Gases and Liquids: The Chemistry of Aqueous Systems
Gas Laws

Fall 2019, Revised Spring 2020

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

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

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

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

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

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

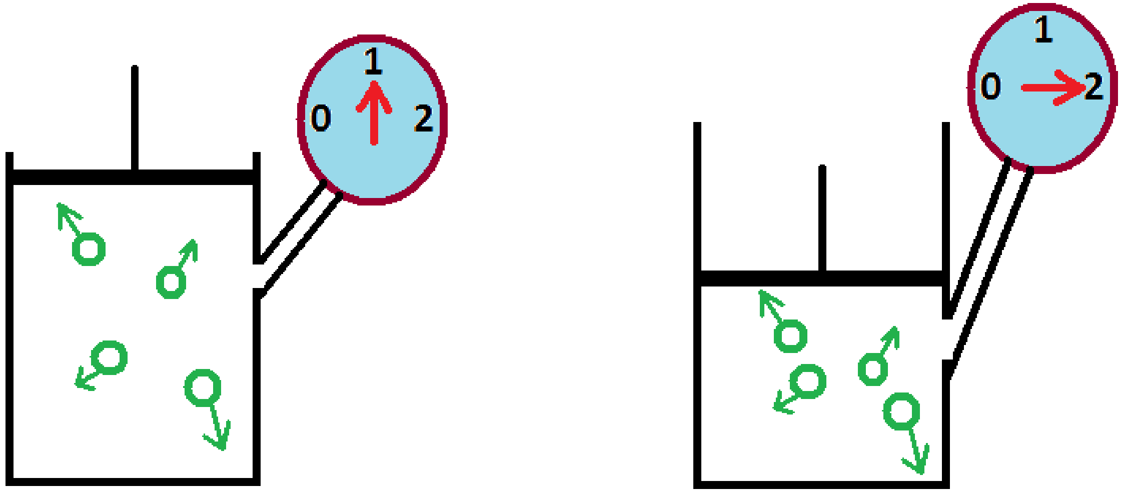
Boyle's Law

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

$$P_1V_1 = P_2V_2$$

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

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



P_1 = 1 atm
V_1 = 1 whatever

P = 2 atm
V = 0.5 whatever

1 x 1 = 2 x 0.5

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?

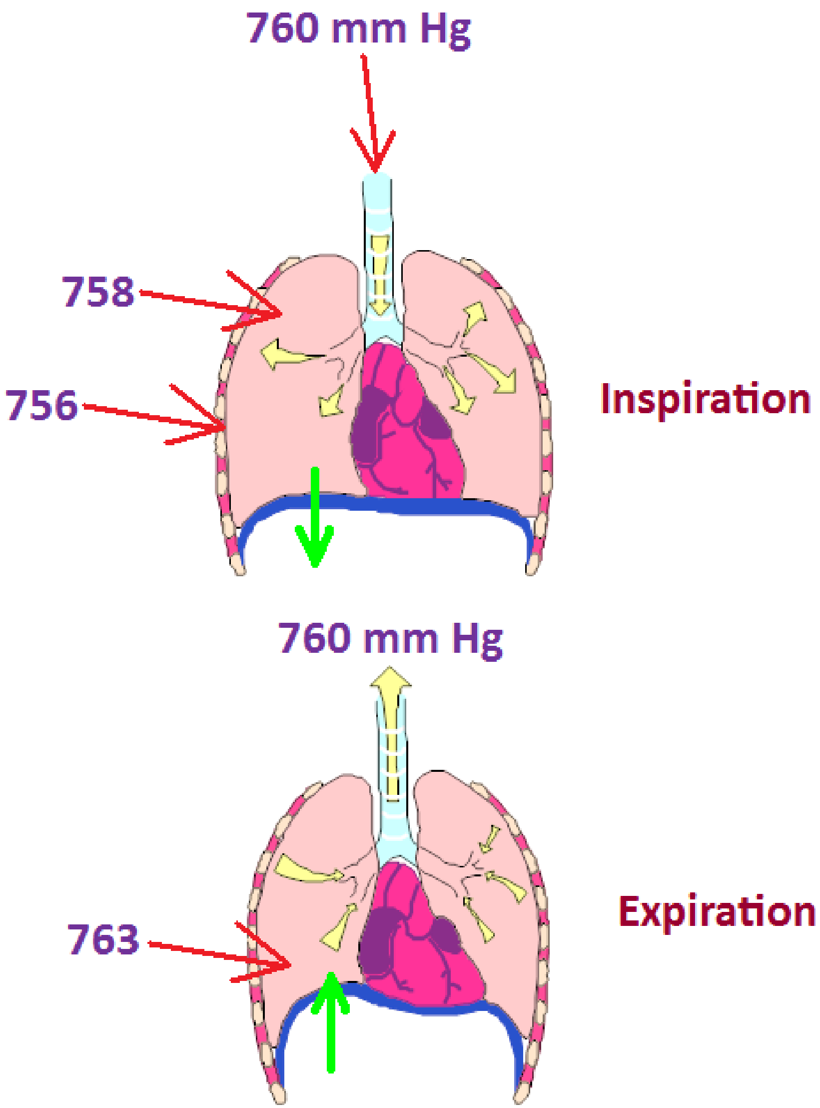
Solution: First, set up Boyle's Law equation:

$$P_1V_1 = P_2V_2$$

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

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

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



Charles' Law

Charles' Law says that the volume of a gas is directly proportional to the absolute temperature of that gas while the pressure is held constant.

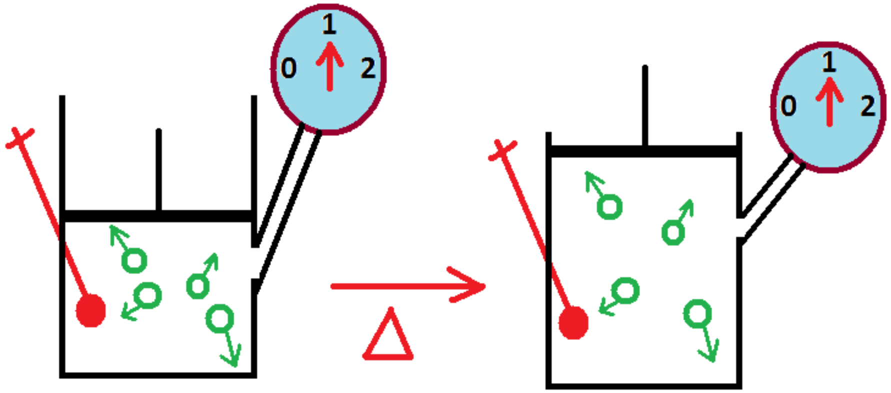
You've all seen this when you watch a hot air balloon fill with air.

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

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

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

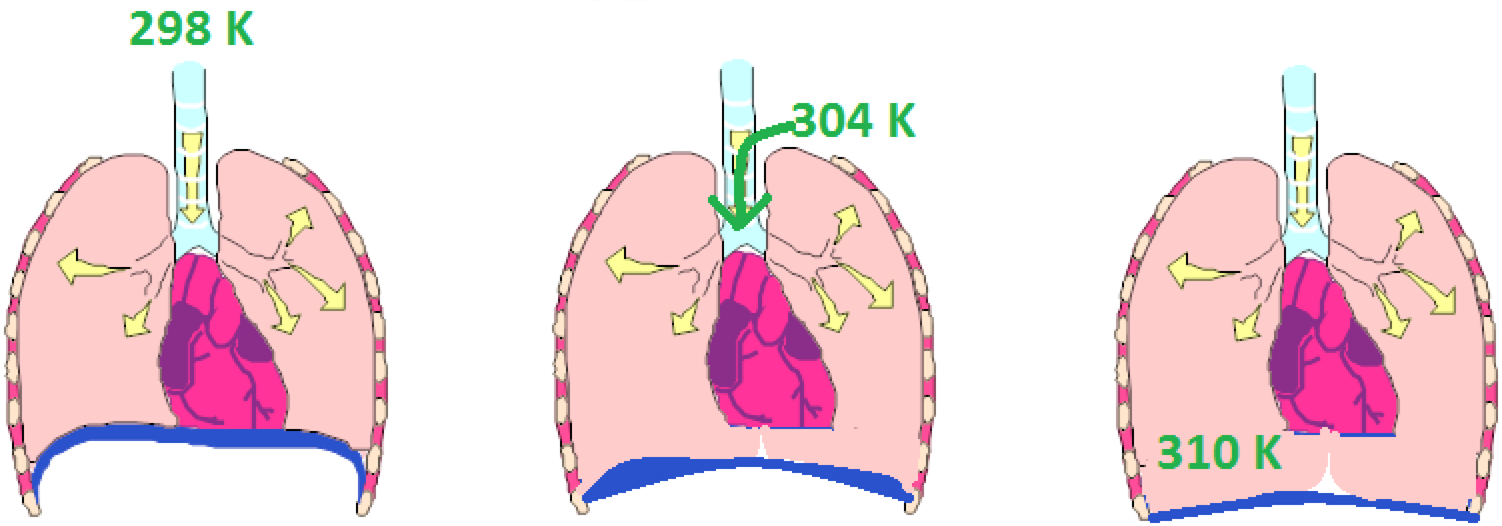
- Note that the pressure never changes when a gas in a cylinder kept at constant pressure is heated and its volume expands.



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?
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":

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

- 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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

Example: 250 mL of oxygen is collected at 30° C at 740 Torr.
What volume will the gas fill at STP?
STP is standard temperature (0° C) and pressure (760 torr).
Solution: rearrange the combined gas law to solve for V_2.
Plug the numbers in and calculate:

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

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?
Solution: As before, rearrange the equation.
Solve for P_2:

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

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:

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

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:

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

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:

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

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:

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

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., $P_T = P_1 + P_2 + P_3 + P_4 + ... + P_n$,
  - where P_T is the total pressure of the gaseous mixture,
  - P_1 is the partial pressure of gas 1,
  - P_2 is the partial pressure of gas 2,
  - P_3 is the partial pressure of gas 3, ad nauseum.

- Example: A sample of air is collected at a pressure of 745 mm Hg. The partial pressure of nitrogen (pN_2) is 600 mm Hg and the pO_2 is 50 mm Hg. If water vapor is the only other gas present, what is the pH_2O vapor?
- $P_T = P_1 + P_2 + P_3$;
  - P_T is 745 mm Hg,
  - P_1 is 600 mm Hg,
  - P_2 is 50 mm Hg and
  - P_3 is to be determined:
- $745 = (600 + 50) + P_3$
- $P_3 = 745 - 650 = 95$ mm Hg $= pH_2O$

- Example: A container has a gas mixture of nitrogen, oxygen and carbon monoxide. The total pressure is 2500 torr. The pN_2 is 800 torr, the pO_2 is 500 torr. What is the pCO?
- Solution: $P_T = P_1 + P_2 + P_3$
- $2500 = (800 + 500) + P_3$
- $P_3 = 2500-1300 = 1200$ 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:

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

Universal Gas Law and Dalton's law: Combined: During a rainstorm in July in New York City the humidity was found to be 100%. The atmospheric pressure was 740 Torr and the temperature was 31°C. Dry air has an average molecular weight of 28.8. Calculate the weight of water in 1.00 liter of the air during the storm.

Analyze: What do you need to solve this problem?
- Table 6.1
- Correct formulas
- Information (data) in Question

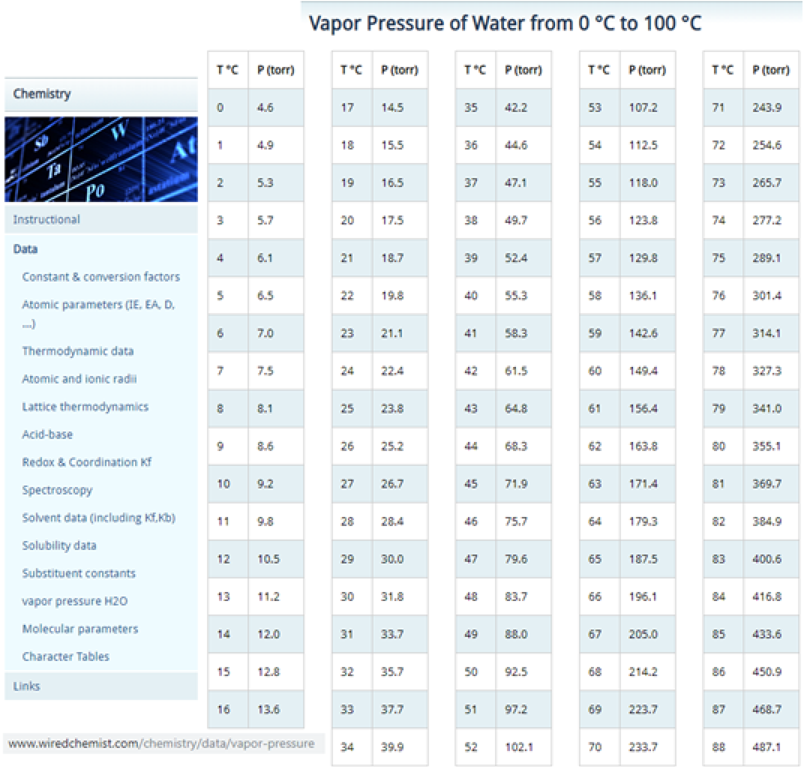
Evaluate: Select appropriate equations
Evaluate: Which gas laws formulas do you need?
Evaluate: Which pressure units do you need

Remember: Appropriate R (units)
Remember: Temp conversion
Remember: Universal Gas Law
Remember: Calculating moles
Remember: Determining molecular weight
Remember: 1 atm of pressure equivalent values

Apply: Determine substitute statement for mol in universaal gas law equation
Apply: Substitute mol expression in universal gas law equation
Apply: Determine water vapor pressure from table 6.1
Apply: plug-n-chug numbers

Create: The answer to the problem

Understand: the answer by using proper units
Understand: how the answer relates to Relative Humidity Concept



Vapor Pressure of Water from 0 °C to 100 °C

T °C	P (torr)
0	4.6
1	4.9
2	5.3
3	5.7
4	6.1
5	6.5
6	7.0
7	7.5
8	8.1
9	8.6
10	9.2
11	9.8
12	10.5
13	11.2
14	12.0
15	12.8
16	13.6
17	14.5
18	15.5
19	16.5
20	17.5
21	18.7
22	19.8
23	21.1
24	22.4
25	23.8
26	25.2
27	26.7
28	28.4
29	30.0
30	31.8
31	33.7
32	35.7
33	37.7
34	39.9
35	42.2
36	44.6
37	47.1
38	49.7
39	52.4
40	55.3
41	58.3
42	61.5
43	64.8
44	68.3
45	71.9
46	75.7
47	79.6
48	83.7
49	88.0
50	92.5
51	97.2
52	102.1
53	107.2
54	112.5
55	118.0
56	123.8
57	129.8
58	136.1
59	142.6
60	149.4
61	156.4
62	163.8
63	171.4
64	179.3
65	187.5
66	196.1
67	205.0
68	214.2
69	223.7
70	233.7
71	243.9
72	254.6
73	265.7
74	277.2
75	289.1
76	301.4
77	314.1
78	327.3
79	341.0
80	355.1
81	369.7
82	384.9
83	400.6
84	416.8
85	433.6
86	450.9
87	468.7
88	487.1

www.wiredchemist.com/chemistry/data/vapor-pressure

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$$P_T = P_{H_2O} @\, 31°\text{C}\ and\ P_{H_2O} = 33.7\ Torr$$

$$MW_{H_2O} = 18 \frac{g}{mol}$$

$$n_{H_2O} = \frac{mass_{H_2O}}{MW_{H_2O}}$$

$$PV = nRT$$

$$PV = \frac{mRT}{MW}$$

$$P = P_{H_2O} = \frac{P_{H_2O}}{P_{1\,atm}} = \frac{33.7\ torr}{760\ \frac{torr}{atm}} = 0.0443\ atm$$

$$m = \frac{(PV)\ MW}{RT}$$

$$m = \frac{(0.0443\ atm)(1\ L)\left(18\ \frac{g}{mol}\right)}{\left(0.0821\ \frac{L-atm}{mol-K}\right)(304\ K)} = 0.03198\ g\ H_2O\ in\ the\ L\ of\ air\ in\ the\ storm$$

Graham's Law

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

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

Effusion is defined as gas "leaking" out of a container through a small hole.

Diffusion is defined as gases mixing on their own when brought together.

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

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

Therefore H_2 diffuses 6 times faster than does Cl_2.

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

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

O_2 diffuses 3 times faster than iodine.

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

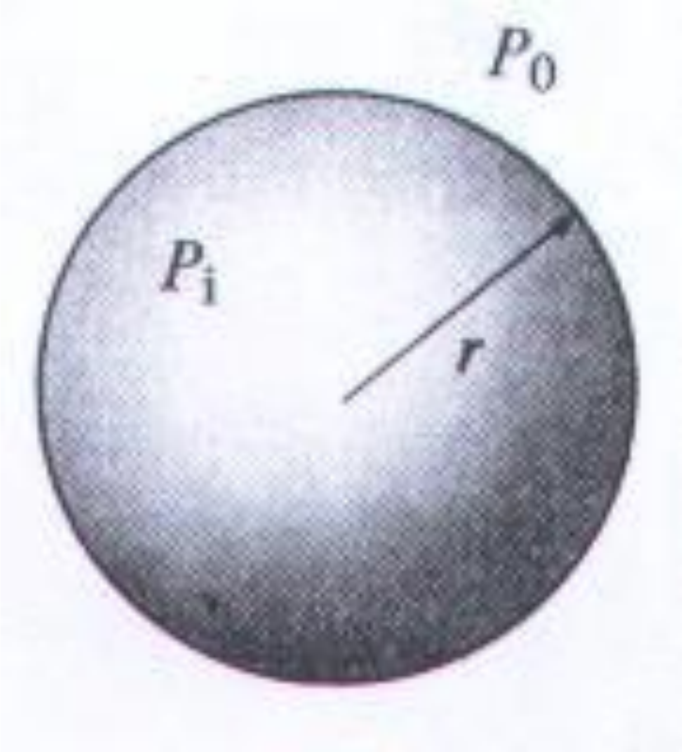
$$\frac{Rate\ of\ N_2}{Rate\ of\ O_2} = \sqrt{\frac{MW_{O_2}}{MW_{N_2}}} = \sqrt{\frac{32}{28}} \approx 1.07$$

Nitrogen and oxygen diffuse at about the same rate.

