

**Objectives for The Chemistry of Aqueous Systems**

Properly prepared students, in random order, **will**

1) Be able to explain, apply and demonstrate the use (verbally, written and arithmetically) of the following gas laws under basic chemistry and applied biological conditions:

- a) Dalton's law
- b) Charles' Law
- c) Boyle's Law
- d) Combined Gas Law
- e) Gay-Lussac's Law
- f) Graham's Law
- g) Henry's Law
- h) Universal Gas Law
- i) LaPlace's Law

2) Be able to describe the water cycle in brief;

3) Be able to describe what acidic and basic anhydrides are;

4) Be able to identify acidic and basic anhydrides and write balanced chemical reactions to demonstrate the synthesis of each.

5) Be able to define and describe relative humidity;

6) Be able to explain the significance of the Reynolds number;

7) Be able to explain the dependency of the Reynolds number on pressure gradients, density, viscosity, radius of the tube or vessel and the length of the tube or vessel;

8) Be able to define and apply "surfactant";

9) Be able to define "eupnea";

10) Be able to explain the difference between "p" in "pH" and  $pX_2$ , where "X" is a gas;

11) Be able to list, and give examples of, the types of surface water impurities;

- 12) Be able to define eutrophication and the most important cause of it;
- 13) Be able to describe and illustrate a simple city water purification system;
- 14) Be able to diagram and explain how a simple still works in the laboratory;
- 15) Be able to describe, and demonstrate on paper the use of, a sling psychrometer;
- 16) Be able to discuss the issues surrounding mercury in the environment and the dangers thereof;
- 17) Be able to define hard water;
- 18) Be able to write chemical reactions, balance and correctly, between soap molecules and heavy metal ions found in hard water;
- 19) Be able to describe and illustrate water softening vis-à-vis zeolite and cation/anion exchangers;
- 20) Be able to define the triple point of water, what the actual values are and illustrate renditions of the three phases of water found at this point;
- 21) Be able to explain, illustrate and diagram the currently accepted model of oxygen's hybridization in water and the role it plays in forming ice and surface tension;
- 22) Be able to describe, write and complete balanced chemical reactions between metals and water and non-metals and water;
- 23) Be able to identify the 5 forms of hydrates and name hydrates properly;
- 24) Be able to begin with the auto-dissociation of water and derive the  $K_w$  and pH;
- 25) Be able to define, apply and give examples of the following liquid laws:
  - a) Pascal's Law
  - b) Bernoulli's Law
  - c) The Venturi Effect
  - d) Poisuille's Law
- 26) Be able to explain, diagram and calculate the flow of liquids in series and in parallel;
- 27) Be able to explain the difference between resistance to flow and conductance of flow of fluids;
- 28) Be able to explain the difference between laminar and turbulent flow of liquids;
- 29) Be able to explain the significance of the Reynold's number;

- 30) Be able to list and apply to chemical reactions the Rules of Solubility;
- 31) Be able to list and apply to chemical reactions the Rules of Strong/Weak Acids/Bases;
- 32) Be able to list and apply to chemical reactions the Rules of Electrolytes;
- 33) Be able to list and apply to chemical reactions the Preparation of Salts;
- 34) Be able to explain the significance of the mean velocity of fluids on the Reynold's number;
- 35) Be able to explain the auto-ionization of water descriptively and chemically;
- 36) Be able to explain and derive the  $K_w$ ;
- 37) Be able to calculate the resistance to flow of a fluid through vessels in series or in parallel;
- 38) Be able to derive, and apply, the determination of pH using the  $K_w$ .
- 39) Be able to explain the difference between unsaturated, saturated and super-saturated solutions;
- 40) Be able to explain what an immiscible mixture is;
- 41) Be able to define, explain and illustrate the difference between osmosis, dialysis and diffusion;
- 42) Be able to define what a salt is;
- 43) Be able to explain Le Chatelier's Principle and illustrate that explanation;
- 44) Be able to explain what a buffer is and how a buffer works from a chemical and a biological perspective;
- 45) Be able to determine the concentrations of solutions using the Common Dilution Methods;
- 46) Be able to describe what colligative properties are and how they impact solutions in an elementary manner;
- 47) Be able to calculate the osmolarity of solutions knowing the rules of solubility, electrolytes and acids/bases;
- 48) Be able to solve problems about or using osmolarity and/or osmotic pressure;
- 49) Be able to explain what chromatography is;
- 50) Be able to explain, apply and demonstrate what the  $K_p$  is;
- 51) Be able to explain (and diagram) how GPC/SEC works;
- 52) Be able to explain (and diagram) how RP-chromatography works;

53) Be able to explain (and diagram) how ion exchange chromatography works and how it applies to water softening with illustrations;

54) Be able to explain, describe and illustrate the various phases in a chromatography column;

55) Be able to explain the difference between a solution and a colloid;

56) Be able to explain what a solvent and a dispersing medium are and the differences between them;

57) Be able to explain what a solute and a dispersed phase are and the differences between them;

58) Be able to explain how particle size determines if a solution is a solution or if a colloid is a colloid;

59) Be able to list several examples of colloids;

60) Be able to give two examples of colloids and their emulsifying agents;

61) Be able to define what a buffer is and explain what a buffer is supposed to do;

62) Be able to derive and apply the  $K_a$  for acids;

63) Be able to derive and apply the  $K_b$  for bases;

64) Be able to derive, demonstrate and apply the relationship between  $K_a$ ,  $K_b$  and  $K_w$ ;

65) Be able to derive, demonstrate and apply the Henderson-Hasselbalch formula for pH determination in buffer solutions;

66) Be able to define what N means;

67) Be able to calculate the equivalent weight of any acid, base and salt;

68) Be able to explain the function of a buffer solution;

69) Be able to explain and define the 4 definitions of acids and bases;

70) Be able to demonstrate using Lewis structures (the octet rule) the bonding between the various entities in an acid or base or ion, including coordinate covalent bonds;

71) Be able to calculate the pH of a solution knowing the concentration of one of the reactants and the  $K_a$ ;

72) Be able to calculate either the pH or pOH from the  $pK_w$  ;

73) Be able to properly name and write the formulas for common acids, bases and salts;

74) Be able to identify conjugate acids and bases in acid-base reactions;

- 75) Be able to explain the qualitative difference between a strong acid and a weak acid;
- 76) Be able to explain the difference between a strong base and a weak base;
- 77) Be able to identify, name and write the correct formulas for the oxo-acids of the halogens;
- 78) Be able to list the 7 mechanisms for acid formation, as well as at least one example thereof;
- 79) Be able to list the 5 mechanisms for base formation, as well as at least one example thereof;
- 80) Be able to identify acids;
- 81) Be able to identify hydroxide, carbonate and bicarbonate bases;
- 82) Be able to identify and explain a titration curve in general terms;
- 83) Be able to identify the number of titration endpoints on titration curves of mono-, di- and tri-protic acids.
- 84) Be able to use the first derivative on a titration curve to identify/determine in a quantitative manner the pK for each endpoint in the titration curve;
- 85) Be able to write out the correct chemical reactions for the dissociation of mono-, di- and tri-protic acids;
- 86) Be able to write out correctly balanced and formulated chemical reactions between acids and the three kinds of bases;
- 87) Be able to write at least one example(chemical reaction) of the formation of HCl;
- 88) Be able to explain which oxo-acid is strongest and why;
- 89) Be able to list the color of the acid and base forms of litmus; phenolphthalein and bromocresol purple;
- 90) Be able to define oxidation and reduction;
- 91) Be able to define oxidizing agents and reducing agents and recognize/identify them in a redox reaction;
- 92) Be able to provide 3 definitions of oxidation;
- 93) Be able to provide 3 definitions of reduction;
- 94) Be able to apply the 7 Oxidation Number Rules to properly balance a redox reaction;
- 95) Be able to use all three redox balancing methods: Oxidation Number Method; Oxidation Number Method for Aqueous Systems; Half Reactions for Aqueous Solutions Method;

- 96) Be able to define oxidation number and state and apply those definitions to redox balancing;
- 97) Be able to list at least 3 examples of oxidizing agents and their common uses;
- 98) Be able to explain what happens at a cathode and an anode;
- 99) Be able to use proper battery nomenclature in short-handing the chemical nature of a battery;
- 100) Be able to explain in an elementary manner how corrosion occurs;
- 101) Be able to explain how a solar panel built from wafers functions;
- 102) Be able to explain the difference between the PVC electron donor wafer and the PVC electron acceptor wafer;
- 103) Be able to explain and diagram how an electrolytic cell works;
- 104) Be able to explain what Piezo electricity is in terms of crystalline structure;
- 105) Be able to explain in simple terms how the Piezo effect impacts bone;
- 104) Be able to explain in simple terms how a muscle cell membrane is made to contract electrically;
- 105) Be able to explain in simple terms how a heart muscle cell contracts using the chemistry of the cell in that explanation

and demonstrate that comprehension and applications thereof per assessment tool at no less than a score of 75%.

## Gases and Liquids

### 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: First, 1 Torr = 1 mm Hg. The Torr was named for the developer of the barometer, Torricelli.

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

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

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

Body temperature (on average) = 98.6°F; 37°C; 310K

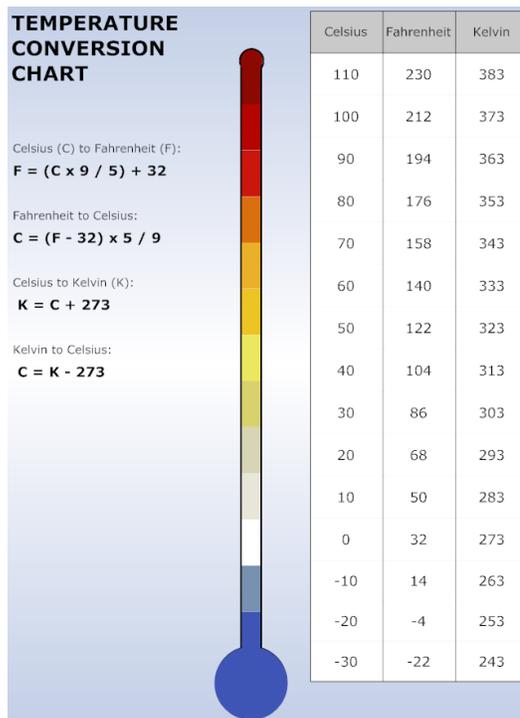
### Boyle's Law

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:

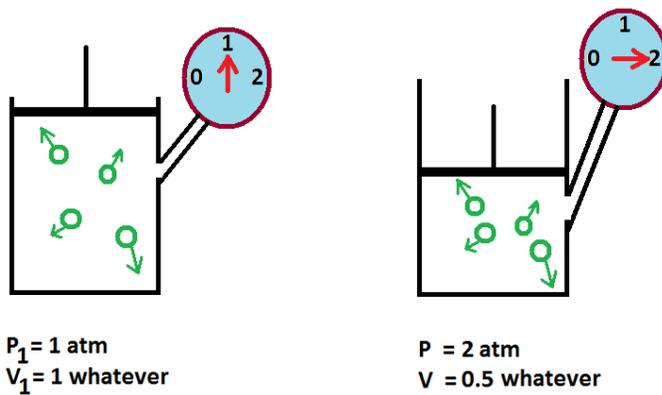
$$P_1 V_1 = P_2 V_2$$

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

Remember, also, your temperature conversions and the points of boiling and freezing on all three temperature scales.



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 (top left following page). 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.



$$1 \times 1 = 2 \times 0.5$$

convert the 65 psi into atm (4.42 atm). Rearrange the equation and solve for "X":

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 of being greater than atmospheric pressure and the air is forced out of the lungs.

### 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.

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

Arithmetically, Charles' Law may be expressed in a manner similar to that of Boyle's Law:

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 (top right following page).

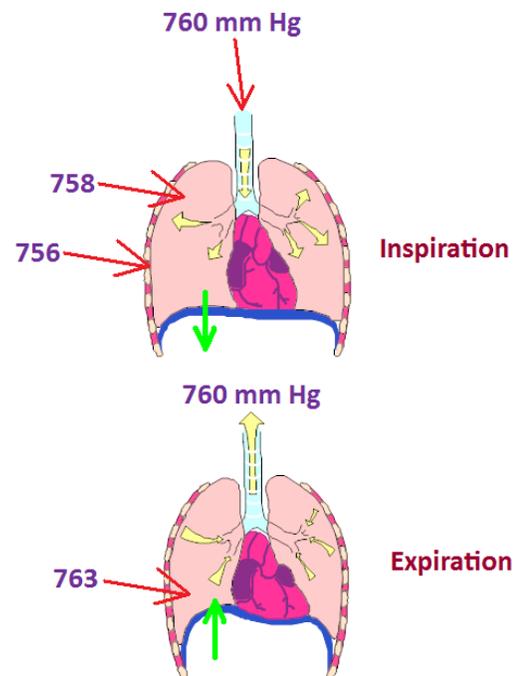
Example: A gas occupies 350 mL at 27° C. The gas is heated until it occupies 700 mL. What is the new temperature of the gas?

Example: How many liters of air at 1 atm need to be pumped into a bicycle tire with a 1 liter volume at a pressure of 65 psi?

$$P_1 V_1 = P_2 V_2$$

$$V_1 = X = \frac{(4.42 \text{ atm})(1 \text{ L})}{1 \text{ atm}} = 4.42 \text{ L of air}$$

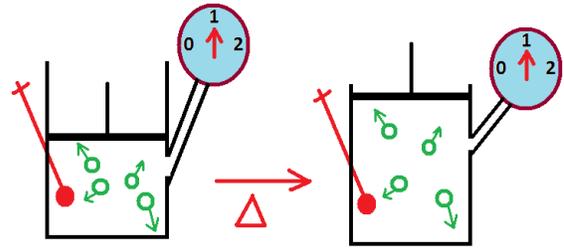
Solution: First, set up Boyle's Law equation:  $P_1$  equals 1 atm;  $V_1$  equals "X",  $P_2$  equals 65 psi and  $V_2$  equals 1 L. Remember, though, that you may not mix units. To bypass this fiasco,





Solution: First set up Charles' Law as above. Second assign values to each variable:  $V_1$  equals 350 mL,  $T_1$  equals 300 K (How'd I get this?),  $V_2$  equals 700 mL and  $T_2$  equals "X". Rearrange, plug in and solve for "X":

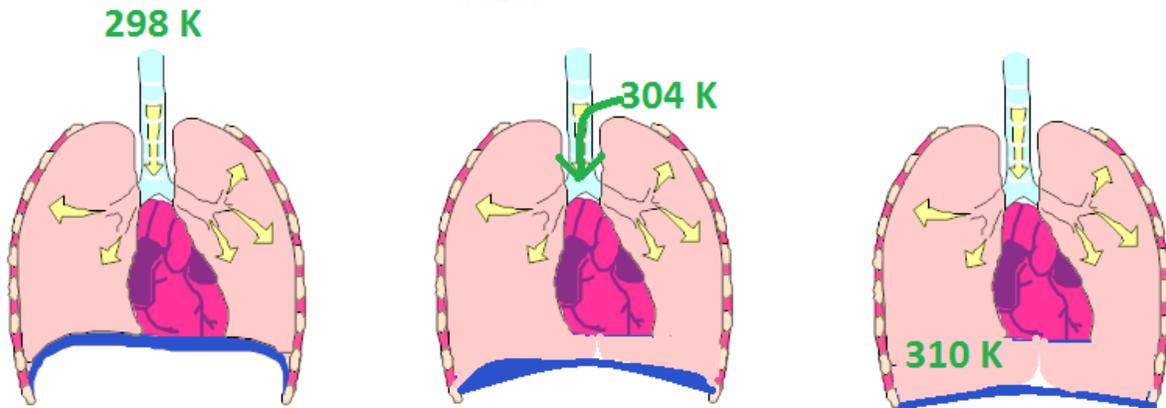
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



$$T_2 = \frac{T_1 V_2}{V_1} = \frac{(300\text{K}) * (700\text{mL})}{350\text{mL}} = 600\text{K} \Leftrightarrow 327^\circ\text{C}$$

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.



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

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

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

Example: 250 mL of oxygen is collected at  $30^\circ\text{C}$  at 740 Torr. What volume will the gas fill at STP? STP is standard temperature ( $0^\circ\text{C}$ ) and pressure (760 torr).

Solution: rearrange the combined gas law to solve for  $V_2$ . Plug the numbers in and calculate:

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

Second Example: 4 L of helium are at STP. The He is compressed into 0.5 L at 50° C. What pressure is the He under?

$$V_2 = \frac{T_2 P_1 V_1}{T_1 P_2} = \frac{(273 \text{ K}) * (740 \text{ Torr}) * (250 \text{ mL})}{(303 \text{ K}) * (760 \text{ Torr})} = 219.3 \text{ mL}$$

Solution: As before, rearrange the equation. Solve for P<sub>2</sub>:

Page | 10

The Ideal Gas Law, aka Universal Gas Law

This equation is easily expressed: PV = nRT, where P is pressure (in atm), V is volume (in liters), n equals the number of moles of the gas present, T is the absolute temperature and R is the universal gas constant (with the units described just above, R = 0.0821 L\*atm/mol\*K. R is determined by substituting standard values into the rearranged equation:

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

$$P_2 = \frac{T_2 P_1 V_1}{T_1 V_2} = \frac{(323 \text{ K}) * (1 \text{ atm}) * (4 \text{ L})}{(273 \text{ K}) * (0.5 \text{ L})} = 9.5 \text{ atm}$$

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm}) * (22.4 \text{ L})}{(1 \text{ mol}) * (273 \text{ K})} = 0.0821 \frac{\text{L} * \text{atm}}{\text{mol} * \text{K}}$$

In other words, 1 mol of any gas at 1 atmosphere of pressure and 273 K will occupy 22.4 liters.

Example: Calculate the volume of a gas in an enclosed container if 0.525 mol of this gas exerts a pressure of 3 atm at 10° C?

Rewrite the equation and plug the numbers into it:

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(0.525 \text{ mol}) * (0.0821 \text{ L} * \text{atm}) * (283 \text{ K})}{(3 \text{ atm}) * (\text{mol} * \text{K})} = 4.07 \text{ L}$$

Example: Calculate the number of mols of a gas that fills a cylinder of 500 mL at 100° C and pressure of 720 torr.

Solution: convert torr to atmospheres (720/760) = 0.95 atm. Rearrange the equation and solve for n:

$$PV = nRT$$

$$\frac{PV}{RT} = n = \frac{(0.95 \text{ atm}) * (0.5 \text{ L}) * (\text{mol} * \text{K})}{(0.0821 \text{ L} * \text{atm}) * (373 \text{ K})} = 0.016 \text{ mol of the gas}$$

Example: A sample of diethyl ether has a mass of 16.5 g and occupies a volume of 5 L at STP. What is the molecular weight (MW) of the diethyl ether?

Solution: There is no "n" term in this question. Remember that the mols of something may be determined by dividing the mass of the substance by its MW and substitute this into the universal gas law equation for "n" after rearrangement:

$$MW = \frac{(\text{mass in grams}) * (R) * (T)}{P * V}$$

$$n = \frac{\text{mass in grams}}{MW}$$

$$MW = \frac{(16.5 \text{ g}) * (0.0821 \text{ L} * \text{atm}) * (273 \text{ K})}{(1 \text{ atm}) * (5 \text{ L}) * (\text{mol} * \text{K})} = 74 \text{ g/mol}$$

### 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.,  $P_T = P_1 + P_2 + P_3 + P_4 + \dots + P_n$ , 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 ( $p_{N_2}$ ) is 600 mm Hg and the  $p_{O_2}$  is 50 mm Hg. If water vapor is the only other gas present, what is the  $p_{H_2O}$  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:

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

$$P_3 = 745 - 650 = 95 \text{ mm Hg} = p_{H_2O}$$

Example: A container has a gas mixture of nitrogen, oxygen and carbon monoxide. The total pressure is 2500 torr. The  $p_{N_2}$  is 800 torr, the  $p_{O_2}$  is 500 torr. What is the  $p_{CO}$ ?

Solution:  $P_T = P_1 + P_2 + P_3$

$$2500 = (800 + 500) + P_3$$

$$P_3 = 2500 - 1300 = 1200 \text{ torr}$$

Continuation: if 1 mole of CO is present, what volume does the gas fill at 0° C? Solution: use the universal gas law equation and solve with rearrangement for V:

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol}) * (0.0821 \text{ L} * \text{atm}) * (273 \text{ K})}{(1.6 \text{ atm}) * (\text{mol} * \text{K})} = 14 \text{ L}$$

## 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:

$$\frac{\text{Rate of Diffusion of Gas}_A}{\text{Rate of Diffusion of Gas}_B} = \sqrt{\frac{MW_B}{MW_A}}$$

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:

$$\frac{\text{Rate of Diffusion of H}_2}{\text{Rate of Diffusion of Cl}_2} = \sqrt{\frac{MW_{Cl_2}}{MW_{H_2}}} = \sqrt{\frac{71}{2}} \approx 6$$

Therefore H<sub>2</sub> diffuses 6 times faster than does Cl<sub>2</sub>.

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

$$\frac{\text{Rate of Diffusion of O}_2}{\text{Rate of Diffusion of I}_2} = \sqrt{\frac{MW_{I_2}}{MW_{O_2}}} = \sqrt{\frac{254}{32}} \approx 3$$

O<sub>2</sub> diffuses 3 times faster than iodine.

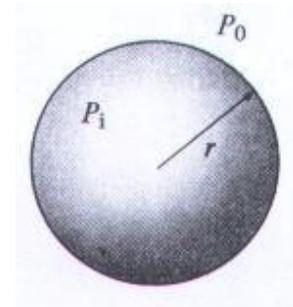
Example: Compare the rate of diffusion of molecular nitrogen with molecular oxygen:

$$\frac{\text{Rate of Diffusion of N}_2}{\text{Rate of Diffusion of O}_2} = \sqrt{\frac{MW_{O_2}}{MW_{N_2}}} = \sqrt{\frac{32}{28}} \approx 1.07$$

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 ( $\Delta P$ ).



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  $\gamma$  = 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. 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  $\pi r$  is common to both sides of the equation, the equations reduce to:

$$2 \gamma = \Delta P r,$$

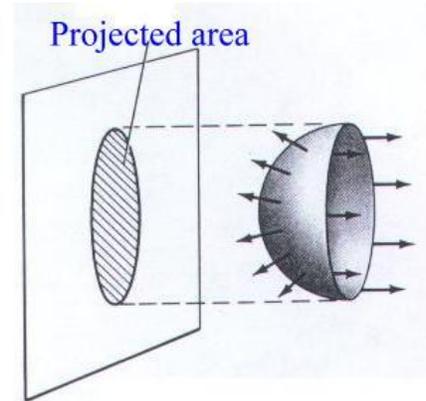
where  $r$  = the radius of the projected circle.

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

$$\gamma = (73.5-14.7) * 3 = 176.4 \text{ psi}$$

#### 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:

$$2 \Delta = \Delta P r.$$

With rearranging:

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

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

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  $\Delta P$ :

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

#### 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  $\Delta P$ :

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

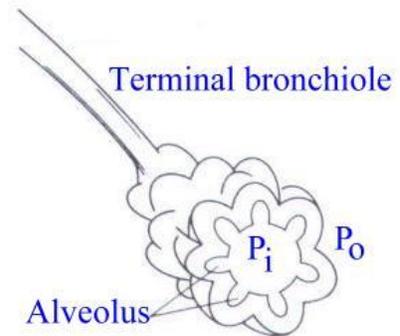
NOTE: a greater pressure gradient is required to maintain a smaller sphere.

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.,  $2 \gamma = \Delta P r$ ? There are some problems with this, see Table below:

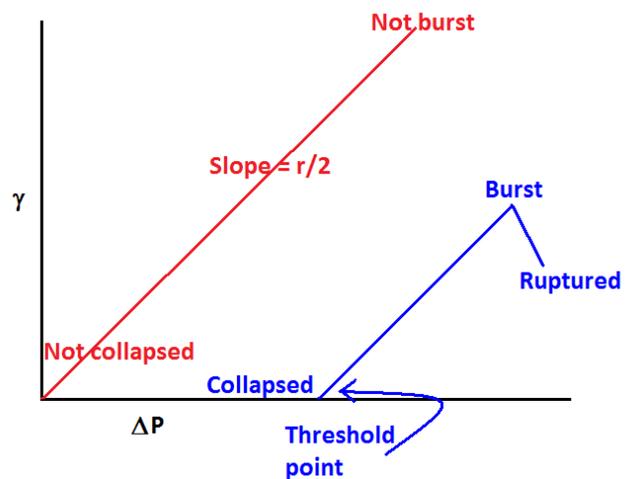


At expiration	At inspiration
$P_o$ increases and $r$ decreases	$P_o$ decreases and $r$ increases
At expiration, the pressure gradient goes down	At inspiration, the pressure gradient goes up

Since  $2 \gamma = \Delta P r$ , 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  $2 \gamma = \Delta P r$ , 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,  $4.42 \times 10^{-5}$  psi.

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

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

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

Gases are Soluble in Water

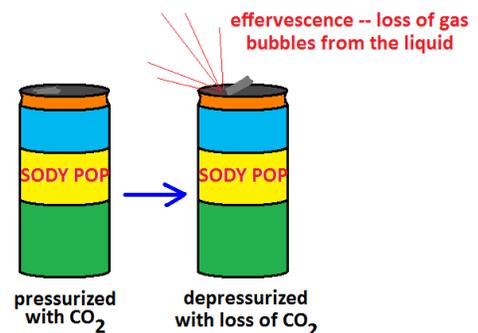
As mentioned shortly, Henry's Law says that the greater the pressure of a gas over a solution, the greater the amount of gas dissolved in the solution. The table, below summarizes the solubilities of 3 gases in water:

Gas	Solubility per 100 g water at 20° C
O <sub>2</sub>	4.3 mg
CO <sub>2</sub>	169 mg
NH <sub>3</sub>	10.6 grams

Henry's Law

Henry's Law says that the greater the pressure of a gas over a solution, the greater the amount of that gas dissolved in the solution.

Consider a soda. When you first open it, the can is under pressure that is greater than atmospheric pressure, hence, the "pfffffftttttt" when you open it. Sodas are canned under pressure with CO<sub>2</sub> to make the "fizz". At sea level, it takes longer for the soda to go flat than it does at Lake Tahoe simply because of pressure differences. If you don't entirely believe this, go to San Francisco, buy a soda and put it in your car. Drive to Lake Tahoe and open it fast. Do this part outside your car and aim the can away from yourself or other people :-)



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.

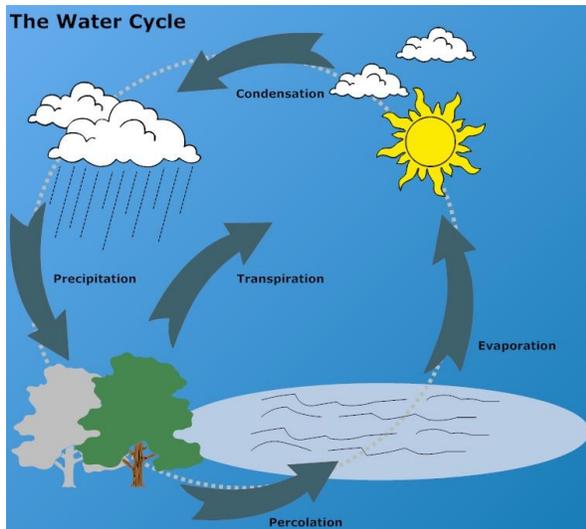
Gas	Solubility Coefficient
CO <sub>2</sub>	0.57
O <sub>2</sub>	0.024
N <sub>2</sub>	0.012
He	0.005±

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.

