the heart (the larger, lower chambers in the heart) during blood ejection.
  - It was this very problem, coupled with the rough surface that eventually caused Barney Clark to have either a stroke or pulmonary embolus that eventually lead to his death after having an artificial heart implanted in himself.
  - As the blood flowed turbulently over the rough surface of the artificial heart, the blood began falling on itself and began clotting.

Water
Fundamentals

- About a half-gallon of water is needed per day by humans for biological needs.

- About 5 gallons of water are used in the production of 1 gallon of milk.

- 10 gallons of water are used per gallon of gasoline produced and roughly 65000 gallons of water are required to turn out a ton of steel.

- Very briefly, the water cycle consists of rain falling from the sky onto the earth.

- This water evaporates to form more clouds, ad nauseum.

The Water Cycle

Condensation

Precipitation

Transpiration

Evaporation

Percolation
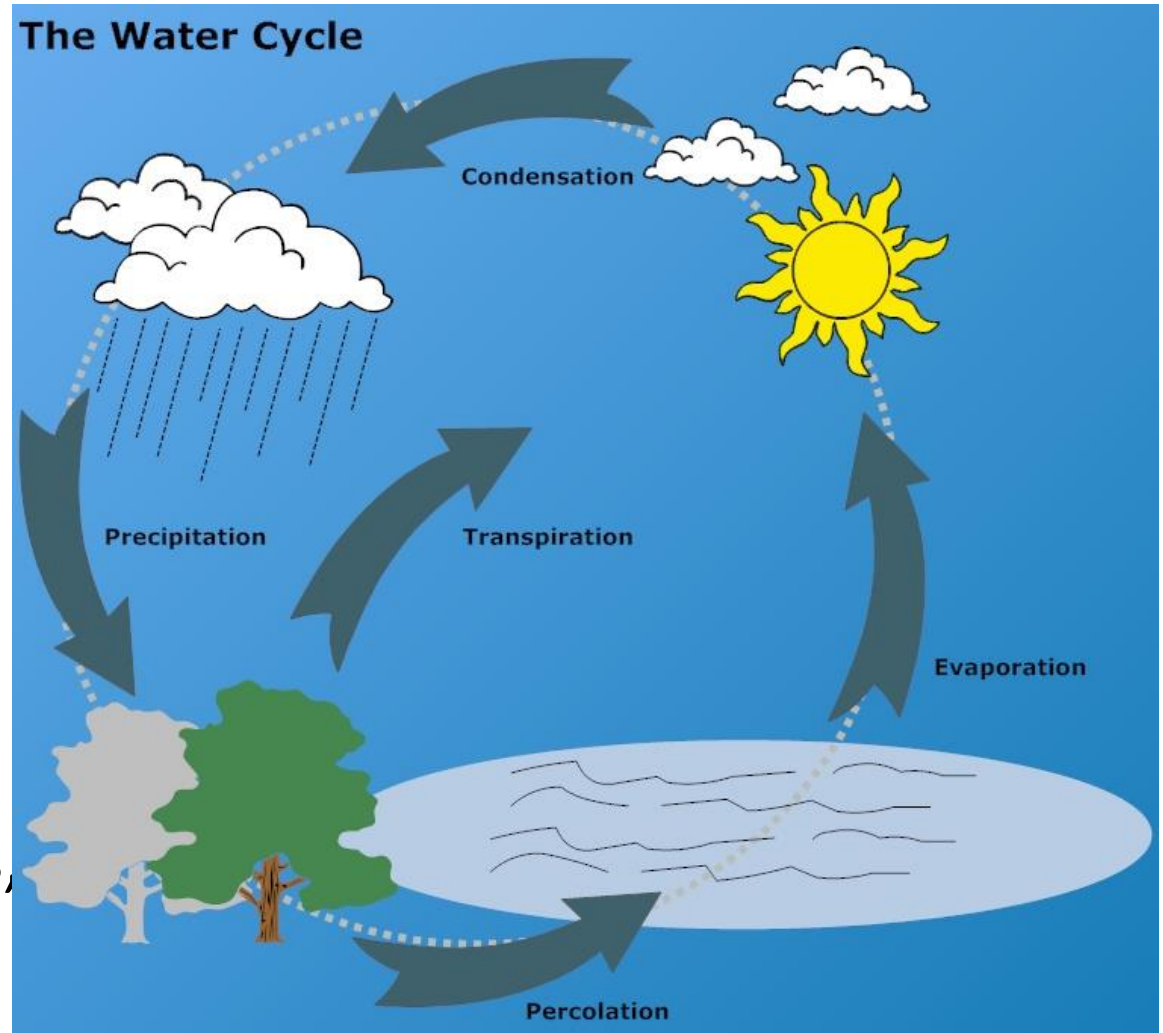
Relative Humidity

- Relative humidities (RH) of 25-50% are comfortable.
- RH's greater than 50% at high temperatures cause your body to not evaporate the produced sweat fast enough to cool you off.
- If RH is greater than 50% at low temperatures (like in a cave), you feel clammy.
- At RH's less than 25%, the inside of your nose and mouth dries out.
- The health implications for the latter are more viral infections with an increased incidence of secondary bacterial infections due to the cracked membranes lining your nose and mouth.
- The RH is measured by a number of different techniques including the use of a sling psychrometer.

- The sling psychrometer contains 2 thermometers.
- One is a dry bulb and the other has a little "sock" on its bulb that is moistened with water.
- When the wet bulb is moistened, one swings the instrument around on its axle until the wet bulb shows no further depression of the temperature.
- The difference between the two thermometers is then compared to a graph at that temperature to see what the relative humidity is.

The relative humidity is determined as follows:

$$R.H. = \frac{air\ vapor\ pressure\ of\ water}{equilibrium\ vapor\ pressure\ of\ water\ at\ the\ same\ temperature} * 100$$

Hard Water

- Hard water contains calcium, magnesium and iron salts (anions include chlorides, sulfates and bicarbonates).
- The problems with hard water are two-fold:
1. It forms bath tub ring:
   1. $Ca^{2+} + 2$ soap $= Ca(soap)_2$;
   2. $Mg^{2+} + 2$ soap $= Mg(soap)_2$;
   3. $Fe^{3+} + 3$ soap $= Fe(soap)_3$.
   4. These have no cleaning power and stick to surfaces. This is the phenomenon that occurs with shampoo, too.
2. Hard water is responsible for "scale" formation in boilers. This is a HUGE problem.
   1. Salts are precipitated as carbonates and sulfates (biggest). Sulfates are sort of strange: they become LESS soluble in hot water than in cold water. This causes their precipitation. The precipitate is called "scale".
   2. Scale is a poor conductor of heat and leads to fuel wasting. Boiler explosions are usually due to scale presence.

- **Here's how the process works: once scale is already present, to keep the water in the boiler at the appropriate temperature, the metal is often red hot. More sulfates precipitate onto the metal and scale inside the boiler. If the scale cracks (and it will, eventually), hot water leaks down to the metal tank where it reacts as follows: $4H_2O + 3Fe = Fe_3O_4 + 4H_2$. The hydrogen bubbles scale from the boiler walls and causes more hydrogen production. Hydrogen eventually explodes from being in contact with red-hot metal and so does the boiler.**

- **How does one get rid of the hard water? By using softeners!**

One type of water softeners will be studied: Ion Exchange softeners.

•The use of ion exchange resins.
•This method consists of using resins or beads that have been conditioned in acid (cation exchangers) or base (anion exchangers).
•Let's start with the cation exchanger, first. If one examines a bead in the cation exchange resin, the surfaces of these beads are covered with protons. As cations run through this resin, the beads exchange the protons for the cations in the hard water, rendering those cations out of the way.
•The same thing occurs with the anion exchanger beads. As the anions in the hard water run through the beads, they are bound by the beads as the hydroxide ions are released. $H^+ + OH^- = H_2O$. The water that is both formed and softened in this process is called deionized water.

WATER with heavy metals, polyatomic anions

Cation Exchanger (resin or beads)

Anion Exchanger (resin or beads)