LaPlace's Law

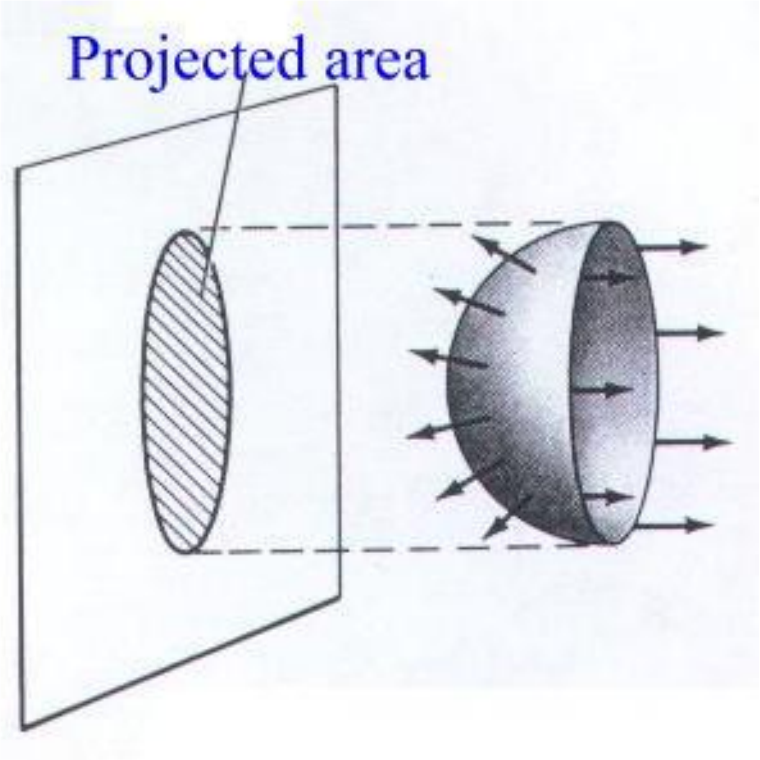
- LaPlace's Law says that a pressure gradient across a closed ELASTIC membrane or liquid film is related to the membrane/film tension -- sort of makes you think of Ficke's Law, doesn't it?!

- The closed sphere shows the pressure inside the balloon (P_i) and the pressure outside the balloon (P_o).
- The difference between the two pressures (P_i - P_o) is the pressure gradient (ΔP).

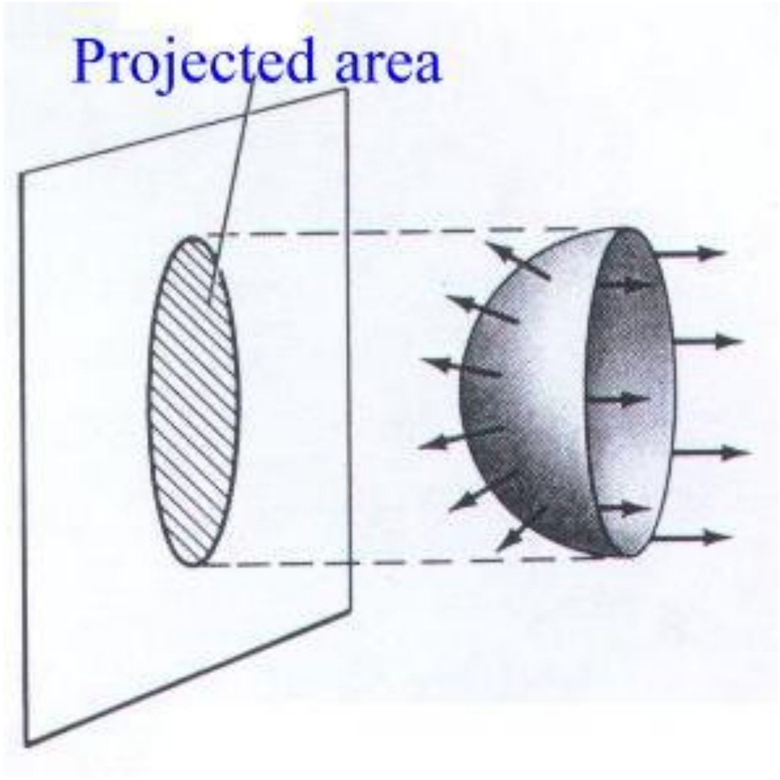


- Why would we even want to study something like LaPlace's Law?
- Let's answer that by asking 2 questions:
- The first question is: you have two balloons inflated at different pressures, joined together by a piece of tubing that has a pinch clamp between the two. Which way will the air move when the pinch clamp is opened? From the largest one into the smallest? From the smallest into the largest?
- The second question is physiologically oriented: why is it that we can breathe without our alveoli either collapsing or exploding?
- LaPlace's Law answers these questions. Let's start examining this law.

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



- The second force (F_2) is the force due to the pressure gradient (or pressure differential, if you prefer). This is arithmetically equal to:
- $(P_i - P_o) \pi r^2 = F_2 = \Delta P \pi r^2$
- This force is represented by the arrows pointing away from the body of the sphere.



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 π 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

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

Arithmetic Example #2

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

This is a sphere question, hence:

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

With rearranging:

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

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

NOTE: With increasing radius comes increasing wall tension.

Arithmetic Example #3

A balloon is blown up to 12 inches in diameter. The wall tension is 240 psi. What is the pressure gradient?

This is another sphere question, hence, we use

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

and we need to solve for ΔP:

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

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 ΔP:

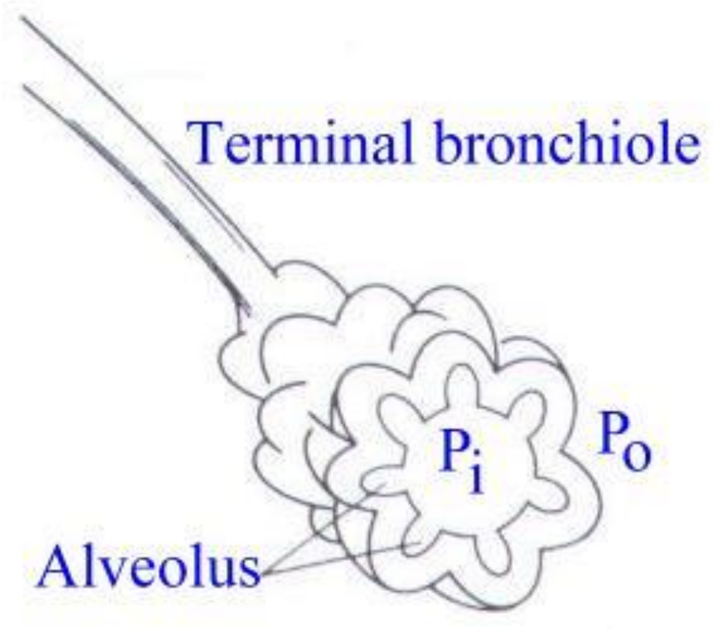
$$2 \gamma /r = \Delta P = \{(2) * (120)\}/8 = 30 \text{ psi}$$

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

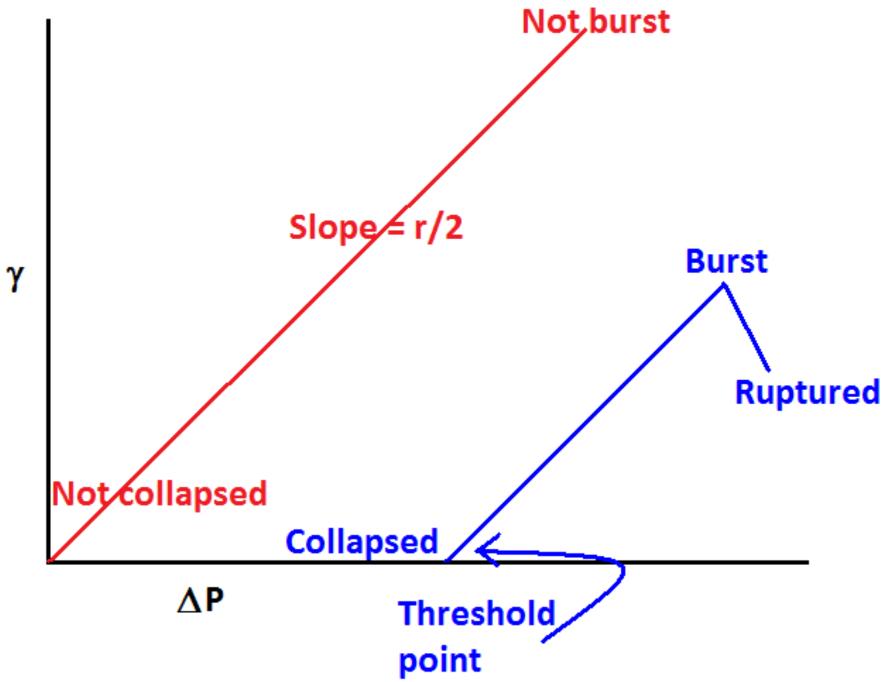
Since $2\gamma = \Delta P\, r$, it suggests that at expiration,
if the wall tension is constant, the alveoli will COLLAPSE and,
at inspiration, if the wall tension is constant,
the alveoli will RUPTURE.
Why doesn't this happen in our lungs?

- 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 $2\gamma = \Delta Pr$, by making the alveolar walls more elastic.
- This makes the alveoli unable to rupture or collapse during eupnea and the alveolar patency is maintained with/for gas exchange.

In short, with surfactant, as the wall tension increases, so does the pressure gradient.
Without surfactant, the alveoli are collapsed until they reach a pressure gradient threshold point, at which point the wall tension increases until the alveoli rupture.
Note that $2\gamma = \Delta P r$ may be re-written as:

$$\gamma = (\Delta P)(r/2) + 0$$

which is in the form of a straight line. WITH surfactant, this relationship is maintained completely. WITHOUT surfactant, this relationship is conditional.



Arithmetic Example

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

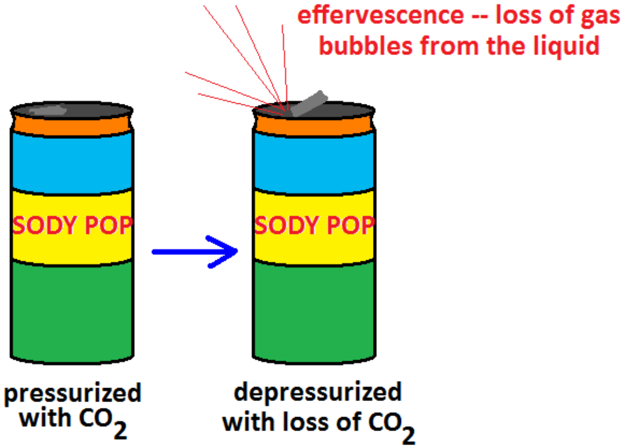
$\gamma = (\Delta P)(r/2) = (-0.058 - (-0.077)) * (0.002/2) = 1.9*10^{-5}$ psi WITH surfactant.

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

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

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 "pfffffffttttttt" when you open it.
- Sodas are canned under pressure with CO_2 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 :-)



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

Gases are Soluble in Water

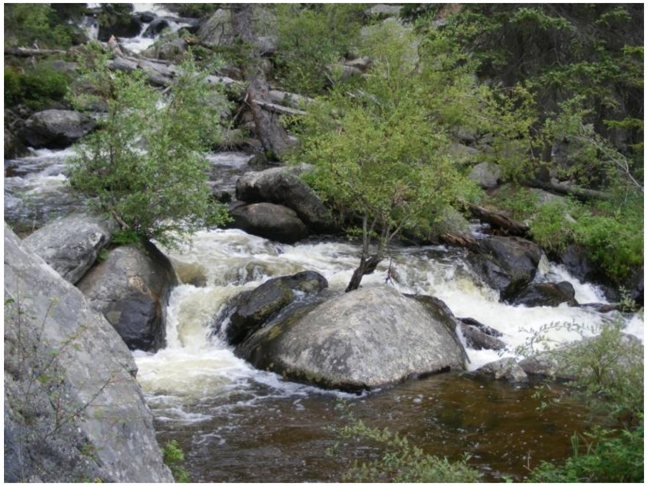
- Henry's Law is also responsible for people getting the "bends".
- When people dive deeply using compressed air, they MUST slowly come back up so that the nitrogen bubbles that are driven into tissues at deep levels (and, hence, with high pressures) may slowly be released and breathed out.
- If the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

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

- 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.

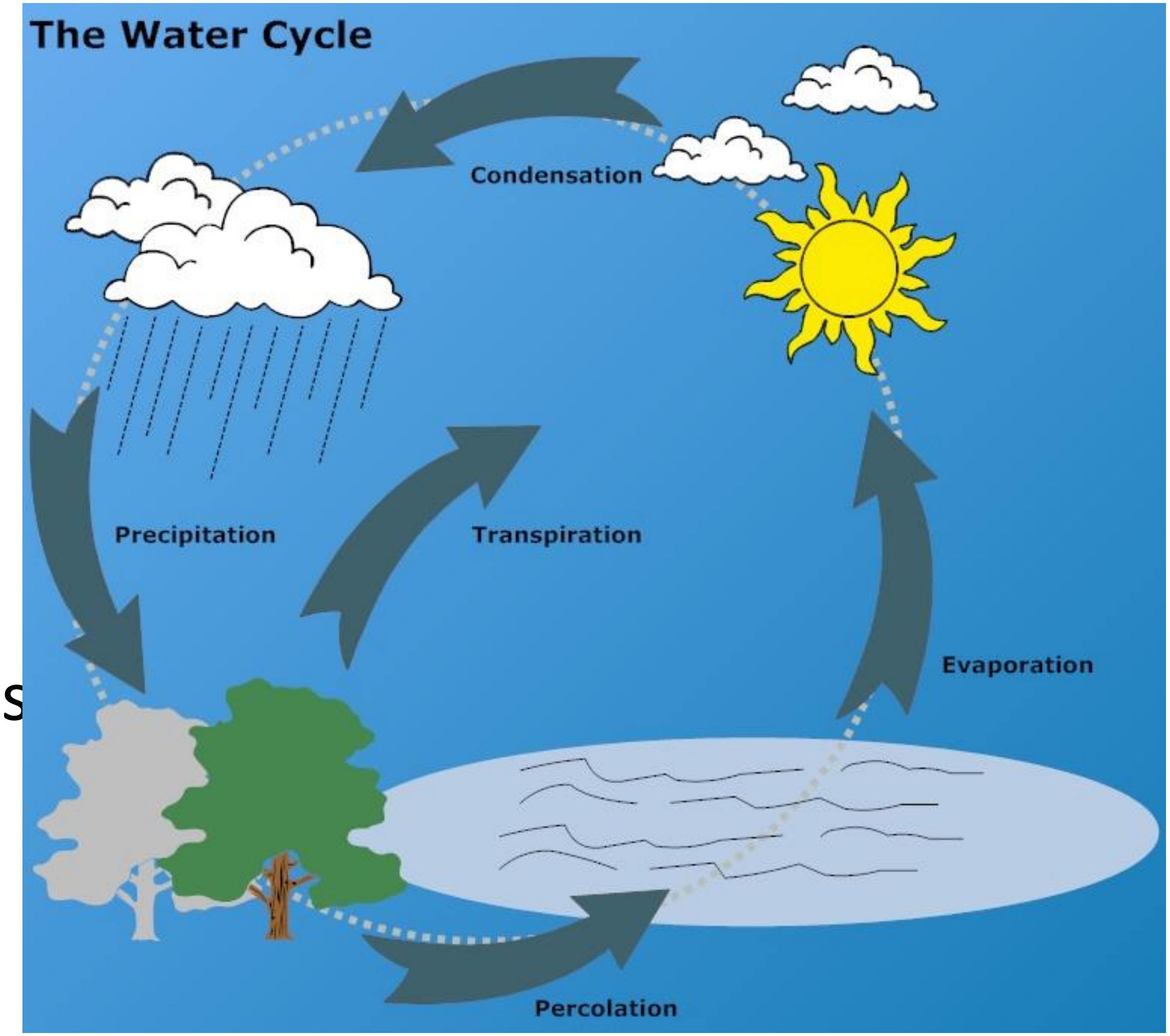
Water and Chromatography

Fundamentals



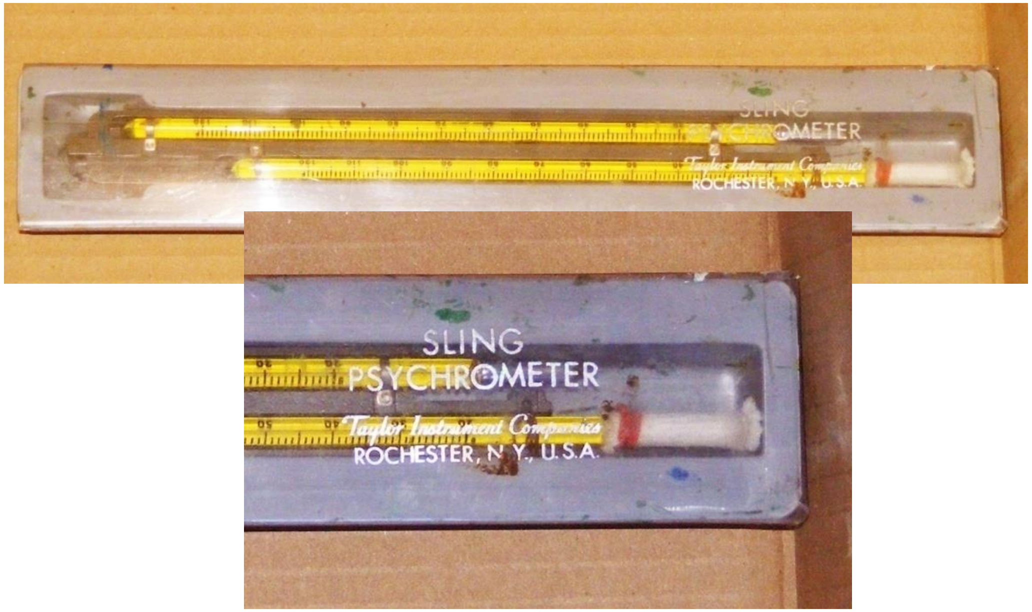
- About a half-gallon of water is needed per day by humans for biological needs.
- About 5 gallons of water are used in the production of 1 gallon of milk.
- 10 gallons of water are used per gallon of gasoline produced and roughly 65000 gallons of water are required to turn out a ton of steel.