### Water and Chromatography

#### 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.

#### 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:

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

#### Natural Waters

Rainwater is relatively pure. Any impurities are dust and dissolved gasses at first. After time has passed, the rainwater is clean and free of impurities.

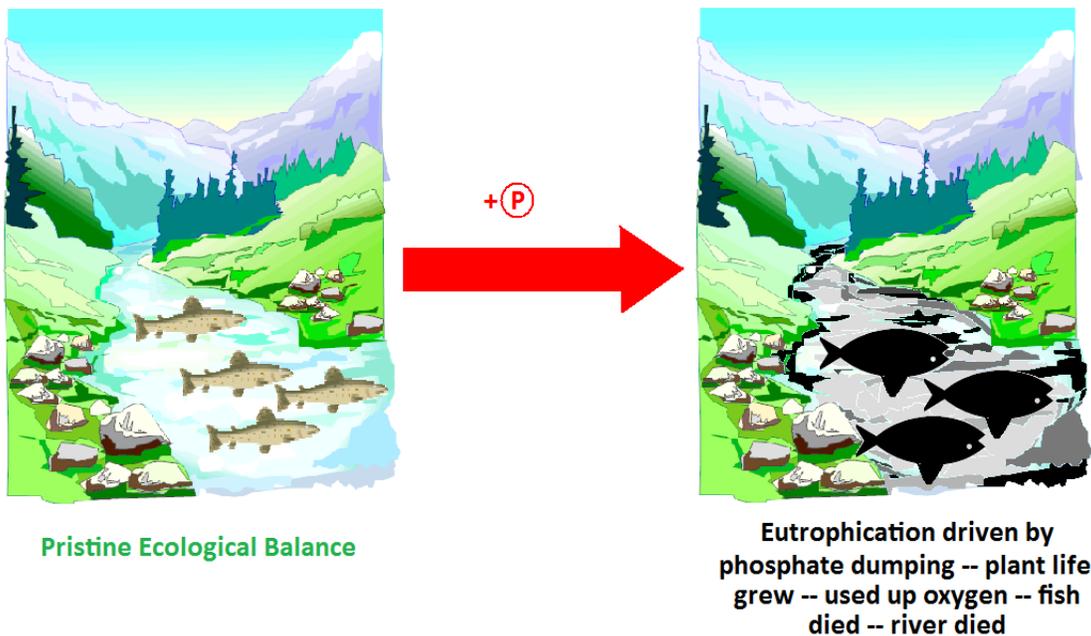
#### Surface Water Impurities

Surface water impurities tend to consist of 4 classes as summarized in the following table:

Type of impurity	Suspended solids	Dissolved gases	Dissolved salts	Dissolved organic substances
Examples	Sand, clay, mud, silt, leaves, sticks, micro-organisms	Oxygen, nitrogen, carbon dioxide, $N_2O_y$ , ammonia, hydrogen sulfide	Chlorides, sulfates, bicarbonates of sodium, potassium, calcium, magnesium, aluminum and iron (III)	From the decay of vegetable and animal matter

### Water Pollution and Pollutants

The biggie of 40 years or so ago were the phosphates. They were primarily used as water softeners (called detergent builders). The big problem with phosphates is that if they were dumped into a body of water, they caused the increased growth of algae, bacteria and plants. This caused an increase in the utilization of oxygen. Because the oxygen was used up faster, fish weren't getting enough oxygen and died. This process is called eutrophication (to increase plant nutrients in a body of water).



A substitute used for phosphate was nitrilotriacetic acid (NTA). It was used for a short time until about 1970, then withdrawn voluntarily. NTA combines with various trace metals in water -- harmful metals. If the combination product is not destroyed in sewage it gets into public water works and causes health problems. The current detergent builder is based off of washing soda, sodium carbonate.

### Mercury

Mercury is still a big problem, particularly here in Nevada. Elsewhere, mercury levels were tested in samples preserved at the Smithsonian (caught between 1878 and 1909, from the Great Lakes) and were

found to be no different than they were in fish caught in 1971. I'm not aware of any follow up to this since that time.

The big problem with mercury is the formation of methyl mercury. This form of mercury is very poisonous. It is synthesized from the action of micro-organisms in inland waters in the bottom mud that contains mercury. Mercury, by itself, is toxic to the liver, kidney and bowel. Methyl mercury attacks the central nervous system, is retained in the body and causes toxicity over a prolonged period of time.

It is also produced and stored in the fish and causes poisoning in the humans that eat the fish. You may be familiar with the Hg problem at Lahontan.

Several years ago, an individual was interviewed on local TV and exclaimed that he was still going to eat the fish he caught there, regardless of the warnings not to. You may also be familiar with "Alice in Wonderland". The Mad Hatter was so called because in "those days" hats were blocked with Hg. It was taken up, crossed the blood-brain barrier and people went "mad".

Sewage waste materials can be a problem, as well. Industrial waste, human waste and animal waste all dump viruses and other micro-organisms into bodies of water. These then get into public water sources. A situation like this occurred in Chicago a number of years ago when a feedlot's sewer system broke and contaminated animal sewage got into the water supply and made a number of people ill.

Pesticides and fertilizers are a problem, as well. Paris Green ( $\text{Cu}_3(\text{AsO}_3)_2 \cdot \text{Cu}(\text{OAc})_2$ , copper (II) arsenite-acetate, calcium and lead arsenates, mercury compounds, DDT and yard fertilizers all create water pollution. Although DDT is not commonly used any more, special use permits may be obtained to control mosquitoes when the benefit to the public far outweighs the risks to the general welfare of the public. All these pesticides and fertilizers eventually lead to or exacerbate the death of something or someone. Fertilizers like urea, nitrates, sulfate compounds all cause eutrophication. Soil conservation is helping with this with new environmental directives.

Thermal pollution is a problem from industry. Discharges from manufacturing plants elevate the temperature of the water into which it is dumped. In 1970, the Department of the Interior directed the following policy regarding Lake Michigan:

"The minimum waste heat shall be added to the waters of Lake Michigan. In no event will heat discharges be permitted to exceed 1° F rise over ambient at the point of discharge."

Even a 2° F rise in temperature causes decreased solubility of oxygen in water, and, hence, increased release of oxygen from that water into the atmosphere.

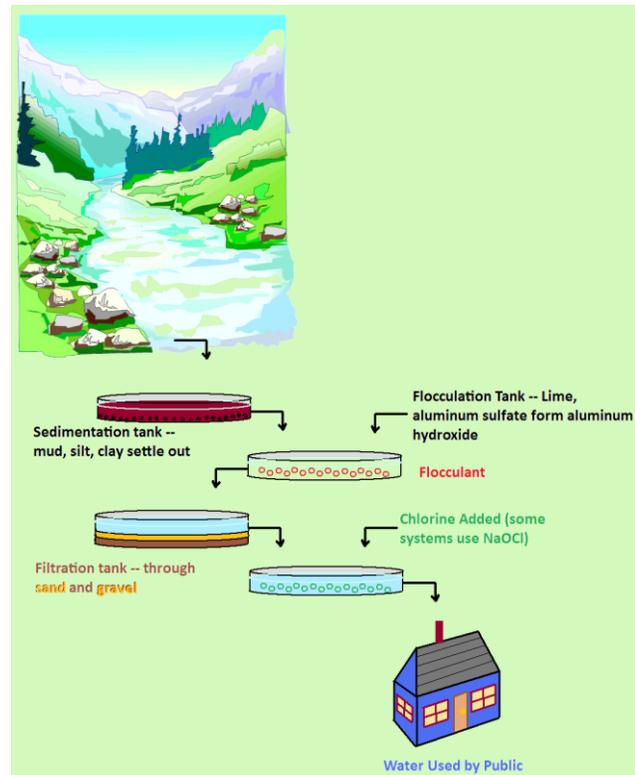
## Water Purification

### City Systems

Although this portion is not inclusive (states, counties and cities seem to have their own "tweaks" on purification), it does give an idea of the basics for water purification.

Water from the stream or river or reservoir flows into a sedimentation tank. In this tank, mud, clay and silt settles out. The water then flows from this tank into the flocculation tank where it is mixed with lime and aluminum sulfate. The latter 2 chemicals form aluminum hydroxide that allows the flocculation of particulate matter not previously filtered out to form.

The flocculate is then filtered through sand and gravel in the filtration tank. In systems that are chlorinated, it seems that while bubbling chlorine gas through this freshly-filtered water is the most popular, there is some use of bleach (sodium hypochlorite) to accomplish the same end. While chlorine gas is tasteless and odorless, we all notice the "chlorine" taste in city water. This is really sodium hypochlorite (bleach) that forms upon reaction of chlorine with the water. The water is then used by all of us in our homes.



### Laboratory Purification

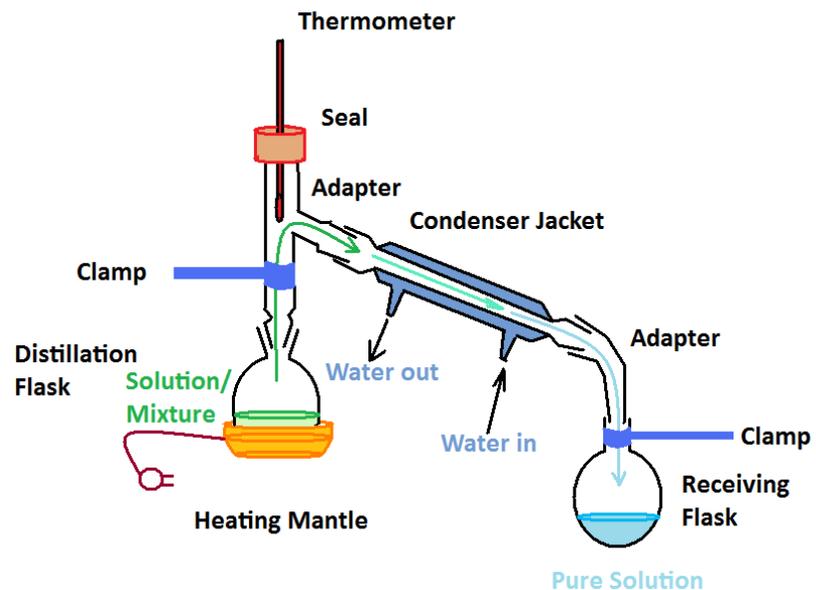
This is accomplished by one of two methods: distillation and de-ionization. The former will be examined first.

Distillation is the purification of water by heating the water to boiling, condensing the vapor and collecting the pure liquid in another vessel.

### A Simple Still

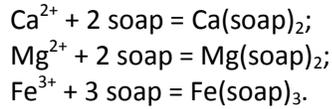
The distilling flask contains the impure water. As it is heated, the vapor rises into the adapter. The point where the thermometer is is the hottest part of the still. The vapor then passes through the condenser.

The condenser is hollow with a cooling jacket of water around it. The cooling water goes in at the bottom of the still and out at the top of the still. The condensate then drips into the collection or distillate flask and is pure.



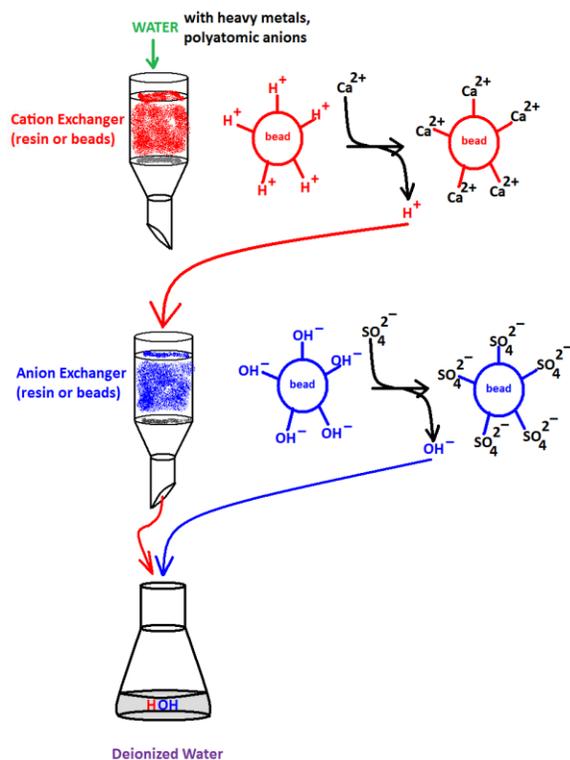
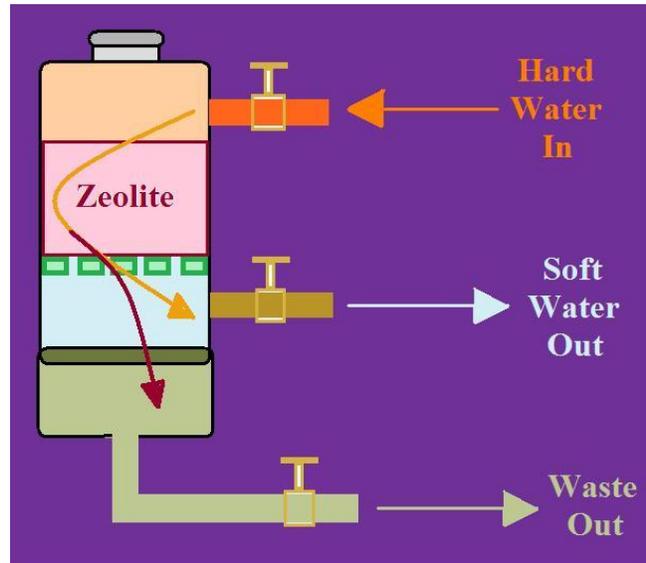
## Hard Water

Hard water contains calcium, magnesium and iron salts (anions include chlorides, sulfates and bicarbonates). The problems with hard water are two-fold: It forms bath tub ring:



These have no cleaning power and stick to surfaces. This is the phenomenon that occurs with shampoo, too. Hard water is responsible for "scale" formation in boilers. This is a HUGE problem. 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". Scale is a poor conductor of heat and leads to fuel wasting. Boiler explosions are usually due to scale presence.

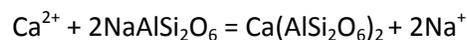
Here's how the process works: once scale is already present, to keep the water in the boiler at the appropriate temperature, the metal is



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:  $4\text{H}_2\text{O} + 3\text{Fe} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ . 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!

Two types of water softeners will be studied: Zeolite and Ion Exchange softeners, respectively.

In the case of zeolite (above), hard water enters the tank and filters through zeolite ( $\text{NaAlSi}_2\text{O}_6$ ). The soft water leaves through a frit beneath the zeolite; the waste leaves beneath that, as well. The reaction that occurs is as follows:



The water is, thus softened. One note of caution: if you are an individual with sodium sensitive

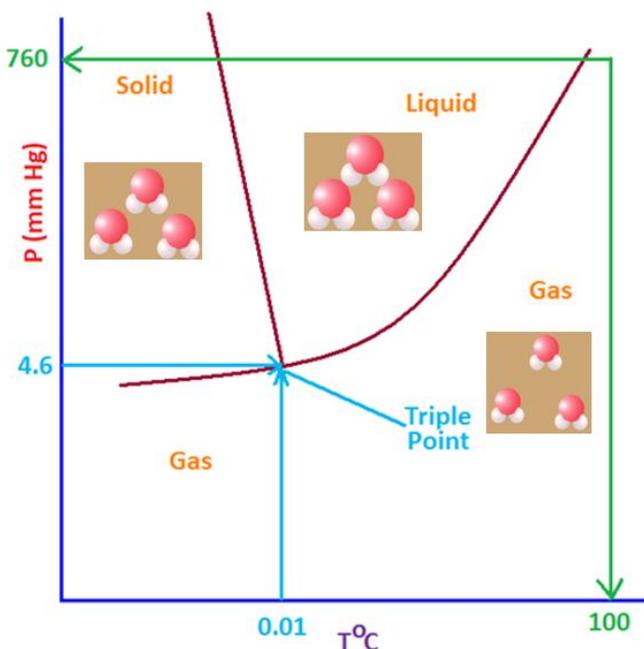
hypertension, this is not the method you want to use as it increases your sodium intake.

The second sort of softener (bottom left previous page) is 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.

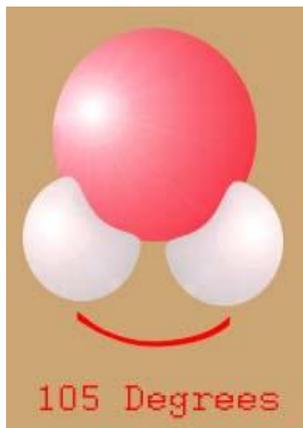
### Physical Properties of Water

The physical properties of water are summarized, below. Expansion of water occurs on cooling below 4° C. Water has an abnormally high melting point (0° C at 760 mm Hg; 760 mm Hg is 1 atmosphere and is also equal to 29.92 inches of Hg). Water has an abnormally high boiling point (100° C at 760 mm Hg). Pure water is odorless, tasteless and colorless. Natural water in a body of water appears blue/green. The taste of drinking water is due to dissolved gases from the air and dissolved salts from the earth.

The unit of mass in the SI is the mass of 1 mL of water at 4° C (the temperature with the maximum density for water). This is exactly equal to 1.00000 grams. The unit of heat in the SI is the calorie (which is equivalent to 4.184 Joules) and is approximately the quantity of heat required to raise 1-g water from 14.5° C to 15.5° C.



Water is capable of forming all three phases, i.e., solid, liquid and gas. At the triple point for water, i.e., 0.01 C and 4.6 mm Hg, all three phases exist at once. Once the temperature and pressure go below this point, solid water (ice) sublimates to the vapor-state, bypassing the liquid state. You may have seen dry ice (solid  $CO_2$ ) do this at parties.



### The Molecular Structure of Water

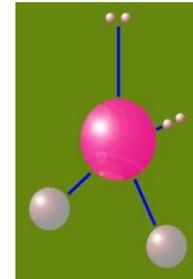
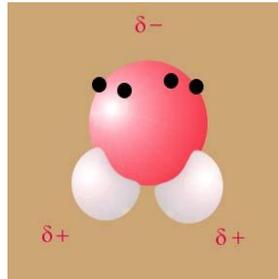
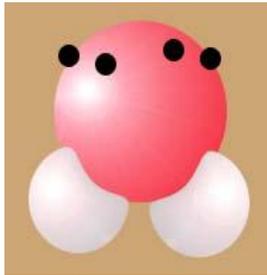
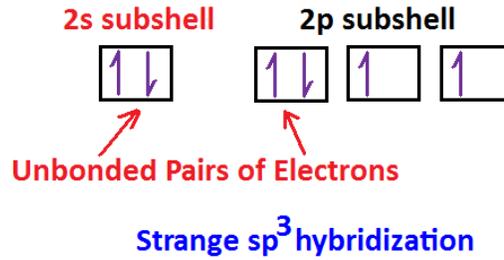
The predicted structure for water is angular with polar covalent bonds and a bond angle of 105° between the hydrogen atoms.

Here's the problem, though: in the old days -- and some days not so long ago -- because of the four 2p electrons, it was believed that the oxygen underwent  $p^2$  hybridization to form this angular geometry.

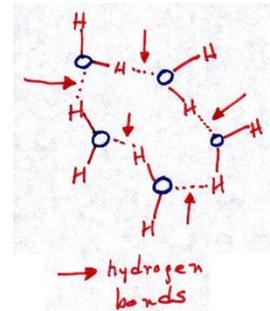
There is a small problem with this: There are 2 pairs of unshared electrons -- one pair of 2s and one pair of 2p electrons. Since these electrons take up space, they lead to a geometry of a tetrahedron (Upper right).



Since these unshared pairs of electrons are partially negative (δ -), they will attract the partially positive (δ +) hydrogen atoms of/from other water molecules to form hydrogen bonds. It is these hydrogen bonds that leads to the high surface tension of water and causes the abnormally high melting and boiling points of water.

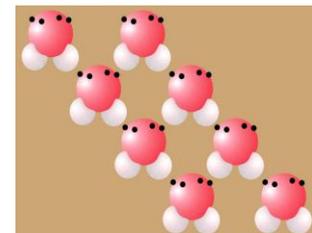


The effects of the aforementioned surface tension are below. If one takes a clean glass and carefully pours water in it, one may pour water over the rim. This forms a bulge on top of the water. That's due to the hydrogen bonds and the polar sites in the glass for the water to bind with. In order to destroy 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.

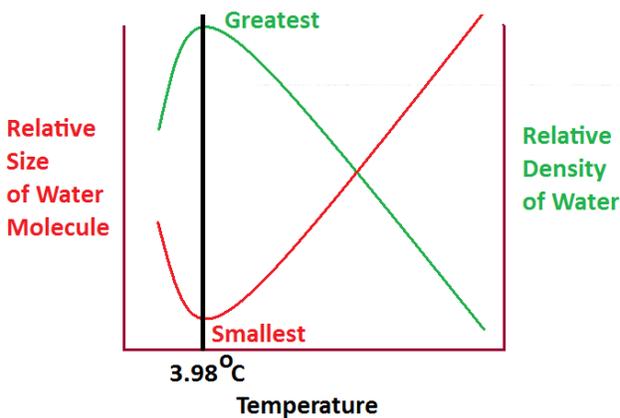
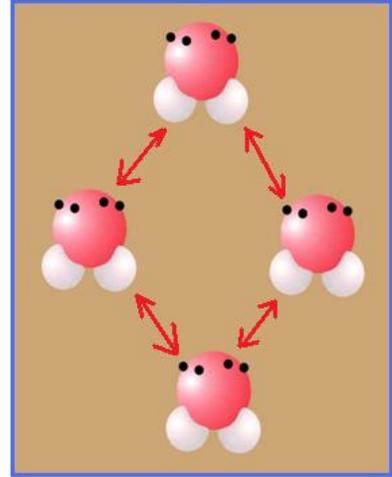




## The Crystal Chemistry of Ice

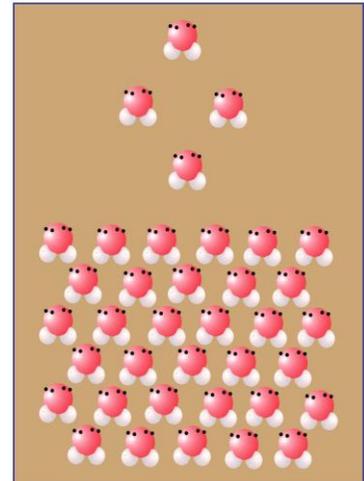
All of us know, empirically, that ice floats in water -- ask the crew on the Titanic. How is it that ice -- solid water -- floats in liquid water? When ice begins to form, it takes on the equivalent of four hydrogen atoms per water molecule: 2 covalently bound and 2 hydrogen bonded.

As this continues, the structure develops "holes" in it that trap air (not quite accurate (bonds actually elongate) -- look at the ice cubes you make in your freezer, though). The ice is less dense than liquid water because of the trapped air in the holes (again, not quite accurate (bonds actually elongate increasing the volume). At 0° C, the density of ice is 0.9168 g/mL, i.e., the density of ice is less than the density of liquid water.



When ice melts, some of the hydrogen bonds are destroyed and the water molecules pack more closely together and the density relationship continues to be maintained.

These relationships are graphically

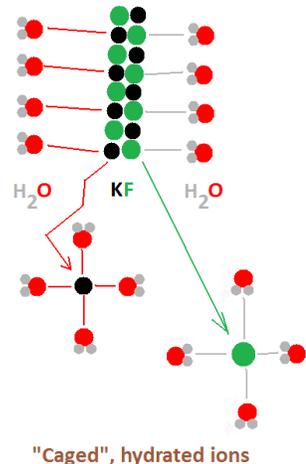
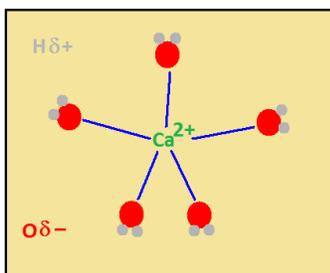


illustrated, below.

You can see that as the temperature increases past 3.98°C, the relative size of the water molecule increases; conversely, the density decreases over the same range. As the temperature goes below 3.98°C, the size of the water molecule rises a bit and the density drops a bit. In short, the smallest molecular size occurs at 3.98°C and the greatest mass of the water molecule is at 3.98°C, as well.

## 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.

#### Chemical Properties of Water

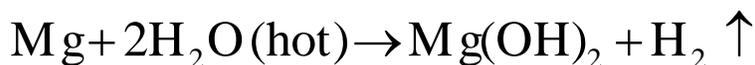
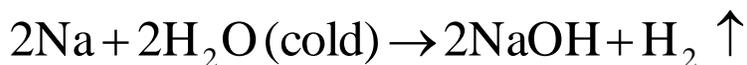
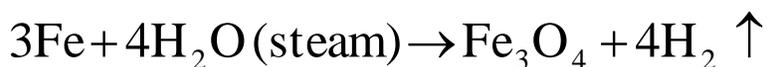
Water is very stable in the presence of high heat. At 2727° C, only 11.1% of water decomposes to form hydrogen and oxygen gases.

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



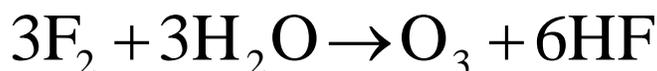
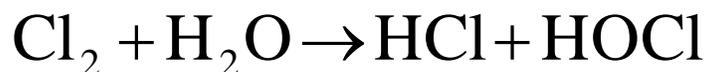
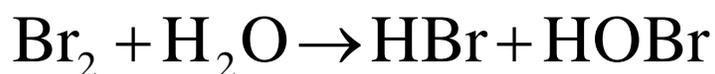
The  $\text{H}_3\text{O}^+$  ions are called hydronium ions and are acidic -- they form the basis for determining the pH of solutions, mixtures and colloids. The  $\text{OH}^-$  ions are the hydroxide ions and are alkaline or basic.

Water reacts with metals as follows:



to form hydroxides, oxides and gaseous hydrogen.

Water reacts with non-metals ( $\text{F}_2$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  at room temperature) as follows:



Acids with "HO" in front of them are the "hypo" acids, e.g., hypochlorous and hypobromous, above.  $\text{O}_3$  is ozone.

HF is not stored in glass containers as it etches the glass. HCl completely ionizes in aqueous solution to the proton and chloride ion. When an acid (or base) does this, it is said to be a strong acid (or base). HOCl does not completely ionize in aqueous solution to the proton and hypochlorite ion. When an acid (or base) does this, it is called a weak acid (or base).

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



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

Non-metal oxides react with water to form acids:



These non-metal oxides are called acidic anhydrides.

Water forms hydrates. A hydrate is defined as the evaporation product of an aqueous solution of a soluble salt. The water with the salt is called water of hydration or water of crystallization. Examples of these follow in the table, below:

Name	Formula	Name
Epsom salts	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Magnesium sulfate heptahydrate
Alum	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Potassium aluminum sulfate dodecahydrate
Plaster of Paris	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	Calcium sulfate hemihydrate
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Calcium sulfate dihydrate
Glauber's salt (cathartic)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Sodium sulfate decahydrate
Blue vitriol	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Copper sulfate pentahydrate

Hydrated compounds that lose water of hydration when exposed to air are said to effloresce. A substance that can remove moisture from the air is called hygroscopic. A deliquescent substance is that substance that is hygroscopic and removes enough water from the air to dissolve itself completely.