HOH

Deionized Water

145

Water up to Brim

Water Bulging Over Brim

Water Spilled Over Brim After Detergent (Surfactant) Added
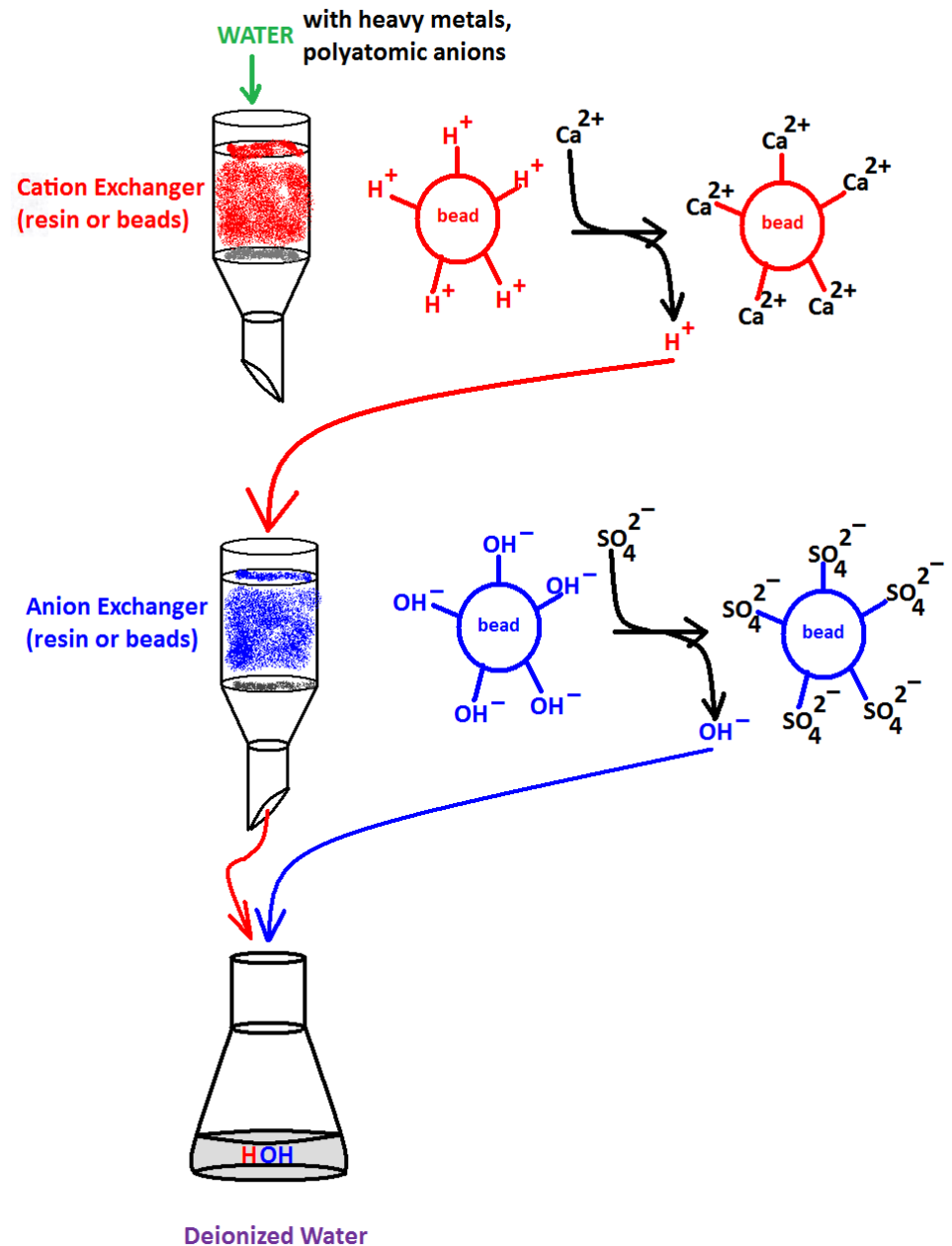
- The effects of surface tension are below.
- If one takes a clean glass and carefully pours water in it, one may pour water over the rim.
- This forms a bulge on top of the water.
- That's due to the hydrogen bonds and the polar sites in the glass for the water to bind with.
- In order to destroy those bonds, something called a surfactant is needed.
- Surfactants reduce the surface tension and make, in this case, water "wet".
- The surfactant, or detergent, "separates" the hydrogen bonds and the water spills down the sides of the glass.
- The same thing happens in our lungs so that we may continue passing oxygen and carbon dioxide across our lungs for utilization or excretion, respectively.

The Solvent "Power" of Water

- Water dissolves substances that strongly attract water, i.e., like dissolves like.
- The way it works is that water molecules surround the substance in three dimensions after the substance has ionized.
- Note that the partially negative portion of the water is that which is attracted to the positively charged ion (and vice versa).
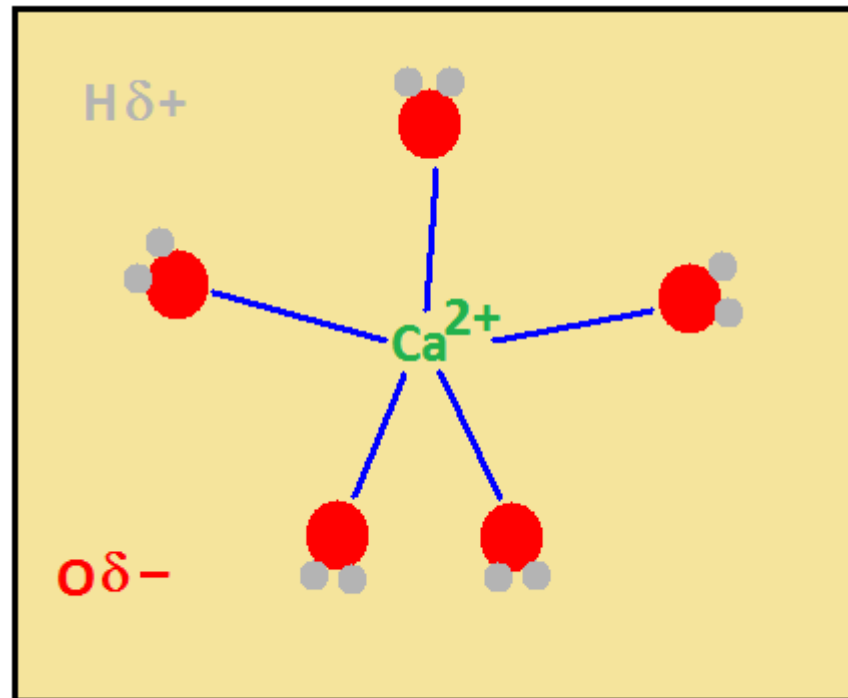
- Ionization is sort of like chiseling a chunk of rock -- only with water molecules instead of a hammer and chisel.

- Water attacks the crystalline structure of the substance and removes an ion at a time.

- Note, again, that the partially negative portion of the water binds with the cations and the partially positive portion binds with the anions.

- Again, the water "cages" are three-dimensional about the ions.

H_2O KF H_2O

"Caged", hydrated ions
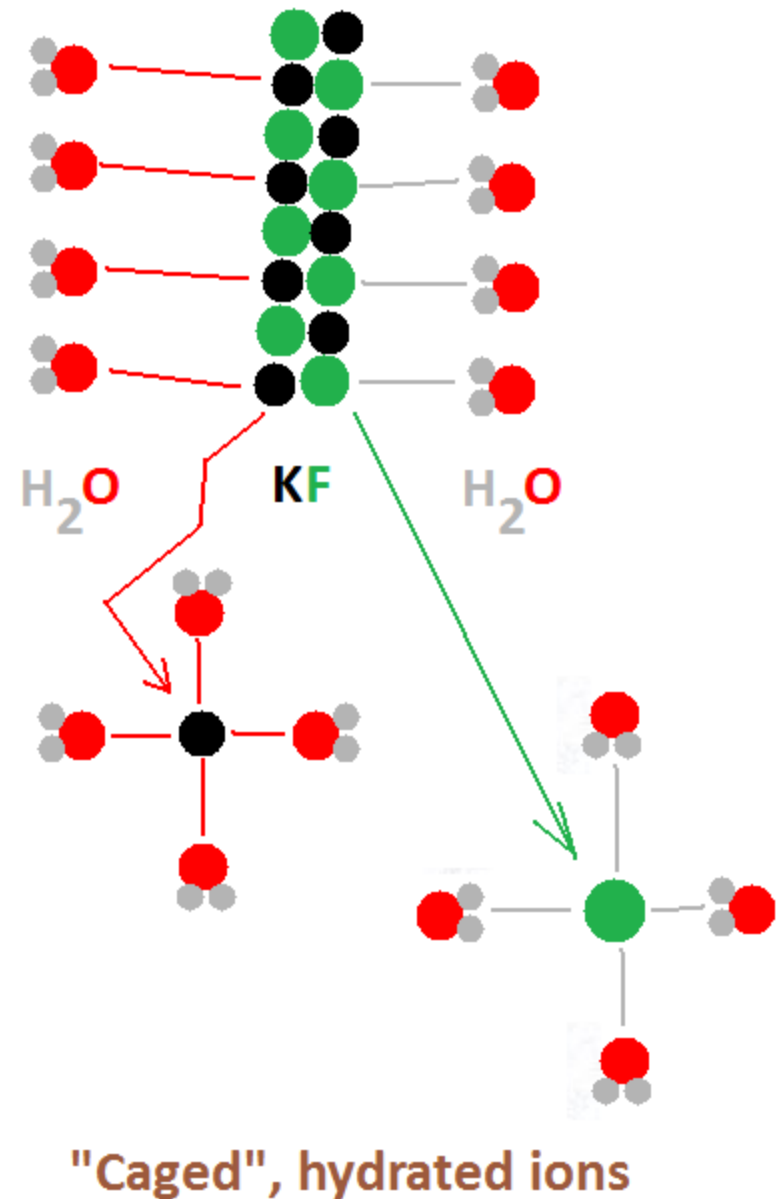
Chemical Properties of Water

- Water is very stable in the presence of high heat.

- At 2727° C, only 11.1% of water decomposes to form hydrogen and oxygen gases.

Water auto-ionizes, i.e., it "separates" or dissociates in itself:

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

- The H_3O^+ ions are called hydronium ions and are acidic -- they form the basis for determining the pH of solutions, mixtures and colloids.

- The OH^- ions are the hydroxide ions and are alkaline or basic.

Solutions, Dilutions and Colloids

Solutions and Colloids

- A solution is a homogeneous mixture of 2 or more substances in which the components are present as atoms, molecules or ions.

- A solvent is the substance present in a solution in the largest amount.

- Solutes consist of one or more substances present in a solution in an amount lesser than that of the solvent.

- Dissolving describes the process of forming a solution when the solvent and solute[s] make a homogeneous mixture,e.g., sugar water.

- Solutions undergo dynamic equilibrium.
- Dynamic means lots of activity.
- Equilibrium means no net change.
- Unsaturated, saturated and super-saturated solutions are constantly "changing".
- In the case of the first, more solute is dissolved than undissolved;
- The second, the dissolved/undissolved solute is at equilbrium;
- In the third solution, more solute is undissolved than is dissolved.

LeChatelier's Principle

- Any shift to the equilibrium of a system may be brought about by outside forces.
- Le Chatelier's Principle says simply, yet eloquently, when a system at rest is acted upon by an outside force, the system responds by moving in a direction to reach equilibrium, again.
- Le Chatelier's Principle may be illustrated using a container that has two joining reservoirs with one external valve.
- At equilibrium, the reservoirs have the same volume.
- Once the outside valve has been turned on (outside force), the reservoir closest to it loses volume more and faster than the one farther away.
- Once the valve is closed (outside force), the two reservoirs balance out, again.