- 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

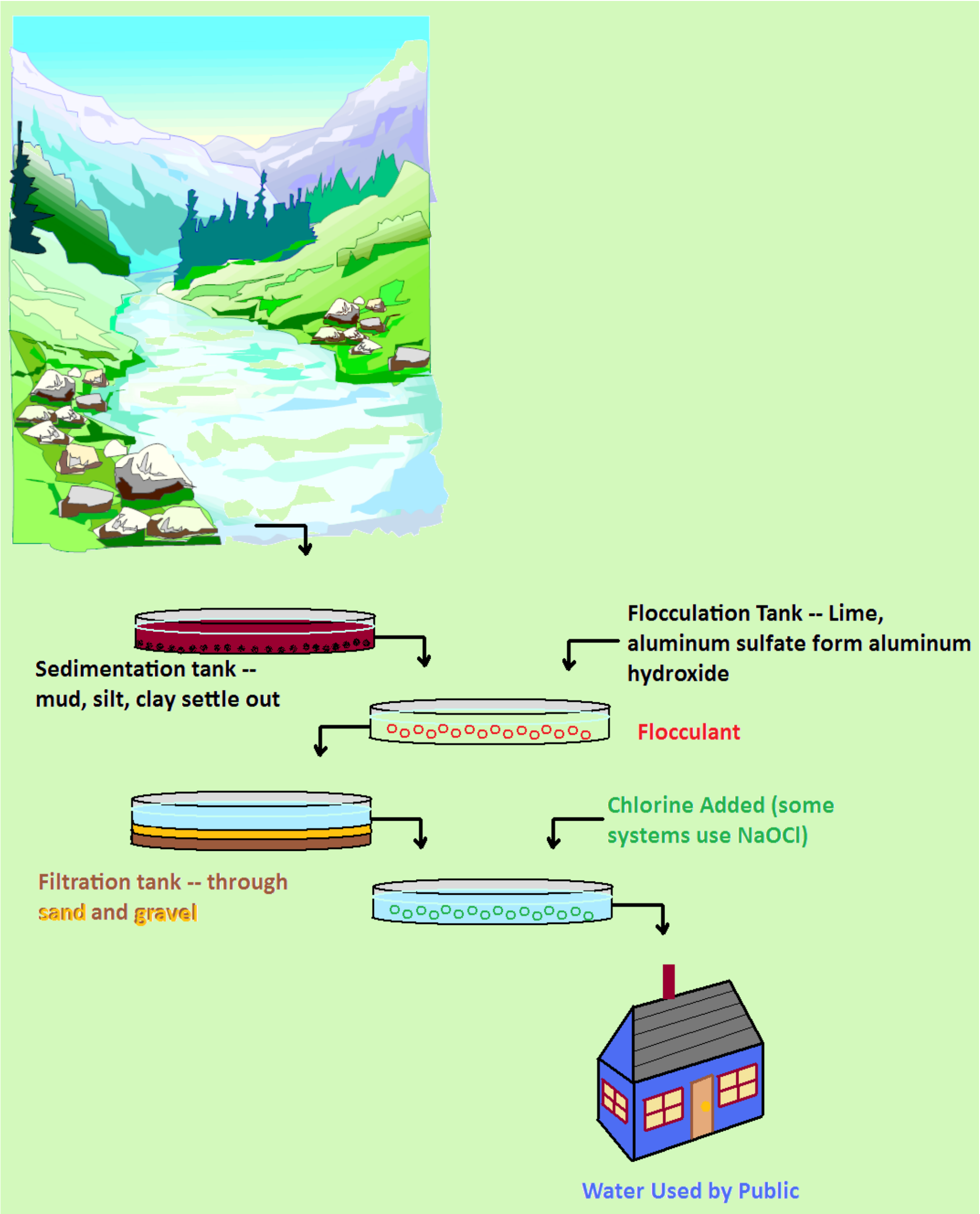
Surface water impurities tend to consist of 4 classes as summarized in the following table:

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_xO_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 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.



Sedimentation tank -- mud, silt, clay settle out

Flocculation Tank -- Lime, aluminum sulfate form aluminum hydroxide

Flocculant

Filtration tank -- through sand and gravel

Chlorine Added (some systems use NaOCl)

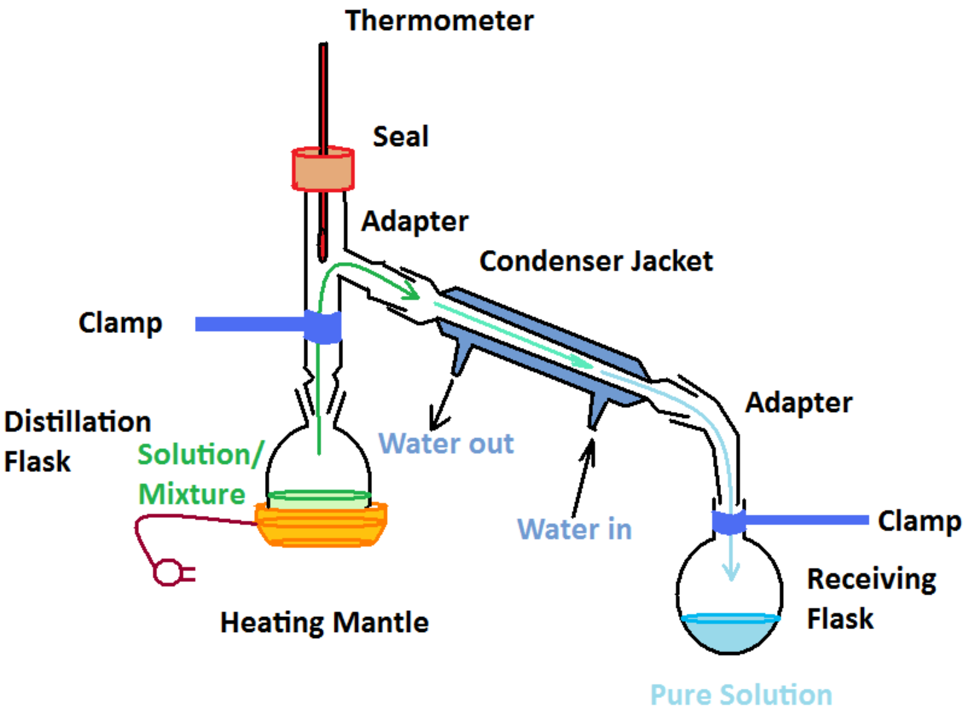
Water Used by Public

- 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.

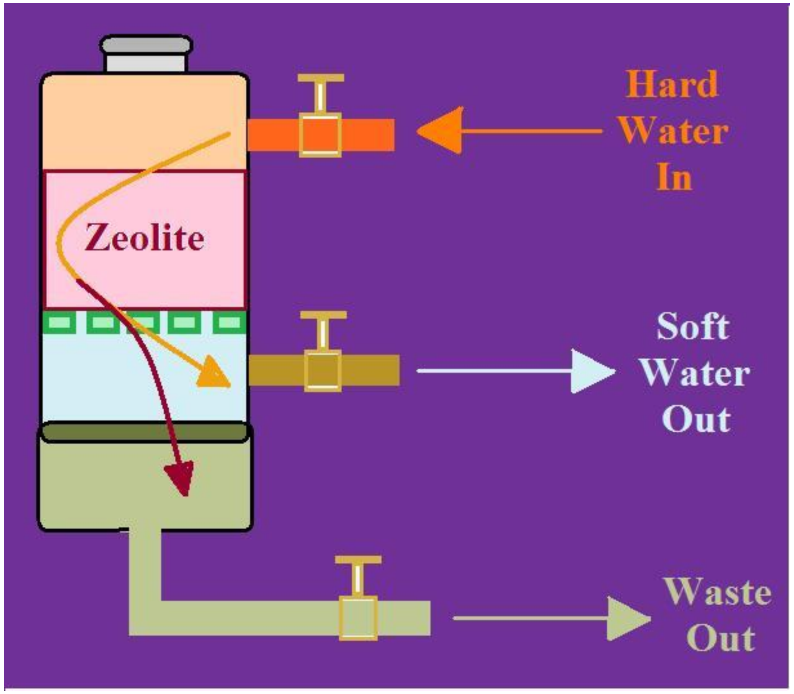
Hard Water

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

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

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

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



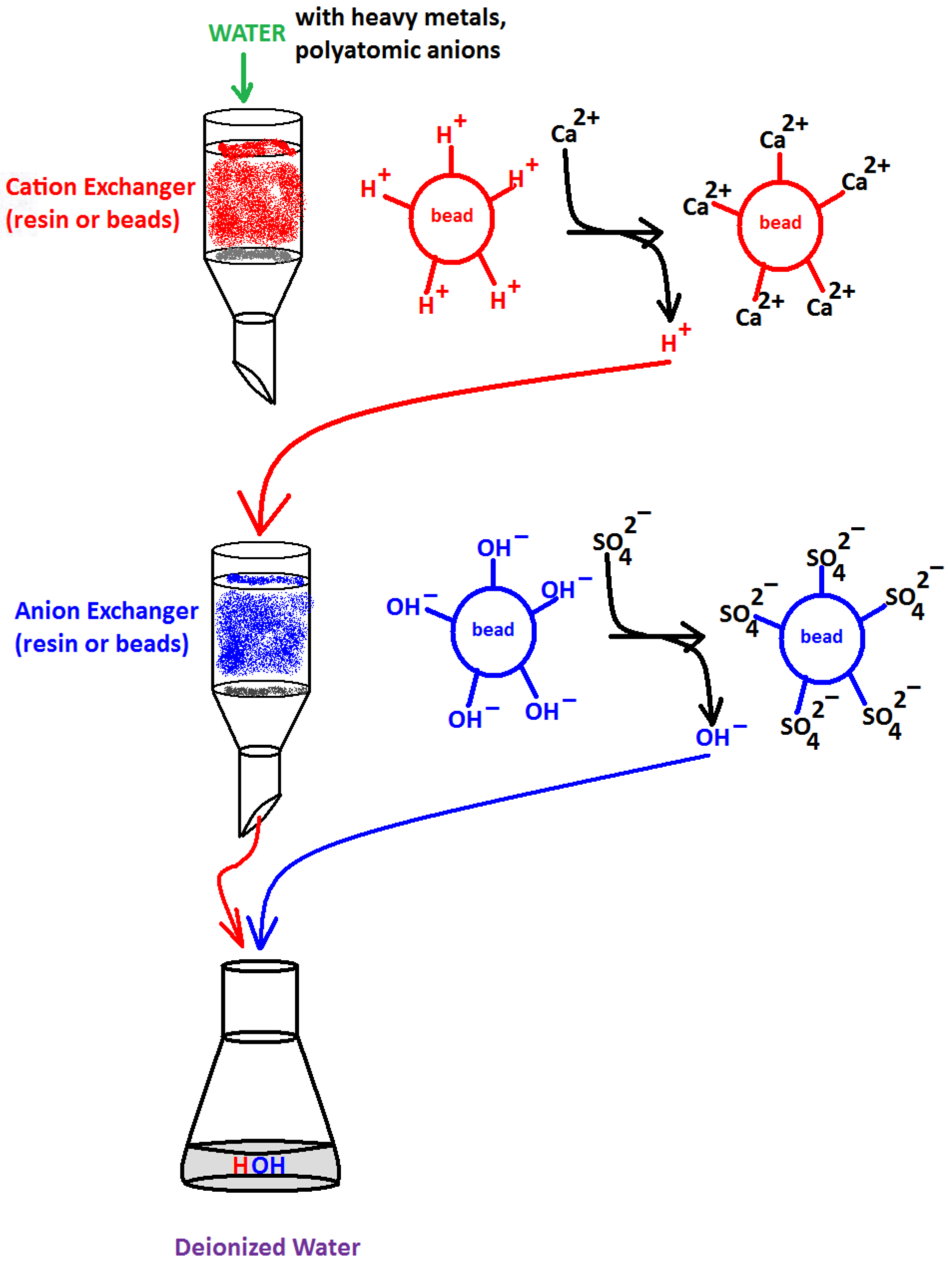
In the case of zeolite, hard water enters the tank and filters through zeolite ($NaAlSi_2O_6$). The soft water leaves through a frit beneath the zeolite; the waste leaves beneath that, as well.

The reaction that occurs is as follows:

$$Ca^{2+} + 2NaAlSi_2O_6 = Ca(AlSi_2O_6)_2 + 2Na^+$$

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 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.**



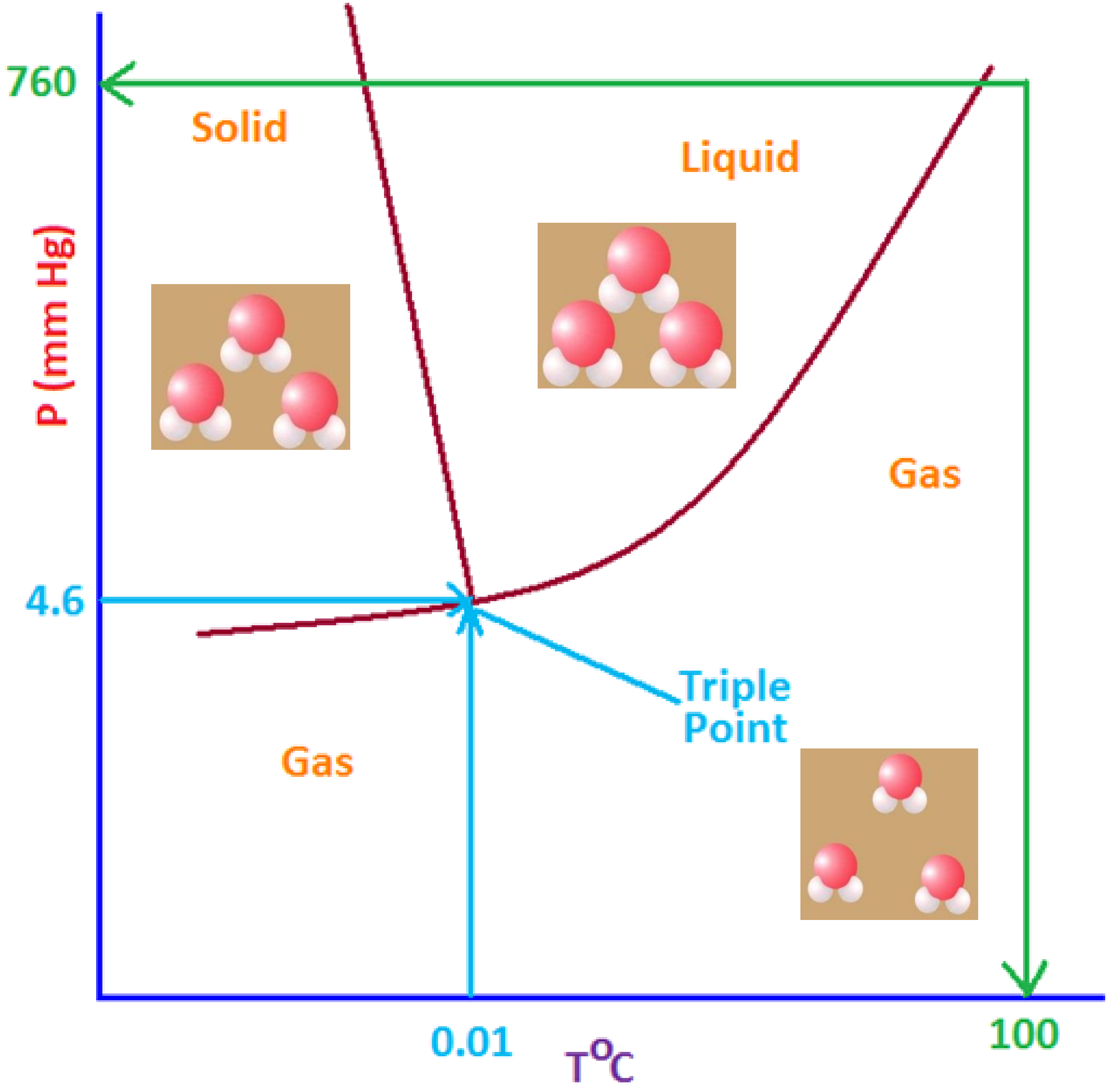
Physical Properties of Water

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.