### Hydrate Structure

There are five forms of hydrates:

**Water of hydroxylation.** The structural unit is the hydroxide ion. Removal of this "water" leads to disruption of the crystalline structure.

**Water of coordination.** In this case the water is joined by the metal ion by coordinate bonds, e.g.,  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  is really  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}[\text{SO}_4]^{2-}$ . This water is essential to the stability of these crystals.

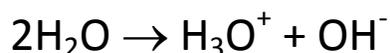
**Anion water.** In this case, the water is attached to the anion by hydrogen bonding, e.g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is really  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  (waters of coordination) and  $[\text{SO}_4(\text{H}_2\text{O})]^{2-}$  (anion water).

**Lattice water.** Water is in the crystalline lattice, but it is not attached to either cation or anion, e.g.,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is really  $\text{K}^+[\text{Al}(\text{H}_2\text{O})_6]^{3+}[\text{SO}_4]_2^{2-}$  (coordination water) plus  $6\text{H}_2\text{O}$  (in lattice, but not bonded with the potassium ion).

**Zeolitic water.** This water occupies random positions in the crystal. Loss or gain of these waters do not change crystalline structure.

### Auto-ionization of Water

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



The reaction is NOT favored as written, although the ratio of protons to hydroxide ions is unity. At  $25^\circ\text{C}$ , the concentration of both ionic species is  $1 \cdot 10^{-7}\text{ M}$ .

Now, let's go back to the acids and bases.  $\text{H}_3\text{O}^+$  is acidic.  $\text{OH}^-$  is alkaline.

In ACIDIC solutions, the molar concentration of  $\text{H}_3\text{O}^+$  ( $[\text{H}_3\text{O}^+]$ ) is greater than the molar concentration of  $\text{OH}^-$  ( $[\text{OH}^-]$ ). In NEUTRAL solutions, they are equal to each other. In ALKALINE solutions,  $[\text{OH}^-]$  is greater than  $[\text{H}_3\text{O}^+]$ .

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  $K_w$ .

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

We can determine the  $K_w$  based off of the equilibrium expression for the dissociation of water as follows:

Note that the coefficient "2" in the equilibrium reaction became the exponent "2" in the equilibrium expression. By rearranging, the equation takes on a slightly different look:

$$K [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+] * [\text{OH}^-]$$

The molar concentration of water is around 55 M -- compared to the small amount that ionizes, it doesn't really change. Since it doesn't really change to any significance, the product of the constant, K, and the square of the  $[\text{H}_2\text{O}]$  are equal to the  $K_w$  and the equation takes on the following look:

$$K_w = [\text{H}_3\text{O}^+] * [\text{OH}^-]$$

At 25° C, the  $K_w$  is equal to the square of  $1*10^{-7}$ , or  $1*10^{-14}$ . How do we use this information to determine the acidity or alkalinity of a solution? From:

$K_w = [\text{H}_3\text{O}^+] * [\text{OH}^-]$ , we substitute the numerical values:

$$1*10^{-14} = (1*10^{-7}) * (1*10^{-7})$$

Next, we take the logs of each side:

$$\log (1*10^{-14}) = \log [ (1*10^{-7}) * (1*10^{-7}) ]$$

which rearranges to:

$$\log (1*10^{-14}) = \log (1*10^{-7}) + \log (1*10^{-7})$$

This gives us:

$$-14 = -7 + -7$$

Take the negative of both sides and we get:

$$14 = 7 + 7$$

Taking the negative log (-log) of this equation may be re-written as "p":

$$pK_w = pH + pOH$$

or:

$$14 = pH + pOH, \text{ where } [\text{H}^+] = [\text{H}_3\text{O}^+]$$

Another way to look at this is that:

$$[\text{H}_3\text{O}^+] = 1*10^{-pH}$$



At neutrality where the hydronium  $[H_3O^+]$  and hydroxide  $[OH^-]$  ion concentrations are equal, the pH is 7 ( $-\log[1 \cdot 10^{-7}]$ ). 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.

### Liquid Laws

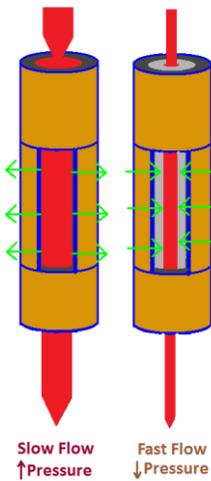
Whether it be in topical product development or in health care, knowledge of how fluids function (flow) is critical. To understand fluids, a number of laws must be

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 Figures. 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.



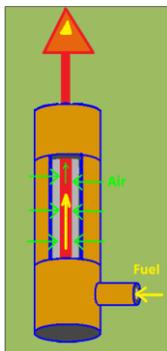
### Bernoulli's Law

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, image left.

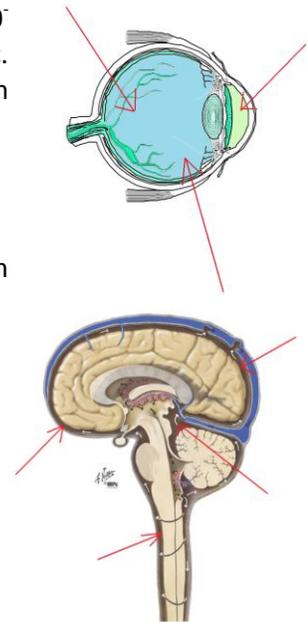
It is this concept by which aspirator "pumps" work on sink faucets, Figure, top following page. Note that in the aspirator that with rapid flow, the pressure on the sides of the tube are reduced (a vacuum) and air rushes into the aspirator to make a suction. A modification on this law is the Venturi effect for gases and liquids.

### Venturi Effect

The Venturi effect happens because fluid pressure drops around the fluid as the fluid speed increases. If a fluid is forced (for example: air or water) down a tube with a narrowing in it, the fluid will move faster through the narrow part. When it starts to move faster the pressure drops.



When the pressure drops below the pressure of the air outside the "jet" (the nozzle, so to speak; the needle valve), other fluids, e.g., fuel, perfume, mixing with the air, creating a mixture that travels through the intake manifold of a car, Bunsen burner or bulb atomizer where it is burnt for energy or sprayed onto oneself.

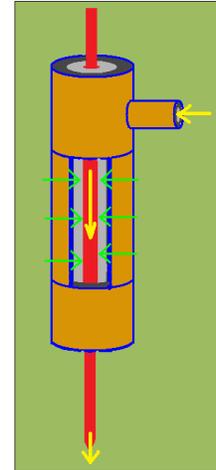




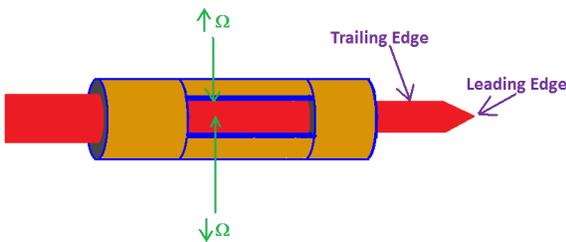
The Venturi effect doesn't really help the gas move faster, but it does encourage fuel and air to mix better giving a more useful and productive fuel burn, as does a bulb atomizer with perfumes give a more uniform spray through which to walk.

### 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.



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:

$$R_e = \frac{vd\rho}{\eta}$$

Where  $R_e$  is the Reynold's number,  $v$  is the velocity of the fluid flow,  $d$  is the diameter of the vessel,  $\rho$  is the density of the solution and  $\eta$  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.

### The Mean Velocity of Fluids

Again, even though I prefer to discuss blood, this section applies to fluids of an aqueous nature, as well. The mean velocity of a fluid through a vessel or tube may be determined as follows, arithmetically:

$$v = \frac{\Delta P r^2}{8 \eta \ell}$$

Where  $v$  is the mean velocity of the fluid,  $\Delta P$  is the pressure gradient between fluid layers,  $r^2$  is the square of the radius of the tube or vessel,  $8$  is a constant,  $\eta$  is the viscosity of the fluid and  $\ell$  is the length of the vessel. If we substitute this equation into the Reynold's number equation, we obtain the following:

$$R_e = \frac{\Delta P 2 r^3 \rho}{8 \eta^2 \ell}$$

Note that  $R_e$  varies in direct proportion to the pressure gradient, the cube of the radius of the vessel and the density of the fluid and inverse proportion to the square of the viscosity of the fluid and the length of the tube or vessel. In general, if the pressure gradient increases, so does the  $R_e$ ; if the radius increases, so does the  $R_e$ ; if the viscosity increases, the  $R_e$  decreases (e.g., if viscosity doubles,  $R_e$  drops by 4-fold); if viscosity decreases,  $R_e$  increases (e.g., if viscosity drops by a half,  $R_e$  increases by four-fold).

### Poiseuille's Law

Poiseuille's Law takes into account the mean velocity of fluid flow. By definition, this law says that the quantity of a fluid ( $Q$ ) flowing through a tube or vessel over a pre-determined period of time is equal to the product of the velocity of the blood flow ( $v$ ) and the cross-sectional area of the vessel or tube:

$$Q = v \pi r^2$$



By substituting the equation for mean velocity into this equation, we obtain:

$$Q = \frac{\Delta P r^4 \pi}{8 \eta l}$$

All but the  $\Delta P$  term is equal to the conductance (the ability to flow) of the fluid. From elementary physics, remember that although conductance (mho) is the ability to flow, resistance ( $\Omega$ ; ohm) is the flow hindering ability. Conductance is the reciprocal of resistance and vice versa. That means that we can write conductance as follows:

$$C = \frac{\pi r^4}{8 \eta l}$$

#### 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:

$$R_T = R_1 + R_2 + R_3 + R_4 + \dots + R_n$$



#### 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:

$$R_T = \left( \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \frac{1}{R_4} + \dots + \frac{1}{R_n} \right)^{-1}$$

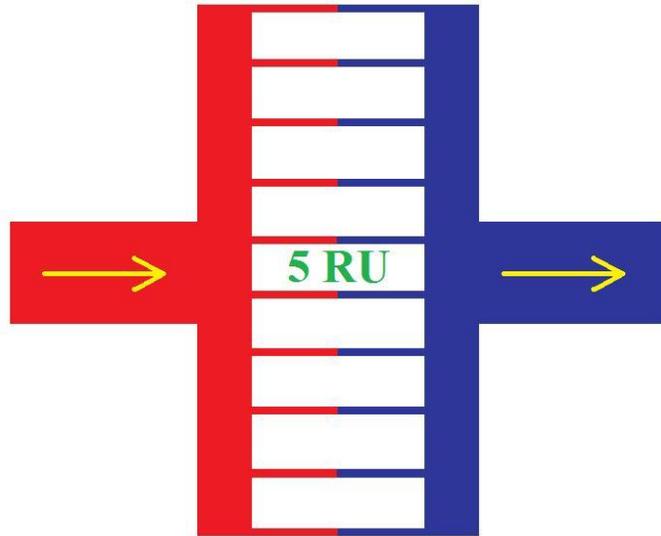
In other words, the conductances are calculated FIRST.

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:



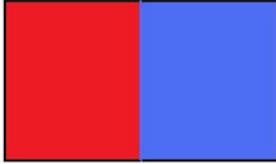
$$\left( \frac{1}{5} + \frac{1}{10} + \frac{1}{15} + \frac{1}{20} \right)^{-1} = (0.2 + 0.1 + 0.067 + 0.05)^{-1} = 2.4 \text{ Units}$$

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, Poiseuille'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 Poiseuille's Equation and their effects on fluid pressure in a vessel or tube:

Flow	Resistance	→	Pressure Gradient
Q	R	→	$\Delta P$
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

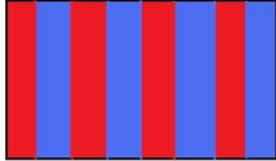
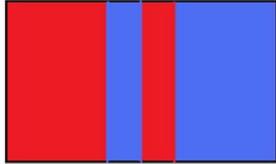


Solutions, Dilutions and Colloids

Solutions and Colloids

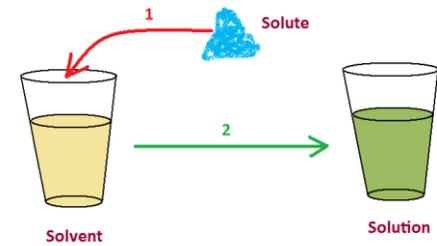
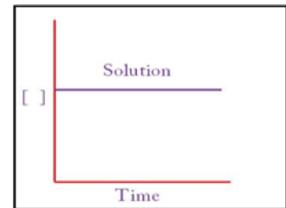
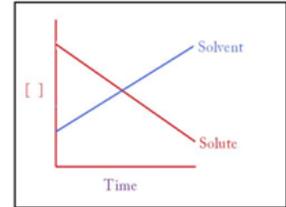
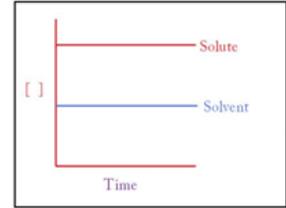
A solution is a homogeneous mixture of 2 or more substances in which the components are present as atoms, molecules or ions. A solvent is the substance present in a solution in the largest amount. Solutes consist of one or more substances present in a solution in an amount lesser than that of the solvent.

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



Diffusion

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.

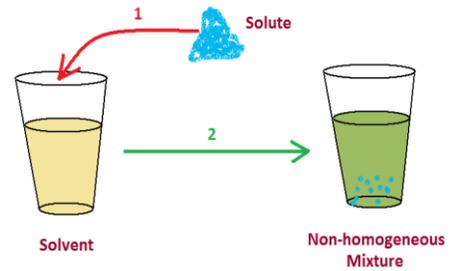


makes a non-homogeneous mixture.

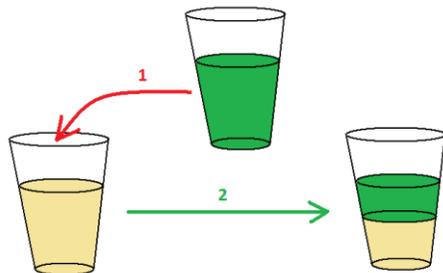
Solubility

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.,



immiscible is used to describe liquids that are insoluble in each other, e.g., oil and water.



Solubility is defined as the maximum amount of a substance dissolved in a specified volume of solvent at a specific temperature and pressure

In very rough terms, Solubility may be defined as summarized in the table, below:

Solubility in grams/0.1 L	Definition
< 0.1	Insoluble
0.1 - 1	Slightly soluble
1 - 10	Soluble
> 10	Very soluble

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).



Solute Dissolved



Solute Undissolved

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

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 equilibrium; In the third solution, more solute is undissolved than is dissolved.



Solute Dissolved



Solute Undissolved

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 <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
NaOCl	LiBr	KNO <sub>3</sub>

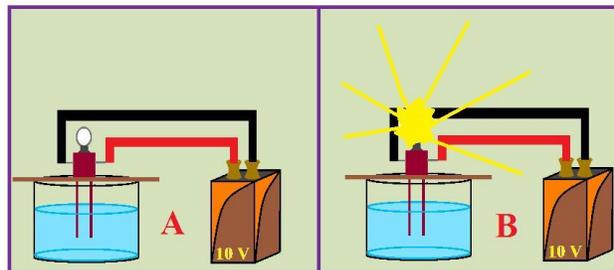
Some common salts are summarized in the table, below:

Salt	Name	Salt	Name
CaSO <sub>4</sub> •½H <sub>2</sub> O	Plaster of Paris	NaHCO <sub>3</sub>	Baking soda
MgSO <sub>4</sub> •7H <sub>2</sub> O	Epsom salts	NaNO <sub>2</sub>	Preservative
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> •10H <sub>2</sub> O	Borax	AgNO <sub>3</sub>	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 tabulated below:

Rule	Exceptions
Alkali metal and $\text{NH}_4^+$ salts are all soluble.	Some cations in analytical group 5 are moderately insoluble
Nitrates and acetates are all soluble.	$\text{AgOAc}$ is moderately insoluble
Chlorides, bromides and iodides are all soluble.	Those salts of $\text{Pb}^{2+}$ , $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ ; $\text{BiOCl}$ and $\text{SbOCl}$
Sulfates are soluble.	Those salts of $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Ag}^+$ , $\text{Pb}^{2+}$ , $\text{Hg}_2^{2+}$
Carbonate and sulfite salts are generally insoluble.	Those of the alkali metals and $\text{NH}_4^+$
Sulfides are generally insoluble.	Those of the alkali metals and $\text{NH}_4^+$ ; alkaline earth sulfides and $\text{Cr}_2\text{S}_3$ and $\text{Al}_2\text{S}_3$ are decomposed by water
Hydroxides are generally insoluble.	Alkali metals and $\text{NH}_4^+$ ; Barium, strontium and calcium hydroxides are moderately soluble.
All other salts are insoluble.	

As a general rule, solubility is defined as being dissolved in aqueous solution to about 3-5%. Soluble salts are electrolytes, i.e., they will conduct an electrical current.



The rules of electrolytes are summarized in the table, below, as well:

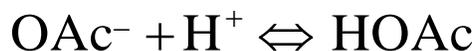
Summary of Strong and Weak Electrolytes	
Rule	Exception
Most acids are weak electrolytes.	The common strong acids: hydrochloric, hydrobromic, hydroiodic, nitric, sulfuric, chloric and perchloric
Most bases are weak electrolytes.	The strong basic hydroxides: Li, Na, K, Rb, Cs, Ca, Sr, Ba hydroxides
Most salts are strong electrolytes	The most importantly weakly ionized salt is $\text{HgCl}_2$ ; occasionally, the following are listed without general agreement: $\text{Hg}(\text{CN})_2$ , $\text{CdCl}_2$ , $\text{CdBr}_2$ , $\text{CdI}_2$ and $\text{Pb}(\text{OAc})_2$

## Preparation of Salts

Mechanism	Representative Reactions
Direct union of their elements.	$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$ $\text{Fe} + \text{S} \rightarrow \text{FeS}$
Reactions of acids with metals, metal hydroxides or metal oxides.	$\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$ $\text{Fe}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$ $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$
Reactions of basic anhydrides with acid anhydrides.	$\text{BaO} + \text{SO}_3 \rightarrow \text{BaSO}_4$ $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$
Reaction of acids with salts.	$\text{BaCO}_3 + 2\text{HCl} \rightarrow \text{BaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$
Reaction of salts with other salts.	$\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$ $\text{ZnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + 2\text{NaCl}$

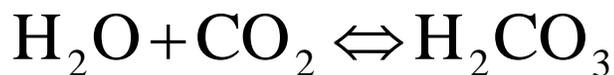
## Buffers

Buffers are solutions of salts that resist changes in pH, i.e., they maintain a relatively constant pH. One example of a buffer pair is the HOAc/OAc<sup>-</sup> pair:



Note that BOTH the hydrogen ion and the hydroxide ion react with the acetate ion.

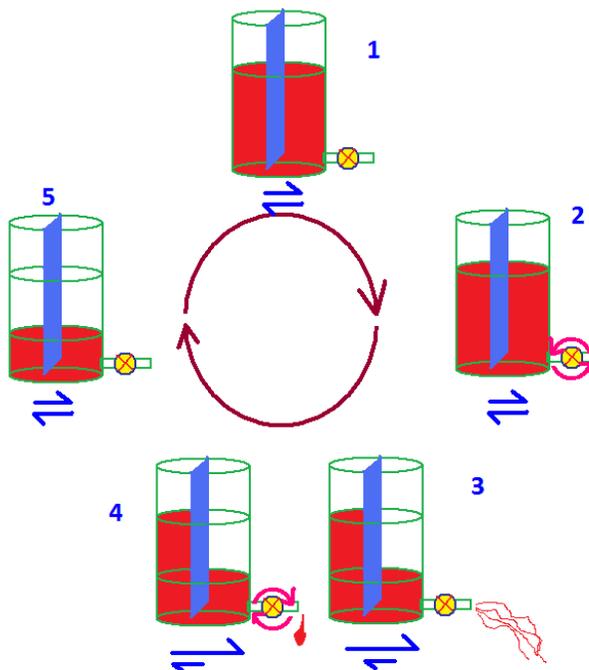
The BUFFER CAPACITY is defined as the amount of hydrogen ion or hydroxide ion "absorbed" by a buffer without causing a significant change in the pH of the system. One system of significance to all humans is the blood. In the blood, the following reactions occur very rapidly and continuously:



It is this particular reaction that plays the most significant role in acid-base balance in the human body -- as you will learn in A&P.

## 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.



## Preparation of Solutions

- 1) Determine the volume needed for the experiment.
- 2) Determine the appropriate units, e.g., M, N, m, %, ppm, ad nauseum.
- 3) Mass out the solute.
- 4) Place the solute in the appropriate container.
- 5) Add solvent and mix.

The volume needed generally reflects the amount of solution that you will need to complete your experiment plus a little bit more to cover mistakes. The units you'll need to use are those units that will work the best with your experiment. Massing out the solute requires either weighing paper or weighing boats, along with spatulas -- remember: if you take it out of the bottle and it's too much, toss it! Do NOT replace it in the bottle.

Placing the solute in the appropriate container can be tricky.

## Common Dilution Methods and Calculations

$$w/w = \text{weight\%} = (\text{mass of solute} / \text{mass of solution}) \cdot 100$$

$$v/v = \text{volume \%} = (\text{volume of solute (mL)} / \text{volume of solution (mL)}) \cdot 100$$

$$w/v = \text{weight-volume \%} = (\text{mass of solute (g)} / \text{volume of solution (mL)}) \cdot 100$$

## Examples

$$85\% \text{ w/w HClO}_4 = 85 \text{ g HClO}_4 \text{ per } 100 \text{ g solution}$$

10% w/v  $\text{NaNO}_3$  = 10 g  $\text{NaNO}_3$  per 100 mL of solution

30% v/v  $\text{NaOH}$  = 30 mL  $\text{NaOH}$  (aq) in 100 mL of solution

Solution-diluent volume ratios are defined as the volume of the more concentrated reagent to the volume of solvent to dilute it, e.g., 1:3 = 1 part concentrated reagent and 3 parts of water. ppm = mg of solute per liter of solution = parts per million

### Solution Diluent Volume Ratios: 2 Methods

#### Method 1

Analytical Chemistry Approach:

1:3 solution of nitric acid = 1 part of concentrated Nitric Acid and 3 parts of Water.

#### Method 2

Biochemistry Approach:

1:3 solution of Nitric Acid = 1 part of Concentrated Nitric Acid and 2 parts Water

ppm

100 ppm  $\text{NaCl}$  = 100 mg  $\text{NaCl}$  dissolved in a final volume of 1 liter of solution

Beakers and Erlenmeyer flasks are for PRE-MIXING ONLY -- they are the "mixing bowls" of chemistry and biology. Even though they have volumes printed on their sides, at best, they are within MAYBE 25% of being correct.



Graduated cylinders are good choices for measuring volumes of liquids. Volumetric flasks (with either rubber, cork or ground glass stoppers) are the most accurate and precise vessel to use for solutions that HAFSA have known concentrations within a very tight range, i.e., with minimal error.



In both graduated cylinders and volumetric flasks, one must use the meniscus of the solvent to determine the appropriate volume. In the graduated cylinder, stay at eye level and consistently use the same part of the meniscus for volume determinations. Once poured into the graduated cylinder, pour the solvent into a beaker with the solute (depending on the solute) and stir to dissolve.



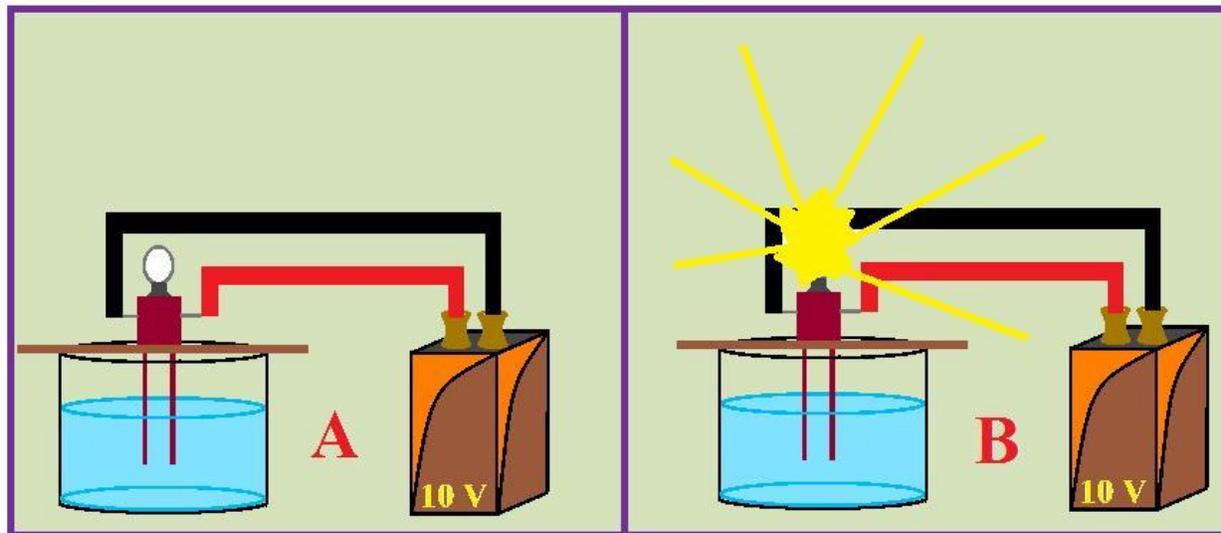
In the volumetric flask, put the solute in the flask and fill the flask to the line in the neck. Stopper and mix by inversion. If it is liquids, invert a minimum of 20 times. If you are dissolving a solid solute, pre-mix the solute with a minimal amount of solvent in a beaker and pour into the flask. Rinse the beaker with minimal amounts of solvent 6-8 times,



pouring the rinse washings into the volumetric flask. Fill the volumetric flask to the line with solvent using either a pipet, medicine dropper or squirt bottle. Stopper and invert to mix 20 times.

### Solution Properties

Electrolyte solutions contain charged particles (ions) in aqueous solution that conduct an electrical current. Nonelectrolyte solutions do not conduct an electrical current. One of the simplest ways in which to determine whether a solution is an electrolyte or not is to use a conductivity tester. Electrolytes will close the circuit and the light comes on. Nonelectrolytes do not and the light stays off.



### 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 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. Does this really work??? At sea level, you don't have to do this. At our elevation and higher elevations, in order to boil potatoes faster, the

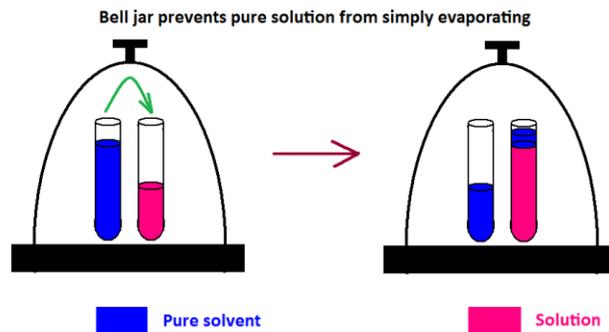
salt raises the boiling point so that the water gets hotter, cooking the potatoes faster. Does this really work???