Diffusion
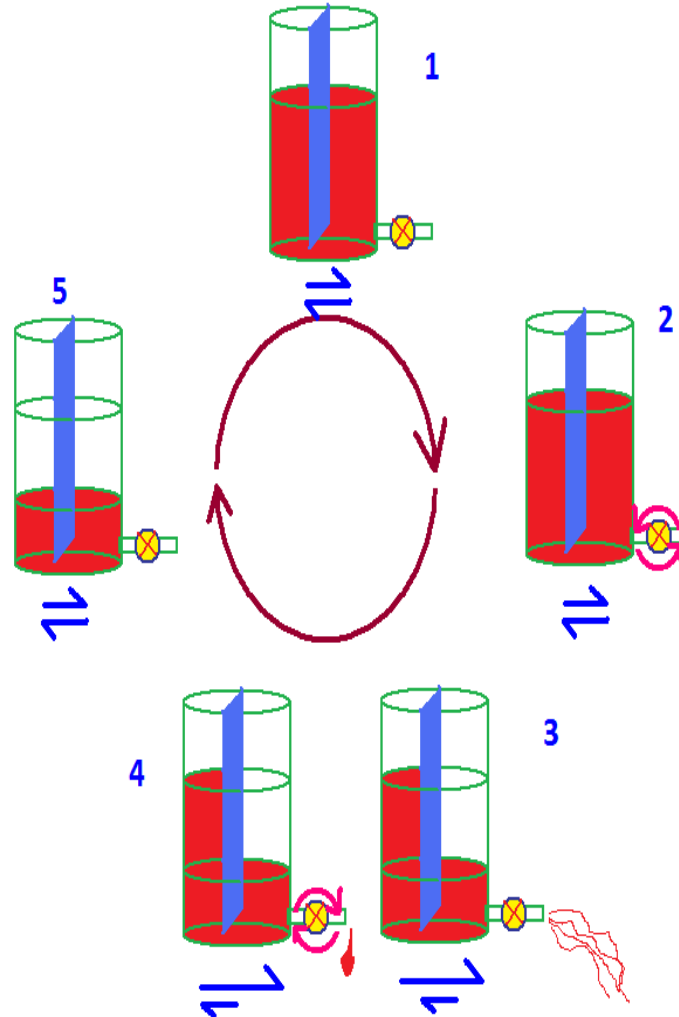
Concentration Gradient
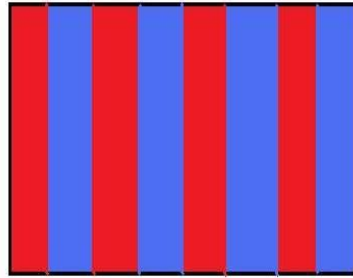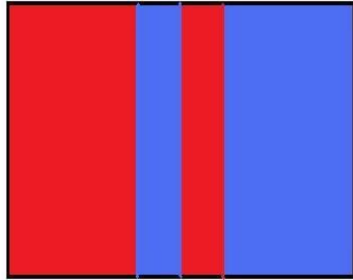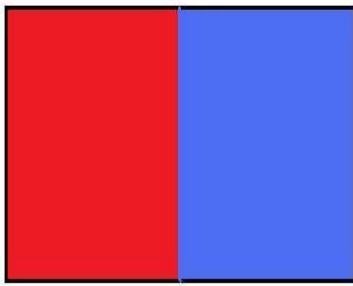
The movement of a solute from a region of higher concentration to a region of lower concentration until the solute is uniformly distributed in solution.
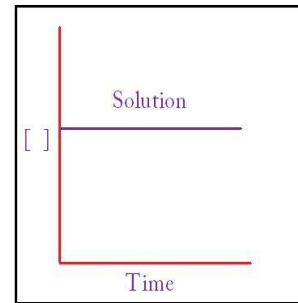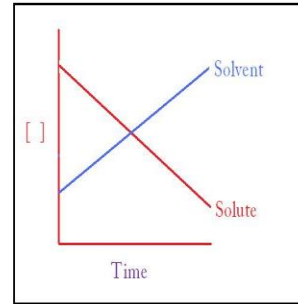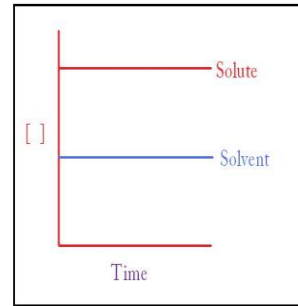
Dialysis

- Dialysis is a process in which solvent molecules, other small molecules and hydrated ions pass from a solution through a membrane.

- Dialysis is used to purify proteins and is used in patients with renal failure to clean their blood, i.e., remove toxins that would have, otherwise, been removed by their kidneys, were they functioning.
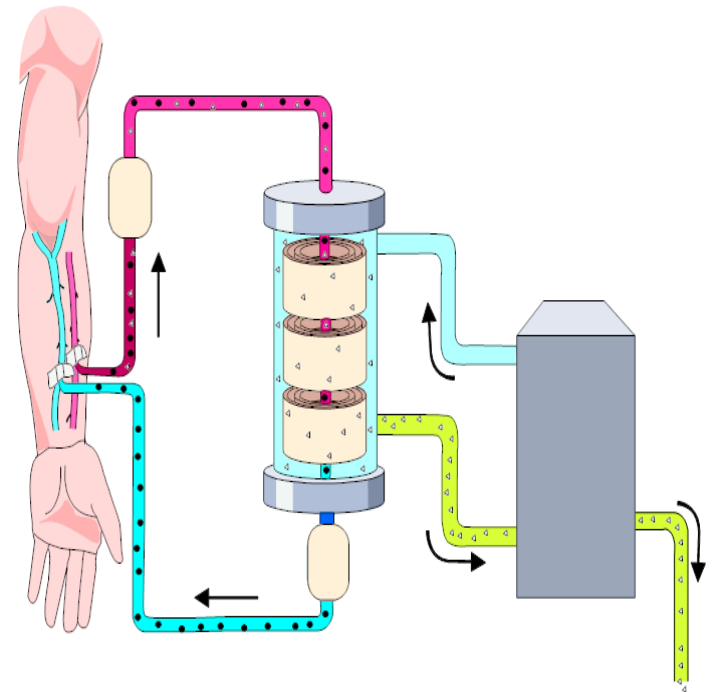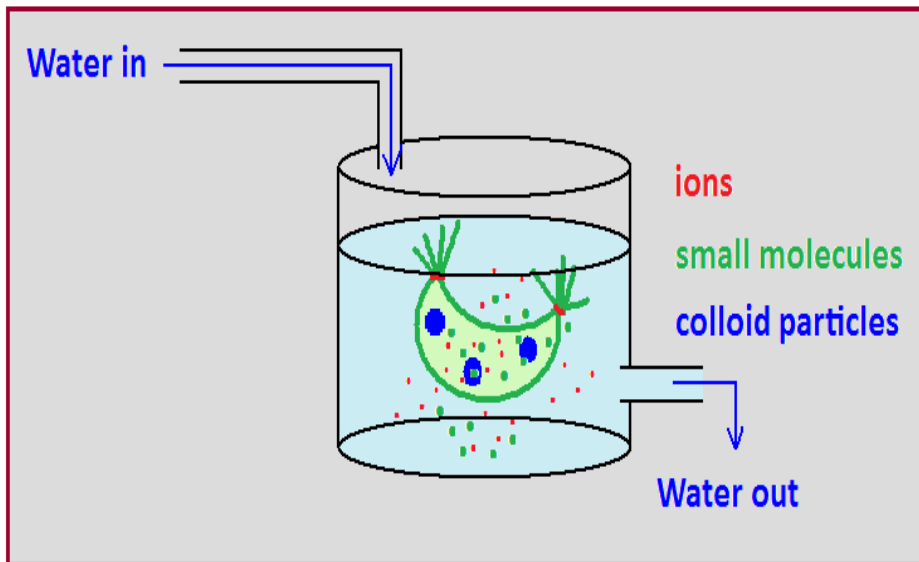
Solubility is defined as the maximum amount of a substance dissolved in a specified volume of solvent at a specific temperature and pressure

Soluble substances are substances that dissolve to a significant extent in the solvent.
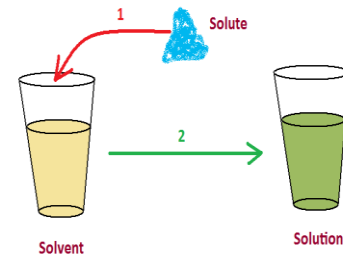
An insoluble substance is the opposite of a soluble substance, i.e., makes a non-homogeneous mixture.
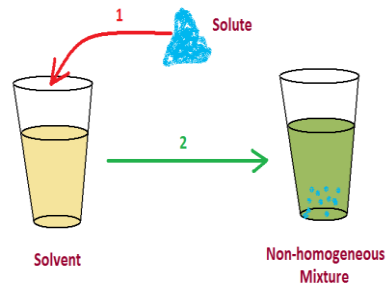
Immiscible is used to describe liquids that are insoluble in each other, e.g., oil and water.
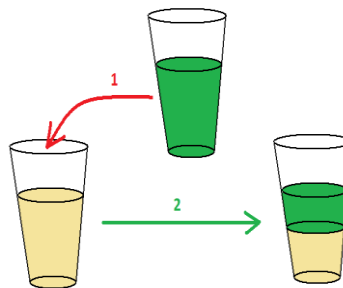
Solubility

Solubility

Unsaturated solutions contain less solute dissolved per unit volume of a solvent. All of the solute in an unsaturated solution is dissolved with excess solvent "caging" the solute.

Saturated solutions are solutions where dissolved solutes are in equilibrium with undissolved solutes, i.e., micro-precipitation occurs but is not observed by the naked eye (dissolved, but at the solubility limit).

Supersaturated solutions are really mixtures. In these solutions, the solution contains more solute in the undissolved state at equilibrium, i.e., precipitate at bottom of container.

Solute Dissolved

Solute Undissolved

Solute Dissolved

Solute Undissolved

Solute Dissolved

Solute Undissolved

Colligative Properties

•Colligative properties are properties of a solution that depend ONLY on the concentration of solute in a solution.
•While we will briefly discuss them, here, they are more thoroughly discussed in CHEM 121 and 122.
•Three colligative properties are summarized, below, in the table:

Colligative property	Abbreviation	Pure solvent	In Solution
Boiling point	BP	Normal	Elevated
Freezing point	FP	Normal	Reduced
Vapor pressure	VP	Normal	Reduced

Boiling Point

- Boiling point elevation is the concept behind both coolant in the radiator of your car in the summer and boiling foods at higher elevations. Impurities raise the boiling point of the pure solvent -- you do this every time you add a bit of salt to your water to boil potatoes.