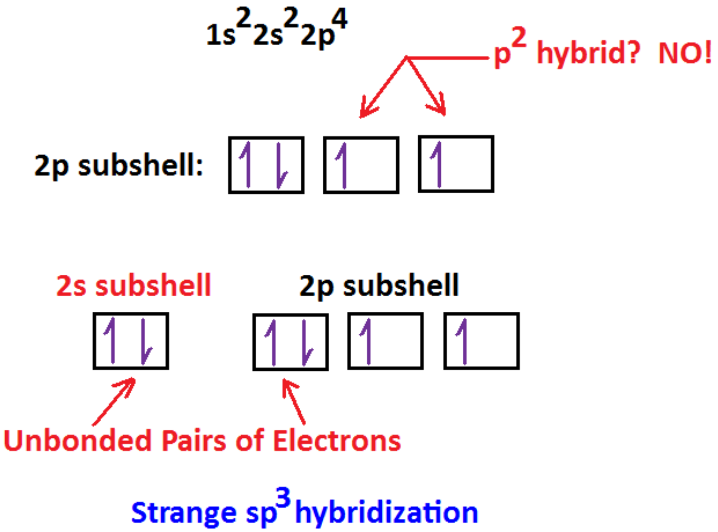
- The unit of mass in the SI is the mass of 1 mL of water at 4° C (the temperature with the maximum density for water).
- This is exactly equal to 1.00000 grams.
- The unit of heat in the SI is the calorie (which is equivalent to 4.184 Joules) and is approximately the quantity of heat required to raise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



$1s^2 2s^2 2p^4$

p^2 hybrid? NO!

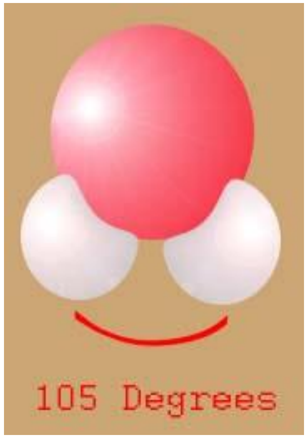
2p subshell:

2s subshell

2p subshell

Unbonded Pairs of Electrons

Strange sp^3 hybridization

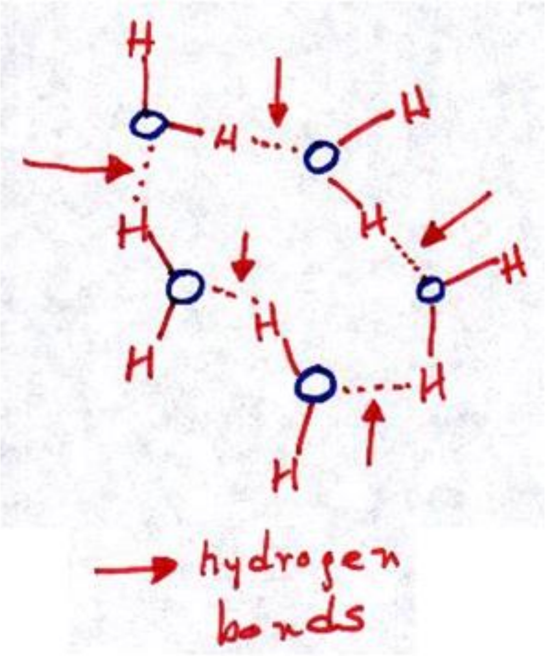


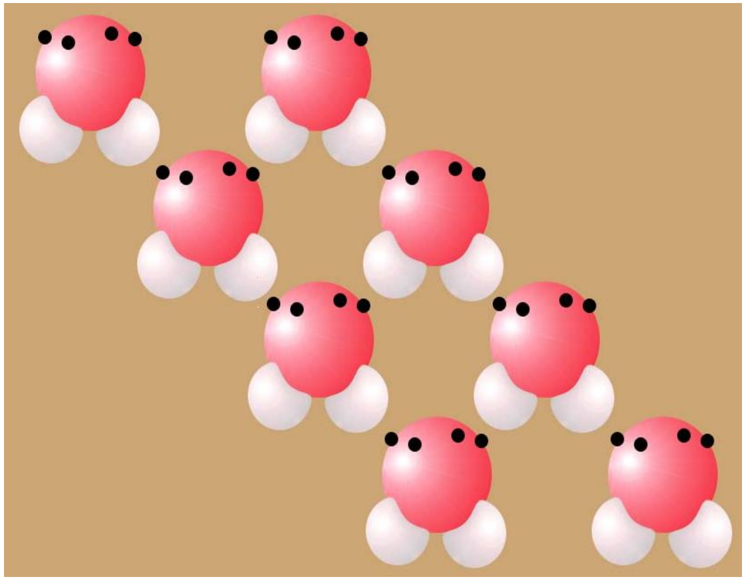
- Here's the problem, though: in the old days -- and some days not so long ago -- because of the four 2p electrons, it was believed that the oxygen underwent p^2 hybridization to form this angular geometry.
- There is a small problem with this: There are 2 pairs of unshared electrons -- one pair of 2s and one pair of 2p electrons.

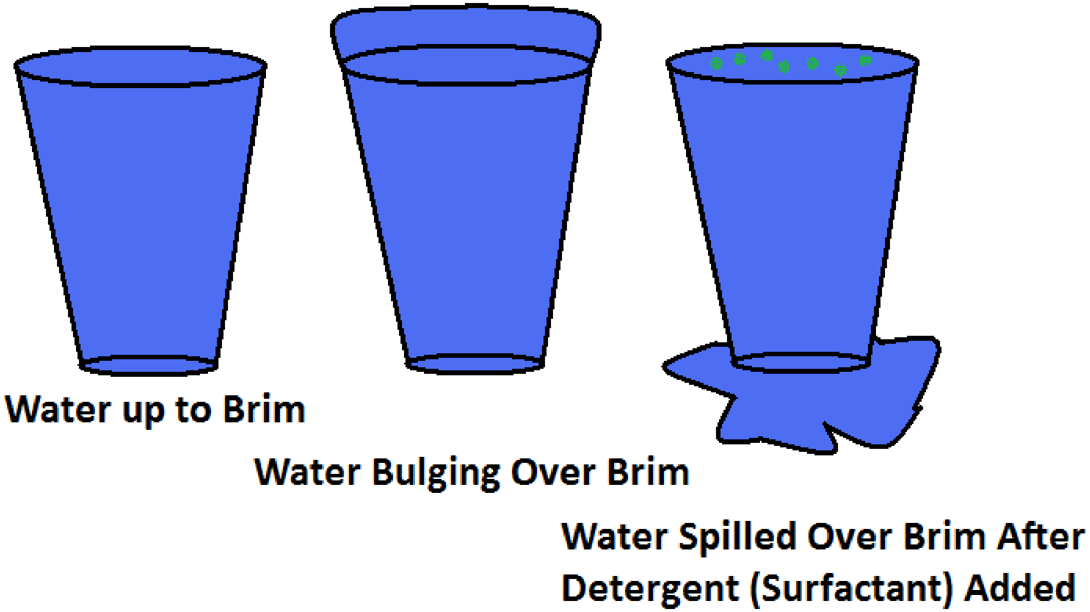
Since these electrons take up space, they lead to a geometry of a tetrahedron as we discussed previously.

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.



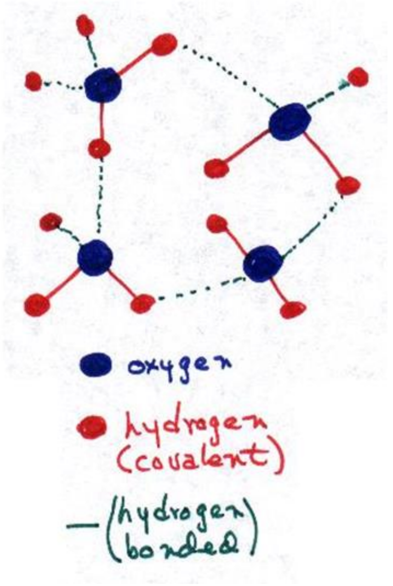


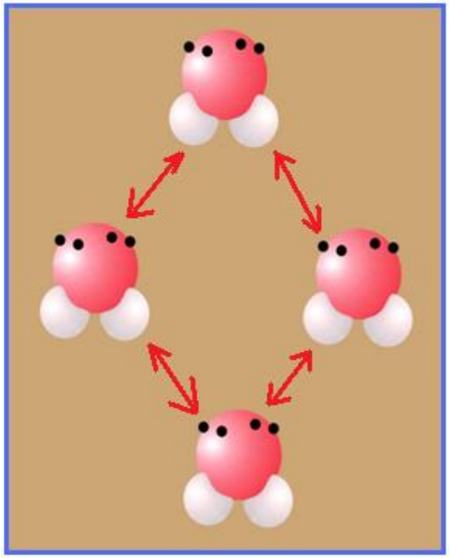


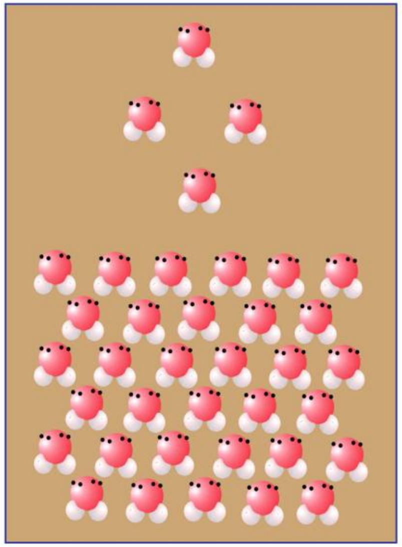
- The effects of the aforementioned surface tension are below.
- If one takes a clean glass and carefully pours water in it, one may pour water over the rim.
- This forms a bulge on top of the water.
- That's due to the hydrogen bonds and the polar sites in the glass for the water to bind with.
- In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

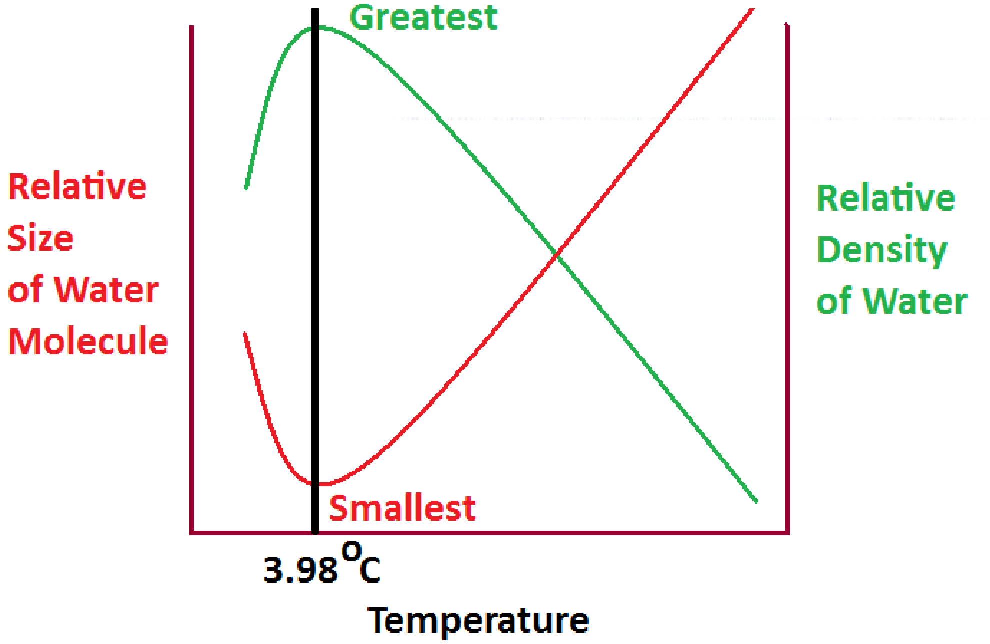
- All of us know, empirically, that ice floats in water -- ask the crew on the Titanic.
- How is it that ice -- solid water -- floats in liquid water?
- When ice begins to form, it takes on the equivalent of four hydrogen atoms per water molecule: 2 covalently bound and 2 hydrogen bonded.
- As this continues,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







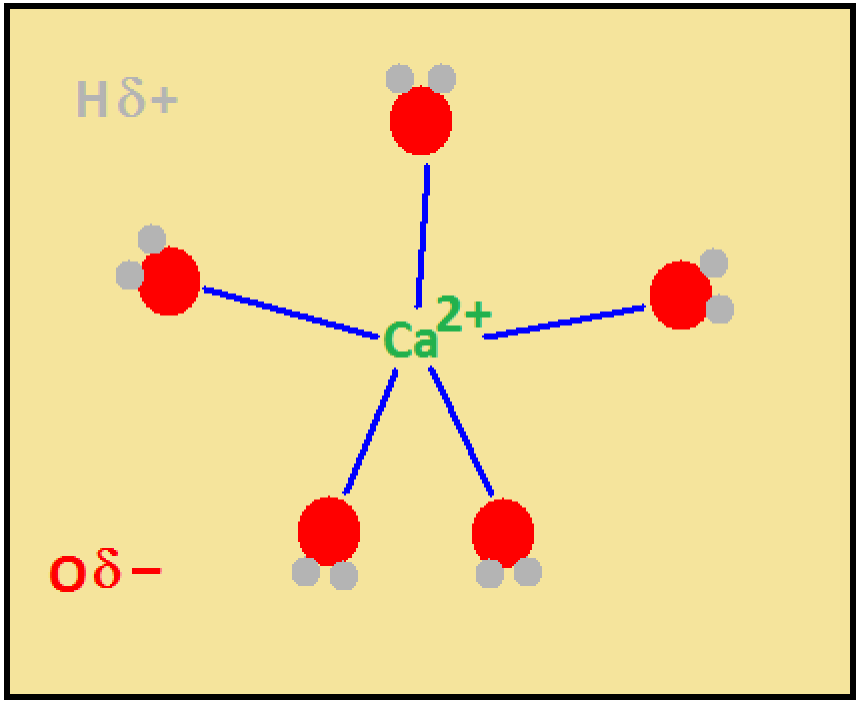
- **When ice melts, some of the hydrogen bonds are destroyed and the water molecules pack more closely together and the density relationship continues to be maintained.**
- **These relationships are graphically illustrated, below.**



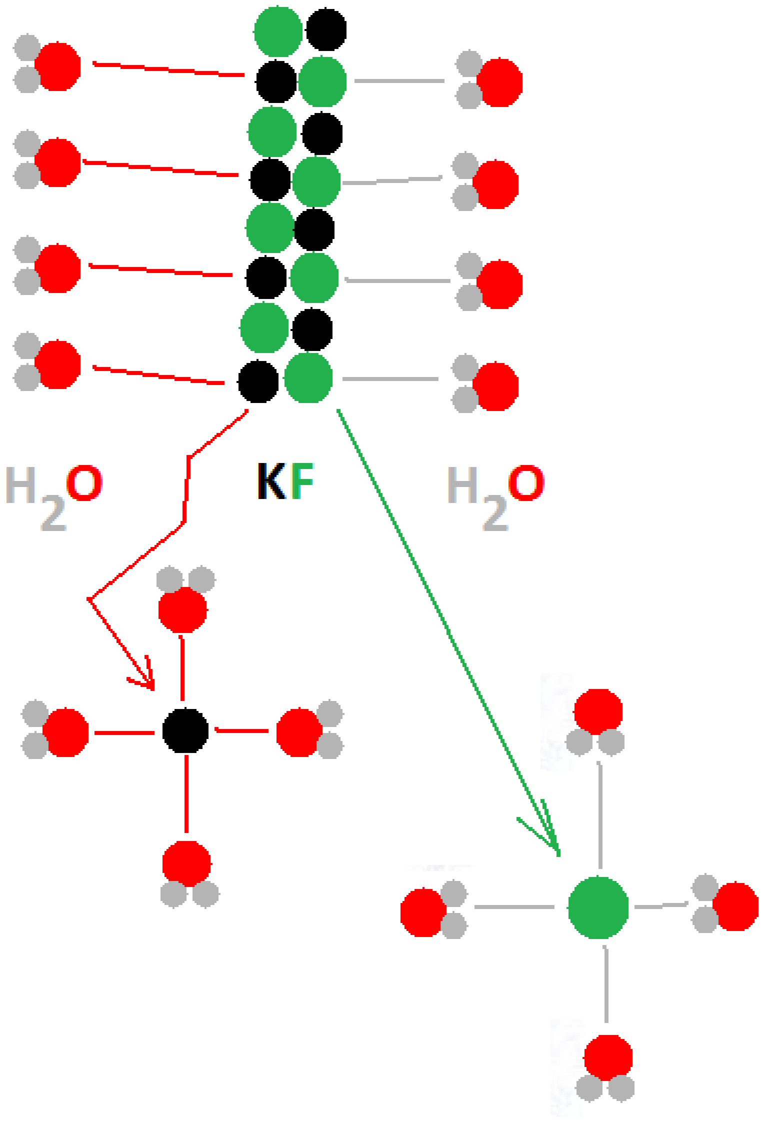
- **You can see that as the temperature increases past 3.98°C, the relative size of the water molecule increases; conversely, the density decreases over the same range.**
- **As the temperature goes below 3.98°C, the size of the water molecule rises a bit and the density drops a bit.**
- **In short, 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.