### 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.

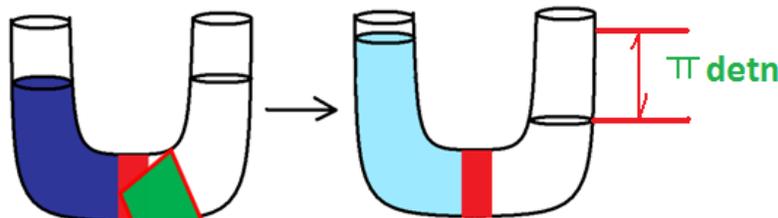
### Vapor Pressure

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.



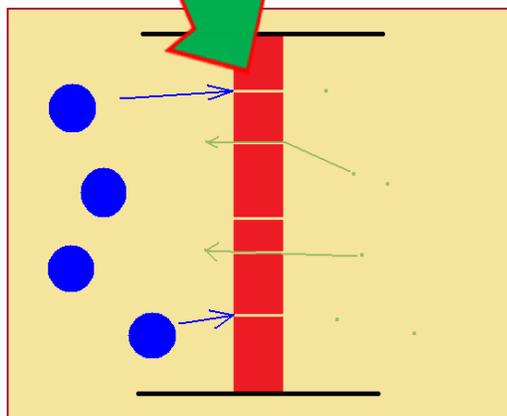
### Osmosis

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:



$$\pi = nMRT$$

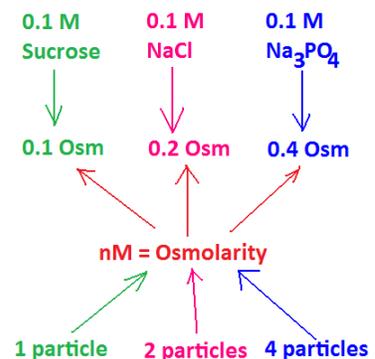
Where  $\pi$  is the osmotic pressure,  $n$  is the number of mols of solute,  $M$  is the molarity of the solution,  $T$  is the absolute temperature and  $R$  is the gas constant (0.0821 L-atm/mol-K or 62.4 torr-L/mol-K).



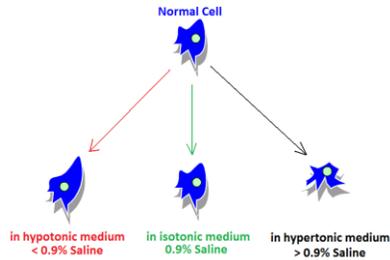
### Osmolarity

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

### 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.

Example: calculate the osmotic pressure of a solution that is 0.25 M in sucrose at 27°C.  $R = 62.4 \text{ torr-L/mol-K}$ .

Solution: Sucrose is a non-electrolyte and has an "n" of 1. Torr are converted to atm. The osmolarity of this sucrose solution is:  $n M = \text{Osm}$  or  $1 * 0.25 = 0.25 \text{ Osm}$

$$\pi = n M R T = (1 \text{ mole}) \left( \frac{0.25 \text{ mol}}{l} \right) \left( \frac{62.4 \text{ torr-L}}{\text{mol-K}} \right) \left( \frac{1 \text{ mmHg}}{1 \text{ torr}} \right) \left( \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) * 300 \text{ K} = 6.16 \text{ atm}$$

Example: calculate the osmotic pressure of a solution that is 0.25 M in  $\text{CaCl}_2$  at 27°C.

Solution:  $\text{CaCl}_2$  is an electrolyte and dissociates into 3 particles. "n" = 3. The osmolarity of this solution is  $3 * 0.25$ . or 0.75 Osm.

$$\pi = n M R T = (3 \text{ mole}) \left( \frac{0.25 \text{ mol}}{l} \right) \left( \frac{62.4 \text{ torr-L}}{\text{mol-K}} \right) \left( \frac{1 \text{ mmHg}}{1 \text{ torr}} \right) \left( \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) * 300 \text{ K} = 18.5 \text{ atm}$$

Example: calculate the molecular weight of a solute that is a non-electrolyte in aqueous solution. The solution contains 14 g of the solute. The osmotic pressure is 2 atm and R is 62.4 torr-L/mol-K and the temperature is 27°C.

Solution: this is a non-electrolyte, hence "n" = 1. M, remember, is the molarity of the solution, which is the number of mols of solute per liter of solution (mol/L). To get the number of mols, the mass of the solute is divided by the molecular weight (grams/MW). We'll substitute, then, grams/MW\*L, for M and rearrange as follows:

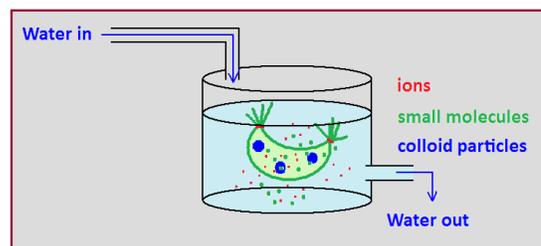
$$\pi = n M R T = M R T = \frac{\text{grams}}{\text{MW} * L} * R T$$

$$\pi = \left( \frac{(14 \text{ grams}) (62.4 \text{ torr-L}) (*300 \text{ K})}{(\text{mol-K}) (2 \text{ atm}) \left( \frac{760 \text{ mmHg}}{1 \text{ atm}} \right)} \right) = 172.42 \text{ g/mol} * 8.5 \text{ atm}$$

### 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.



## Chromatography

Chromatography is a technique that allows for the separation of a liquid/dissolved mixture/solution of molecule[s] based upon molecular weight, polarity (hydrophobic versus hydrophilic) or charge, to give three examples. In order to cause the separation of molecules, some must separate from the solution and interact with some sort of solid support. This process is called partitioning.

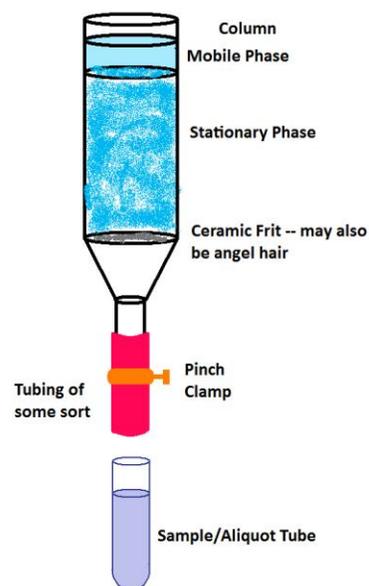
Partitioning may be viewed arithmetically to give us an idea of how the molecules are distributed between the solid support (stationary phase) and a liquid (mobile phase). This is done by looking at the partition coefficient (a constant similar to  $K_a$ ,  $K_b$ ,  $K_{eq}$ , etc), the  $K_p$ :

$$K_p = \frac{[\text{solute}] \text{ in stationary phase}}{[\text{solute}] \text{ in mobile phase}} = \frac{[S]_S}{[S]_M}$$

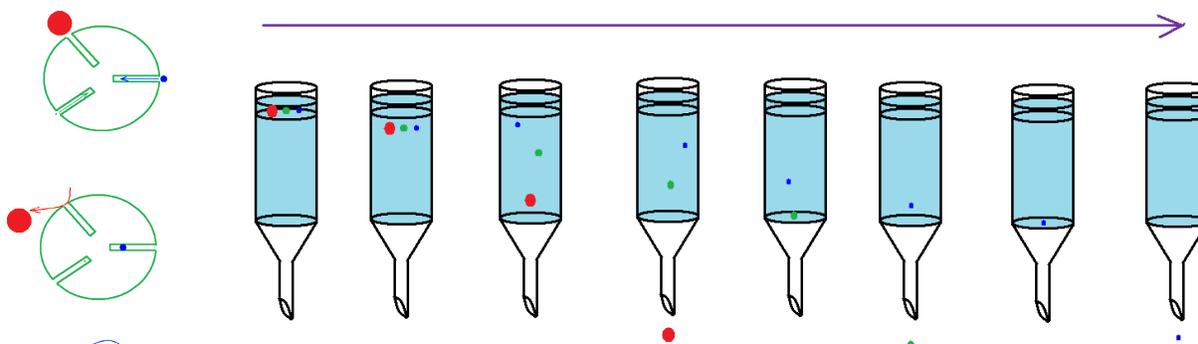
A partition coefficient of 1 says that the solutes (molecules) are equally distributed (partitioned) between both phases. A partition coefficient less than one says that the solutes are primarily in the mobile phase. A partition coefficient greater than one says that the solutes are primarily in the stationary phase.

What are these phases? The stationary phase may be complex carbohydrates, a silicate bonded to octadecane, octane or ethane or it may be a resin that may be modified to change its ionic characteristics (remember cation exchangers for water softening? -- same thing). The mobile phase is some liquid, e.g., may be water, a buffer, an organic solvent or a mixture of organic/aqueous solvents.

Where are these phases? They are kept in a column, a tube made out of glass, metal or non-reactive plastic. A simple column consists of a glass tube that has a ceramic frit or a plug of angel hair in the bottom of the tube, just above the exiting tip. This graphic illustrates and labels a simple chromatography column.



How does this simple column work? In general, a sample in liquid form (may be a vapor if gas chromatography is used -- here we are restricting our discussion to liquid samples) is added to the top of the wet column. The pinch clamp is opened just enough to allow the mobile phase to migrate into the stationary phase (known as packing). The pinch clamp is then closed and solvent is carefully added to the top of the column. The pinch clamp is then opened and the mobile phase is allowed to leave the column, i.e., the mobile phase is eluted. The eluant is collected in fixed, pre-determined volumes (aliquots) for later analysis. Solvent is continuously added so that the column never runs dry -- this may cause cracking of the column, which disrupts the whole process.



### Gel Permeation (GPC) or Size Exclusion Chromatography (SEC)

In the case of GPC/SEC, porous particles (stationary phase) are used to separate molecules by molecular weight. In a nutshell, molecules that fit through the pores are retained by the stationary phase.

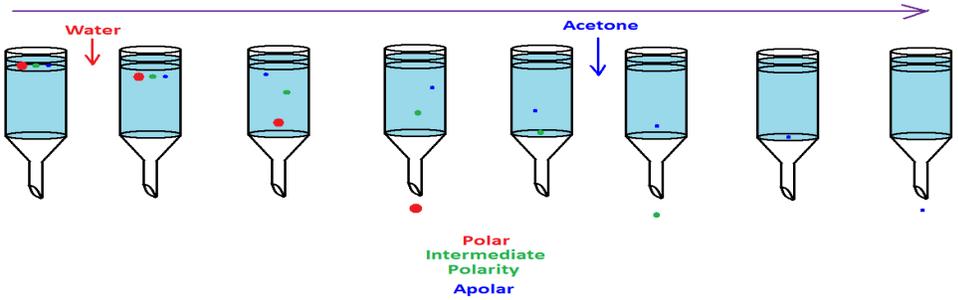
Those molecules that are too large to fit into the pores remain in the mobile phase and are the first to be eluted, i.e., the large molecules are "excluded" from the stationary phase by their large "size".

### Reverse Phase Chromatography (RPC)

In the case of RPC, a hydrophobic bonded packing phase (stationary phase) is combined with a hydrophilic mobile phase. The bonded phase is stable over a pH range of 2-7.5. The stationary phase is typically a silicate with a C-18, C-8 or C-2 functional group attached to it. The mobile phase is either a graduated or 100% aqueous solvent. As a rule, hydrophilic particles partition into the solvent and will elute first. Apolar compounds partition into the stationary phase and have longer retention times (time of being "bound" to the packing material). The retention times of both kinds of compounds may be altered by using appropriate solvent mixtures.

The table, below, provides some introductory RPC applications:

Polarity of Particles	Particles	Stationary Phase	Solvent	Polarity of Solvent
Low	Aliphatic hydrocarbon soluble	C-18	Aqueous methanol	High
Moderate	Methyl ethyl ketone soluble	C-8	Aqueous acetonitrile	Moderate
High	Lower alcohol soluble	C-2	Aqueous dioxane	Low



As one might expect, water is the weakest eluant in RPC. Typically, RPC is accomplished with a pump that pushes the mobile phase through the column. The pump may be mechanical and adjustable -- this is called RP-HPLC (Reverse Phase-High Pressure [or Performance] Liquid Chromatography). The pump may be as simple as a syringe placed onto a Sep-Pak™ from Waters (at top right following page). This is also RPC, but lacks the finesse to be called RP-HPLC. Note the application of the organic solvent following the aqueous solvent, bottom previous page.

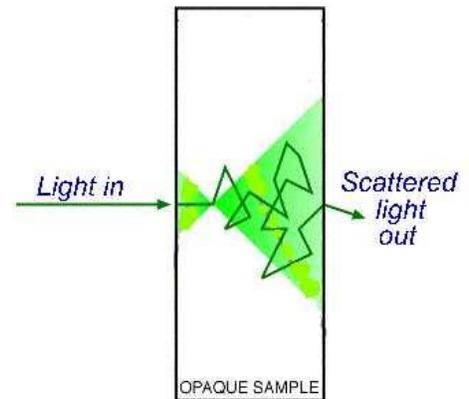
### Ion Exchange Chromatography

Ion Exchange Chromatography (IEC) has already been discussed in an earlier section (Water and Chromatography), i.e., cation and anion exchanging columns rid water of metals and harmful anions. The technique works the same way in IEC with smaller columns, more sophisticated equipment and more complex biomolecules.

### 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 <math> < 10^{-7}</math> cm	Particle size $\geq 10^{-5}</math> cm$
Particle size does not lead to light scattering	Particle size causes light scattering



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, above right. 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, 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.

### Acid-Base Titrations

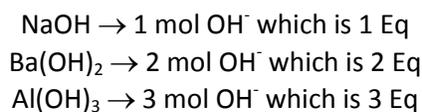
Knowing now what we know about acids, how may we apply this information to the lab? By studying acid/base titrations. Acids and hydroxide bases react to form water and a salt. This sort of reaction is called a neutralization reaction. Bases that contain bicarbonate or carbonate in them also produce carbon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

$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
$\text{H}_2\text{SO}_4 + 2 \text{KOH} \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$
$2\text{HNO}_3 + \text{Ba}(\text{OH})_2 \rightarrow \text{Ba}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
$\text{H}_3\text{PO}_4 + \text{Al}(\text{OH})_3 \rightarrow \text{AlPO}_4 + 3\text{H}_2\text{O}$
$2\text{HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
$6\text{HNO}_3 + \text{Al}_2(\text{CO}_3)_3 \rightarrow 2\text{Al}(\text{NO}_3)_3 + 3\text{CO}_2 + 3 \text{H}_2\text{O}$
$\text{H}_2\text{SO}_4 + \text{MgCO}_3 \rightarrow \text{MgSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$

### Normality

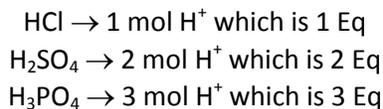
In reactions, thus far, we've looked at grams and moles. Sometimes, though, we need to express units in terms of protons, hydroxide ions or charges. When we do this we use a unit called EQUIVALENTS.

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

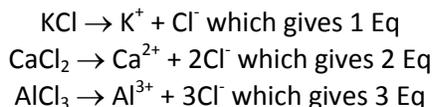


By definition, an equivalent (Eq) of acid is that amount of acid that contributes or provides 1 mol of hydronium ( $\text{H}_3\text{O}^+$ ) or hydrogen ( $\text{H}^+$ ) ion:





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:



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  $\text{AlCl}_3$  -- this has a molecular weight of 133.5 g/mol

$$\frac{133.5 \text{ g}}{\text{mol}} * \frac{1 \text{ mol AlCl}_3}{3 \text{ Eq}} = \frac{44.5 \text{ g}}{\text{Eq}} \Leftrightarrow 44.5 \text{ g/Eq}$$

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, LiCl and magnesium hydroxide:

$$\begin{aligned} \frac{98 \text{ g H}_2\text{SO}_4}{\text{mol}} * \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ Eq}} &= \frac{49 \text{ g H}_2\text{SO}_4}{\text{Eq}} \\ \frac{42.5 \text{ g LiCl}}{\text{mol}} * \frac{1 \text{ mol LiCl}}{1 \text{ Eq}} &= \frac{42.5 \text{ g LiCl}}{\text{Eq}} \\ \frac{58.3 \text{ g Mg(OH)}_2}{\text{mol}} * \frac{1 \text{ mol Mg(OH)}_2}{2 \text{ Eq}} &= \frac{29.15 \text{ g Mg(OH)}_2}{\text{Eq}} \end{aligned}$$

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 = mol/L). 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 = Eq/L). 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, and, then, let's calculate the normality of a solution of 29.15 g Mg(OH)<sub>2</sub> that is dissolved in 500 mL of water.

$$40 \text{ g NaOH} * \frac{1 \text{ mol}}{40 \text{ g NaOH}} * \frac{1 \text{ Eq}}{1 \text{ mol}} * \frac{1}{1 \text{ Liter}} = 1 \text{ N} = 1 \frac{\text{Eq}}{\text{L}}$$

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

Notice how the units cancel out.

There Are at Least 4 Definitions of Acids and Bases.

#### Arrhenius Definition of Acids and Bases

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	$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$	Sodium hydroxide	$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$
Sulfuric	$\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$	Potassium hydroxide	$\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$
Nitric	$\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-$	Magnesium hydroxide	$\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2 \text{OH}^-$
Phosphoric	$\text{H}_3\text{PO}_4 \rightarrow 3\text{H}^+ + \text{PO}_4^{3-}$	Barium hydroxide	$\text{Ba(OH)}_2 \rightarrow \text{Ba}^{2+} + 2 \text{OH}^-$
Perchloric	$\text{HClO}_4 \rightarrow \text{H}^+ + \text{ClO}_4^-$	Aluminum hydroxide	$\text{Al(OH)}_3 \rightarrow \text{Al}^{3+} + 3 \text{OH}^-$
Carbonic	$\text{H}_2\text{CO}_3 \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}$	Tin (IV) hydroxide	$\text{Sn(OH)}_4 \rightarrow \text{Sn}^{4+} + 4\text{OH}^-$

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

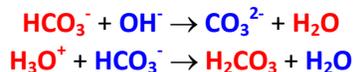
By this set of definitions, an acid is a proton donor and a base is a proton acceptor when they dissociate in water. Representative reactions are summarized in the table, below:

Acid dissociation in water	Reaction of Hydroxide with an Acid
$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$	$\text{HCl} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Cl}^-$
$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$	$\text{HNO}_3 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{NO}_3^-$
$\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$	$\text{H}_2\text{SO}_4 + \text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{SO}_4^{2-}$

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

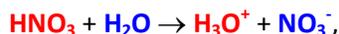


Where **RED** indicates the acid and **BLUE** indicates the base form of each molecule.

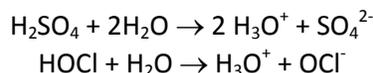


Where **RED** indicates the acid and **BLUE** indicates the base form of each molecule.

When a reaction is written in the following form,



the nitric acid is the acid and the water is the base. Once they react, a NEW acid and a NEW base are formed. The new acid is the  $\text{H}_3\text{O}^+$  and the new base is the nitrate ion ( $\text{NO}_3^-$ ). The nitric acid and the nitrate ion make up a conjugate acid-base pair, respectively. The water and the hydronium ion ( $\text{H}_3\text{O}^+$ ) make up a conjugate base-acid pair, respectively. Two more examples of reactions that produce conjugate acid-base pairs follow:



$\text{H}_2\text{SO}_4$  and  $\text{SO}_4^{2-}$  are one conjugate acid-base pair in the first reaction. What is the other?  $\text{HOCl}$  and  $\text{OCl}^-$  is one of the conjugate acid-base pairs in the second reaction. What is the other?

The table, below summarizes a few acids with their conjugate bases:

Acid	Conjugate Base
Nitric ( $\text{HNO}_3$ )	Nitrate ion ( $\text{NO}_3^-$ )
Acetic ( $\text{HC}_2\text{H}_3\text{O}_2$ or $\text{HOAc}$ )	Acetate ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ or $\text{OAc}^-$ )
Water ( $\text{H}_2\text{O}$ )	Hydroxide ion ( $\text{OH}^-$ )
Phosphoric ( $\text{H}_3\text{PO}_4$ )	Dihydrogen phosphate ion ( $\text{H}_2\text{PO}_4^-$ )

In general, a strong acid gives a weak conjugate base; a weak acid gives a strong conjugate base; a strong base gives a weak conjugate acid; a weak base gives a strong conjugate acid. Strong acids are those that dissociate 100% in water. Examples include perchloric, sulfuric, hydrochloric and nitric acids.

Weak acids are those that ionize less than fully in water. Examples include ammonia, water and carbonic acids.

Strong bases are those that, like the acids, dissociate 100% in water. Examples include sodium hydroxide.

Weak bases are those that, like the acids, dissociate less than fully in water. Examples include the perchlorate ion, the iodide ion and the bromide ion.

#### Acid Formation and Dissociation

The formation of protonic acids may occur by 6 different mechanisms. These mechanisms and examples are summarized in the table, below: Page | 52

Acid Formation Mechanism	Representative Reactions
Direct union of elements	$\begin{aligned} \text{H}_2 + \text{Cl}_2 &\rightarrow 2 \text{HCl} & \text{H}_2 + \text{S} &\rightarrow \text{H}_2\text{S} \\ \text{H}_2 + \text{Br}_2 &\rightarrow 2 \text{HBr} & \text{H}_2 + \text{F}_2 &\rightarrow 2 \text{HF} \\ & & \text{H}_2 + \text{I}_2 &\rightarrow 2 \text{HI} \end{aligned}$
Action of water on non-metal oxides	$\begin{aligned} \text{CO}_2 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{CO}_3 & \text{SO}_3 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_4 \\ \text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} &\rightarrow 4 \text{H}_3\text{PO}_4 & \text{SO}_2 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_3 \end{aligned}$
Heating salts of volatile acids with NON-volatile or SLIGHTLY volatile acids	$\begin{aligned} \text{NaCl} + \text{H}_2\text{SO}_4 &\rightarrow \text{NaHSO}_4 + \text{HCl} \\ \text{NaBr} + \text{H}_3\text{PO}_4 &\rightarrow \text{NaH}_2\text{PO}_4 + \text{HBr} \end{aligned}$
By the action of salts with other acids producing a precipitate	$\begin{aligned} \text{H}^+ + \text{Cl}^- + \text{Ag}^+ + \text{NO}_3^- &\rightarrow \text{AgCl} + \text{H}^+ + \text{NO}_3^- \\ 2\text{H}^+ + \text{SO}_4^{2-} + \text{Ba}^{2+} + 2\text{ClO}_3^- &\rightarrow \text{BaSO}_4 + 2\text{H}^+ + 2\text{ClO}_3^- \end{aligned}$
By hydrolysis	$\begin{aligned} \text{PBr}_3 + 3 \text{H}_2\text{O} &\rightarrow \text{H}_3\text{PO}_3 + 3 \text{HBr} \\ \text{PCl}_5 + 4 \text{H}_2\text{O} &\rightarrow \text{H}_3\text{PO}_4 + 5 \text{HCl} \end{aligned}$
By oxidation-reduction reactions	$\begin{aligned} \text{H}_2\text{S} + \text{I}_2 &\rightarrow 2 \text{HI} + \text{S} \\ 2\text{HNO}_3 + 2\text{SO}_2 + \text{H}_2\text{O} &\rightarrow 2\text{H}_2\text{SO}_4 + \text{NO} + \text{NO}_2 \end{aligned}$

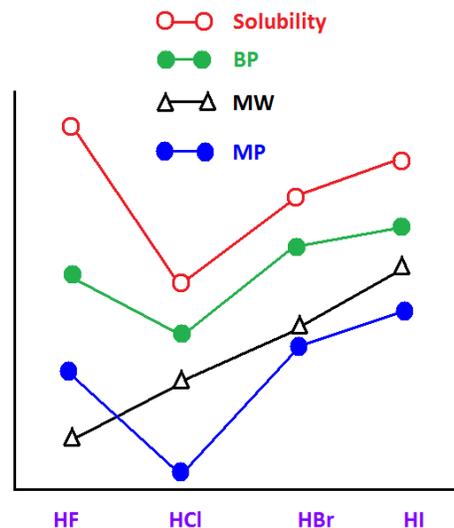
If the acid has one ionizable proton, it is called a mono-protic acid. If it has 2, a di-protic acid. If it has three ionizable protons, it is called a triprotic acid. The significance has to do with eventually using this information in reaction-type calculations. Each proton has its own dissociative 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 -- $1 \text{H}^+$	Diprotic Dissociation -- $2 \text{H}^+$	Triprotic Dissociation -- $3 \text{H}^+$
$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$	$\begin{aligned} \text{H}_2\text{CO}_3 + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \\ \text{HCO}_3^- + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \end{aligned}$	$\begin{aligned} \text{H}_3\text{PO}_4 + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^- \\ \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} \\ \text{HPO}_4^{2-} + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{PO}_4^{3-} \end{aligned}$
$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$	$\begin{aligned} \text{H}_2\text{SO}_4 + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- \\ \text{HSO}_4^- + \text{H}_2\text{O} &\rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \end{aligned}$	
$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CN}^-$		

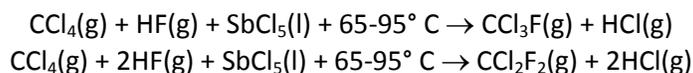
## Hydrogen Halides

### Properties, Chemical Characteristics and Uses of/for Hydrogen Halides

Hydrogen halide→	HF	HCl	HBr	HI
MW	20	36.5	80.9	127.9
Solubility in g/100 mL water	$\infty$ @ 0 ° C	82.3 @ 0 ° C	221 @ 0 ° C	234 @ 10 ° C
BP (° C)	120	110	126	127
MP (° C)	-83.1	-114.2	-86.8	-50.8

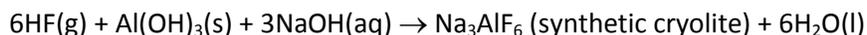


About  $8 \times 10^8$  pounds of HF are used each year to make freons:



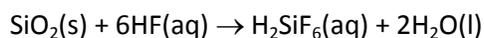
Freons are used in air conditioners and refrigerators, but they are destructive to the ozone layer (15-30 km layer above the earth).

Another  $8 \times 10^8$  pounds of HF are used per year to produce aluminum:



Bauxite, the ore that contains aluminum ( $\text{Al}_2\text{O}_3$ ) is subjected to electrolysis in the cryolite solvent to form elemental aluminum.