- At sea level, you don't have to do this.

- At our elevation and higher elevations, in order to boil potatoes faster, the salt raises the boiling point so that the water gets hotter, cooking the potatoes faster.

- NOTE!!! Pressure Cooker!

Freezing Point

- Freezing point depression is the idea behind anti-freeze in your radiator in the winter and using salt on the ice in your ice cream freezer/maker.

- As impurities are added to aqueous systems, the FP goes below 0° C, preventing your radiator from freezing.

Vapor Pressure

- Vapor pressure reduction is best explained from a visualized perspective.

- The bottom line with VP is that the VP of a solution is less than that of the VP of the pure solvent.

Bell jar prevents pure solution from simply evaporating

Pure solvent

Solution
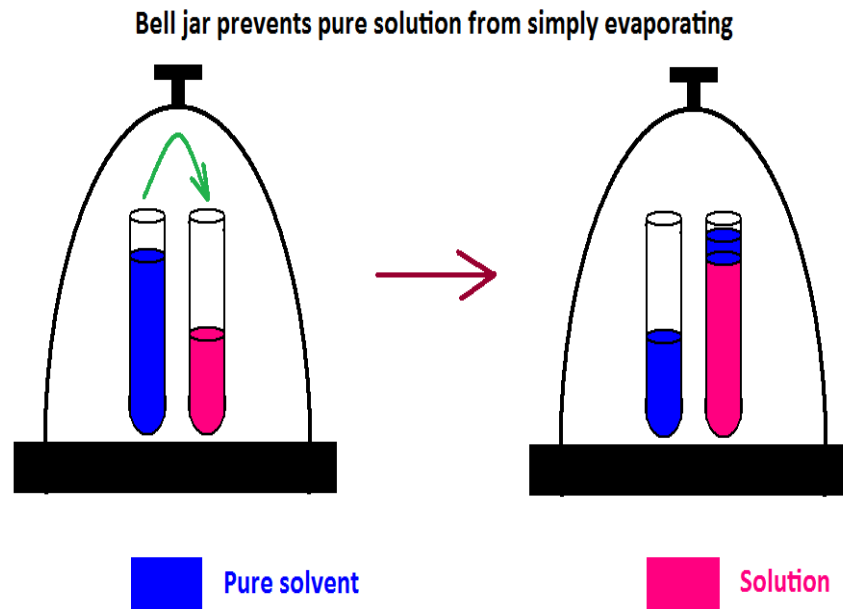
Osmosis

- Osmosis is defined as the movement of water from a region of higher water concentration to a region of lower water concentration across a semi-permeable membrane.

- Osmotic pressure is the pressure required to halt the net flow of water through a semi-permeable membrane into a solution.

- Osmolarity is a function of osmotic pressure:

$$\pi = nMRT$$

- Where π is the osmotic pressure, n is the number of mols of solute, M is the molarity of the solution, T is the absolute temperature and R is the gas constant (0.0821 L-atm/mol-K or 62.4 torr-L/mol-K).
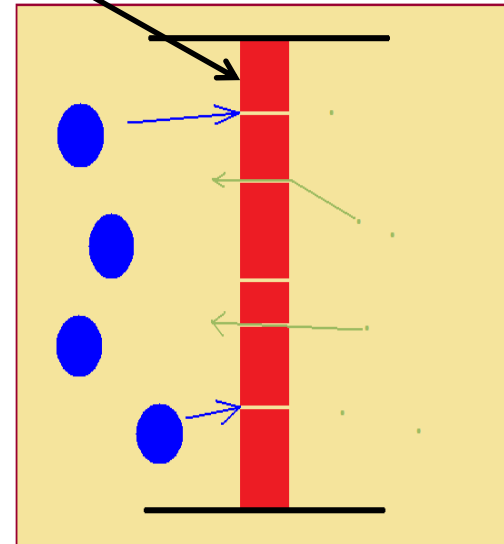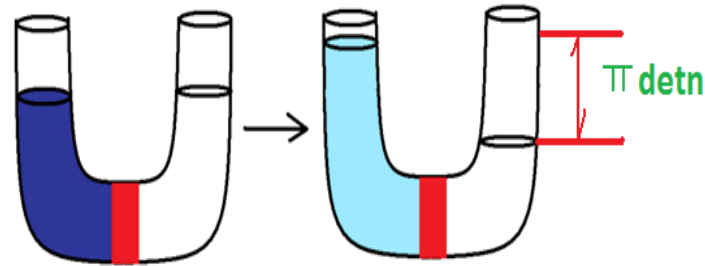
Osmolarity

- Osmolarity equals the product of the number of particles of the solute after dissociation times the molarity of the solution (n*M).

0.1 M Sucrose	0.1 M NaCl	0.1 M Na_3PO_4
↓	↓	↓
0.1 Osm	0.2 Osm	0.4 Osm

nM = Osmolarity

1 particle   2 particles   4 particles
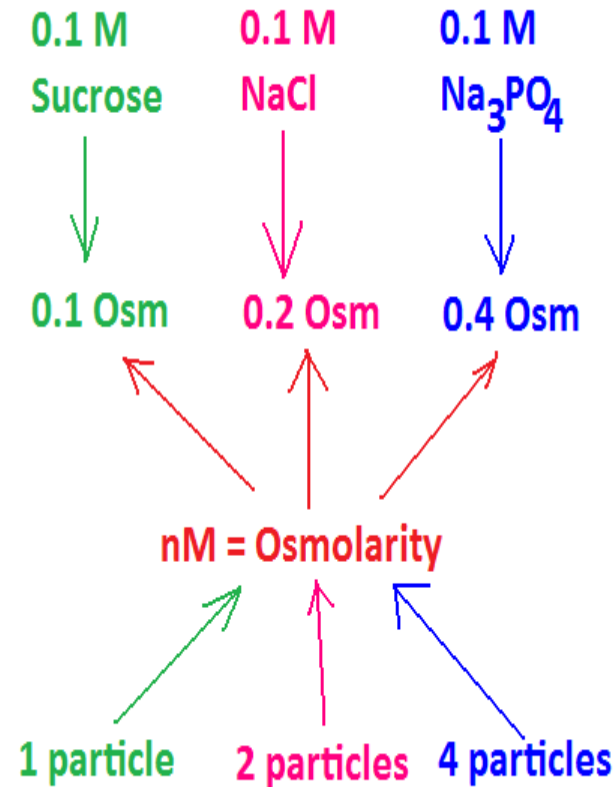
Biological Application

- One classical application of osmosis is the effects of different fluids on cells in the human body.
- As you can see in the graphic, cells bathed in hypotonic (dilute) solutions rupture if not done with care, cells bathed in hypertonic (concentrated) solutions shrink and cells bathed in isotonic solutions exhibit no changes, at all.

Normal Cell

in hypotonic medium
< 0.9% Saline

in isotonic medium
0.9% Saline

in hypertonic medium
> 0.9% Saline
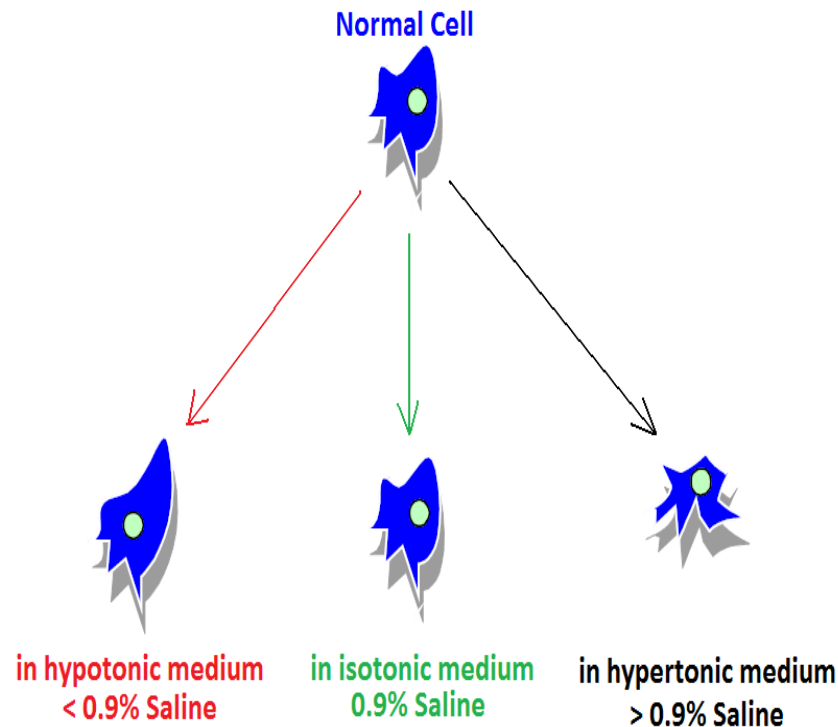
Colloids

Before we define some terms in and about colloids, let's first compare these terms to those we've already learned about with solutions:

Solution	Colloid
Solvent	Dispersing medium
Solute	Dispersed phase
Particle size $< 10^{-7}$ cm	Particle size $\leq 10^{-5}$ cm
Particle size does not lead to light scattering	Particle size causes light scattering

Light in → Scattered light out

OPAQUE SAMPLE
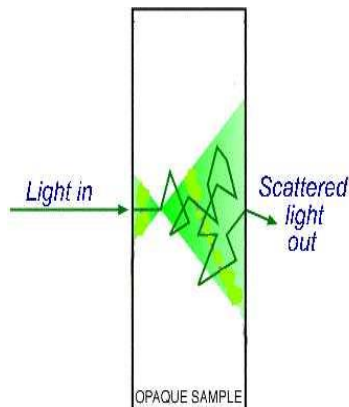
- By definition, a colloid is a homogeneous mixture of 2 substances in which the dispersed substances are present as larger particles than are found in solutions.

- The dispersing medium is the substance present in a colloidal dispersion in the greatest amount.

- The dispersed phase is the substance present in amounts less than the amount of dispersing medium.