"Caged", hydrated ions

Chemical Properties of Water

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

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

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

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

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

Water reacts with metals as follows:

$$3Fe + 4H_2O\,(steam) \rightarrow Fe_3O_4 + 4H_2\uparrow$$

$$2Na + 2H_2O\,(cold) \rightarrow 2NaOH + H_2\uparrow$$

$$Mg + 2H_2O\,(hot) \rightarrow Mg(OH)_2 + H_2\uparrow$$

$$Mg + H_2O\,(steam) \rightarrow MgO + H_2\uparrow$$

to form hydroxides, oxides and gaseous hydrogen.

Water reacts with non-metals (F_2, Cl_2 and Br_2 at room temperature) as follows:

$$Br_2 + H_2O \rightarrow HBr + HOBr$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$3F_2 + 3H_2O \rightarrow O_3 + 6HF$$

- **Acids with "HO" in front of them are the "hypo" acids, e.g., hypochlorous and hypobromous, above.**
- **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:

$$Li_2O + H_2O \rightarrow 2LiOH$$

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$K_2O + H_2O \rightarrow 2KOH$$

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

Non-metal oxides react with water to form acids:

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

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

These non-metal oxides are called acidic anhydrides.

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	$MgSO_4 \cdot 7H_2O$	Magnesium sulfate heptahydrate
Alum	$KAl(SO_4)_2 \cdot 12H_2O$	Potassium aluminum sulfate dodecahydrate
Plaster of Paris	$CaSO_4 \cdot 1/2H_2O$	Calcium sulfate hemihydrate
Gypsum	$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate
Glauber's salt (cathartic)	$Na_2SO_4 \cdot 10H_2O$	Sodium sulfate decahydrate
Blue vitriol	$CuSO_4 \cdot 5H_2O$	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:

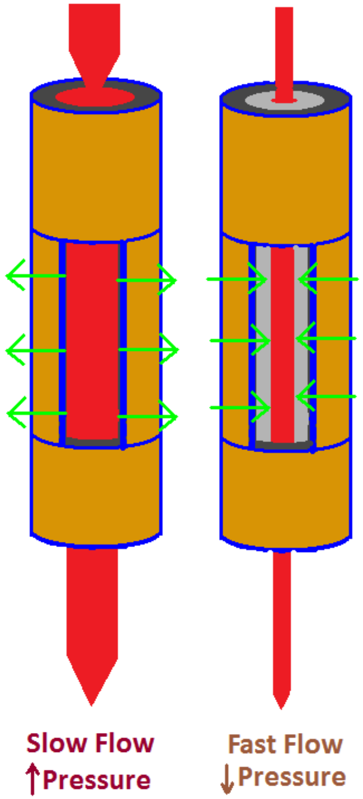
1. **Water of hydroxylation. The structural unit is the hydroxide ion. Removal of this "water" leads to disruption of the crystalline structure.**
2. **Water of coordination. In this case the water is joined by the metal ion by coordinate bonds, e.g., $BeSO_4 \cdot 4H_2O$ is really $[Be(H_2O)_4]^{2+}[SO_4]^{2-}$. This water is essential to the stability of these crystals.**
3. **Anion water. In this case, the water is attached to the anion by hydrogen bonding, e.g., $CuSO_4 \cdot 5H_2O$ is really $[Cu(H_2O)_4]^{2+}$ (waters of coordination) and $[SO_4(H_2O)]^{2-}$ (anion water).**
4. **Lattice water. Water is in the crystalline lattice, but it is not attached to either cation or anion, e.g., $KAl(SO_4)_2 \cdot 12H_2O$ is really $K^+[Al(H_2O)_6]^{3+}$ $[SO_4]_2{}^{2-}$ (coordination water) plus $6H_2O$ (in lattice, but not bonded with the potassium ion).**
5. **Zeolitic water. This water occupies random positions in the crystal. Loss or gain of these waters do not change crystalline structure.**

Liquid Laws

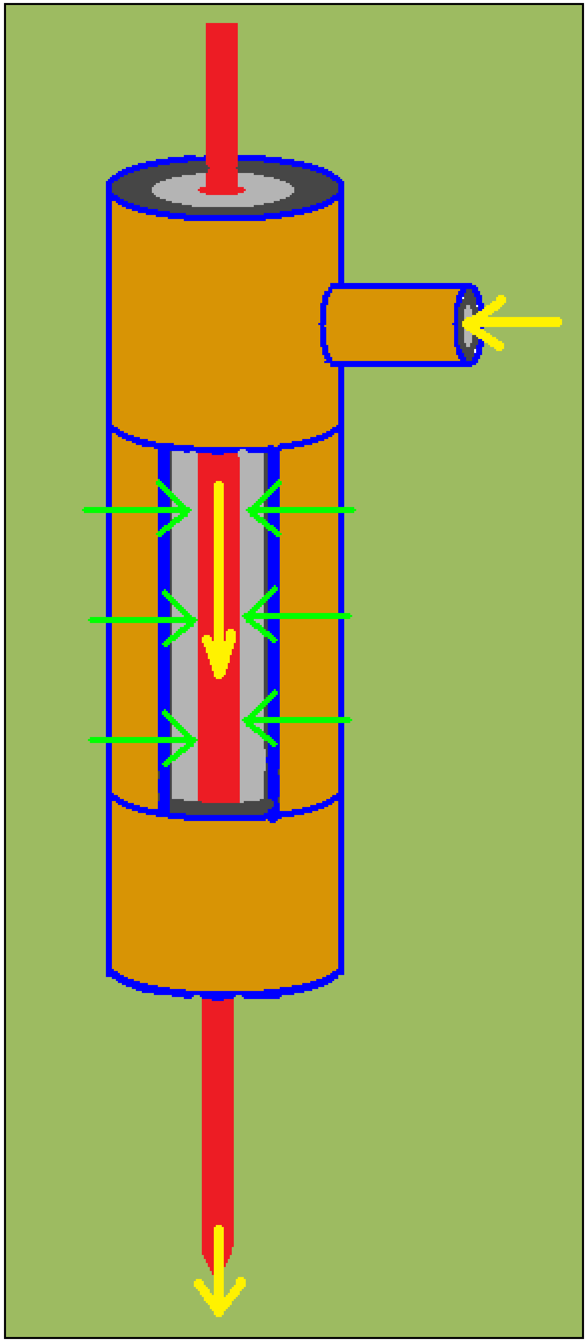
- Whether it be in topical product development or in health care, knowledge of how fluids function (flow) is critical.
- To understand fluids, a number of laws must be examined.

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 :

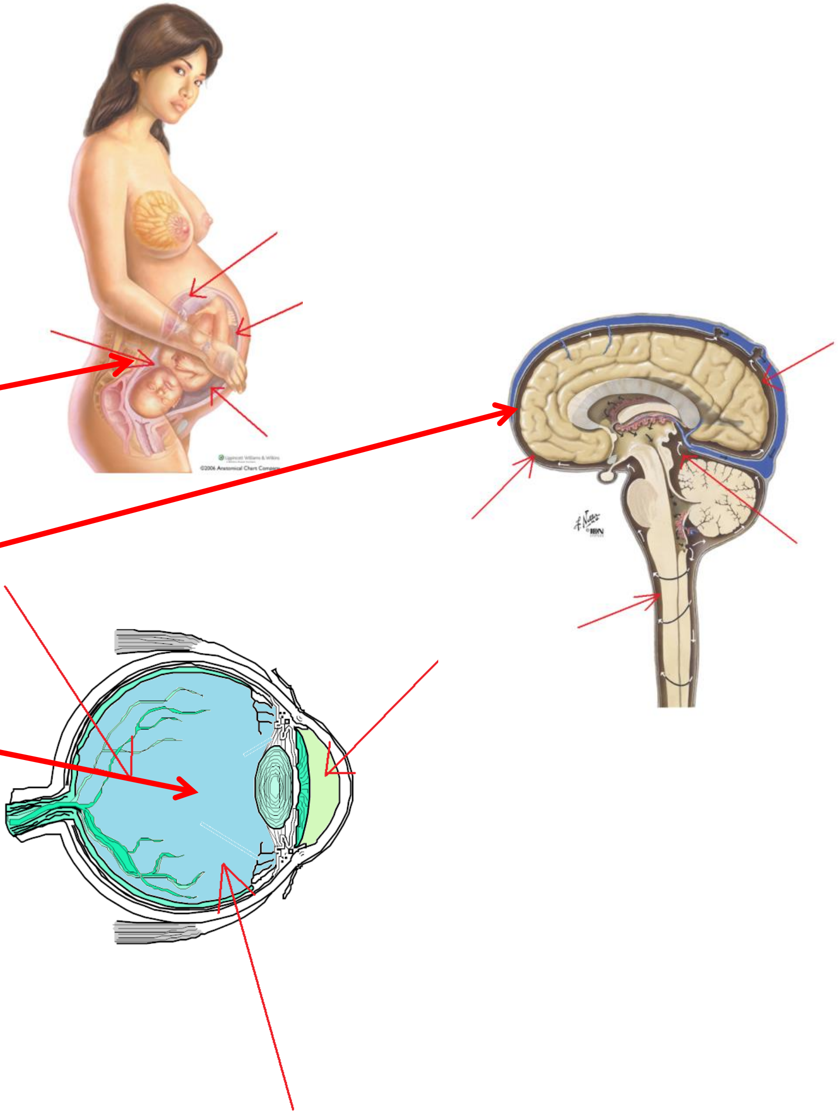


- It is this concept by which aspirator "pumps" work on sink faucets, Figure, right.
- Note that in the aspirator that with rapid flow, the pressure on the sides of the tube are reduced (a vacuum) and air rushes into the aspirator to make a suction.
- A modification on this law is the Venturi effect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



Pascal's Law

- Pascal's Law says that when a pressure is applied to a confined liquid, the pressure is spread out over the liquid.
- Three really good examples of this are illustrated in the Figure.
- These examples are amniotic fluid, fluid in the eye and cerebrospinal fluid.
- Keep in mind that these fluids are wonderful shock absorbers at low pressure, but that at high pressure, they become a "weapon", i.e., these fluids are double edged swords.

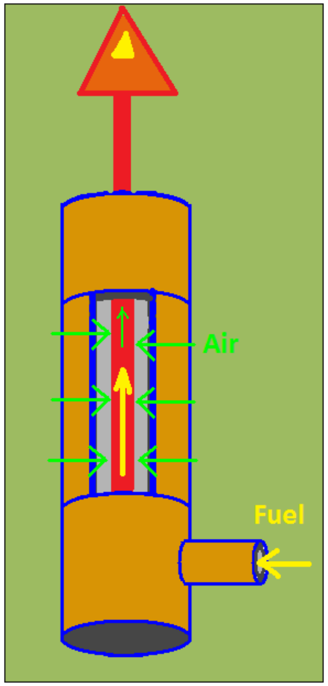


Venturi Effect

- 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.

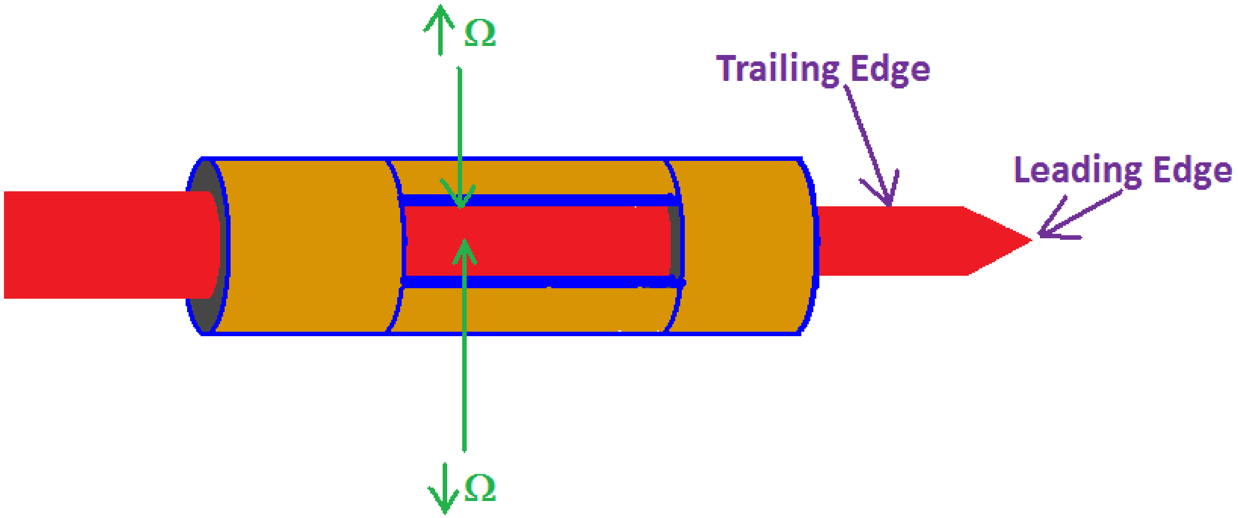
- When the pressure drops below the pressure of the air outside the "jet" (the nozzle, so to speak; the needle valve), other fluids, e.g., fuel, perfume, mixing with the fluid are sprayed into the air, creating a mixture that travels through the intake manifold of a car, Bunsen burner or bulb atomizer 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:

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

Where R_e is the Reynold's number,

v is the velocity of the fluid flow,

d is the diameter of the vessel and

η is the viscosity of the fluid, whether it be blood, fuel, or perfume.

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

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,
ΔP is the pressure gradient between fluid layers,
r^2 is the square of the radius of the tube or vessel,
8 is a constant,
η is the viscosity of the fluid and
ℓ 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

a) direct proportion to the pressure gradient,

the cube of the radius of the vessel and the density of the fluid and

b) 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 ∆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 (Ω ; ohm) is the flow hindering ability.

Conductance is the reciprocal or 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.

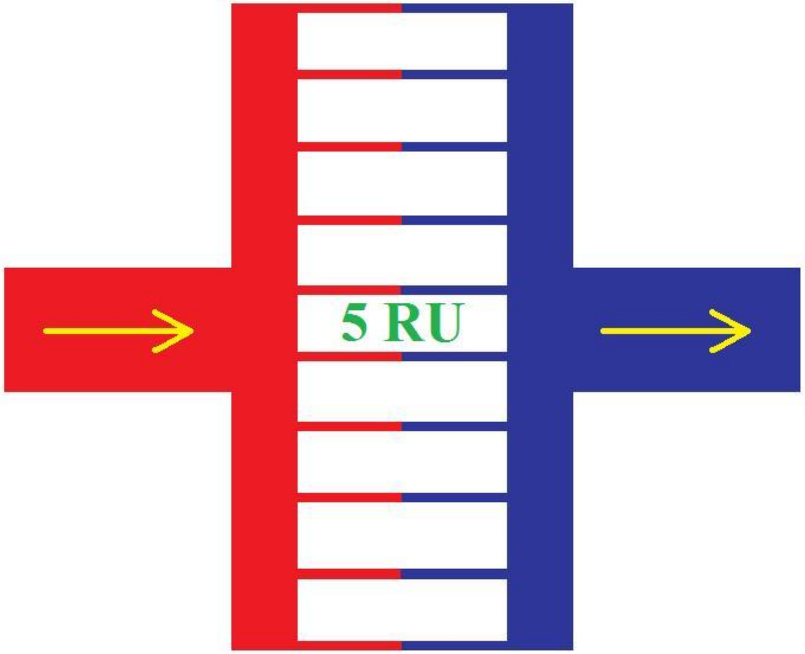
Vessels in series.
This sort of arrangement has the least amount of flow and the most resistance to flow.
The total resistance to flow in this model is equal to the sums of the individual resistances:

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

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:

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

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:

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

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

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

$$\Delta P = Q\ R$$

This equation is useful in thinking about fluid pressures, including blood pressure regulation.