HF is used for glass etching and frosting bulbs. The reaction for this is:

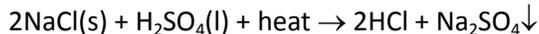
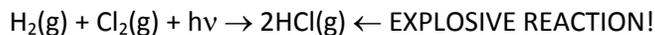


and



HCl is produced in one of three ways and follows:





The primary use of HCl is to remove oxide scale from rusted steel or metals. Bromides and iodides are formed in the same manners, the ONLY difference is that the reactions with these 2 halogens require  $\text{H}_3\text{PO}_4$  instead of  $\text{H}_2\text{SO}_4$ . Page | 54

The Halogens Form Oxo-Acids

Hypohalous acids	HOCl	HOBr	HOI
Halous acids	$\text{HClO}_2$	$\text{HBrO}_2$	$\text{HIO}_2$
Halic acids	$\text{HClO}_3$	$\text{HBrO}_3$	$\text{HIO}_3$
Perhalic acids	$\text{HClO}_4$	$\text{HBrO}_4$	$\text{HIO}_4$

$\text{HClO}_4$  is explosive by shock alone in the pure state. In terms of acid strengths, the acids with the halogen in the lowest oxidation state are the weakest while those that have the halogen in the highest oxidation state are the strongest oxo-acids:

<b>Weakest</b>			<b>Strongest</b>
<b>HClO (HOCl)</b>	<b><math>\text{HClO}_2</math></b>	<b><math>\text{HClO}_3</math></b>	<b><math>\text{HClO}_4</math></b>
<b>Hypochlorous acid</b>	<b>Chlorous</b>	<b>Chloric</b>	<b>Perchloric</b>
<b>+1 Oxidation state</b>	<b>+3 Oxidation state</b>	<b>+5 Oxidation state</b>	<b>+7 Oxidation state</b>

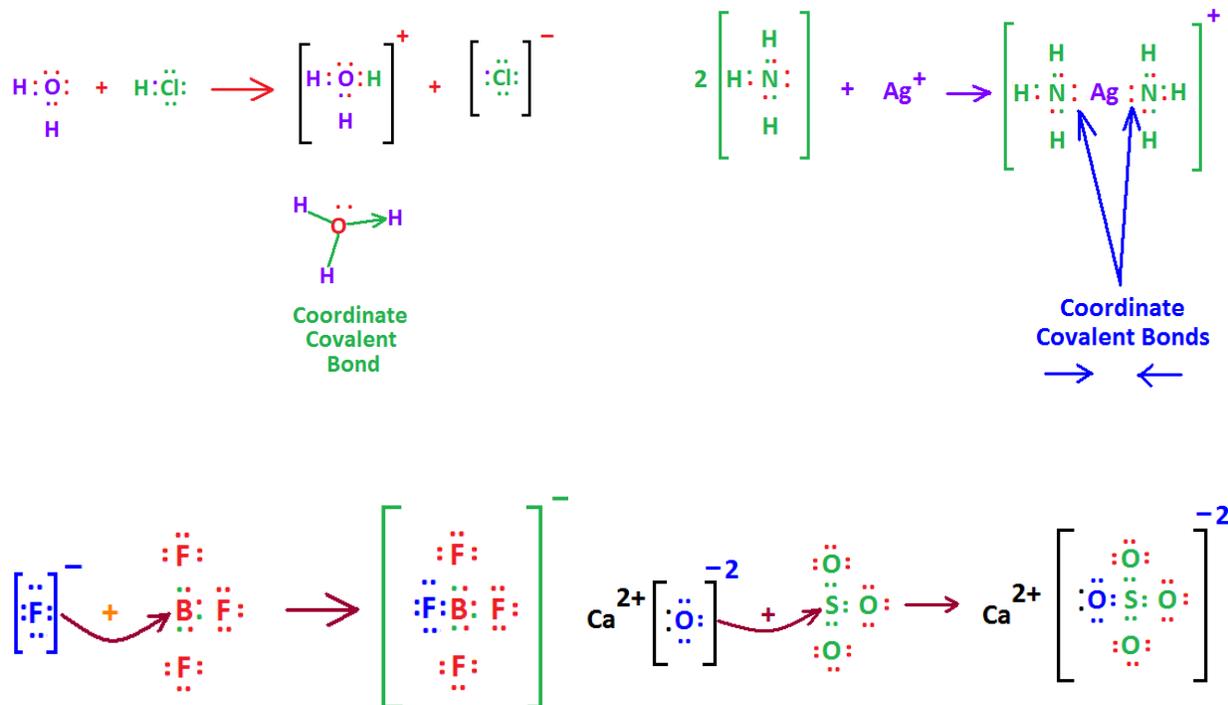
Base Formation

There are 5 mechanisms by which hydroxides are formed. These mechanisms and representative reactions are summarized in the table, below:

Base Mechanism	Representative Reactions
Alkali metals or alkaline earth metals react with water	$2\text{K} + 2\text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{OH}^- + \text{H}_2$ $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- + \text{H}_2$ $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2$
Water reacting with oxides of alkali/alkaline earth metals	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^-$ $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$
Salts with other bases with a resulting precipitate	$2\text{Na}^+ + \text{CO}_3^{2-} + \text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{CaCO}_3\downarrow + 2\text{Na}^+ + 2\text{OH}^-$ <b>IONIC REACTION</b>
Electrolysis	$2\text{Na}^+ + 2\text{Cl}^- + 2\text{H}_2\text{O} + \text{Electrolysis} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2 + \text{Cl}_2$
Dissolving $\text{NH}_3$ in water	$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$

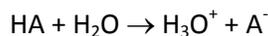
## Lewis Definition of Acids and Bases

By this definition, acids are a molecule or ion which can accept a pair of electrons. A base is a molecule or ion which can donate a pair of electrons, 4 examples follow.



## Acids and Bases Dissociate in Water

Fortunately for us, acids and bases dissociate in water:



Where HA is any acid and A<sup>-</sup> is the anion left behind after the proton has separated from the acid.

We may determine the acid dissociation constant (like we did for water) as follows. The water concentration doesn't change as we saw in the K<sub>w</sub> determination, so we'll rearrange the equation as follows. Where K<sub>a</sub> is the acid dissociation constant.

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

We can do the same for a base:



$$K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

The equilibrium expression is as follows:

Again, since the water concentration doesn't change, we'll rearrange and manipulate:

$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$$

Where  $K_b$  is the base dissociation constant.

Note that in all cases, these equilibrium expressions are the quotient of the product concentrations and the reactant concentrations.

$$K[\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_b$$

Would you suspect, then, that there is some sort of relationship between  $K_a$ ,  $K_b$  and  $K_w$ ? Let's see.

Remember that

$$K_w = [\text{H}^+][\text{OH}^-] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

and that

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

and that

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Let's multiply  $K_a$  by  $K_b$  and see what happens:

$$K_w = [\text{H}^+][\text{OH}^-] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

and that

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \text{ and } K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_a K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} * \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Note that all we're left with after canceling is  $K_w$ . So that we now know that the product of the acid and base dissociation constants for the same compound is equal to the  $K_w$ .

Since  $K_a K_b = 1 * 10^{-14}$ , if the  $K_a$  or the  $K_b$  is in a reference table in a textbook or online, the other can easily be calculated.

Additionally, we can also use this same method with conjugate acid-base pairs, e.g. HF and  $\text{F}^-$  and  $\text{NH}_4^+$  and  $\text{NH}_3$ , following page.



$$K_w = K_a \{HF\} * K_b \{F^-\}$$

$$K_a K_b = \frac{[H_3O^+][HF][F^-][OH^-]}{[HF][F^-]} = [H_3O^+][OH^-] = K_w \text{ YES!}$$

$$K_w = K_a \{NH_4^+\} * K_b \{NH_3\}$$

$$K_a K_b = \frac{[H_3O^+][NH_3][NH_4^+][OH^-]}{[NH_3][NH_4^+]} = [H_3O^+][OH^-] = K_w \text{ YES!}$$

Why is all of this important? How would you know if a salt solution or any solution from an acid and/or a base will be acidic, alkaline or neutral with both  $H^+$  and  $A^-$  present?

Method 1:

Eyeball the pH of Solutions of Acids and Bases

A strong acid and a strong base mixed together yields a neutral solution, e.g., hydrochloric acid with sodium hydroxide.

A strong acid and a weak base yields an acidic solution, e.g., hydrochloric acid and ammonia.

A weak acid plus a strong base yields a basic solution, e.g., acetic acid and sodium hydroxide.

A weak acid and a weak base mixed together can be complex. BUT! If they are equal in strength they will yield a neutral solution, e.g., acetic acid and ammonia.

Method 2:

Determining the pH of A Solution

If a solution of 0.3M HOAc dissociates in water by the following reaction:

$HOAc + H_2O \rightarrow H_3O^+ + OAc^-$ , what is the pH of the solution?  $K_a$  for HOAc is  $1.8 \times 10^{-5}$

Solution: Always write out the equation, first, in these types of questions as laid out below:

	HOAc	+	H <sub>2</sub> O	→	H <sub>3</sub> O <sup>+</sup>	+	OAc <sup>-</sup>
[Before reaction]	0.3M				0M		0M
[After reaction]	- x				+ x		+ x
Total concentration of species	0.3 - x				x		x

Note that the concentrations change in proportion to the amount (number of mols) of reactants and products, i.e., 1 mol of HOAc begets 1 mol of hydronium ion and 1 mol of acetate ion.

Write the equilibrium expression, substitute and rearrange and solve:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} = \frac{X * X}{0.3 - X} \approx \frac{X^2}{0.3}$$

$$K_a * 0.3 = X^2$$

$$\sqrt{(1.8 * 10^{-5})(0.3)} = X = 0.0023 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.0023 = 2.64 = \text{pH}$$

What is the pOH for this aqueous solution? Since  $\text{pH} + \text{pOH} = 14$ , it follows that  $14 - 2.64 = 11.36$  is the pOH.

Example #1: What is the pH of a solution that is 0.8M in ammonia?  $K_b$  for  $\text{NH}_3 = 1.8 * 10^{-5}$ .

Solution: Set up as before:

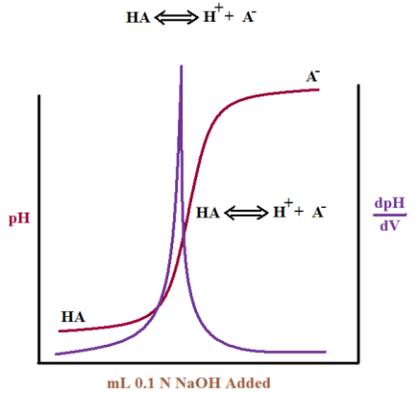
	$\text{NH}_3$	+	$\text{H}_2\text{O}$	→	$\text{NH}_4^+$	+	$\text{OH}^-$
[Before reaction]	0.8M				0M		0M
[After reaction]	- x				+ x		+ x
Total concentration of species	0.8 - x				x		x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{X * X}{0.8 - X} \approx \frac{X^2}{0.8}$$

$$\sqrt{(1.8 * 10^{-5})(0.8)} = X = 0.0038 \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log 0.0038 = 2.42$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 2.42 = 11.58 = \text{pH}$$

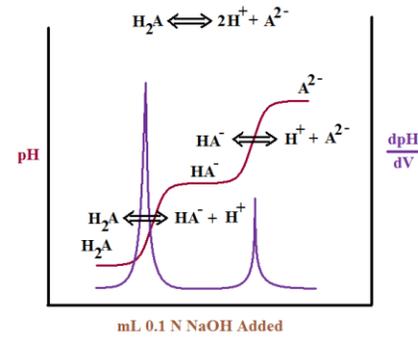
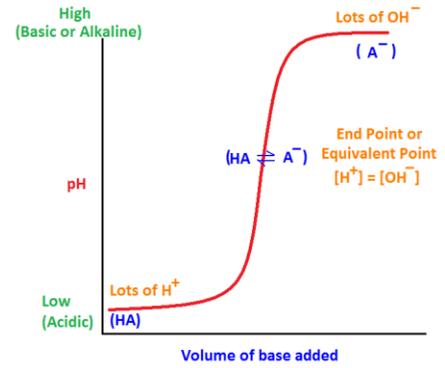


Acid-Base Titrations: In General:

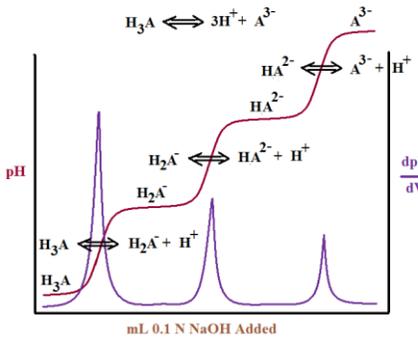
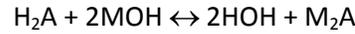
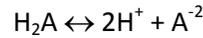
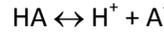
Titrations of acids and bases follow a general sigmoid-shaped curve for a monoprotic acid:

Acid-Base Titrations

Mono-protic Acid



Di-protic Acid



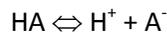
Tri-Protic Acids have THREE Endpoints

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".

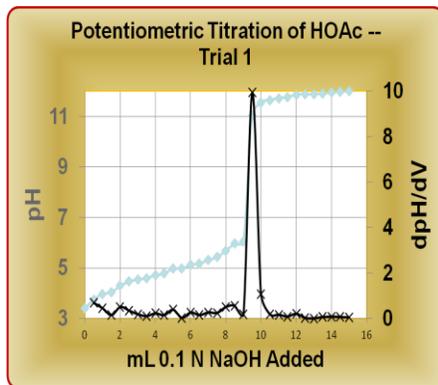
The value of the equivalence point is that it is the pH at which the  $[H^+] = [OH^-]$ . At that point, divide the volume at the endpoint in half, read from that volume up onto the sigmoid-shaped curve, then over to the pH curve and you will be at the numerical value for the negative log of the acid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

Amino Acid Titration: 3 Endpoints – top right following page

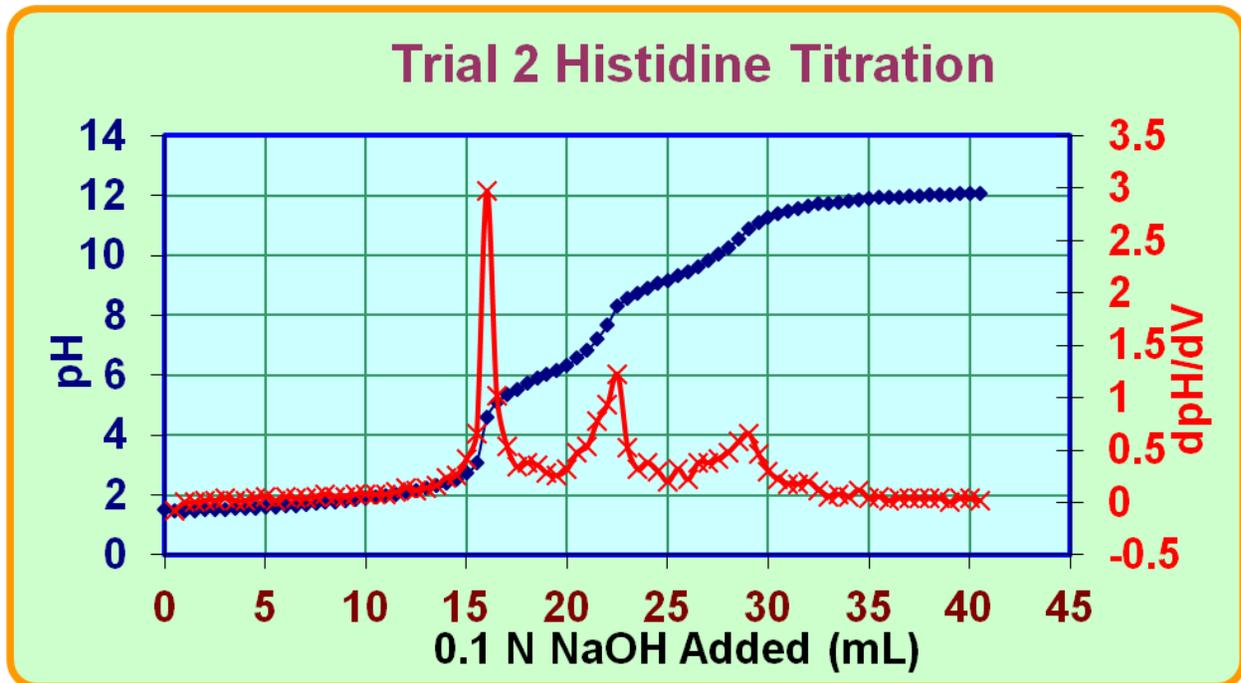
The  $K_a$  is equal to the arithmetic relationship between the undissociated and dissociated acid:



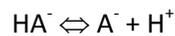
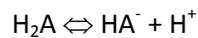
$$K_a = \frac{[H^+][A^-]}{[HA]}$$



and notice that the  $K_a$  is directly proportional to  $[H^+]$  -- more on this later.



Acids (and bases, as well) like  $H_2A$  and  $H_3A$  have multiple dissociation steps. Each step is represented by its own  $K_a$  or  $K_b$ :



where

$$K_{a_1} = \frac{[HA^-][H^+]}{[H_2A]} \qquad K_{a_2} = \frac{[A^-][H^+]}{[HA^-]}$$

$$K_{a_1} * K_{a_2} = \frac{[HA^-][H^+]}{[H_2A]} * \frac{[A^-][H^+]}{[HA^-]} = K_{a_{TOTAL}} = \frac{[H^+]^2 [A^-]}{[H_2A]}$$

The total  $K_a$  for this reaction is equal to the product of the two dissociation constants:

A tri-protic acid has three dissociations, hence the total  $K_a$  is equal to the products of the three dissociation constants. Likewise, the  $K_b$ 's for bases are calculable in the same manner; an exception for bases is that you are focusing on the  $OH^-$ 's instead of the protons.

## Henderson-Hasselbalch Equation for Calculating the pH of a Weak Acid

The derivation of this equation is a rather lengthy one and is summarized, below. Note that it starts from the very simple mono-protic acid dissociation that we've pretty much beaten to death. The salt concentration is equivalent to the anion concentration. This equation is very useful in biomedical research when making buffers.

Example #1: Find the pH of a solution that is 0.05M in carbonic acid and 0.025M in bicarbonate ion. The  $K_{a1}$  for carbonic acid is  $4.4 \times 10^{-7}$ .

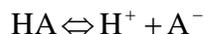
Solution: First get the  $pK_a$

Secondly, set up, manipulate and plug into the equation:

$$\begin{aligned}
 -\log\left(\frac{[HA]}{[A^-]}\right) - \log 4.4 \times 10^{-7} &= pH \\
 -\log\left(\frac{[HA]}{[A^-]}\right) + 6.357 &= pH \\
 \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) + 6.357 &= pH \Leftrightarrow pK_a + \log\left(\frac{[0.025]}{[0.05]}\right) \\
 pH &\Leftrightarrow 6.357 + \log\left(\frac{[0.025]}{[0.05]}\right) \\
 pH &= 6.357 - 0.301 = 6.056
 \end{aligned}$$

Example #2: If a solution of carbonic acid was at a pH of 7.35 and was 0.03M in carbonic acid, what molar concentration of bicarbonate ion is present? Use the same  $K_{a1}$  as in Example 1, above.

Solution: Manipulate the equation right off the bat and substitute right into it:



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging sequentially

$$\frac{[HA]}{[A^-]} * K_a = [H^+]$$

$$-\log\left(\frac{[HA]}{[A^-]} * K_a\right) = -\log[H^+]$$

$$-\log\left(\frac{[HA]}{[A^-]}\right) - \log K_a = pH$$

$$-\log\left(\frac{[HA]}{[A^-]}\right) + pK_a = pH$$

$$\log\left(\frac{[A^-]}{[HA]}\right) + pK_a = pH \Leftrightarrow pK_a + \log\left(\frac{[salt]}{[acid]}\right)$$

$$pH \Leftrightarrow pK_a + \log\left(\frac{[salt]}{[acid]}\right)$$

$$pH - pK_a = \log[HCO_3^-] - \log[H_2CO_3]$$

$$pH - pK_a + \log[H_2CO_3] = \log[HCO_3^-]$$

$$\text{antilog}(pH - pK_a + (\log 0.03)) = [HCO_3^-]$$

$$\text{antilog}(7.35 - 6.357 + (\log 0.03)) = [HCO_3^-]$$

$$\text{antilog}(-0.530) = [HCO_3^-] = 0.295 M$$

## Redox Reactions: Oxidation-Reduction

Reduction ALWAYS occurs with oxidation -- you can not have one without the other. One substance is oxidized and the other is reduced. 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.

### Oxygen

Fossil fuels burn in the presence of oxygen. More than 90% of the energy in our society comes from fossil fuels. Oxygen causes iron to rust, copper to corrode and wood to rot. All of these processes are processes of OXIDATION.

Representative oxidation reactions are illustrated, below:

Process	Reaction	Comment
Rust formation	$4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$	The product is Iron (III) oxide or ferric oxide.
Charcoal burning	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	This is what happens on your charcoal grill.
Burning sulfur	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$	This is one process that occurs in catalytic converters.
Automobile engines at high temperatures	$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$	Another wonderful thing that came from catalytic converters.
Burning methane (natural gas)	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	Just like in the winter time when you run your gas furnace.
Burning off hydrogen sulfide	$2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{SO}_2$	
Oxidizing carbon disulfide	$\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$	

The combination of substances with oxygen is the classic definition of oxidation. When oxygen has combined with substances, they are said to have been OXIDIZED.

### Three Definitions of Oxidation

1) A substance is oxidized when it GAINS oxygen atoms, e.g.:



2) A substance is oxidized when it LOSES hydrogen atoms, e.g.:

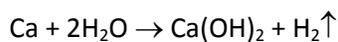
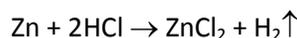


3) A substance is oxidized when it LOSES electrons, e.g.:



### Hydrogen

Let's examine hydrogen, briefly. Nearly all compounds derived from living organisms contain hydrogen in fats, carbohydrates and proteins. Petroleum and natural gas are hydrocarbons that are derived from previously living organisms. Hydrogen is synthesized with ease in the lab (just like in the clock reaction you did at the beginning of this course):

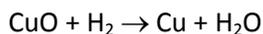


Pt, Pd, and Ni "collect" condensed hydrogen on their surfaces. The absorbed hydrogen has a greatly increased activity (making it more reactive) and Pt, Pd and Ni (in the form of Raney nickel -- his name was Raney) are used as catalysts in hydrogenation reactions. Do you remember the orbital hybridization and molecular geometry of these three metals?

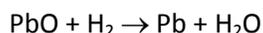
Hydrogen reacts with oxygen, e.g.:



Hydrogen reacts with cupric oxide, e.g.,

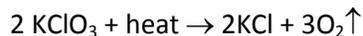


Hydrogen reacts with lead (II) oxide, e.g.:



### Three Definitions of Reduction

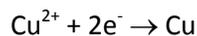
1) A substance is reduced when it LOSES oxygen atoms, e.g.:



2) A substance is reduced when it GAINS hydrogen atoms, e.g.:



3) A substance is reduced when it GAINS electrons, e.g.:



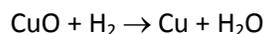
### Summary Thus Far

The table, below, summarizes oxidation and reduction definitions:

Oxidation	Substance/Particle Involved	Reduction
Gains	O <sub>2</sub>	Loses
Loses	H <sub>2</sub>	Gains
Loses	e <sup>-</sup>	Gains

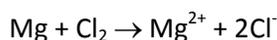
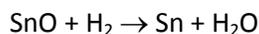
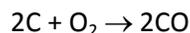
### Redox Reactions -- More Terms

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.:



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<sub>2</sub> is the reducing agent as the H<sub>2</sub> 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<sub>2</sub>) 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):





The table below summarizes examples of common oxidizing and reducing agents:

Common Oxidizing Agents	Common Reducing Agents
$O_2$ $Cr_2O_7^{2-}$ * See below for example reaction $H_2O_2$ Halogens	$C$ $H_2$ Silver halides# See below for example reaction
$* 8H^+ + Cr_2O_7^{2-} \text{ (orange)} + 3C_2H_5OH \rightarrow 2Cr^{3+} \text{ (green)} + 3C_2H_4O + 7H_2O$	$\# C_6H_4(OH)_2 \text{ (hydroquinone -- "developer")} + 2Ag^+ \rightarrow C_6H_4O_2 + 2Ag \text{ (dark part of the negative)} + 2H^+$

### Applications of Oxidizing Agents

Oxidizing Agent	Use/Comments
NaOCl -- sodium hypochlorite	Clorox -- used to be used in wound irrigation, not any more -- used to be used to treat bladder infections, not any more
$(C_6H_5COO)_2$ -- benzoyl peroxide	POWERFUL oxidizing agent; 5-10% ointments are used to treat acne; when used on regions that are exposed to sunlight, has been known to cause skin cancer, i.e., stay out of the sun OR cover up if you use this
$Ca(OCl)_2$ -- calcium hypochlorite	Bleach -- disinfect clothing, bedding
$Cl_2$ -- gaseous chlorine	Water purifier

NaOCl + $Ca(OCl)_2$	Bleach
$H_2O_2$ -- hydrogen peroxide $NaBO_2 \cdot H_2O_2$ -- sodium perborate $Cl_2$	All work through redox -- when hydrogen peroxide and cold water are used on fresh blood stains, the stain is removed -- gotta be careful, though, as the stain will return. If you really want to get the blood out, rinse it out of the fabric while it's still fresh and use normal saline -- won't lyse the cells so that they "stick" to the fabric like they do with $H_2O_2$ .
$KMnO_4$ -- potassium permanganate	Removes most stains from white fabrics EXCEPT rayon. The purple $MnO_4^-$ stain may be removed with oxalic acid ( $H_2C_2O_4$ ): $5H_2C_2O_4 + 2MnO_4^- \text{ (purple)} + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} \text{ (colorless)} + 8H_2O$ ; oxalic acid also removes rust stains -- not by redox, though, by complex formation
$Na_2S_2O_3$ -- sodium thiosulfate	Removes iodine stains: $I_2 \text{ (brown)} + 2Na_2S_2O_3 \rightarrow 2NaI \text{ (colorless)} + Na_2S_4O_6$

Many stain removers are adsorbants: corn starch for grease, acetone for ballpoint pen and detergents for mustard.

### Oxidation Number/Oxidation State Defined

We now have some introductory terms and ideas about redox reactions. The next step is to learn how to use this information with new skills so that we may balance redox reactions. Before we begin, though, understand that oxidation number and oxidation state mean the same thing.

The oxidation number of a covalently bonded element is the charge the element would have if all the shared pairs of electrons in the Lewis structure for the species were transferred to the more electronegative atoms.

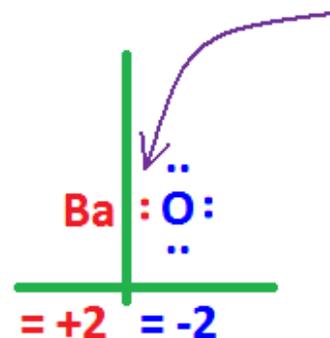
The oxidation number of covalently bound elements are not real charges like the charges on ions. Hence, they may not be experimentally measured. Only for simple mono-atomic ions such as  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{S}^{2-}$  and for elements such as  $\text{N}_2$ ,  $\text{O}_3$ , are oxidation numbers real numbers that are easily obtained in the lab. In binary ionic compounds, the bonding electrons are already on the more electronegative atom because ionic bonds result from electron transfer, therefore, the oxidation number of mono-atomic ions equals the ionic charge. Electrons shared between 2 unlike atoms are counted with the more electronegative atom and electrons shared between 2 like atoms are divided between the sharing atoms.

#### E.g., determine the oxidation number of $\text{N}_2$ :

Three (3) electron pairs are shared by two (2) identical atoms, hence, by #2, above, half the electrons are counted with each atom. The nitrogen nucleus has a +7 charge (7 protons) and with 7 negative charges (7 electrons), the apparent charge is 0. Therefore, the oxidation number of  $\text{N}_2$  is zero (0).