- Superficially, the path of a beam of light through the colloid is visible due to light scattering and is called the Tyndall effect.

Examples of colloids are summarized, below, in the table:

Name	Example
Aerosol	Fog, air pollutants
Foam	Whipped cream, shaving cream
Emulsion	Milk, mayonnaise
Solid foam	Marshmallow, foam rubber

An emulsifying agent is a substance that when added to colloids, prevents them from coalescing and settling.
These are also known as (aka) stabilizing agents.
The table below summarizes some of these stabilizing agents:

Mayonnaise	Bowel Fat
Oil in water	Fat in water
Egg yolk acts as the emulsifier	Bile acts as the emulsifier

- Soaps and detergents act as emulsifiers, as well.

Acids and Bases -- Importance

- Acids and bases are of incredible importance in the functioning of the human body.

- If we become too acidic or too alkaline, our hearts, our brains and our muscles, to name three examples, stop functioning properly.

Acids, Bases, Salts and Buffers

Centuries ago, certain substances were recognized for:

Sour taste	Turned vegetable blues to red	Solvent power	Ability to neutralize alkalies to form salts

These were called "acids" from "ac" which means sharp,
as in *acetum*.

Other substances were recognized for:

Soapiness	Cutting grease	Having the reverse effect of acids

These were called "alkalies" which is from Arabic for plant ashes.
They are also called bases.

Most Significant Properties

1) Their effect on acid/base indicators.
The table, below, summarizes the acid and base forms of
6 different acid/base indicators:

Acid Form (color)	Indicator	Base Form (color)
Red	Litmus	Blue
Clear	Phenolphthalein	Pink
Yellow	Bromocresol green	Green
Yellow	Phenol red	Red
Red	Methyl red	Yellow
Yellow	Bromocresol purple	Purple

2) Their ability to react with each other to produce salts.
3) Their catalytic action.
4) Their ability to displace weaker acids or bases.
5) Aqueous solutions conduct an electrical current.

There are at least 4 definitions of acids and bases: This Course Focuses on Two Definitions.
First Definition: <u>Arrhenius Definition of Acids and Bases</u>

The first definitions are those of Arrhenius. By this set of definitions, an acid is a substance that dissociates in water to yield a proton (hydrogen ion). A base is a substance that dissociates in water to yield hydroxide ions. Examples of these sorts of reactions are summarized in the table, below:

Acid Name	Acids	Base Name	Bases
Hydrochloric	$HCl \rightarrow H^+ + Cl^-$	Sodium hydroxide	$NaOH \rightarrow Na^+ + OH^-$
Sulfuric	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$	Potassium hydroxide	$KOH \rightarrow K^+ + OH^-$
Nitric	$HNO_3 \rightarrow H^+ + NO_3^-$	Magnesium hydroxide	$Mg(OH)_2 \rightarrow Mg^{2+} + 2\ OH^-$
Phosphoric	$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$	Barium hydroxide	$Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^-$
Perchloric	$HClO_4 \rightarrow H^+ + ClO_4^-$	Aluminum hydroxide	$Al(OH)_3 \rightarrow Al^{3+} + 3\ OH^-$
Carbonic	$H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$	Tin (IV) hydroxide	$Sn(OH)_4 \rightarrow Sn^{4+} + 4OH^-$

# Second Definition: Brønsted-Lowry Definition of Acids and Bases

By this set of definitions, an acid is a proton donor and a base is a proton acceptor when they dissociate in water. Representative reactions are summarized in the table, below:

Acid dissociation in water	Reaction of Hydroxide with an Acid
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$	$HCl + OH^- \rightarrow H_2O + Cl^-$
$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$	$HNO_3 + OH^- \rightarrow H_2O + NO_3^-$
$HClO_4 + H_2O \rightarrow H_3O+ + ClO_4^-$	$H_2SO_4 + OH^- \rightarrow 2H_2O + SO_4^{2-}$

Species/substances that may either gain or lose protons (the hydrogen ion) are called amphipathic or amphiprotic or ampholytes. Examples are shown, below:

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Where RED indicates the acid and BLUE indicates the base form of each molecule.

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
$$H_3O^+ + HCO_3^- \rightarrow H_2CO_3 + H_2O$$
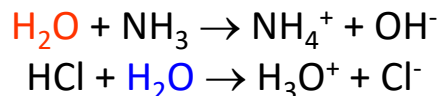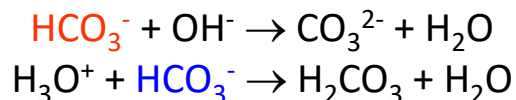
Where RED indicates the acid and BLUE indicates the base form of each molecule.

Water reacts with compounds.
Alkali metal oxides react exothermically
with water to form hydroxides:

$$Li_2O + H_2O \rightarrow 2LiOH$$

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$K_2O + H_2O \rightarrow 2KOH$$

These metal oxides that react with water
to form hydroxides are called basic anhydrides.

Non-metal oxides react with water to form acids:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

These non-metal oxides are called acidic anhydrides.

- If the acid has one ionizable proton, it is called a mono-protic acid.
- If it has 2, a di-protic acid.
- If it has three ionizable protons, it is called a triprotic acid.
- The significance has to with eventually using this information in reaction-type calculations.
- Each proton has its own dissociative step, i.e., the protons don't just "fall off" the acids all at once.
- They are removed a proton at a time.

Monoprotic Dissociation -- 1 H$^+$	Diprotic Dissociation -- 2 H$^+$	Triprotic Dissociation -- 3H$^+$
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$	$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$ $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$	$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$ $H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$ $HPO_4^{2-} + H_2O \rightarrow H_3O^+ + PO_4^{3-}$
$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$	$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$	
$HCN + H_2O \rightarrow H_3O^+ + CN^-$		

Auto-ionization of Water

Let's for a moment forget about acids and bases and focus on water. Water auto-ionizes in itself:

$$2H_2O \rightarrow H_3O^+ + OH^-$$
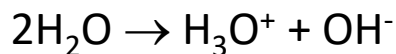
The reaction is NOT favored as written, although the ratio of protons (hydronium ions) to hydroxide ions is unity.

At 25° C, the concentration of both ionic species is $1*10^{-7}$ M.

Now, let's go back to the acids and bases.

H_3O^+ is acidic.

OH^- is alkaline.

In ACIDIC solutions, the molar concentration of H_3O^+ ($[H_3O^+]$) is greater than the molar concentration of OH^- ($[OH^-]$.

In NEUTRAL solutions, they are equal to each other.

In ALKALINE solutions, $[OH^-]$ is greater than $[H_3O^+]$.

In any dilute solution of water, the product of the hydronium ion concentration and hydroxide ion concentration is a constant, regardless of the solute.

This constant is called the dissociation constant of water and is represented by K_w.

$$pK_w = pH + pOH$$

or:
$$14 = pH + pOH, \text{ where } [H^+] = [H_3O^+]$$

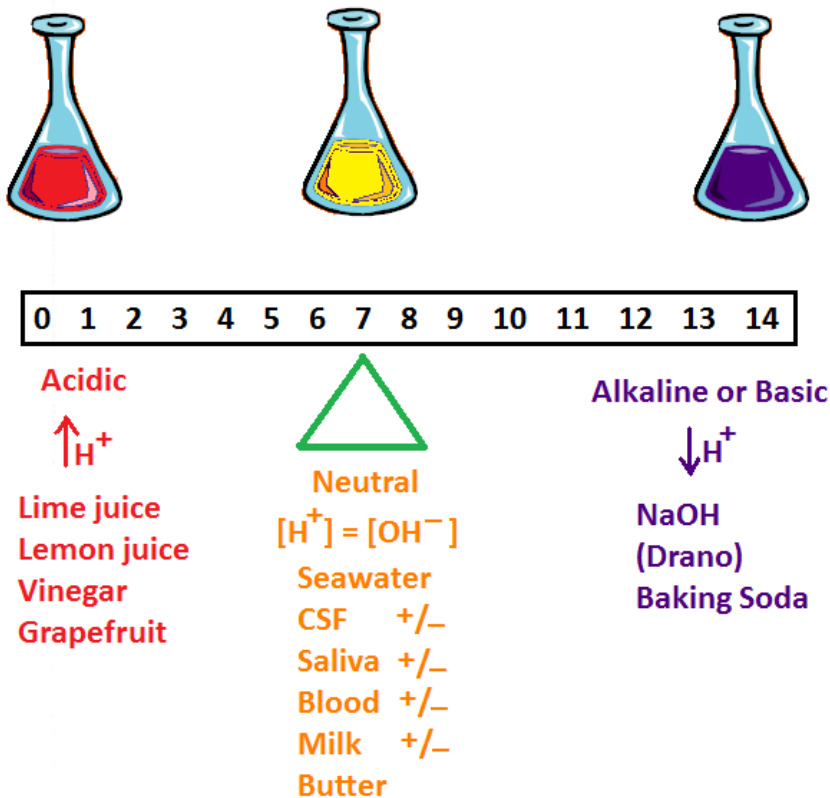Another way to look at this is that:

$$[H_3O^+] = 1*10^{-pH}$$

At neutrality where the hydronium and hydroxide ion concentrations are equal, the pH is 7:   ($-\log[1*10^{-7}]$).