The table, below, summarizes the effects of altering one or two parts of Poisueille's Equation and their effects on fluid pressure in a vessel or tube:

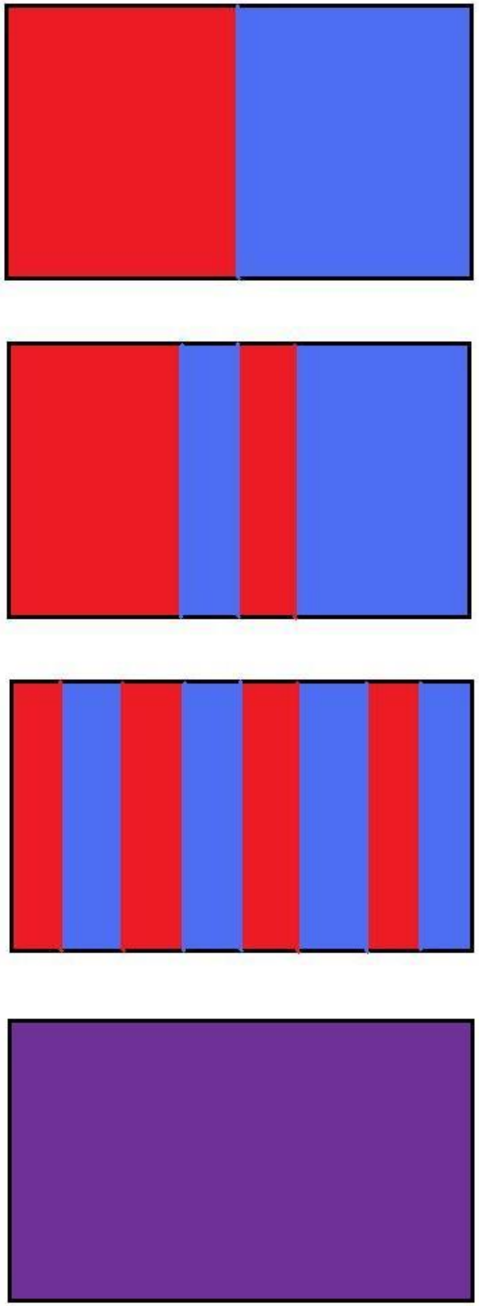
Flow	Resistance	→	Pressure Gradient
Q	R	→	ΔP
Up	No change	→	Up
No change	Up	→	Up
Up	Down	→	No change
Down	Up	→	No change
Down	No change	→	Down
No change	Down	→	Down
Up	Up	→	Up
Down	Down	→	Down

Solutions, Dilutions and Colloids

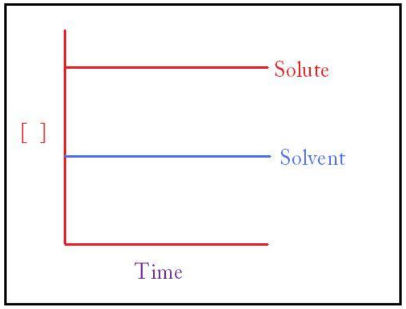
Solutions and Colloids

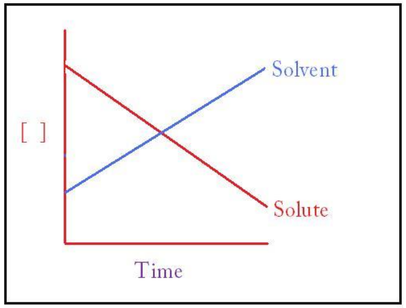
- A solution is a homogeneous mixture of 2 or more substances in which the components are present as atoms, molecules or ions.
- A solvent is the substance present in a solution in the largest amount.
- Solutes consist of one or more substances present in a solution in an amount lesser than that of the solvent.
- Dissolving describes the process of forming a solution when the solvent and solute[s] make a homogeneous mixture,e.g., sugar water.

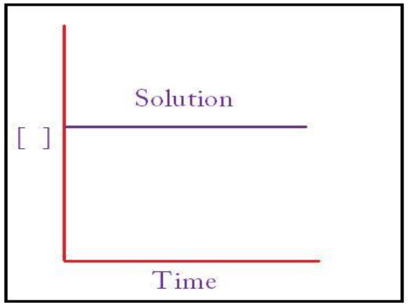
Diffusion



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.







Concentration Gradient

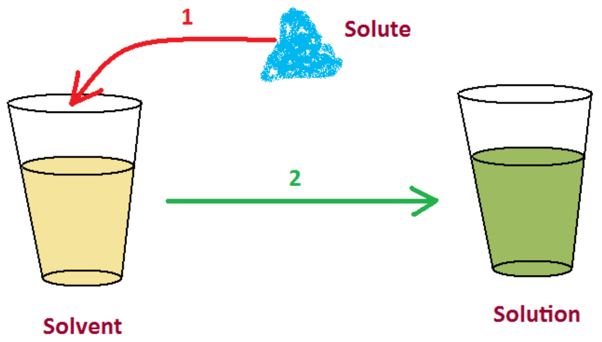
Solubility

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

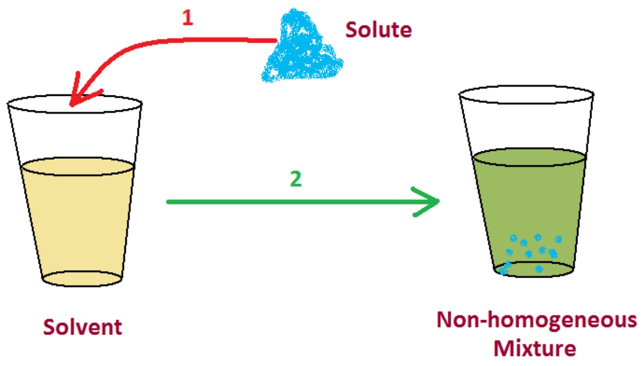
In very rough terms,
Solubility may be defined as summarized in the table, below:

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

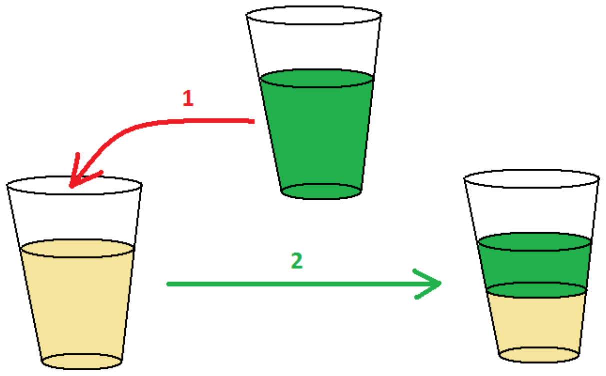
Soluble substances are substances that dissolve to a significant extent in the solvent.



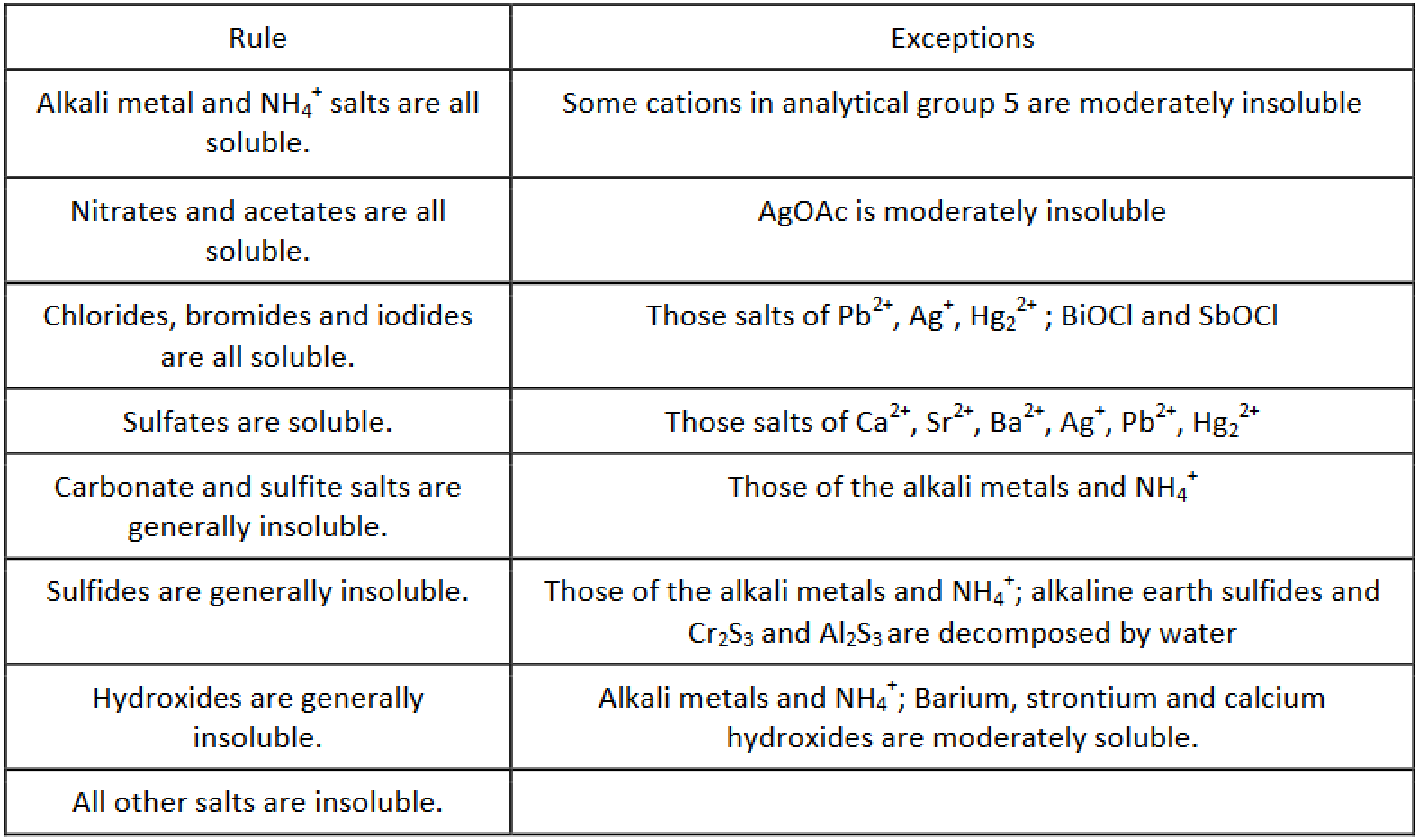
An insoluble substance is the opposite of a soluble substance, i.e., makes a non-homogeneous mixture.



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



Solubility Rules

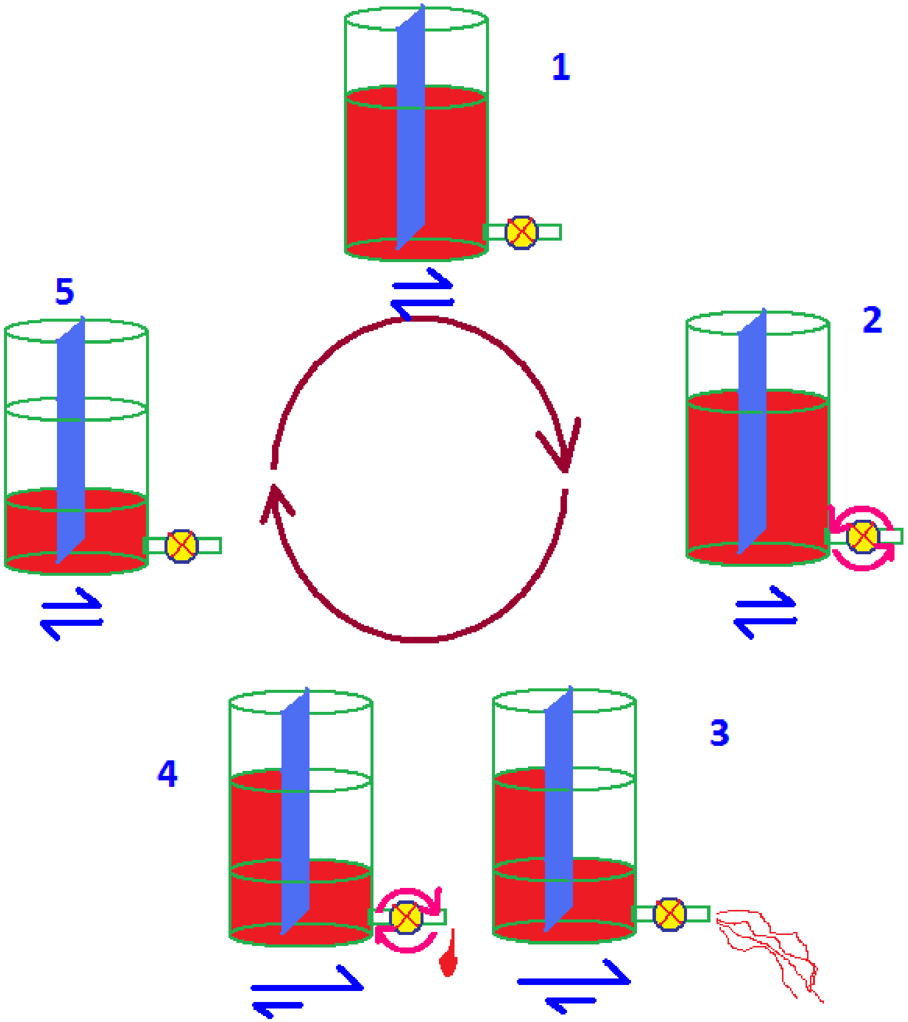


Rule	Exceptions
Alkali metal and NH_4^+ salts are all soluble.	Some cations in analytical group 5 are moderately insoluble
Nitrates and acetates are all soluble.	AgOAc is moderately insoluble
Chlorides, bromides and iodides are all soluble.	Those salts of Pb^{2+}, Ag^+, Hg_2^{2+} ; BiOCl and SbOCl
Sulfates are soluble.	Those salts of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Pb^{2+}, Hg_2^{2+}
Carbonate and sulfite salts are generally insoluble.	Those of the alkali metals and NH_4^+
Sulfides are generally insoluble.	Those of the alkali metals and NH_4^+; alkaline earth sulfides and Cr_2S_3 and Al_2S_3 are decomposed by water
Hydroxides are generally insoluble.	Alkali metals and NH_4^+; Barium, strontium and calcium hydroxides are moderately soluble.
All other salts are insoluble.	

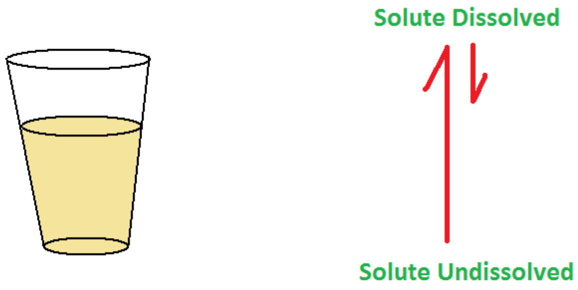
- Solutions undergo dynamic equilibrium.
- Dynamic means lots of activity.
- Equilibrium means no net change.
- Unsaturated, saturated and super-saturated solutions are constantly "changing".
- In the case of the first, more solute is dissolved than undissolved;
- The second, the dissolved/undissolved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

LeChatelier’s Principle

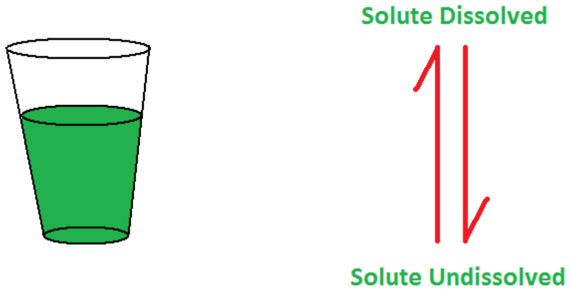
- Any shift to the equilibrium of a system may be brought about by outside forces.
- Le Chatelier's Principle says simply, yet eloquently, when a system at rest is acted upon by an outside force, the system responds by moving in a direction to reach equilibrium, again.
- Le Chatelier's Principle may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



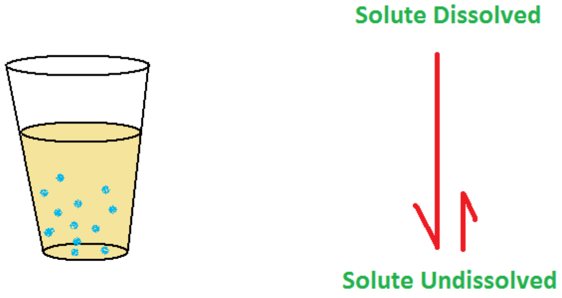
Unsaturated solutions contain less solute dissolved per unit volume of a solvent. All of the solute in an unsaturated solution is dissolved with excess solvent "caging" the solute.



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

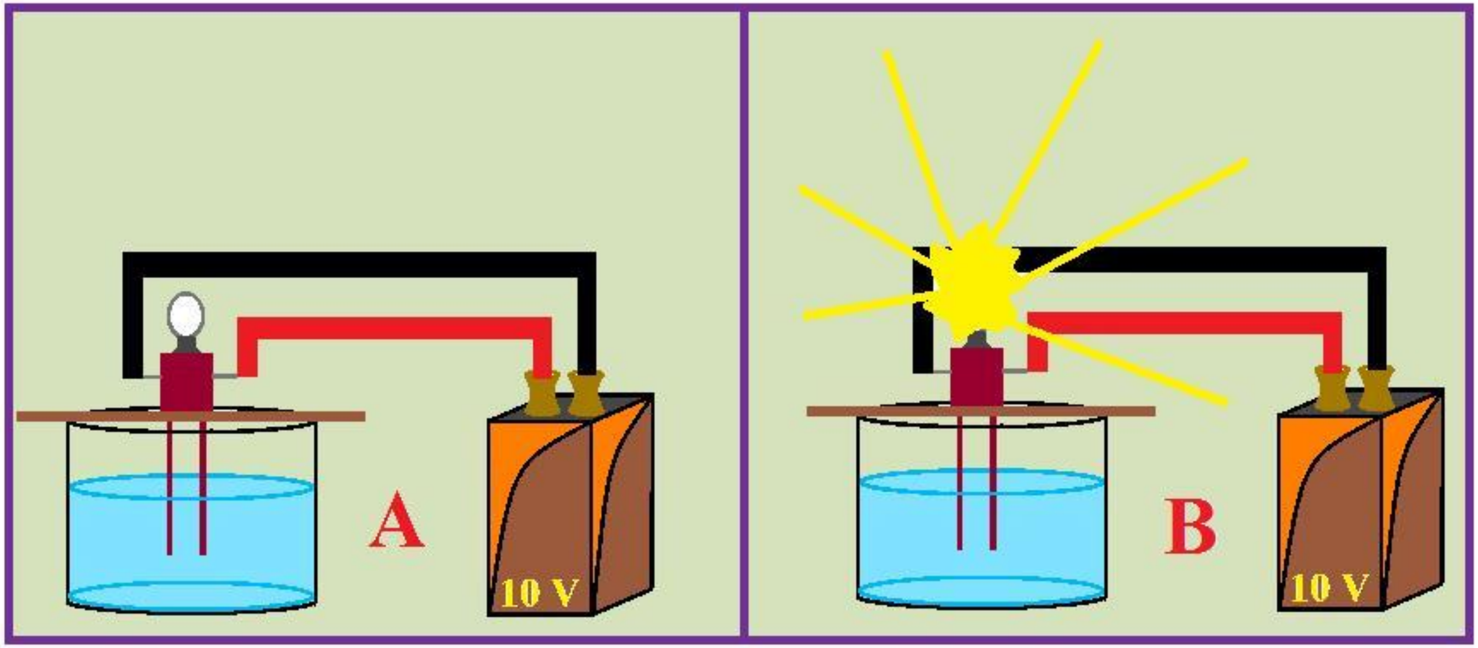


Supersaturated solutions are really mixtures. In these solutions, the solution contains more solute in the undissolved state at equilibrium, i.e., precipitate at bottom of container.