#### E.g., determine the oxidation numbers of Ba and O in $\text{BaO}$ :

Oxygen is more electronegative and so, by #1, above, the shared electrons are counted with oxygen as shown right:. The line shows the SHIFTING of electrons. Since oxygen has 6 protons and APPEARS to have 8 electrons, the oxidation state of oxygen is -2. Note the movement of the 2 electrons away from the Ba and towards the O (arrows pointing to). Ba APPEARS to have "lost" 2 electrons and its oxidation state is +2 since its nucleus now has an excess of 2 protons relative to the number of electrons left behind.



## Oxidation Number Rules

1) All elements have an oxidation number of zero (0):

E.g.	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ca
Oxidation Number	0	0	0	0

2) Monoatomic ions' charges equal the oxidation number of that monoatomic ion:

E.g.	Na <sup>+</sup>	K <sup>+</sup>	Sr <sup>2+</sup>	F <sup>-</sup>
Ionic Charge	+1	+1	+2	-1
Oxidation Number	+1	+1	+2	-1

3) Cations from Groups I and II have oxidation numbers equal to +1 and +2, respectively:

E.g.	Na <sup>+</sup>	Ba <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>
Ionic Charge	+1	+2	+1	+2
Oxidation Number	+1	+2	+1	+2

4) With only a few exceptions, the oxidation number of H is +1:

E.g.	H <sup>+</sup>	H <sup>-</sup>
Ionic Charge	+1	-1
Oxidation Number	+1	-1 (as the HYDRIDE ion)

5) The oxidation number of O is -2; exception: when it's in a peroxide, it's oxidation number is then -1:

E.g.	O <sup>0</sup>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub> (hydrogen peroxide)	NaOH
Ionic Charge of O	0	-2	-1	-2
Oxidation Number of O	0	-2	-1	-2

6) The sum of all the oxidation numbers in a compound is equal to zero (0):

E.g.	KMnO <sub>4</sub>	K <sup>+</sup>	Mn <sup>+7</sup>	O <sup>-2</sup>
Oxidation Numbers	0	+1	+7	-2
TOTAL Oxidation Numbers	0	+1	+7	-8 (4 of them in the compound)
Sum of TOTAL Oxidation Numbers	0			

Arithmetic example:

$$1(\text{ox \# of K}^+) + 1(\text{ox \# of Mn}^{+7}) + 4(\text{ox \# of O}^{-2}) = (1*1) + (1*7) + (4*-2) = 0$$

7) The sum of all the oxidation numbers in an ion is equal to the charge on the ion:

E.g.	Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	Cr <sup>+6</sup>	O <sup>-2</sup>
Oxidation Numbers	-2	+6	-2
TOTAL Oxidation Numbers	-2	+12 (2 of them in the ion)	-14 (7 of them in the ion)
Sum of TOTAL Oxidation Numbers	-2		

Arithmetic example:

$$2(\text{ox \# of Cr}^{+6}) + 7(\text{ox \# of O}^{-2}) = (2*6) + (7*-2) = -2$$

Typical Oxidation Numbers of Common Elements : Positive Ox #'s

Positive Oxidation Numbers							
Ox #	+1	+2	+3	+4	+5	+6	+7
Examples	H, Na, K, Cu, Ag, Hg, N, Cl, Br, I	Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, N, Sn, Pb	Al, Cr, Mn, Fe, Co, N, P, As, Sb, Bi, Cl, Br	C, N, Si, S, Mn, Sn, Pb	N, P, As, Sb, Bi, Cl, Br, I	S, Cr, Mn	Cl, I, Mn, Br

Typical Oxidation Numbers of Common Elements : Negative Ox #'s

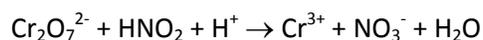
Negative Oxidation Numbers				
Ox #	-1	-2	-3	-4
Examples	H, F, Cl, Br, I	O, S, Se	N, P	C, Si

### Three Methods of Balancing Redox Reactions

Method 1	Method 2	Method 3
Oxidation Number Method	Oxidation Number Method for Aqueous Solutions	Half-Reactions for Aqueous Solutions Method

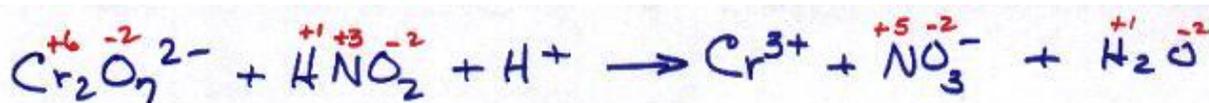
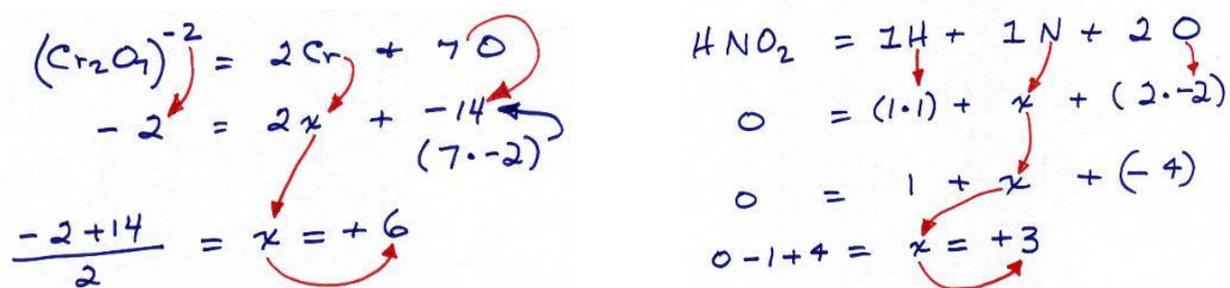
#### EXAMPLE 1

For the first example for ALL three methods (after you get through the homework, I don't care which method you utilize as long as you can do it), we'll use the following UNBALANCED equation:

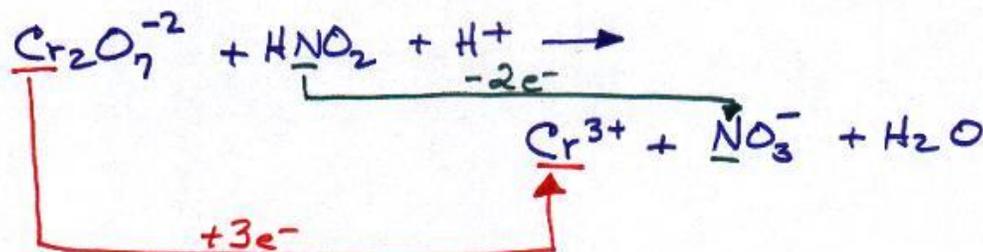


#### Method 1: Oxidation Number Method

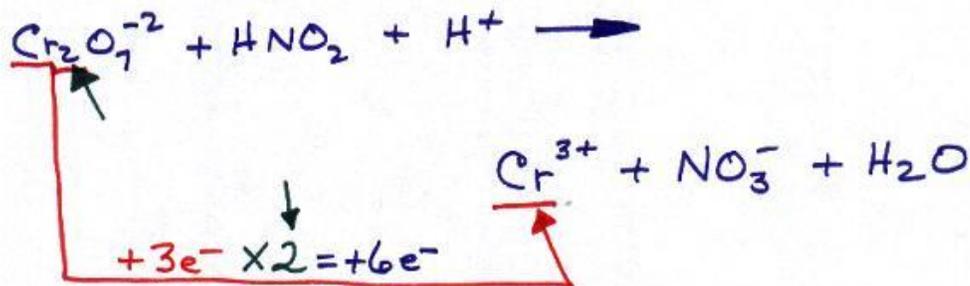
Step Number One: Assign oxidation numbers. Do this just as I set up the rules for oxidation numbers, above, in the multiple tables. Keep track of your charges.



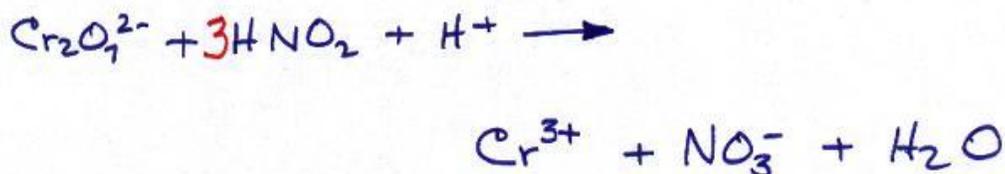
Step Number Two: You need to determine which reactant gains (oxidizing agent) or loses (reducing agent) electrons and identify how many electrons are lost per individual atom ONLY at this point.



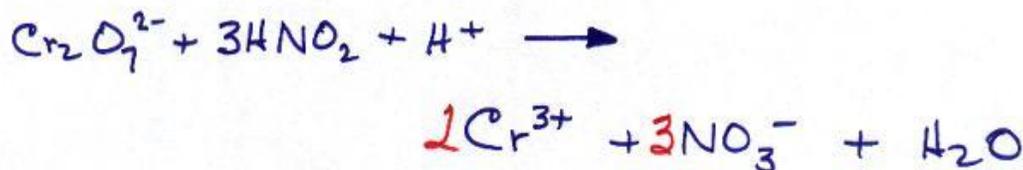
Step Number three: Determine the gain or loss of electrons per formula unit -- this reaction is a great example: dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) has 2 Cr's. That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



Step Number Four: Balance the left side of the reaction for gain and loss of electrons.



Step Number Five: Balance the redox pair, now, by balancing the right side of the reaction.

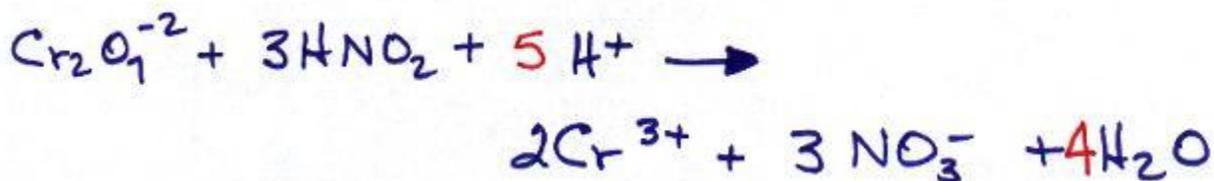


Step Number Six: Balance everything EXCEPT oxygen and hydrogen.

Step Number Seven: Balance the oxygens.

Step Number Eight: Balance the hydrogens.

Step Number Nine: Write the balanced equation/reaction.

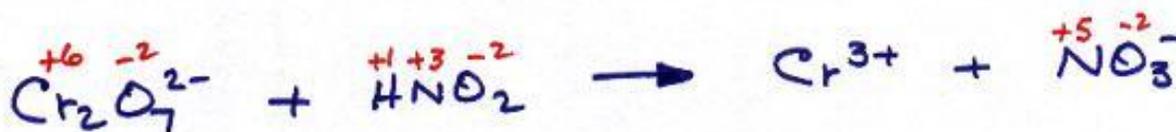


## Method 2: Oxidation Number Method for Aqueous Solutions

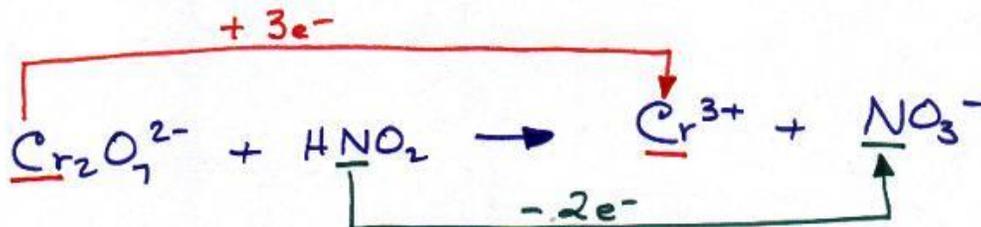
We'll still use the same example reaction, above. This method requires a slightly different approach.

Step Number One: write the net ionic reaction. This means to write the reaction that is going to occur between the redox pair ONLY.

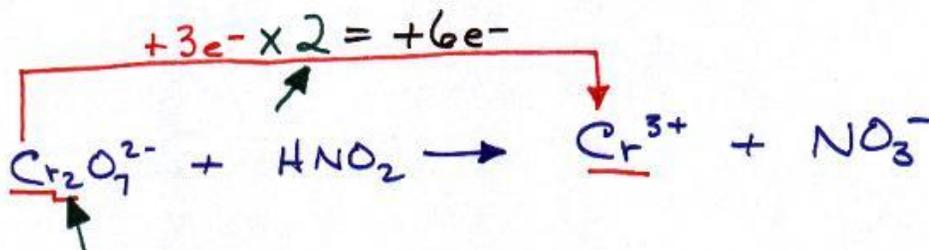
Step Number Two: Assign oxidation numbers just as we did in the first method.



Step Number Three: Determine which reactant gains and loses electrons.



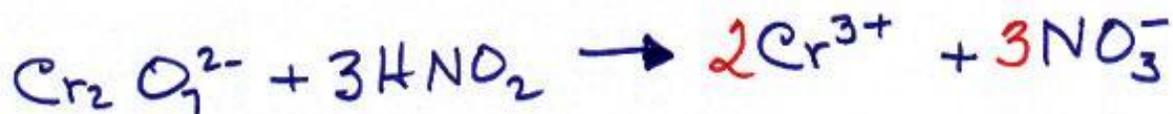
Step Number Four: determine the loss and gain of electrons per formula unit -- this reaction is a great example: dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) has 2 Cr's. That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



Step Number Five: Balance the left side of the reaction based on electron gain/loss.



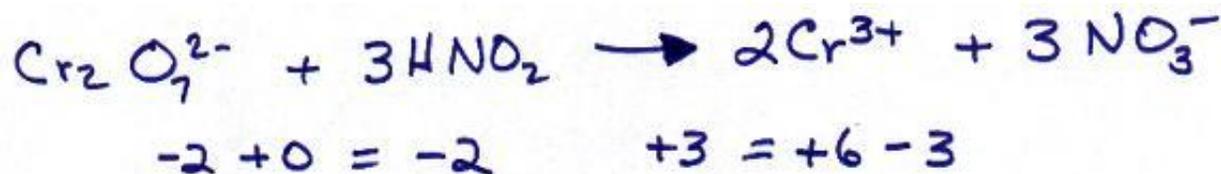
Step Number Six: balance the right side of the reaction.



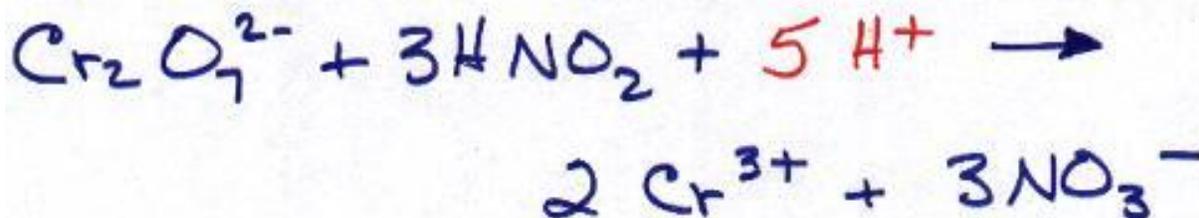
Page | 72

Step Number Seven: balance all but oxygen and hydrogen.

Step Number Eight: Add up the charges on both sides of the reaction.



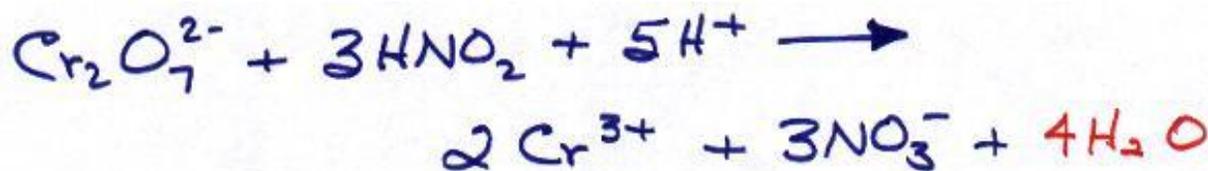
Step Number Nine: balance the charges by adding  $\text{H}^+$  for positive charges and  $\text{OH}^-$  for negative charges.



Step Number Ten: Balance the oxygens by putting water ( $\text{H}_2\text{O}$ ) on the side opposite the hydroxide ions.

Step Number Eleven: hydrogens ought to balance.

Step Number Twelve: Write the balanced reaction.

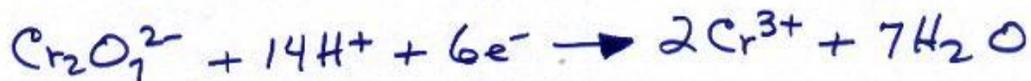


### Method 3: Half-Reactions for Aqueous Solutions Method

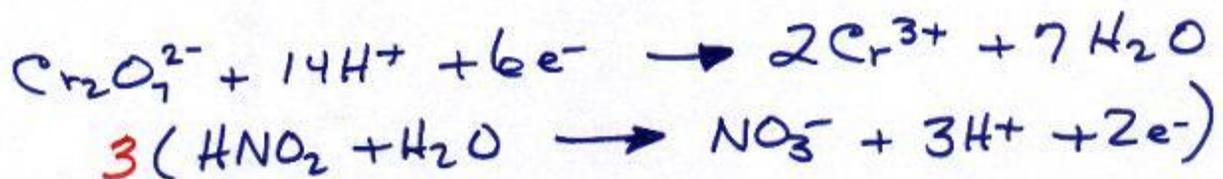
Step Number One: write out the unbalanced reaction.

Step Number Two: find the half reactions for each of the redox pair. This is done by looking them up in the appendix of traditional chemistry texts (Redox Potentials) or in the CRC Handbook of Chemistry and Physics. They will be given to you during the exams if they are needed and if they actually exist in the literature -- there are times there are no accessible half reactions for use; when that occurs, these problems are usually fairly simple.





Step Number Three: Balance all but the oxygen and hydrogen in each half reaction.

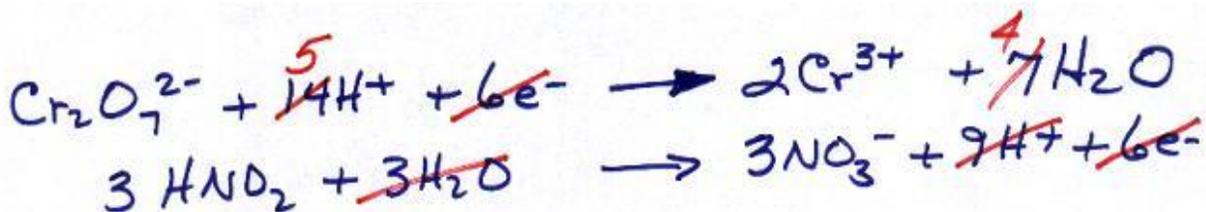


Step Number Four: Balance oxygens with water added to the oxygen deficient side of the reaction.

Step Number Five: Balance the hydrogens: 1) in ACID with  $\text{H}^+$ ; 2) in BASE with 1  $\text{H}_2\text{O}$  per needed hydrogen with an equal number of  $\text{OH}^-$  on the opposite side of the reaction.

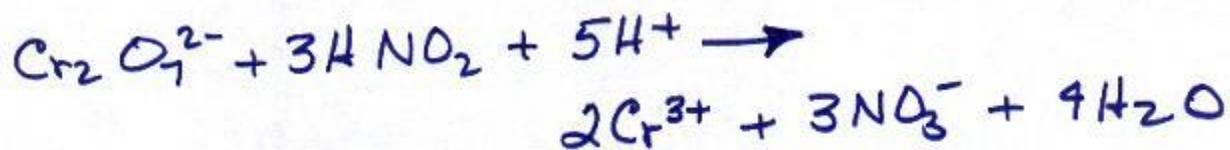
Step Number Six: Balance the charges with electrons on the side of each half reaction with the least negative charge.

Step Number Seven: between the two half reactions, now balance electron gain and loss. In this step, it becomes necessary to turn one of the reactions around so that it will add to the other half-reaction, eventually. Note that two half reactions will make a whole reaction.



Step Number Eight: Cancel out common elements, ions, and/or electrons between the 2 half reactions now balanced.

Step Number Nine: Add them up and write out the balanced reaction.

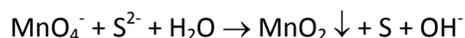


One key concept to keep in mind is that if you've balanced the same reaction by each method above, and you don't get the same answer each time, then there is an error in the balancing. Go back and find it -- it usually jumps right out at you.

### EXAMPLE 2

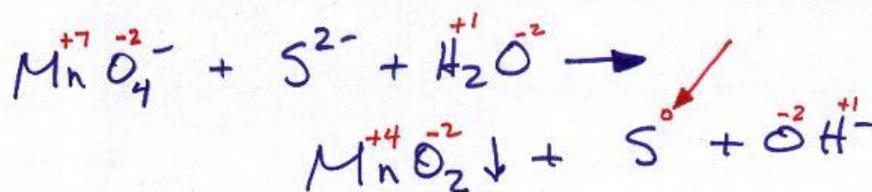
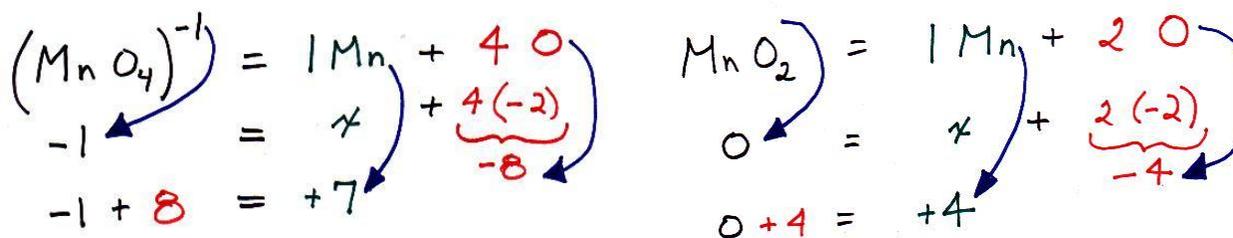
#### Method 1: Oxidation Number Method

For this example for ALL three methods (after you get through the homework, I don't care which method you utilize as long as you can do it), we'll use the following UNBALANCED equation:

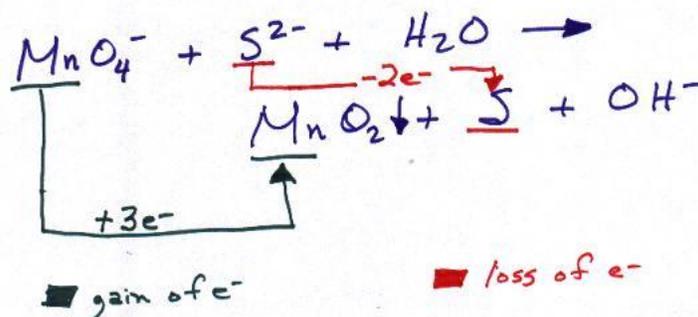


Note that the S on the right is in the elemental form and has an oxidation number of zero (0).

Step Number One: Assign oxidation numbers. Do this just as I set up the rules for oxidation numbers, above, in the multiple tables. Keep track of your charges.



Step Number Two: You need to determine which reactant gains (oxidizing agent) or loses (reducing agent) electrons and identify how many electrons are lost per individual atom ONLY at this point. (The sulfide loses 2 electrons and the manganese gains three.)

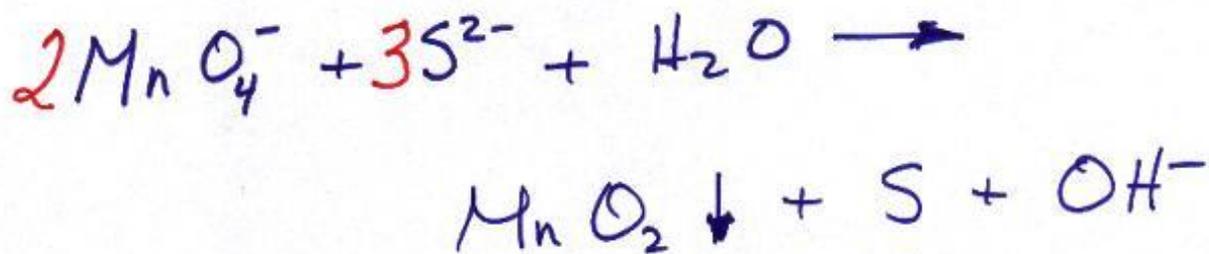


Step Number Three: Determine the gain or loss of electrons per formula unit -- this reaction is a bad example as there is only one formula unit for each -- the first of the examples illustrated this idea.

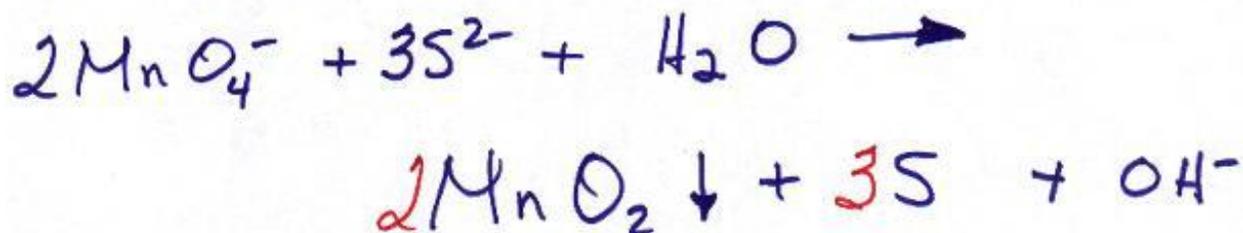
Step Number Four: Balance the left side of the reaction for gain and loss of electrons.

This balancing is done by looking at the numbers of electrons gained and lost. They must be equal.

Sometimes the easiest thing to do is to just multiply them together if there is no obvious lowest common multiple. Page | 75



Step Number Five: Balance the redox pair, now, by balancing the right side of the reaction.



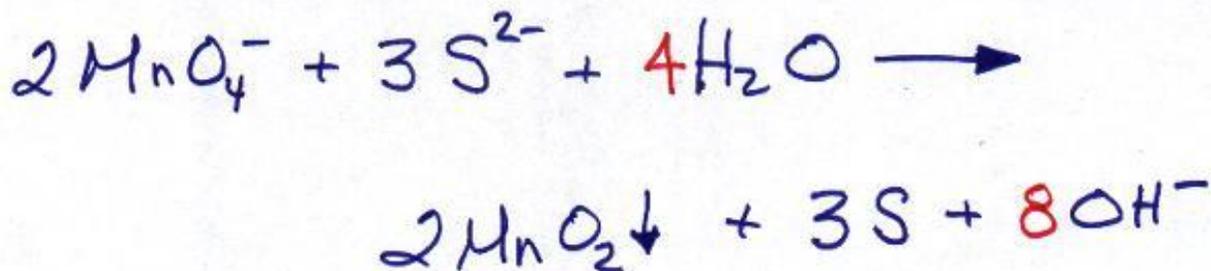
Make sure you've got as many atoms on the right as you do on the left.

Step Number Six: Balance everything EXCEPT oxygen and hydrogen.

Step Number Seven: Balance the oxygens. See below.

Step Number Eight: Balance the hydrogens. See below.

Step Number Nine: Write the balanced equation/reaction.