When the pH is less than 7, the solution is acidic.
When pH equals 7, is neutral.
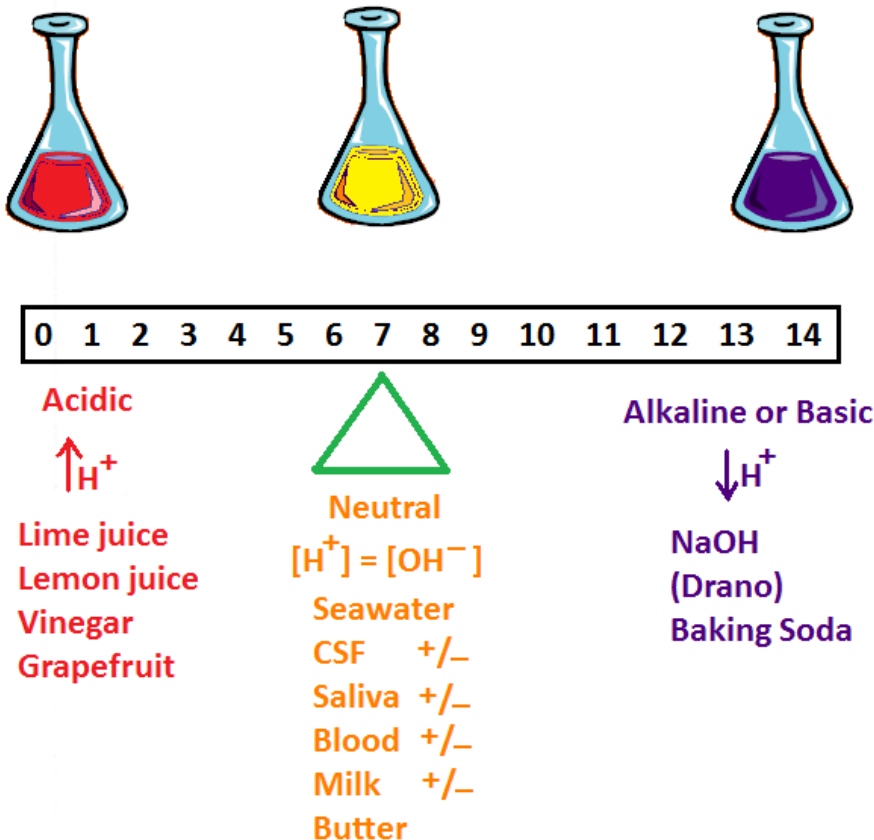**When the pH is greater than 7, the solution is alkaline or basic.**

pH

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Acidic ↑H^+

Lime juice
Lemon juice
Vinegar
Grapefruit

Neutral
$[H^+] = [OH^-]$
Seawater
CSF   +/−
Saliva +/−
Blood   +/−
Milk   +/−
Butter

Alkaline or Basic ↓H^+

NaOH
(Drano)
Baking Soda

- A solution that has a very acidic pH has lots of hydrogen ions (protons; H^+) in it;

- Conversely, a solution that has a very alkaline pH has lots of base in it (e.g., bicarbonate in the body).

$$pH = -\log[H^+]$$

$$[H^+] = 1 * 10^{-pH}$$

pH

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Acidic

↑H⁺

Lime juice
Lemon juice
Vinegar
Grapefruit

Neutral
$[H^+] = [OH^-]$
Seawater
CSF   +/_
Saliva +/_
Blood +/_
Milk   +/_
Butter

Alkaline or Basic

↓H⁺

NaOH
(Drano)
Baking Soda

- Examples of solutions that are very acidic include lime and lemon juices, vinegar and grapefruit.
- Examples of solutions that are very alkaline include lye and Drano (same thing, different name).
- When the proton concentration equals the base, or alkali, concentration, the pH is neutral.
- This occurs at a pH of 7 - the derivation of pH is reserved for CHEM 121.
- Solutions that are close to neutral include seawater, cerebrospinal fluid, milk, butter and blood.
- Note that the pH scale goes from most acidic at pH = 0 to most alkaline at pH = 14.

An Application of pH in Milk Left Out to Spoil
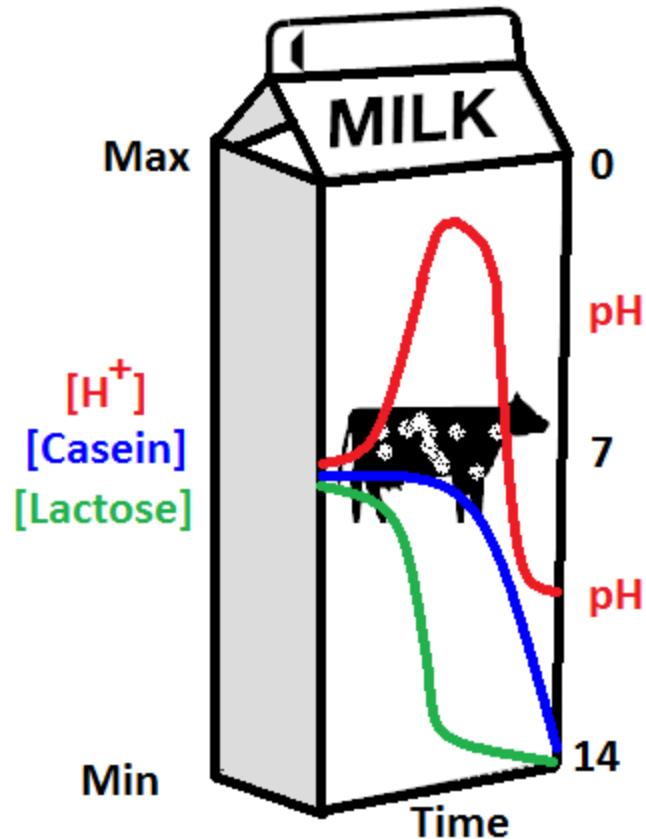
- Note that over time, the casein concentration remains fairly stable, while the lactose concentrations go DOWN with DECREASING pH.

- The reason for this is that the lactose, when left out in milk as it spoils, is metabolized from a 12 carbon sugar to a 3 carbon acid called lactic acid (or lactate as it is ionized).

- This lowers the pH of the milk.

An Application of pH in Milk Left Out to Spoil

Max

MILK

0

[H$^+$]
[Casein]
[Lactose]

pH

7

pH

Min

14

Time
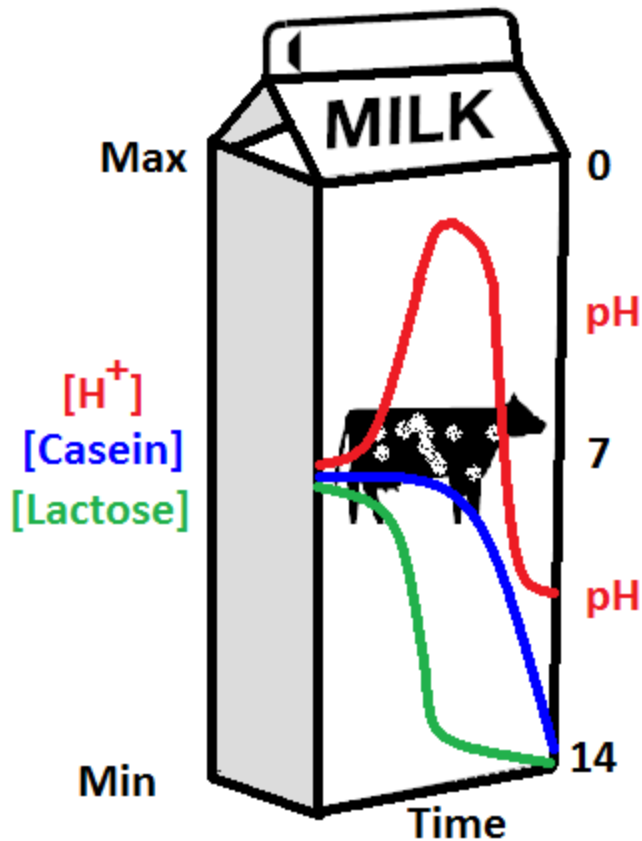
- Note, also, though, that at the lowest point of the pH the casein concentration begins to decrease.

- This occurs because the casein tries to absorb (or neutralize) the excessive number of protons bringing the pH, not only back to normal, but way above normal.

- This alkalization of the milk is a form of cannibalism: as the pH goes higher and higher, the casein is metabolized (specifically, it's catabolized).

Blood and pH

- Blood is slightly alkaline.
- Arterial blood runs a pH between 7.35 and 7.45.
- In venous blood, it runs less than 7.35 due to the high amount of carbon dioxide in it.
- Protons (hydrogen ions) come from aerobic metabolism of glucose, from hydrolysis of carbonic acid, from the oxidation of sulfur containing amino acids, from the anaerobic metabolism of glucose, from lactate, from ketone bodies and from phosphate containing proteins and nucleic acids.

- Under normal conditions, the bicarbonate to proton ratio is about 20 to 1 and the hydrogen ion concentration may be calculated by multiplying 24 times the ratio of pCO$_2$ over bicarbonate ion concentration:

$$[H^+] = 24 * \frac{pCO_2}{[HCO_3^-]}$$

- That means, then, that the pH is proportional to the ratio of bicarbonate ion concentration (the metabolic contributor to pH balance) to the pCO$_2$ levels (the respiratory contributor to pH balance).

Bicarbonate, Protons and Their Relationship
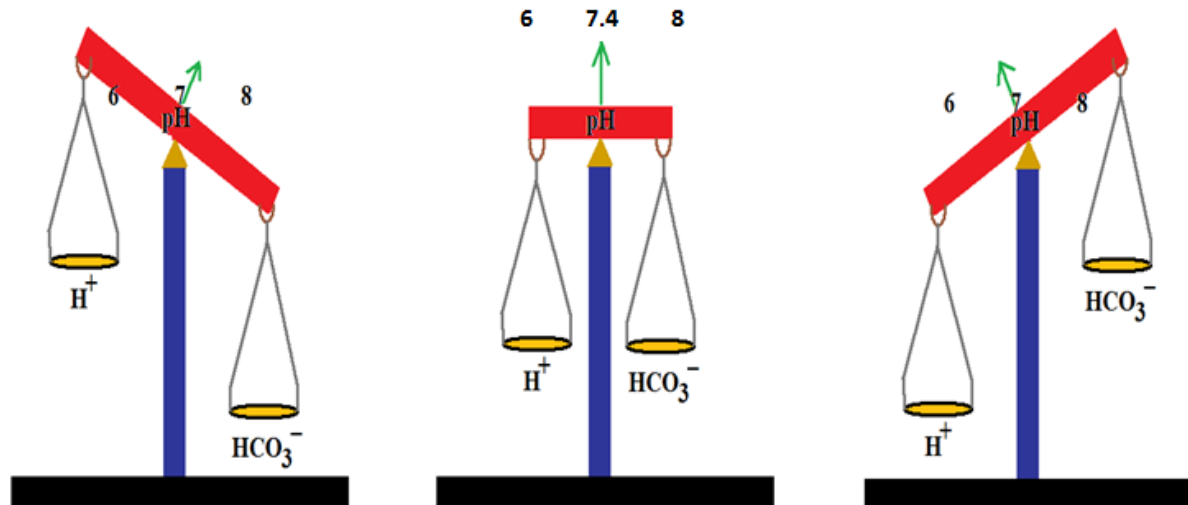
Condition:	Alkaline	Normal	Acidic
Bicarbonate to proton ratio:	44 to 1	20 to 1	8 to 21
Shifts to:	Right making the blood alkaline	7.35-7.45 or normal balance	Left making the blood acidic