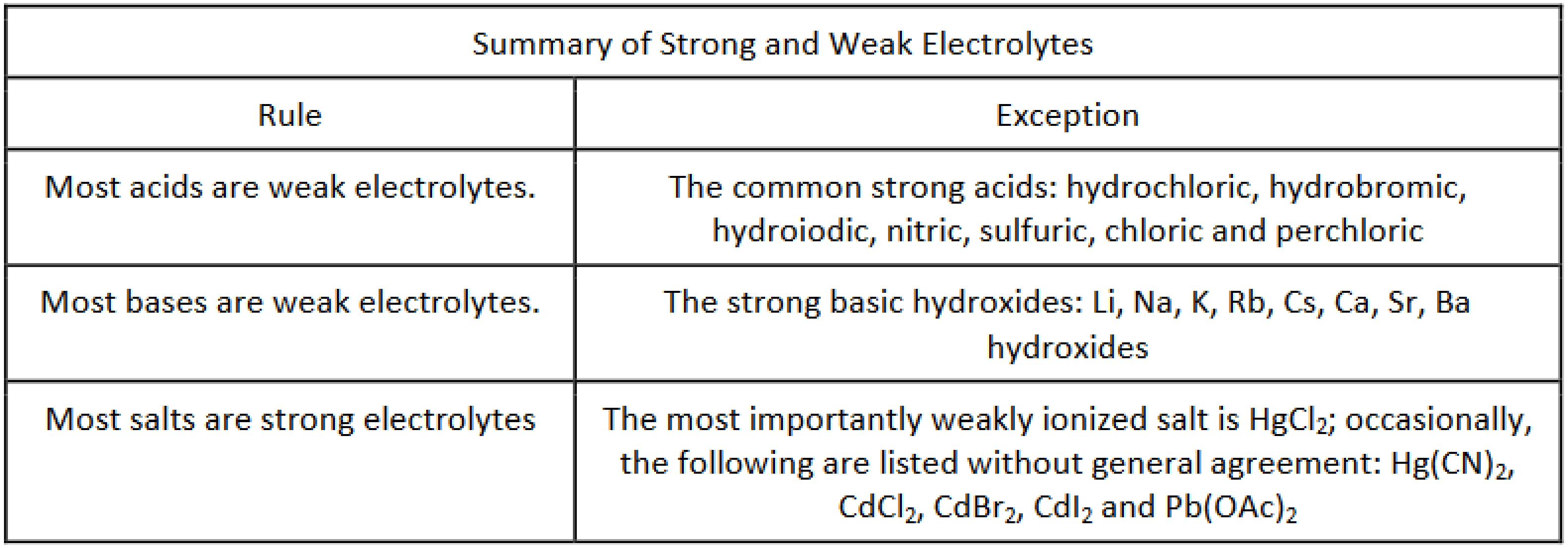


Electrolyte/Solution Properties

- **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.**



Electrolyte Rules



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 $HgCl_2$; occasionally, the following are listed without general agreement: $Hg(CN)_2$, $CdCl_2$, $CdBr_2$, CdI_2 and $Pb(OAc)_2$

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

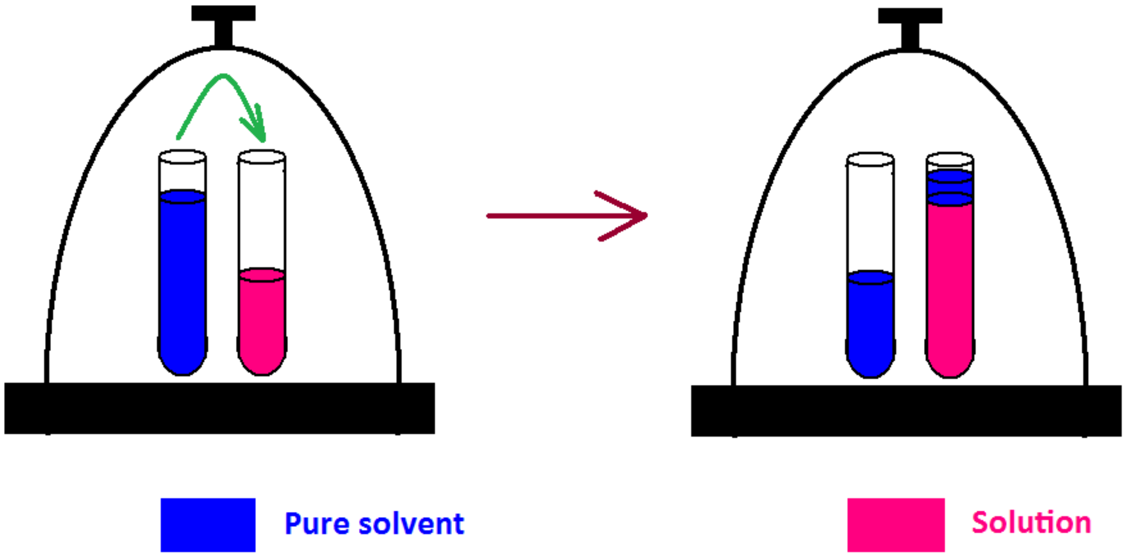
- Boiling point elevation is the concept behind both coolant in the radiator of your car in the summer and boiling foods at higher elevations. Impurities raise the boiling point of the pure solvent -- you do this every time you add a bit of salt to your water to boil potatoes.
- At sea level, you don't 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.

Freezing Point

- Freezing point depression is the idea behind anti-freeze in your radiator in the winter and using salt on the ice in your ice cream freezer/maker.
- As impurities are added to aqueous systems, the FP goes below 0° C, preventing your radiator from freezing.

Vapor Pressure

- Vapor pressure reduction is best explained from a visualized perspective.
- The bottom line with VP is that the VP of a solution is less than that of the VP of the pure solvent.

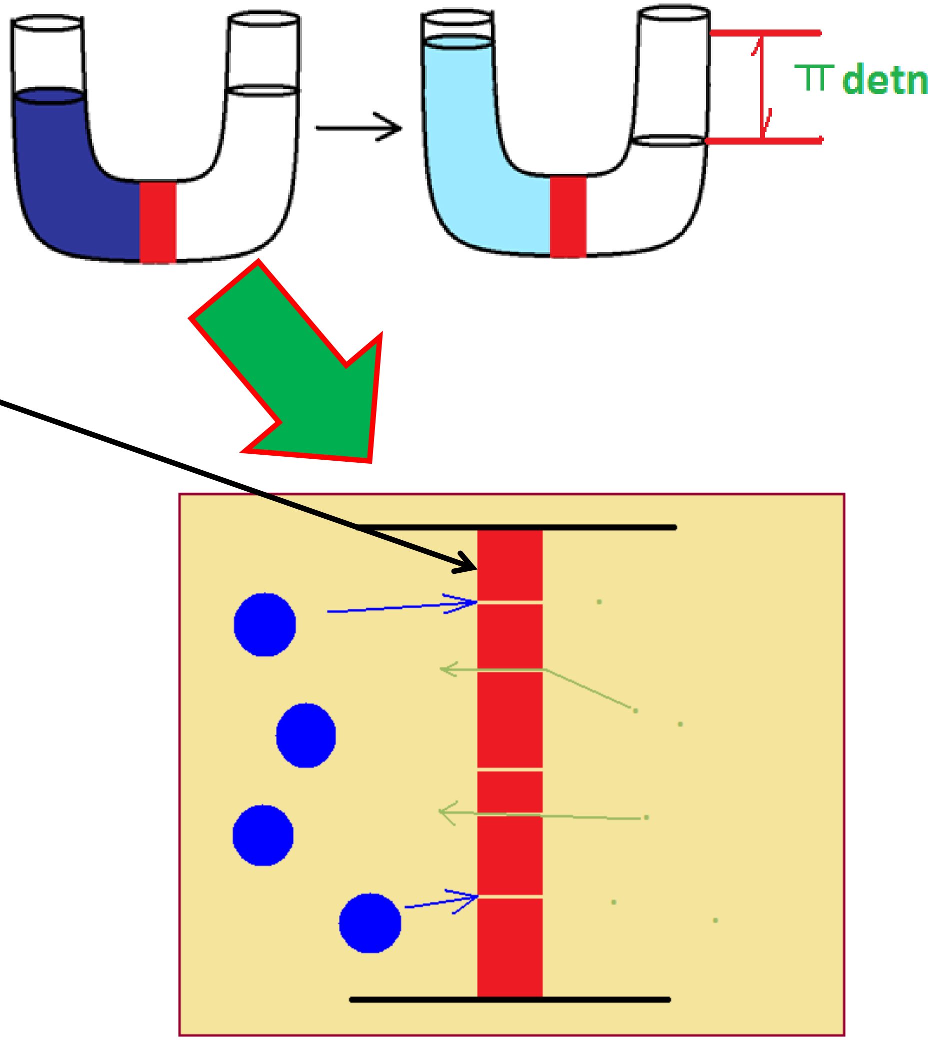

Bell jar prevents pure solution from simply evaporating

Osmosis

- Osmosis is defined as the movement of water from a region of higher water concentration to a region of lower water concentration across a semi-permeable membrane.
- Osmotic pressure is the pressure required to halt the net flow of water through a semi-permeable membrane into a solution.
- Osmolarity is a function of osmotic pressure:

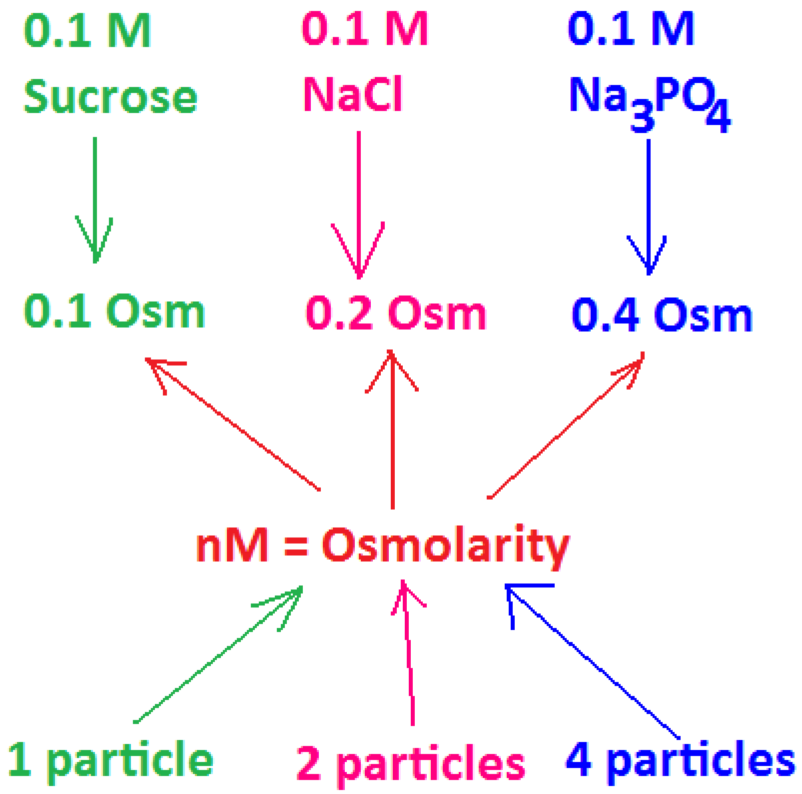
$$\pi = nMRT$$

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



Osmolarity

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



0.1 M Sucrose

0.1 M NaCl

0.1 M Na_3PO_4

0.1 Osm

0.2 Osm

0.4 Osm

nM = Osmolarity

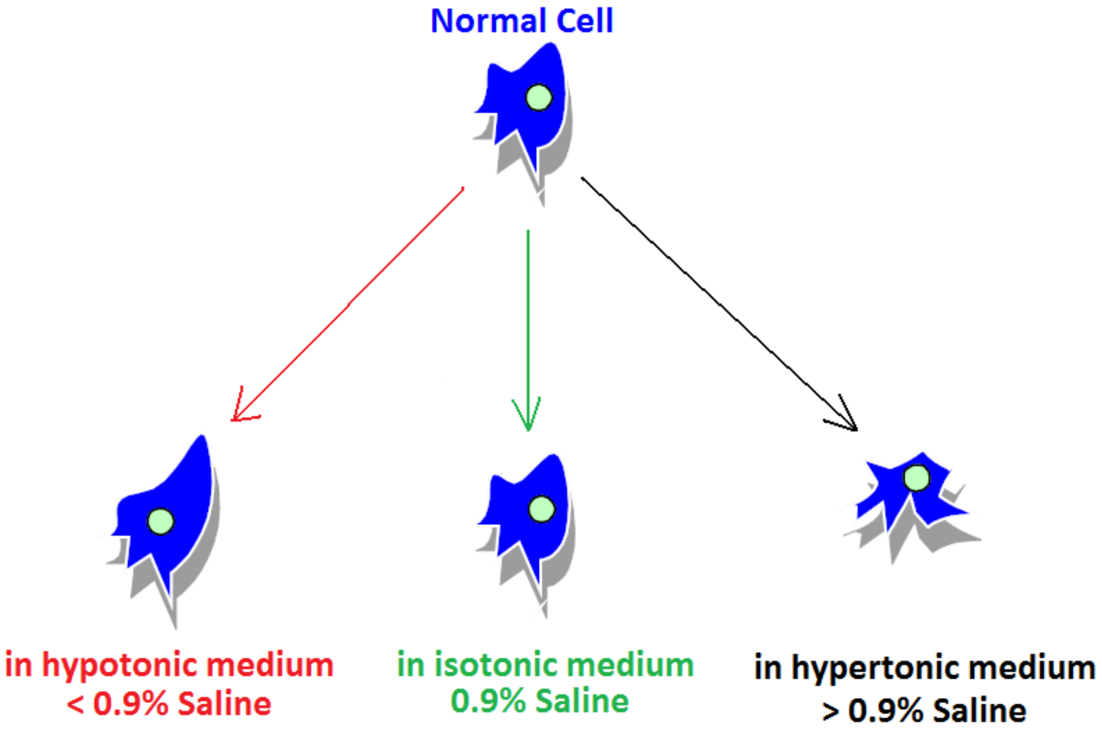
1 particle

2 particles

4 particles

Biological Application

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



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

Solution:

$$\pi = n\,M\,RT = (1\,mole) * \frac{62.4\,torr - L}{mol - K} * \frac{1\,mm\,Hg}{1\,torr} * \frac{1\,atm}{760\,mm\,Hg} * 300\,K = 6.16\,atm$$

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 = Osm or 1 * 0.25 = 0.25 Osm

Example: calculate the osmotic pressure of a solution that is 0.25 M in $CaCl_2$ at 27° C.
Solution: $CaCl_2$ is an electrolyte and dissociates into 3 particles. "n" = 3.

$$\pi = n\ M\ RT = (3\,mols) * \frac{0.25\,mol}{L} * \frac{62.4\,torr - L}{mol - K} * \frac{1\,mm\,Hg}{1\,torr} * \frac{1\,atm}{760\,mm\,Hg} * 300\,K = 18.5\,atm$$

The osmolarity of this solution is 3 * 0.25. or 0.75 Osm.

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:

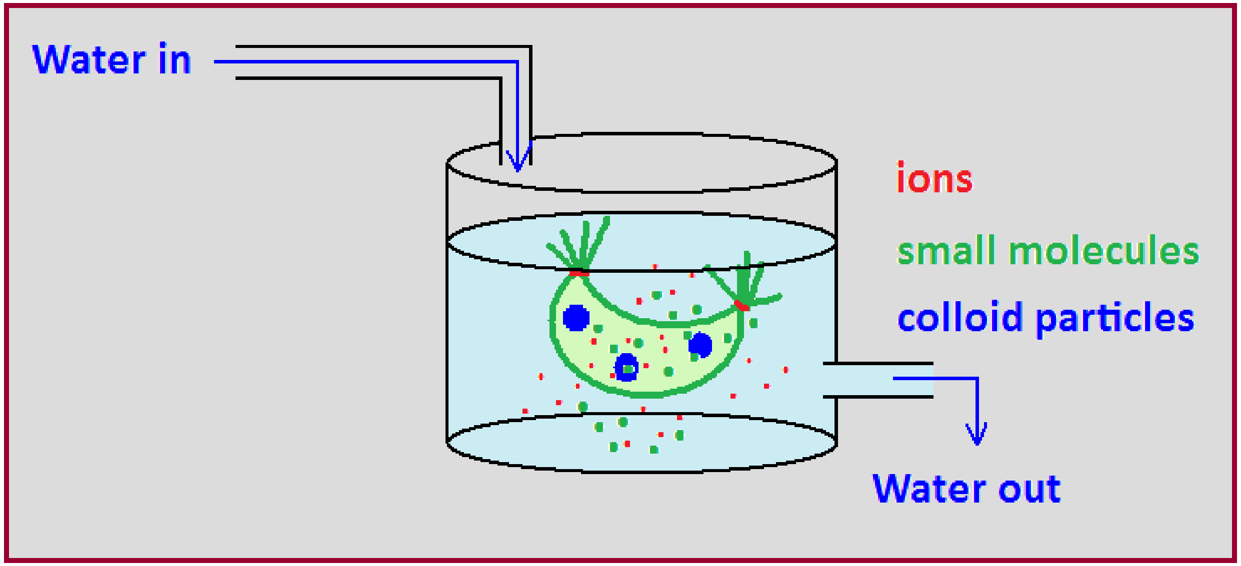
$$\pi = n\,M\,RT = M\,RT = \frac{grams}{MW * L} * RT$$

Rearranging:

$$MW = \frac{grams * R * T}{\pi * L} = \frac{(14\,grams) * 62.4\,torr - L * 300\,K}{(mol - K) * (2\,atm) * (\frac{760\,torr}{1\,atm})} = 172.42\,g/mol$$

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.