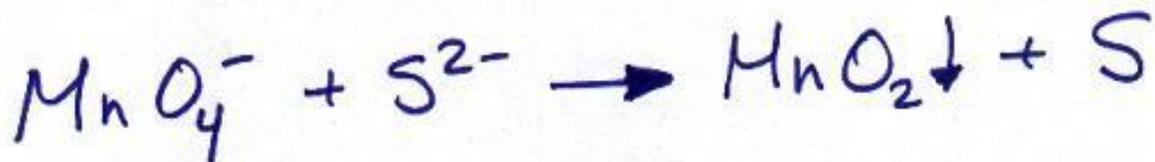


## Method 2: Oxidation Number Method for Aqueous Solutions

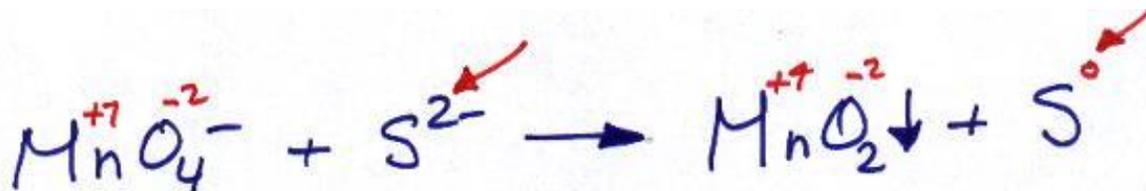
We'll still use the same example reaction, above. This method requires a slightly different approach.

Step Number One: write the net ionic reaction. This means to write the reaction that is going to occur between the redox pair ONLY.

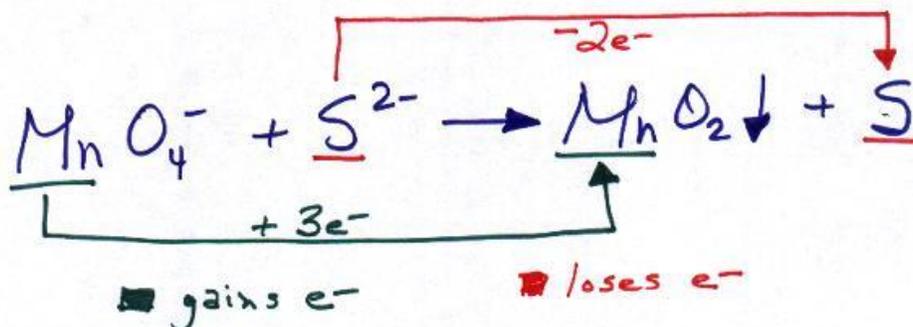
Page | 76



Step Number Two: Assign oxidation numbers just as we did in the first method.



Step Number Three: Determine which reactant gains and loses electrons.



Step Number Four: determine the loss and gain of electrons per formula unit (again, this is not a good example and was dealt with in the first example).

Step Number Five: Balance the left side of the reaction based on electron gain/loss.



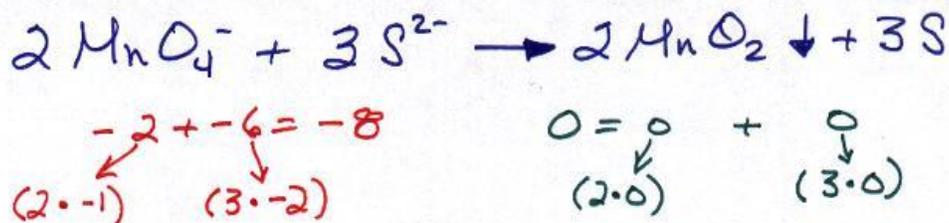
Step Number Six: balance the right side of the reaction.



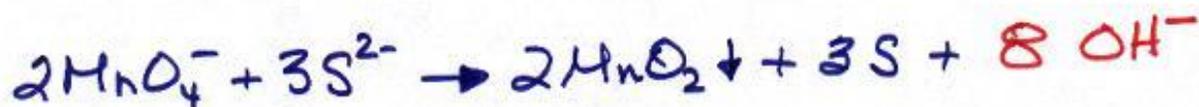
Step Number Seven: balance all but oxygen and hydrogen.

Page | 77

Step Number Eight: Add up the charges on both sides of the reaction.

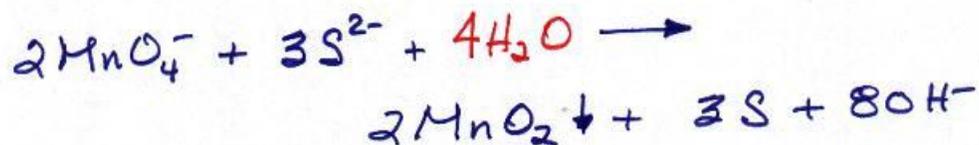


Step Number Nine: balance the charges by adding  $\text{H}^+$  for positive charges and  $\text{OH}^-$  for negative charges.



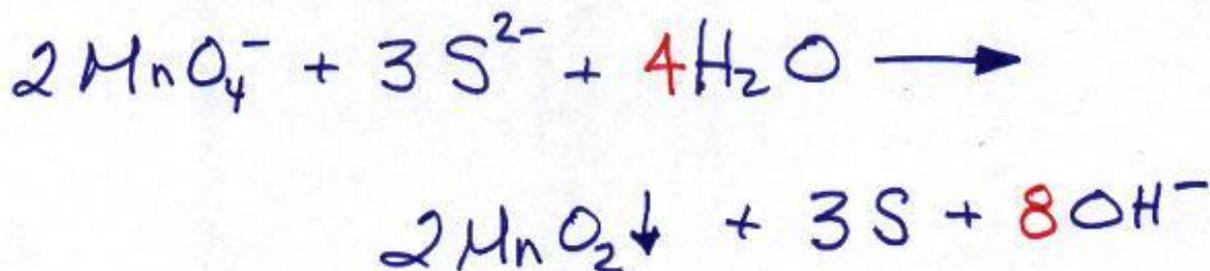
Note that I used  $\text{OH}^-$  to balance the negative charges on the right.

Step Number Ten: Balance the oxygens by putting water ( $\text{H}_2\text{O}$ ) on the side opposite the hydroxide ions.



Step Number Eleven: hydrogens ought to balance.

Step Number Twelve: Write the balanced reaction, just as above.

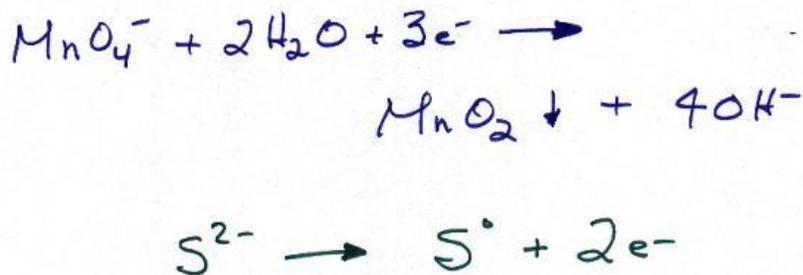


### Method 3: Half-Reactions for Aqueous Solutions Method

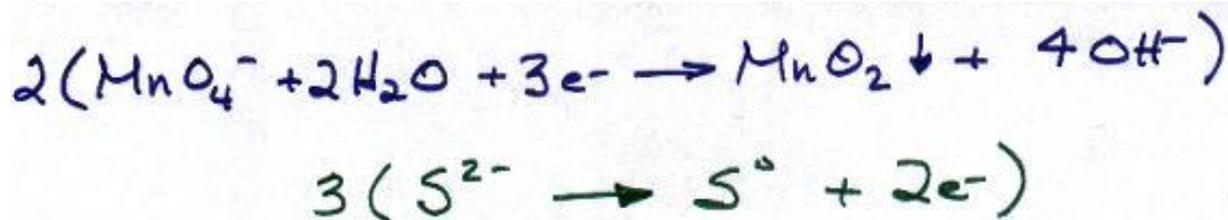
Step Number One: write out the unbalanced reaction.

Step Number Two: find the half reactions for each of the redox pair. This done by looking them up in the appendix of traditional chemistry texts (Redox Potentials) or in the CRC Handbook of Chemistry and Physics. They will be given to you during the exams if they are needed and if they actually exist in the literature -- there are times there are no accessible half reactions for use; when that occurs, these problems are usually fairly simple. Note that for each reactant there is a half reaction -- eventually, we'll add 'em up to make a whole reaction.

Page | 78



Step Number Three: Balance all but the oxygen and hydrogen in each half reaction.

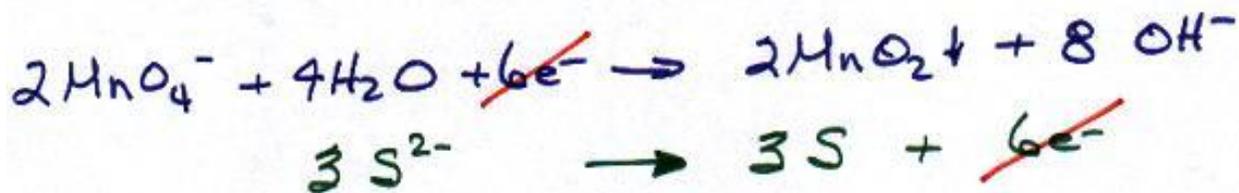


Step Number Four: Balance oxygens with water added to the oxygen deficient side of the reaction.

Step Number Five: Balance the hydrogens: 1) in ACID with  $\text{H}^+$ ; 2) in BASE with 1  $\text{H}_2\text{O}$  per needed hydrogen with an equal number of  $\text{OH}^-$  on the opposite side of the reaction.

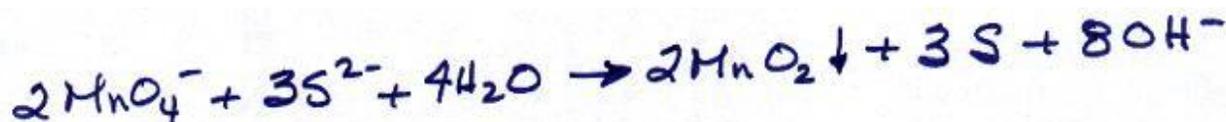
Step Number Six: Balance the charges with electrons on the side of each half reaction with the least negative charge. Note that we multiply the top half reaction by the number of electrons from the bottom reaction and vice versa. While this works in most cases, remember that once the reaction is balanced, you must use the lowest possible coefficients, i.e., if the coefficients are divisible by the same number across the reaction, the final reaction must be divided by that number to yield numbers that are no longer divisible, yet consist of a whole number.

Step Number Seven: between the two half reactions, now balance electron gain and loss. In this step, it becomes necessary to turn one of the reactions around so that it will add to the other half-reaction, eventually. Note that two half reactions will make a whole reaction.



Step Number Eight: Cancel out common elements, ions, and/or electrons between the 2 half reactions now balanced.

Step Number Nine: Add them up and write out the balanced reaction.



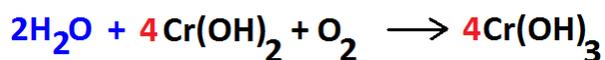
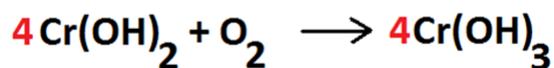
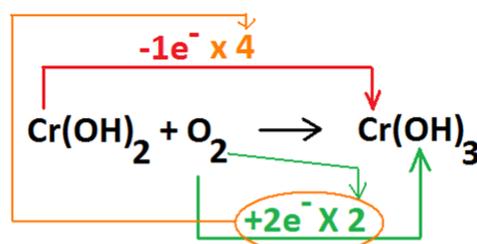
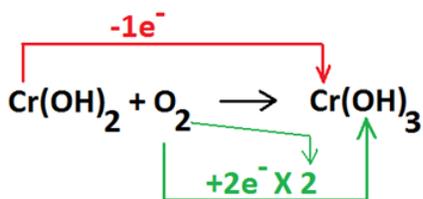
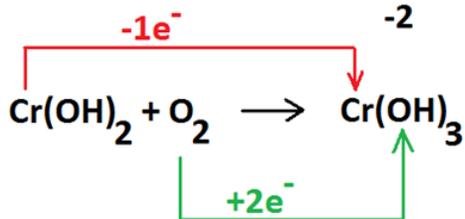
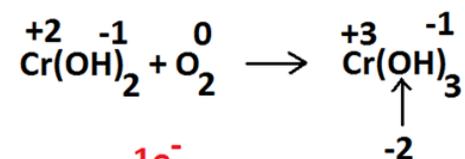
### Redox Reactions with OH<sup>-</sup>—Containing Reactions

Students have asked over the years about balancing redox reactions with hydroxide ions present.

For the most part, they are, overall, no different than traditional redox reactions.

There is, though, some logic that must be applied, i.e., a basic understanding of chemistry in these reactions helps comprehend how they work out.

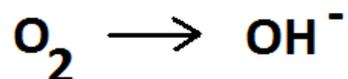
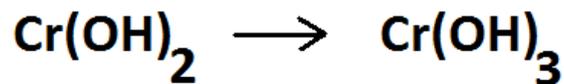
Traditional Example:  $\text{Cr}(\text{OH})_2 + \text{O}_2 \rightarrow \text{Cr}(\text{OH})_3$



## Non-Traditional Approach to The Same Reaction

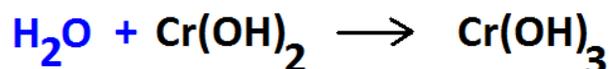
1. Write out the half-reaction for the redox pair – NOT the half reaction in the Tables of Electrochemical Potential. This comes from working with redox pairs so you can identify them. Do you see the “extra”  $\text{OH}^-$  in the top half reaction?

Page | 80

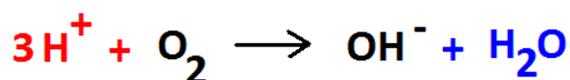
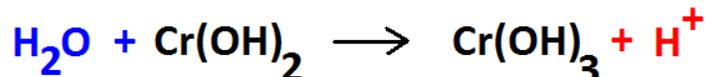


2. Balance all but H and O: DONE

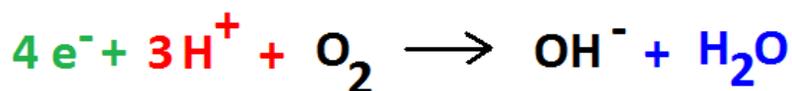
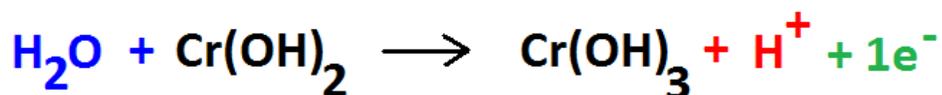
3. Balance O with water ( $\text{H}_2\text{O}$ )



4. Balance H with  $\text{H}^+$  as needed

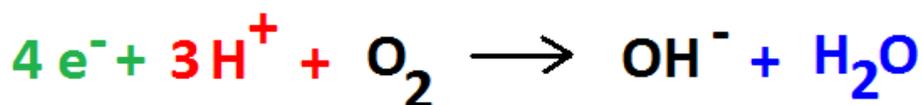
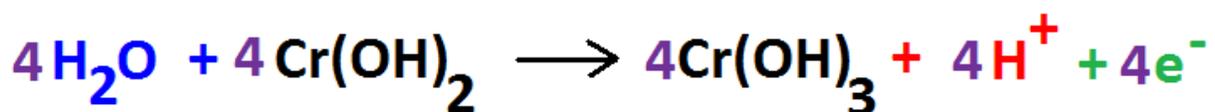


5. Balance the charge in each half-reaction by adding electrons as needed:

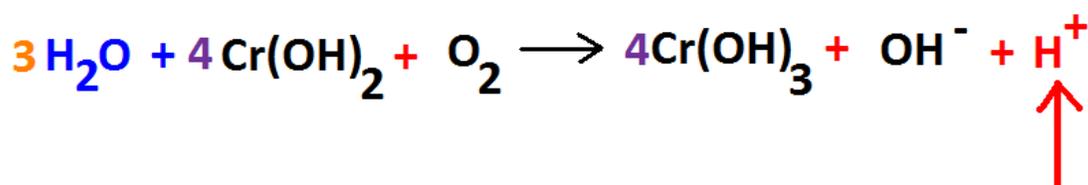
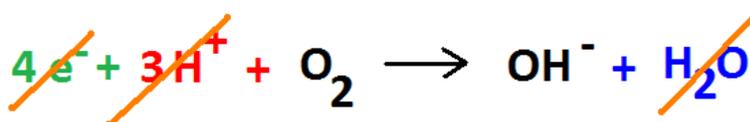
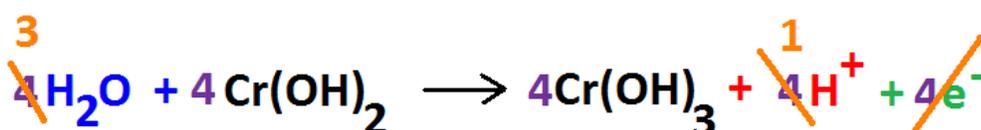


6. Balance the gain-n-loss of electrons per each half reaction:

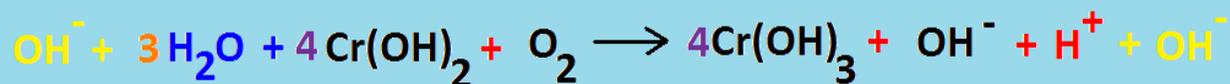




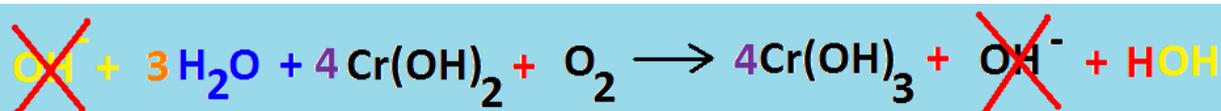
7. Add the two reactions, cancelling common entities to both sides of the reaction:



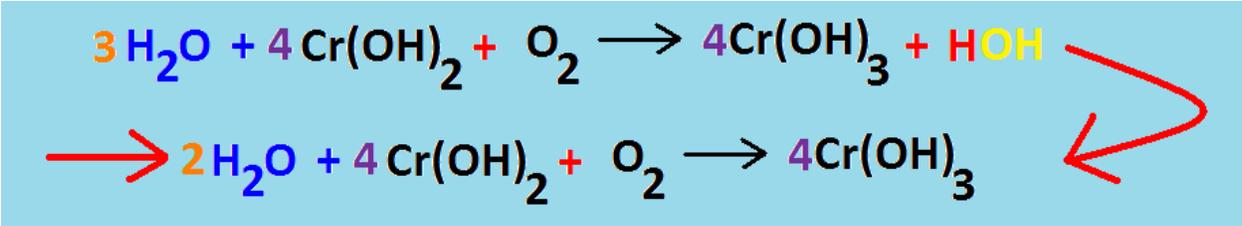
8. Now switch to a basic (alkaline) solution by adding an equal number of hydroxide ions as there are hydrogen ions to both sides of the reaction:



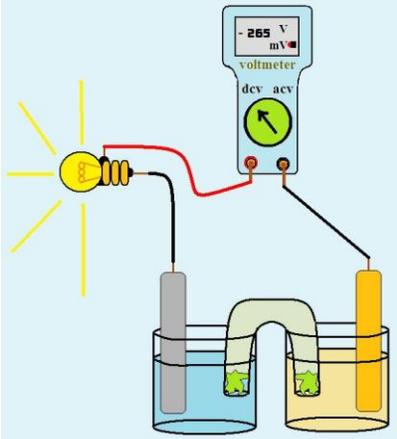
9. Combine and remove:



10. Write the final balanced reaction:

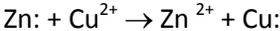
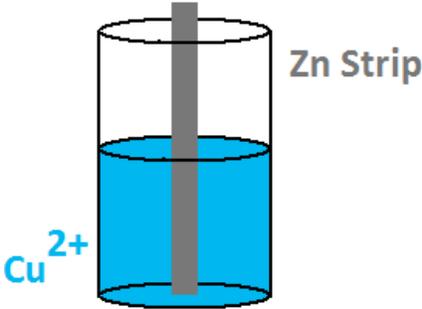


Batteries

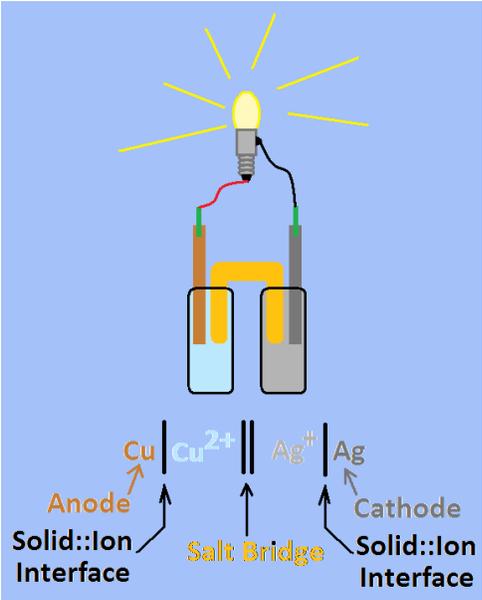


Batteries are classic redox reactions, which is why the tables of redox potentials are called just that: tables of redox POTENTIALS. A potential is, in common terms, volts. Chemical changes can produce electricity. A classic demonstration is to touch the two terminals of a 9-volt battery to your tongue -- the shock you get is a chemical change.

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:



where the "2+" represent the two electrons that were removed from the Zn by the Cu<sup>2+</sup>.



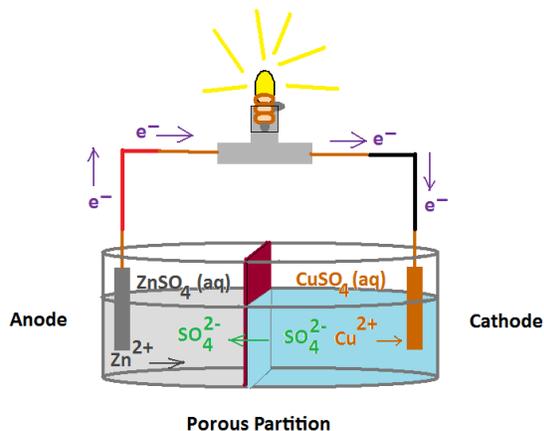
Battery Nomenclature

In the graphic you can see a simple battery. Beneath the battery is how batteries are illustrated without writing out the complete redox reaction (although you can derive the overall redox reaction and the flow of electrons using this format: Cu loses 2 e- and donates them to the Ag(I) ion to reduce it to Ag).

By convention, the anode is ALWAYS written on the left in this format. One solid vertical line indicates the solid::ion interface (where you dip the metal electrode in the corresponding ionic solution). Two solid vertical lines indicate the salt bridge (this maintains the flow of the anions to make sure that the circuit continues to flow and to ascertain that there is no increase in the anion concentration on the cathode side of the battery – vice versa on the anode side).

## Another Example Using an Inert Electrode

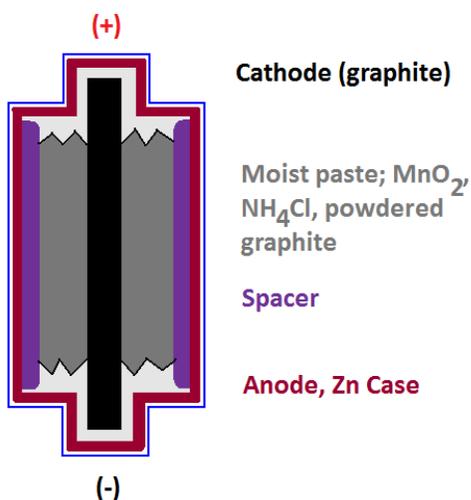
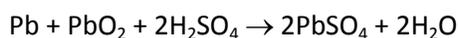
Same format – simply using an inert (non-reactive) electrode. This concept can be used to electroplate cheaper metals with a thin layer of a more expensive (precious) metal. The flow of electrons is called the electric current. This can be confirmed by using a voltmeter or by putting a light in the circuit and observing the light glowing.



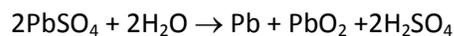
The graphic at left is an example of a fairly simple battery set up with a light in the circuit. Note the flow of electrons from the elemental zinc strip to the copper (II) side.

The 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 (the one that lit the light) 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:



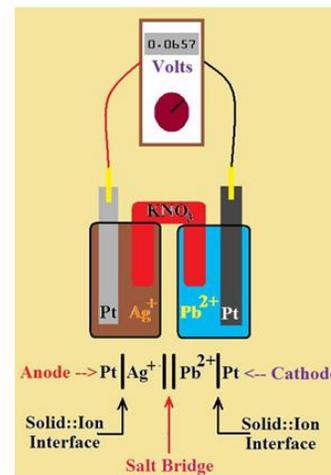
And on recharge (when your car is running and the generator or alternator is recharging it), the following reaction occurs:



Alkaline (Dry Cell) Batteries

Anode = Zinc (Zn)

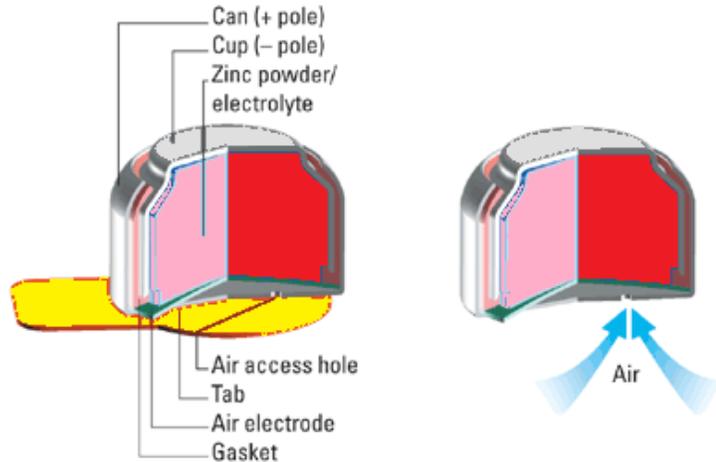
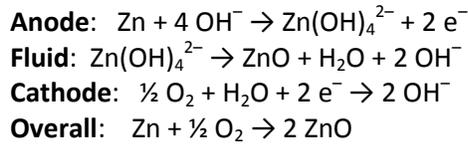
Cathode = manganese dioxide (MnO<sub>2</sub>)



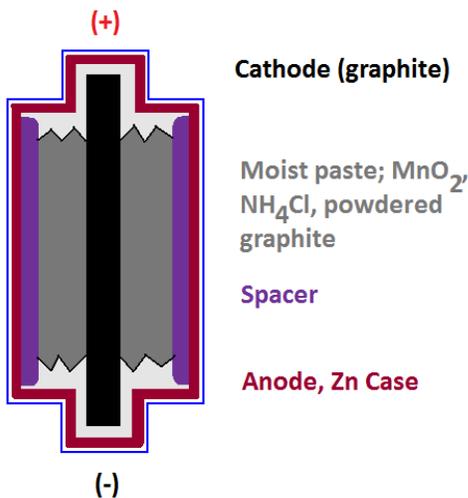
Watch-Type Batteries (Zinc-Air)

Left: Inactivated (tab in place)  
 Right: Activated (tab removed)

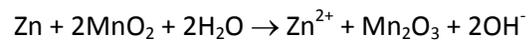
Research is exploring battery development to run off of a person's blood sugar - ramifications: pacer's/defib's



ca 1.60 V produced theoretically



Dry cells have been around quite a while, now. While each manufacturer has its own style, they all pretty much follow, in very general terms, the graphic of a generic dry cell. The cathode is a piece of graphite and the anode is the zinc case. It is the latter "disappearing" as the battery runs down that can cause corrosion inside your electronic whatever's when the paste leaks out. The paste may be a combination of  $MnO_2$ ,  $NH_4Cl$  and powdered graphite -- or something altogether different depending on the battery. For the battery I've described, the following chemical reaction occurs as it's used:

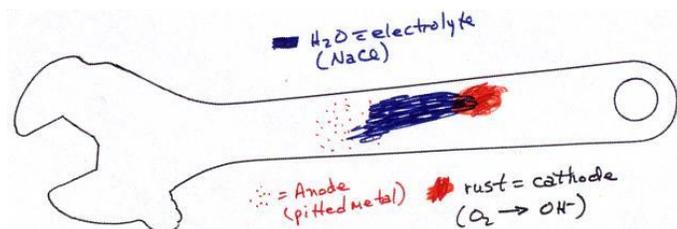


Corrosion

Corrosion is another form of a battery -- tools are meant to be cared for, kept away from water of any form (including ice in freezers) and wrapped in greasy or lightly oiled cloths. If, for example, a prized flat-blade screwdriver is taken from its protected place in the toolbox and used to scrape ice out of a freezer or if a wrench is carelessly tossed out in the salted slush while one puts tire chains on, the tool will rust. How does this happen? Let's use the wrench as our example.