Acid-Base Titrations

- Knowing now what we know about acids, how may we apply this information to the lab?
  - By studying acid/base titrations.
- Acids and hydroxide bases react to form water and a salt.
  - This sort of reaction is called a neutralization reaction.
- Bases that contain bicarbonate or carbonate in them also produce carbon dioxide in addition to the water and the salt.
- Examples of these sorts of [neutralization] reactions are summarized, below, in the table:

$HCl + NaOH \rightarrow NaCl + H_2O$
$H_2SO_4 + 2\,KOH \rightarrow K_2SO_4 + 2H_2O$
$2HNO_3 + Ba(OH)_2 \rightarrow Ba(NO_3)_2 + 2H_2O$
$H_3PO_4 + Al(OH)_3 \rightarrow AlPO_4 + 3H_2O$
$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$
$6HNO_3 + Al_2(CO_3)_3 \rightarrow 2Al(NO_3)_3 + 3CO_2 + 3\,H_2O$
$H_2SO_4 + MgCO_3 \rightarrow MgSO_4 + CO_2 + H_2O$

Acid-Base Titrations: In General:

Titrations of acids and bases follow a general sigmoid-shaped curve for a mono-protic acid:
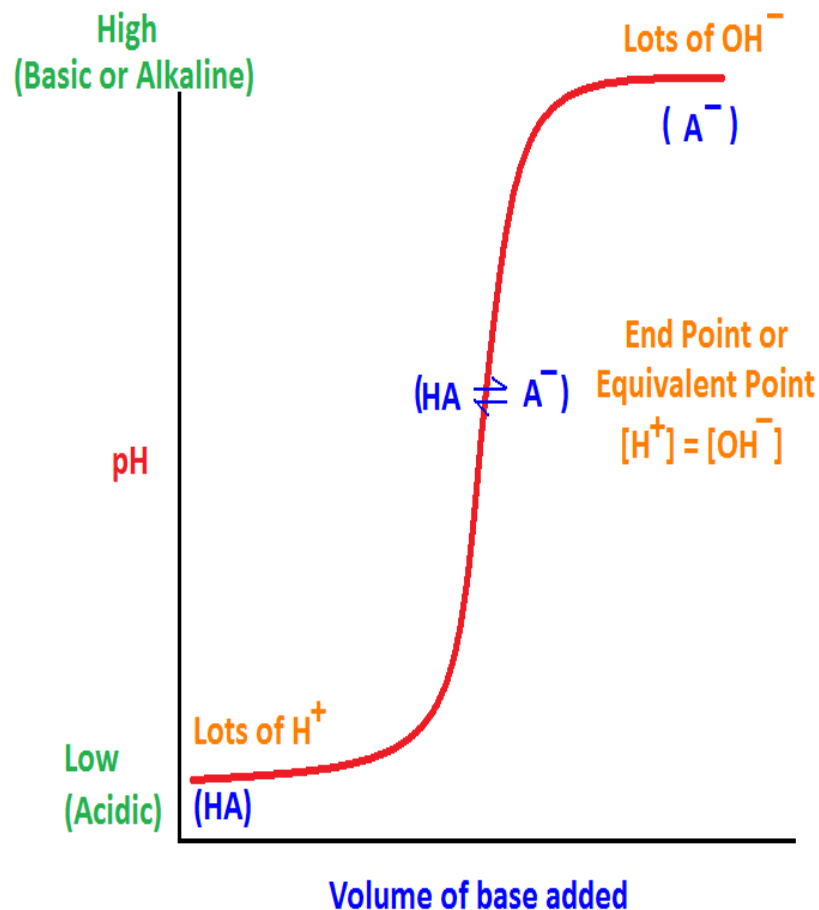
When using a pH meter to keep track of the titration, the equivalent point/end point are not obvious. Typically a technique called "taking the first derivative" of the pH curve (the sigmoid shaped curve) is used to determine these points. Without going into detail, this involves manipulating the sigmoid curve data to take on a sort of "backwards, inside out parabolic shape".

Potentiometric Titration of HOAc -- Trial 1
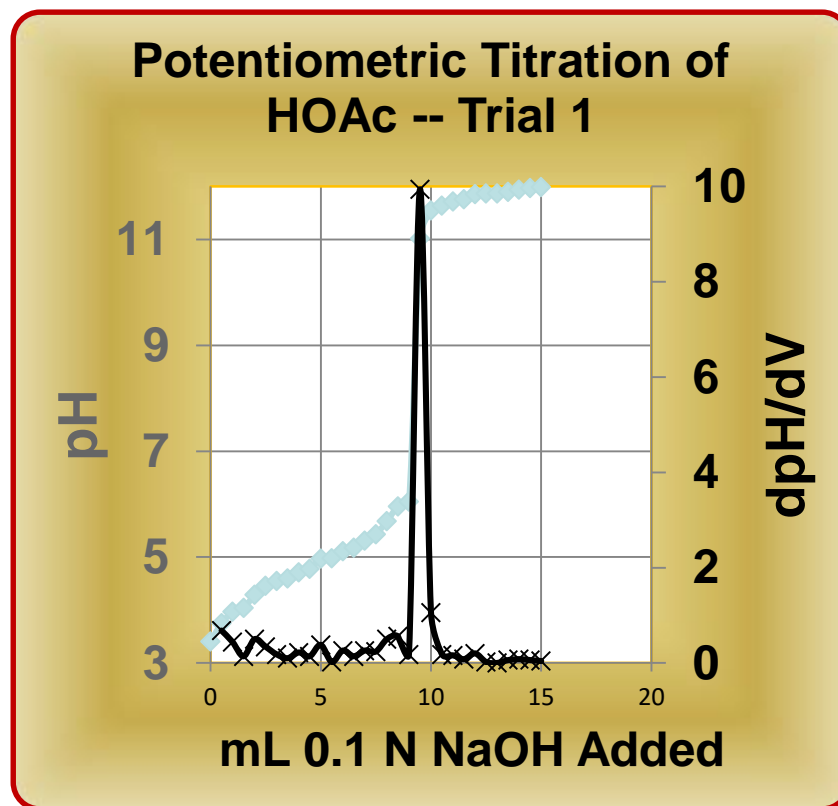
The value of the equivalence point is that it is the pH at which the $[H^+] = [OH^-]$. At that point, divide the volume at the endpoint in half, read from that volume up onto the sigmoid-shaped curve, then over to the pH curve and you will be at the numerical value for the negative log of the acid dissociation constant (pK_a)
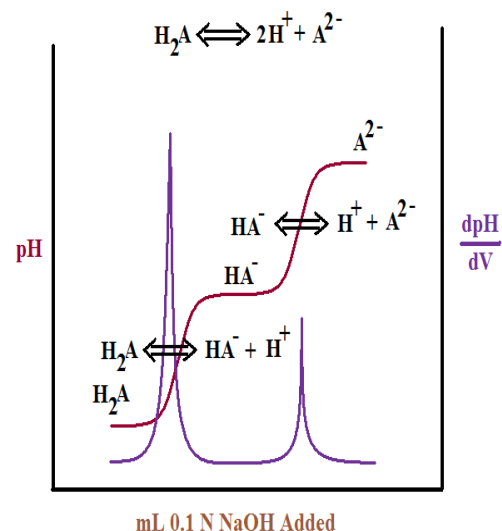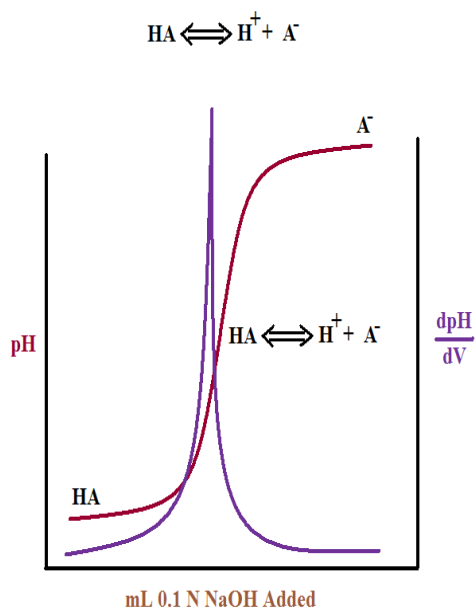
Acid-Base Titrations

$$HA \leftrightarrow H^+ + A^-$$
Or
$$HA + MOH \leftrightarrow HOH + MA$$
Mono-protic Acid
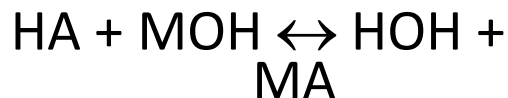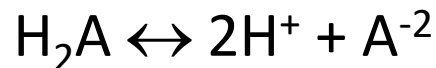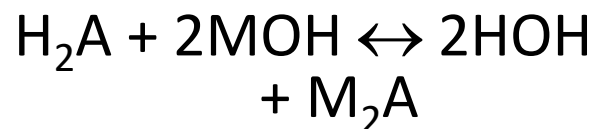
$$H_2A \leftrightarrow 2H^+ + A^{-2}$$
Or
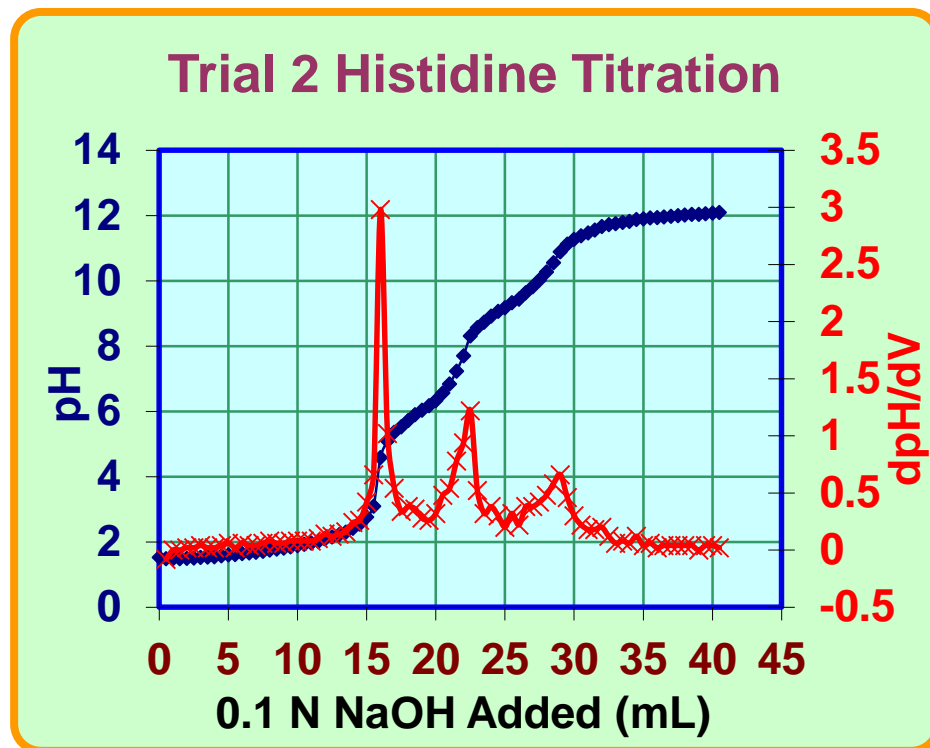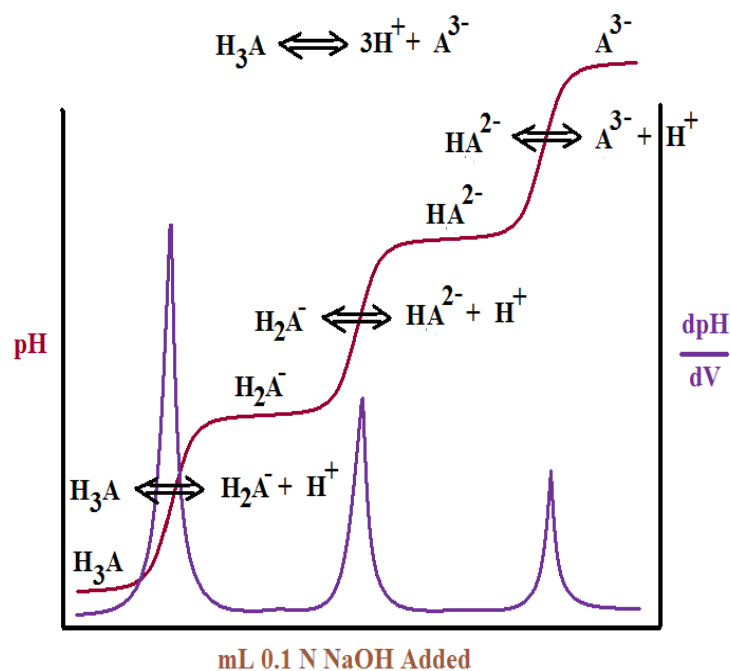$$H_2A + 2MOH \leftrightarrow 2HOH + M_2A$$
Di-protic Acid

# Tri-Protic Acids have THREE Endpoints

Amino Acid Titration: 3 Endpoints

Salts

Salts are solid crystalline substances at room temperature that contains the cation of a base and the anion of an acid, e.g.:

NaCl	$Mg_3(PO_4)_2$	$Al_2(SO_4)_3$
NaOCl	LiBr	KNO_3

Some common salts are summarized in the table, below:

Salt	Name
$CaSO_4 \cdot \frac{1}{2}H_2O$	Plaster of Paris
$MgSO_4 \cdot 7H_2O$	Epsom salts
$Na_2B_4O_7 \cdot 10H_2O$	Borax
$NaHCO_3$	Baking soda
$NaNO_2$	Preservative
$AgNO_3$	Antiseptic/germicide

The formation of salts necessarily depend on their solubility -- or the lack thereof -- in water. Solubility rules that actually help make chemical reactions make sense are covered in more detail in CHEM 121 and 122.

$$MgNH_4PO_4 \Leftrightarrow Mg^{2+} + NH_4^{+} + PO_4^{3-}$$
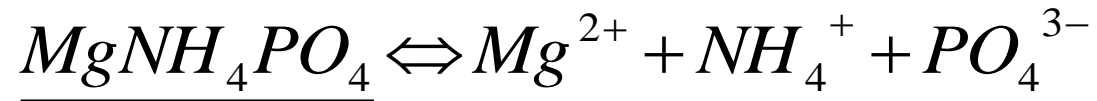
$$K_{sp} = [Mg^{2+}][NH_4^{+}][PO_4^{3-}]$$

Example – a more complex salt – "triple phosphate" – found in some urinary tract infections – precipitates so rapidly that it forms "staghorn calculi":


These calculi are so-called because of their similarities to the head of a stag – male deer.

Buffers

- Buffers are solutions of salts that resist changes in pH, i.e., they maintain a relatively constant pH.
- Consist of a weak acid and its conjugate base.
  - In this case: H_2CO_3 and HCO_3^-
- The acid-base pair serves to maintain an essentially constant pH.
- The acid-base pair can NOT regulate excessive amounts of acid/alkaline substances secondary to a pathology of respiration or of metabolism.

- Buffers work to:
  - Neutralize excess acid to elevate the pH
  - Neutralize excess base to reduce the pH
  - End result: keep pH within normal (7.35-7.45 in human arterial blood) limits under normal circumstances
- This is simply a physiological TITRATION!!
- It just doesn't use phenolphthalein or a pH checker or meter.
- The BUFFER CAPACITY is defined as the amount of hydrogen ion or hydroxide ion "absorbed" by a buffer without causing a significant change in the pH of the system.

Carbonic Acid-Bicarbonate Ion: Physiological Interactions

- CO_2 is fairly soluble in water (more soluble in cold water like in cold soda; less soluble in warm water like in "flat" soda).

- A saturated solution at 1 atm and 25° C is approximately 0.033M. At equilibrium only 0.17% of dissolved CO_2 is in the form of carbonic acid (H_2CO_3).
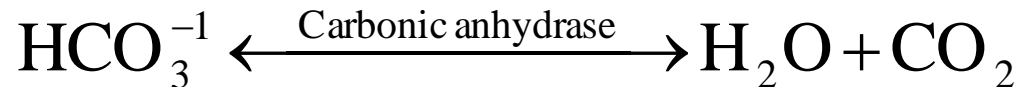
- An aqueous solution of CO_2 is typically acidic:
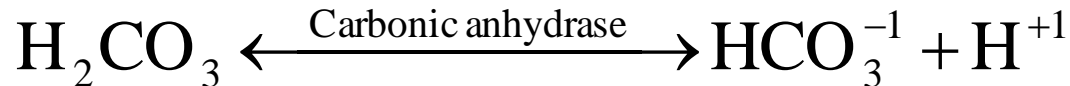
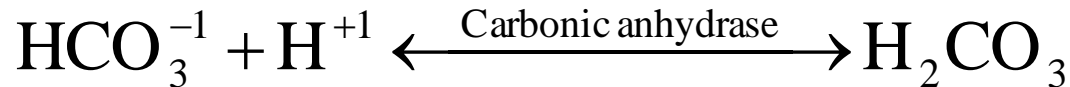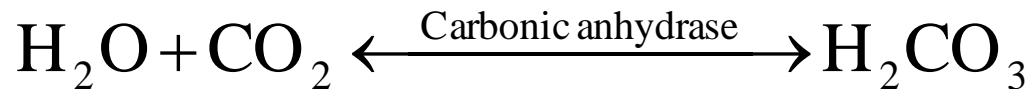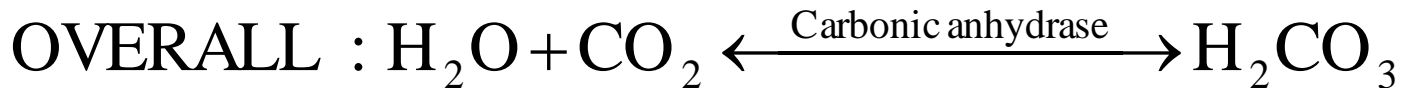$$CO_2(g) + H_2O(l) \rightarrow H^+ + HCO_3^-$$
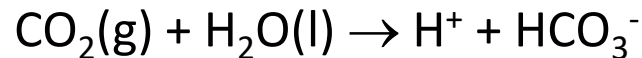
- CO_2 plays a major role in maintaining the pH of blood (and sea water).

- CO_2 is not normally transported as such, rather as HCO_3^-.

- This occurs via an enzymatic reaction catalyzed by carbonic anhydrase:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+$$
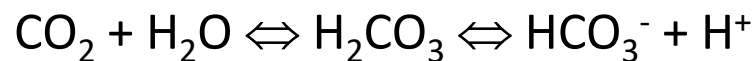
- IMPORTANT in acid/base balance

One system of significance to all humans is the blood. In the blood, the following reactions occur very rapidly and continuously:

$$\text{OVERALL}: H_2O + CO_2 \xleftrightarrow{\text{Carbonic anhydrase}} H_2CO_3$$

$$H_2O + CO_2 \xleftrightarrow{\text{Carbonic anhydrase}} H_2CO_3$$

$$HCO_3^{-1} + H^{+1} \xleftrightarrow{\text{Carbonic anhydrase}} H_2CO_3$$

$$H_2CO_3 \xleftrightarrow{\text{Carbonic anhydrase}} HCO_3^{-1} + H^{+1}$$

$$HCO_3^{-1} \xleftrightarrow{\text{Carbonic anhydrase}} H_2O + CO_2$$

It is these particular reactions that play the most significant role in acid-base balance in the human body.