The wrench is made out of metal. No matter how carefully the wrench is crafted, it will have lots of pits in its surface. These pits will act as the anode.



If only pure water is exposed to these pits, it's more or less protected from oxygen by the water. If, however, the water has salt (NaCl) in it (an ionic compound), an electrolytic solution is made. If these pits in contact with the ionic compound "connect" with an area of rust (cathode) on the wrench, a battery is set up and more corrosion will occur on the wrench. Hammer, above, obtained ca 1945; Wrench and screwdriver ca 1970.



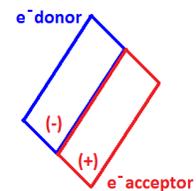
The reactions that occur on this wrench are as follow:

Location	Reaction
At anode	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
At cathode	$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$
Also at cathode	$\text{Fe}(\text{OH})_2 + \text{O}_2 \rightarrow \text{Fe}(\text{OH})_3$ ; $\text{Fe}(\text{OH})_3 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$

The pitting makes the wrench more chemically reactive.

### Solar Batteries

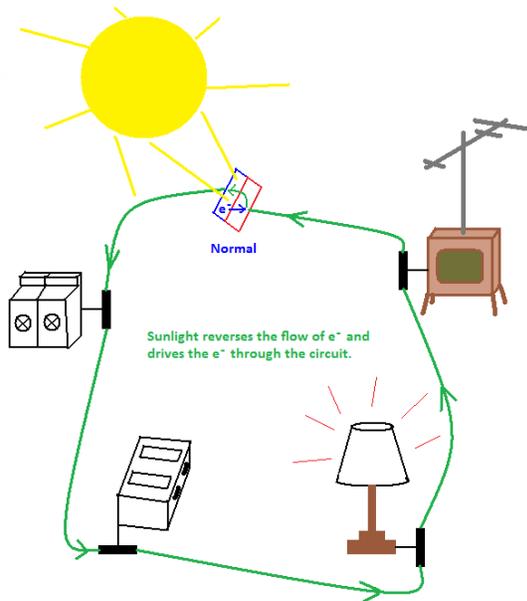
Since I developed this part of the lecture, solar power has gone through numerous changes. At the time I put this together, solar cells were only about 10% efficient in energy conversion. Efficiencies, now, range from 8-20% depending on the technology and manufacturer. I have given up trying to keep 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.



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).

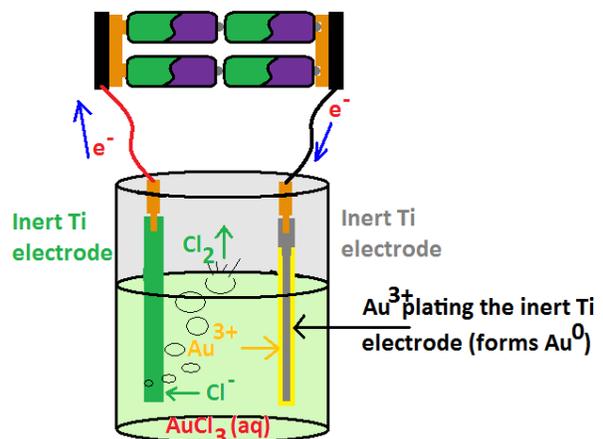
By itself, electrons flow from the electron donor plate to the electron acceptor plate. Sunlight, though, reverses the "natural process" and electrons are driven through the circuit via the donor layer to the acceptor layer. This closes the circuit and runs electric appliances and toys (TV, stereos,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



What the 10% efficiency 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).

### Electrolytic Cells

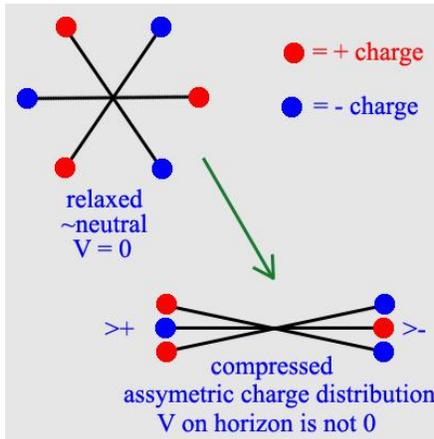
Electrical energy is used to drive an otherwise "not runnable" reaction to completion. This is done with an electrolytic cell. In general, inert electrodes are used as both anode (which one is this?) and cathode (which one is this?). They are "dipped" in a solution or solutions and an electrical current (out of the wall, a power source or batteries) is sent between them. In the graphic example, the solution is gold (III) chloride.



The reactions that occur in this electrolytic cell are tabulated, below:

Location	Reaction
Anode	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
Cathode	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$

In other words, the gold plates onto the inert electrode. You'll learn more about electroplating in CHEM 122.



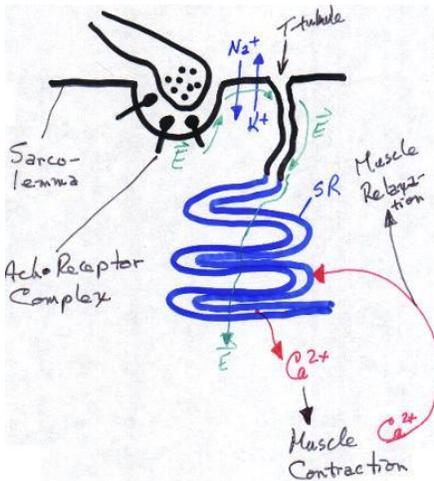
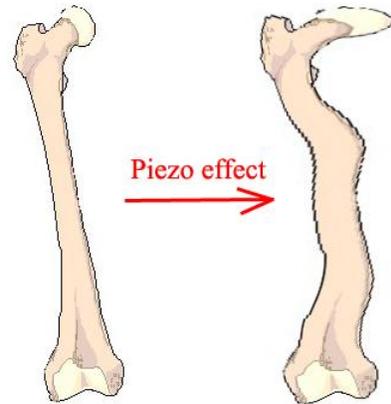
### Piezo Electric Effect

Piezoelectricity = pressure electricity. We know it from BBQ grills with the propane "starter". 1<sup>st</sup> discovered in quartz and tourmaline. It was also found to occur in tendon, dentin, aorta, trachea, elastin and BONE!

The Piezo 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.

### Piezo – Bone

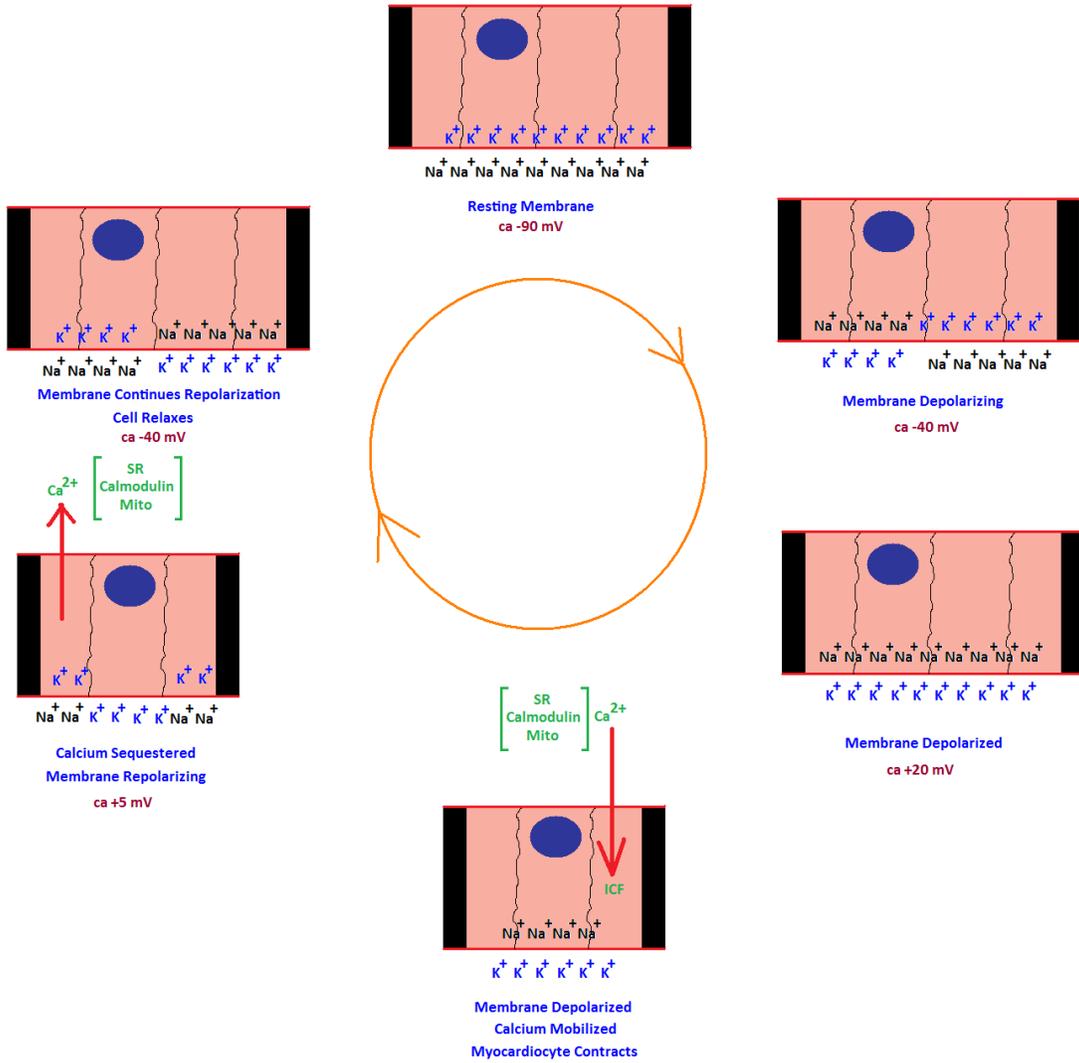
This stress effect causes osteoblasts to secrete osteoid (CHON that permits Ca salt ppt'ation on/in it) to make/remodel new bone.



### Elementary Muscular Electrical Transmission/Conduction

The part that gets detailed is the next graphic. Probably the best simple way to describe this graphic is that energy flows into the muscle cell, causing it to contract.

# Electrical Events During Myocardial Contraction/Relaxation





## Problem Sets

### Problem Set 25

1. Your bicycle tire is flat and you need to fill it with air. If the air is at 1 atm and your bicycle tire holds 4.5 L at 80 psi, how much air do you need to pump into your tire?
2. At full expiration a rabbit's lungs hold 2.4 L of air at 765 mm Hg. At full inspiration, the intrapulmonary pressure is 750 mm Hg. How large is the volume of the rabbit's lungs at full inspiration?
3. A hot air balloon at deflation has a volume of 5 L at 760 mm Hg. After inflation, the balloon has a volume of 450 L. What is the pressure of the hot air in the balloon?
4. As you drive along in your automobile, the air in your tires (and the tires, too) heats up. If you started a 500 mile trip at 10°C with 50 L of air in your tires, what volume would be occupied by air in your tires at the end of the trip when the air temperature is 40°C?
5. The air in a deflated hot air balloon occupies 5 L at 5°C. What is the volume of the air in the balloon at 60°C?
6. Air that we breathe in has to be heated for breathing ease. If we breathe in air at 10°C and the temperature in the lungs is 37°C with a volume of 6 L, how much air did we breathe in?
7. A gas at 300 Torr and 5°C occupies 350 mL. How many mol of gas is/are present in this volume?
8. If 0.8 mol of a gas exerts 4 atm of pressure at 75°C, how much volume does it occupy?
9. 0.8 mol of a gas occupies 50 L at 25°C. How much pressure does this gas exert against the walls of its container?
10. A sample of  $\text{NH}_3$  has a mass of 3.04 g and occupies a volume of 4 L at STP (0°C and 760 mm Hg). What is the molecular weight of  $\text{NH}_3$ ?
11. The total pressure of a mixture of gases ( $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CH}_4$ ) is 1800 Torr. The  $p_{\text{CO}_2}$  is 500 Torr and the  $p_{\text{O}_2}$  is 600 Torr. What is the  $p_{\text{CH}_4}$ ?
12. Air is collected at a barometric pressure of 600 mm Hg. If the primary gases in the air are  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  and the  $p_{\text{N}_2}$  is 400 mm Hg and the  $p_{\text{O}_2}$  is 160 mm Hg, what is the  $p_{\text{H}_2\text{O}}$ ?

### Problem Set 26

1. Compare the rate of diffusion of each pair of gases:  
A.  $\text{Cl}_2$  with  $\text{H}_2$                       B.  $\text{Br}_2$  with  $\text{H}_2$                       C.  $\text{O}_2$  with  $\text{N}_2$   
D.  $\text{I}_2$  with  $\text{O}_2$                           E.  $\text{I}_2$  with  $\text{F}_2$                           F.  $\text{CH}_4$  with  $\text{O}_2$   
G.  $\text{CH}_4$  with  $\text{N}_2$     H.  $\text{CH}_4$  with air (MW = 29)    I.  $\text{H}_2\text{S}$  with air

2. Describe Bernoulli's Law.
3. Describe how an aspirator pump works.
4. Describe the dependency of  $R_e$  on  $V$ ,  $d$ ,  $\rho$  and  $\eta$ .
5. Describe the dependency of the resistance of blood flow on the radius of the vessel.

Based on the following table, determine under which conditions you would have the greatest flow: vessels in series or in parallel:

#6	#7	#8
$R_1 = 7$ units	$R_1 = 2$ units	$R_1 = 1$ unit
$R_2 = 10$ units	$R_2 = 4$ units	$R_2 = 2$ units
$R_3 = 12$ units	$R_3 = 6$ units	$R_3 = 3$ units
	$R_4 = 8$ units	$R_4 = 4$ units
		$R_5 = 5$ units

#### PROBLEMS to Accompany This Topic

1. A solution is prepared with 250 mg  $\text{Fe}_2(\text{SO}_4)_3$  in 2M HCl and diluting to 1.50 L. Calculate the following:
  - The molarity of the ferric sulfate solution.
  - The w/v% of the ferric sulfate solution
  - The ppm of the ferric sulfate solution
2. A solution is prepared with 565 mg  $\text{K}_4\text{Fe}(\text{CN})_6$  in water and diluted to 1375 mL. Calculate the following:
  - The molarity of the potassium ferrocyanide solution
  - The w/v% of the potassium ferrocyanide solution
  - The ppm of the potassium ferrocyanide solution
3. How would you prepare:
  1. 400 mL of 8% w/v aqueous ethyl alcohol (EtOH)
  2. 400 mL of 8% w/w aqueous EtOH
  3. 400 mL of 8% v/v aqueous EtOH
  4. 5 L of 16% w/v aqueous propylene glycol
  5. 5 L of 16% w/w aqueous propylene glycol
  6. 5 L of 16% v/v aqueous propylene glycol
  7. 1200 mL of 34% w/v aqueous acetic acid
  8. 1200 mL of 34% w/w aqueous acetic acid
  9. 1200 mL of 34% v/v aqueous acetic acid

4. How would you prepare 500 mL of the following nitric acid solutions with the Analytical Chemistry approach?

1. 1:4
2. 2:3
3. 4:5
4. 1:16
5. 1:24
6. 1:2

5. How would you prepare 750 mL of the following nitric acid solutions with the Biochemistry approach?

1. The same solutions as above in #4 -- REMEMBER to use the correct approach for dilution.

#### Problem Set 14

1. Draw and generally explain how a still works and what it does.
2.  $\text{H}_3\text{C}(\text{CH}_2)_{16}\text{CO}_2\text{K}$  is the formula for potassium stearate ("lye" soap). Predict what the chemical products between potassium stearate and the following ions would be.

- A)  $\text{Fe}^{2+}$       B)  $\text{Fe}^{3+}$       C)  $\text{Cu}^{2+}$       D)  $\text{Mg}^{2+}$   
E)  $\text{Mn}^{2+}$       F)  $\text{Ca}^{2+}$

3. Briefly explain how cation exchange resins work.

4. Briefly explain how anion exchange resins work.

5. Explain how detergents make water "wet".

6. Name the following hydrates chemically:

- A)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$       B)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$       C)  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$   
D)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$       E)  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$       F)  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$

7. Define hygroscopic, effloresce and deliquescent.

8. Explain the surface tension exhibited by  $\text{H}_2\text{O}$ .

9. Explain why ice is less dense than liquid water.

10. Define basic and acidic anhydrides.

11. Why is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  blue and  $\text{CuSO}_4$  white?

12. What is the triple point of water in definition terms and in actual numbers?

## Problem Set 21

1. What are the two "R" values in determining osmotic pressure?
2. Define osmosis and dialysis.
3. Define Henry's Law.
4. Compare and contrast colloids and solutions.
5. Define the Tyndall effect.
6. Define osmolarity.
7. Describe how an electrolyte solution would have a different osmotic pressure than a non-electrolyte solution.

## Problem Set 22

1. A solution of  $\text{Al}_2(\text{SO}_4)_3$  is 0.5 M. If the solution is at  $30^\circ\text{C}$ , what is the osmotic pressure for this solution?
2. What is the osmolarity of the solution in #1?
3. A solution of glucose is 1 M. If the solution is at  $25^\circ\text{C}$ , what is the osmotic pressure for this solution?
4. What is the osmolarity for the solution in #3?
5. A solution of  $\text{CaCO}_3$  is 0.25 M. If the solution is at  $35^\circ\text{C}$ , what is the osmotic pressure of the solution?
6. What is the osmolarity of the solution in #5?
7. If salt is added to pure water, what happens to its boiling point, freezing point and vapor pressure?

## Problem Set 15

1. If a solution of 0.5 M HOAc dissociates as follows:  $\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^-$ , what is the final  $[\text{H}_3\text{O}^+]$  in the solution?  $K_a$  for HOAc =  $1.8 \cdot 10^{-5}$ .
2. What is the pH of the above solution?
3. What is the  $K_b$  for HOAc?

4. If a solution of 0.25 M HA dissociates as follows:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$ , what is the final  $[\text{H}_3\text{O}^+]$  in the solution?  $K_a$  for HA =  $5.4 \cdot 10^{-7}$ .
5. What is the pH for the above solution (question 4)?
6. What is the  $K_b$  for HA?
7. If a solution of 1.3 M  $\text{H}_2\text{M}$  dissociates as follows:  
 $\text{H}_2\text{M} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{O}^+ + \text{M}^{2-}$ , what is the  $[\text{H}_3\text{O}^+]$  of the solution?  $K_a$  for  $\text{H}_2\text{M} = 2 \cdot 10^{-8}$ .
8. What is the pH of the above solution (in question 7)?
9. What is the  $K_b$  for  $\text{H}_2\text{M}$ ?
10. Prove that  $K_a K_b = K_w$

#### Problem Set 16

1. Mark the pH with "A" for Acidic, "B" for Neutral or "C" for Alkaline or Basic:
 

A) 2.5	B) 6.8	C) 10	D) 12
E) 7.0	F) 9.4		
G) 6	H) 14	I) 3.5	J) 4
K) 1.5	L) 13.6		
2. Calculate the  $[\text{H}_3\text{O}^+]$  for all of the above pH's in Question #1.
3. Which of the following compounds are soluble in water?
 

A) $\text{PbCl}_2$	B) $\text{LiCl}$	C) $(\text{NH}_4)_2\text{SO}_4$
D) $\text{AlF}_3$		
E) $\text{SrCl}_2$	F) $\text{LiOAc}$	G) $\text{H}_2\text{SO}_4$
H) $\text{H}_3\text{PO}_4$		
4. Determine the equivalent weight for the following compounds:
 

A) $\text{HCl}$	B) $\text{Ba}(\text{OH})_2$	C) $\text{MgSO}_4$
D) $\text{AlF}_3$		
E) $\text{SrCl}_2$	F) $\text{LiOAc}$	G) $\text{H}_2\text{SO}_4$
H) $\text{H}_3\text{PO}_4$		

#### Problem Set 17

1. 20 g NaOH are dissolved in 1 L  $\text{H}_2\text{O}$ . What is the N of the NaOH solution?
2. 25 g HCl are dissolved in 500 mL of water. What is the N of the HCl solution?

- 30 g  $\text{Sr}(\text{OH})_2$  are dissolved in 750 mL water. What is the N of the  $\text{Sr}(\text{OH})_2$  solution?
- 150 g  $\text{H}_2\text{SO}_4$  are dissolved in 750 mL water. What is the N of the  $\text{H}_2\text{SO}_4$  solution?
- 75 g  $\text{BaSO}_4$  are dissolved in 3 L  $\text{H}_2\text{O}$ . What is the N of the  $\text{BaSO}_4$  solution?

Problem Set 18

- A solution of HA and  $\text{A}^-$  is at a pH of 6.4. If the  $[\text{HA}] = 0.4 \text{ M}$  and the  $[\text{A}^-] = 0.25 \text{ M}$ , what is the  $\text{pK}_a$  for HA?
- A solution of HB and  $\text{B}^-$  is at a pH of 8.5. If the  $[\text{HB}] = 0.05 \text{ M}$  and the  $[\text{B}^-] = 0.15 \text{ M}$ , what is the  $\text{pK}_a$  for HB?
- A solution of HC and  $\text{C}^-$  is at a pH of 7. If the  $[\text{HC}] = 0.5 \text{ M}$  and the  $[\text{C}^-] = 0.5 \text{ M}$ , what is the  $\text{pK}_a$  for HC?
- A solution of HA and  $\text{A}^-$  is at a pH of 12. If the  $[\text{HA}] = 0.01 \text{ M}$  and the  $[\text{A}^-] = 0.75 \text{ M}$ , what is the  $\text{pK}_a$  for HA?
- A solution of HA and  $\text{A}^-$  is at an unknown pH. The  $\text{K}_a$  for HA is  $7.2 \cdot 10^{-8}$ . If  $[\text{HA}] = 0.5 \text{ M}$  and  $[\text{A}^-] = 0.125 \text{ M}$ , what is the pH of the solution?

Problem Set 19

- Define Arrhenius acids and bases.
- Define Bronsted-Lowry acids and bases.
- Define Lewis acids and bases.
- Describe the 5 forms of hydrates and give examples where possible.

Problem Set 20

- Identify from which acids the following salts were obtained:

- |                                 |                               |                    |                   |
|---------------------------------|-------------------------------|--------------------|-------------------|
| A) $\text{K}_2\text{SO}_4$      | B) $\text{LiCl}$              | C) $\text{AlPO}_4$ |                   |
| D) $\text{MgSO}_4$              |                               |                    |                   |
| E) $\text{Al}_2(\text{SO}_4)_3$ | F) $\text{BPO}_4$             | G) $\text{SrCl}_2$ | H) $\text{NaOCl}$ |
| I) $\text{Be}_3(\text{PO}_4)_2$ | J) $\text{Mg}(\text{NO}_3)_2$ | K) $\text{NaNO}_3$ | L) $\text{KNO}_3$ |

- Define buffers and what the effective range of a buffer is.
- Design a 3-column table describing unsaturated, saturated and super-saturated solutions.

Additional Problems – Do with Your Other Redox Problem Set Questions

Balance the following reactions using the non-traditional method of balancing redox reactions that use hydroxide ion.

- Nickel(II) hydroxide + oxygen = Nickel(III) hydroxide
- Copper(I) hydroxide + oxygen = Copper(II) hydroxide
- Cobalt(II) hydroxide + oxygen = Cobalt(III) hydroxide
- Iron(II) hydroxide + Oxygen = Iron(III) hydroxide
- Mercury(I) hydroxide + Oxygen = Mercury(II) hydroxide

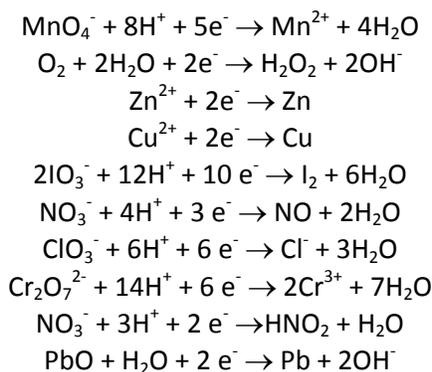
- NOTE: Don't forget that Mercury(I) is a little weird when you write out the formula for Mercury(I) hydroxide!**

- Tin(II) hydroxide + Oxygen = Tin(IV) hydroxide

Problem Set 23

Table of Half Reactions

IMPORTANT: When necessary, turn the reactions around to fit your needs – do NOT, however, change the contents of the half-reactions

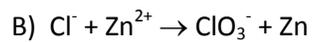
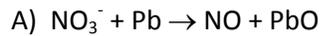


1. Balance the following reactions by each of the first two methods of balancing redox reactions:

- |   |  |
|---|--|
| A) $\text{Zn} + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{N}_2\uparrow$                | B) $\text{NO}_3^- + \text{I}_2 \rightarrow \text{IO}_3^- + \text{NO}_2\uparrow$              |
| C) $\text{Cu} + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{NO}_2\uparrow$               | D) $\text{H}_2\text{O}_2 + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \text{O}_2\uparrow$   |
| E) $\text{CuS} + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{S} + \text{NO}\uparrow$     | F) $\text{NO}_3^- + \text{Zn} \rightarrow \text{NH}_3\uparrow + \text{Zn}(\text{OH})_4^{2-}$ |
| G) $\text{ClO}_3^- + \text{I}_2 \rightarrow \text{IO}_3^- + \text{Cl}^-$                      | H) $\text{Cr}_2\text{O}_7^{2-} + \text{HNO}_2 \rightarrow \text{Cr}^{3+} + \text{NO}_3^-$    |
| I) $\text{H}_2\text{SO}_4 + \text{HBr} \rightarrow \text{SO}_2\uparrow + \text{Br}_2\uparrow$ | J) $\text{C} + \text{HNO}_3 \rightarrow \text{NO}_2\uparrow + \text{CO}_2\uparrow$           |

2. Balance the following reactions from #1, above, by the third method: D, G and H.

3. Balance the following reactions by whichever methods you so desire:



Problem Set 24

1. Draw a simple battery and label its parts.
2. Oxidation in a battery occurs at which electrode?
3. Reduction in a battery occurs at which electrode?
4. Draw and label an electrolytic cell.
5. Explain how corrosion on a piece of metal works as a battery.