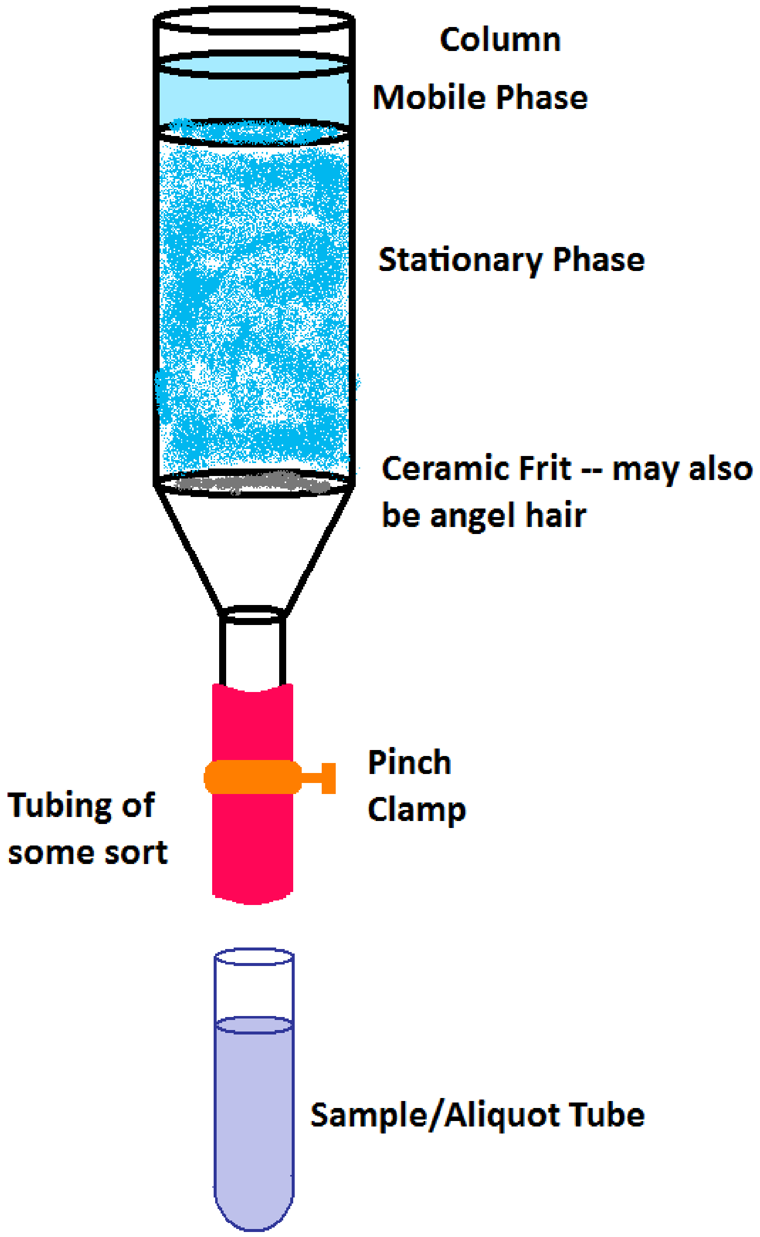
Partitioning may be viewed arithmetically to give us an idea of how the molecules are distributed between the solid support (stationary phase) and a liquid (mobile phase). This is done by looking at the partition coefficient (a constant similar to K_a, K_b, K_{eq}, etc), the K_p:

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

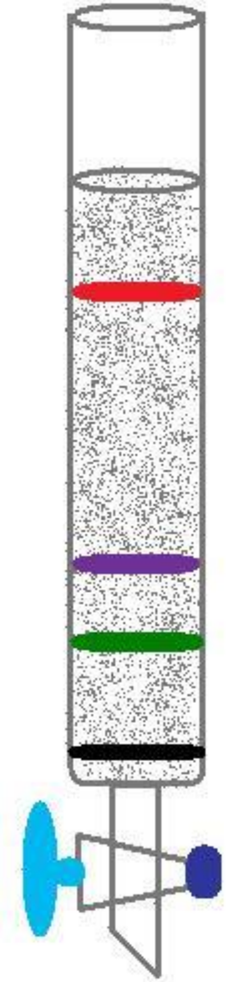
- A partition coefficient of 1 says that the solutes (molecules) are equally distributed (partitioned) between both phases.
- A partition coefficient less than one says that the solutes are primarily in the mobile phase.
- A partition coefficient greater than one says that the solutes are primarily in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

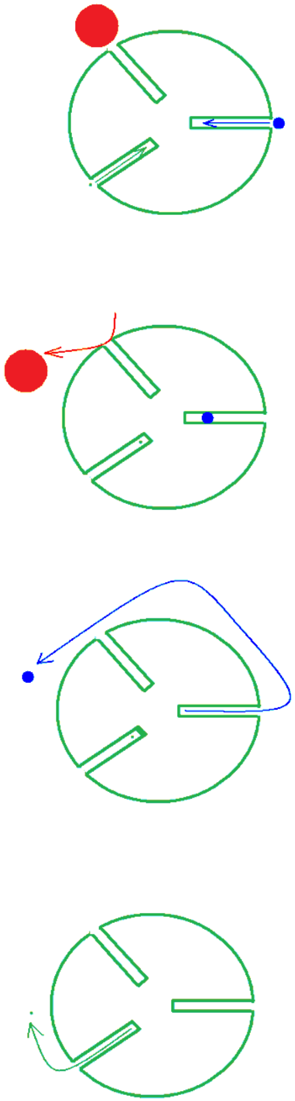
- Where are these phases?
- They are kept in a column, a tube made out of glass, metal or non-reactive plastic.
- A simple column consists of a glass tube that has a ceramic frit or a plug of angel hair in the bottom of the tube, just above the exiting tip.
- This graphic illustrates and labels a simple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



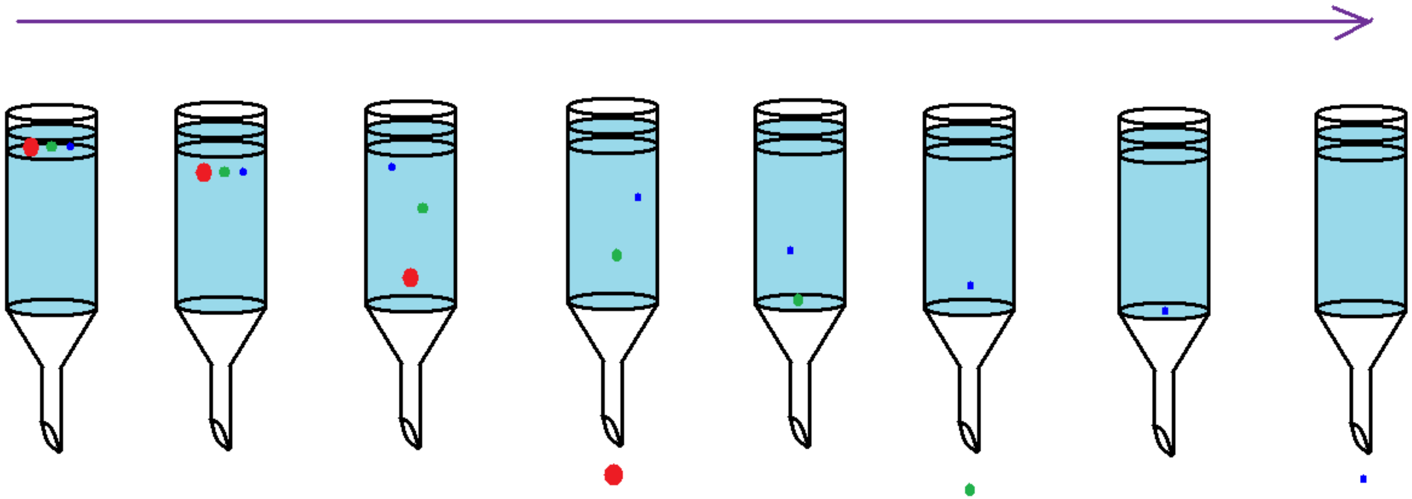
Gel Permeation (GPC) or Size Exclusion Chromatography (SEC)



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".



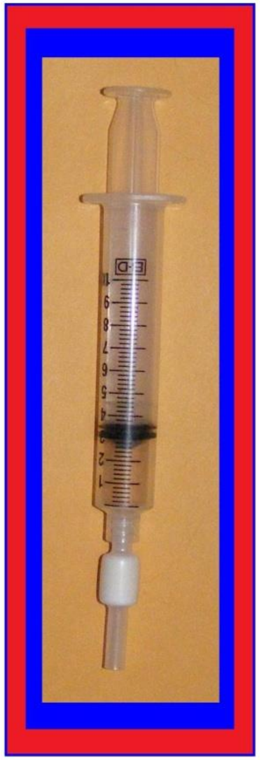
Reverse Phase Chromatography (RPC)

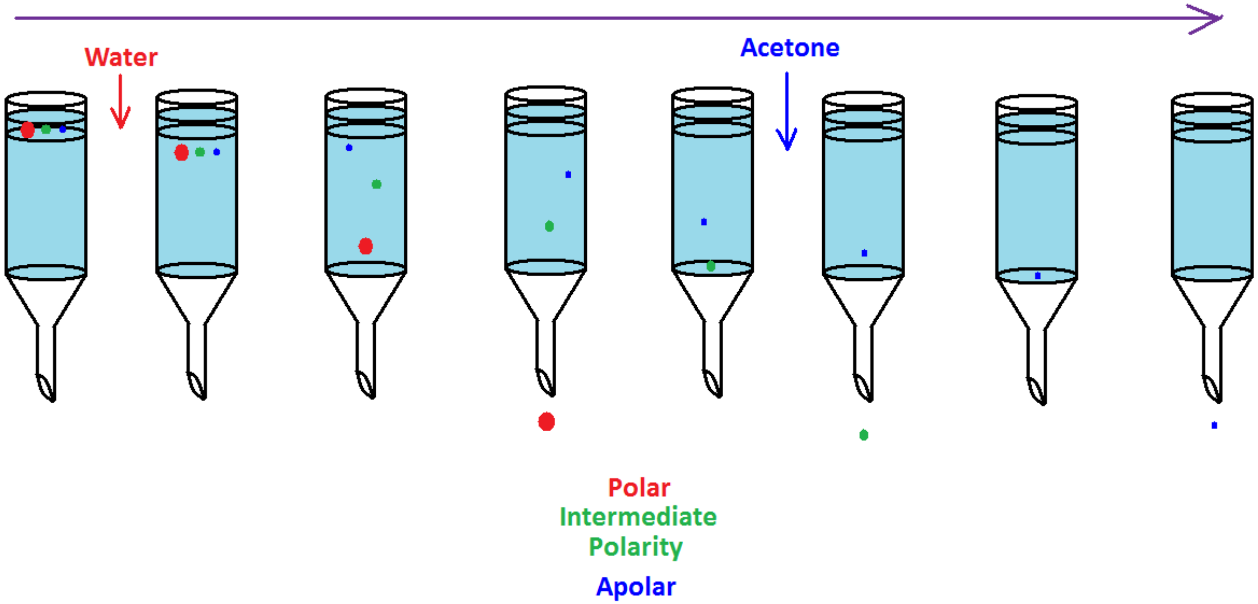
- In the case of RPC, a hydrophobic bonded packing phase (stationary phase) is combined with a hydrophilic mobile phase.
- The bonded phase is stable over a pH range of 2-7.5.
- The stationary phase is typically a silicate with a C-18, C-8 or C-2 functional group attached to it.
- The mobile phase is 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 eluent 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 right).
- This is also RPC, but lacks the finesse to be called RP-HPLC.
- Note the application of the organic solvent following the aqueous solvent, below.





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

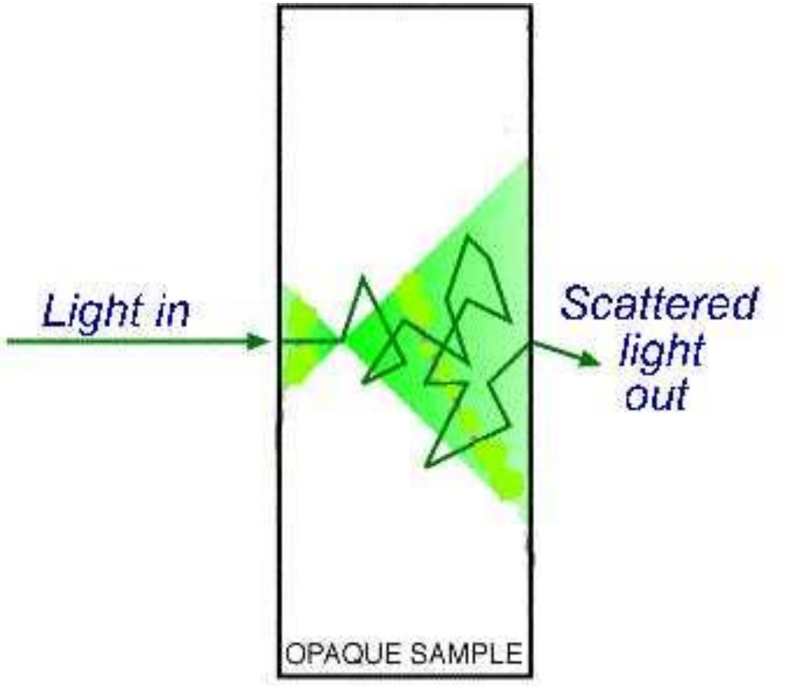
Before we define some terms in and about colloids, let's first compare these terms to those we've already learned about with solutions:

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

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**

- 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.



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:

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

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

Brønsted-Lowry Definition of Acids and Bases

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

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

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

$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

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

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

$H_3O^+ + HCO_3^- \rightarrow H_2CO_3 + H_2O$

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

When a reaction is written in the following form,

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$,

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 H_3O^+ and the new base is the nitrate ion (NO_3^-). The nitric acid and the nitrate ion make up a conjugate acid-base pair, respectively. The water and the hydronium ion (H_3O^+) make up a conjugate base-acid pair, respectively. Two more examples of reactions that produce conjugate acid-base pairs follow:

$$H_2SO_4 + 2H_2O \rightarrow 2\ H_3O^+ + SO_4^{2-}$$
$$HOCl + H_2O \rightarrow H_3O^+ + OCl^-$$

H_2SO_4 and SO_4^{2-} are one conjugate acid-base pair in the first reaction. What is the other? HOCl and 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 (HNO_3)	Nitrate ion (NO_3^-)
Acetic ($HC_2H_3O_2$ or HOAc)	Acetate ion ($C_2H_3O_2^-$ or OAc^-)
Water (H_2O)	Hydroxide ion (OH^-)
Phosphoric (H_3PO_4)	Dihydrogen phosphate ion ($H_2PO_4^-$)

- 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:

Acid Formation Mechanism	Representative Reactions
Direct union of elements	$H_2 + Cl_2 \rightarrow 2\ HCl$ $H_2 + S \rightarrow H_2S$ $H_2 + Br_2 \rightarrow 2\ HBr$ $H_2 + F_2 \rightarrow 2HF$ $H_2 + I_2 \rightarrow 2HI$
Action of water on non-metal oxides	$CO_2 + H_2O \rightarrow H_2CO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$ $P_4O_{10} + 6\ H_2O \rightarrow 4H_3PO_4$ $SO_2 + H_2O \rightarrow H_2SO_3$
Heating salts of volatile acids with NON-volatile or SLIGHTLY volatile acids	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ $NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr$
By the action of salts with other acids producing a precipitate	$H^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + H^+ + NO_3^-$ $2H^+ + SO_4^{2-} + Ba^{2+} + 2ClO_3^- \rightarrow BaSO_4 + 2H^+ + 2ClO_3^-$
By hydrolysis	$PBr_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HBr$ $PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$
By oxidation-reduction reactions	$H_2S + I_2 \rightarrow 2HI + S$ $2HNO_3 + 2SO_2 + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$

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

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

Hydrogen Halides

- $CaF_2(s) + H_2SO_4(l) + 200\text{-}250° \rightarrow CaSO_4\downarrow + 2HF$
- About $8*10^8$ pounds of HF are used each year to make freons:
- $CCl_4(g) + HF(g) + SbCl_5(l) + 65\text{-}95°\ C \rightarrow CCl_3F(g) + HCl(g)$
- $CCl_4(g) + 2HF(g) + SbCl_5(l) + 65\text{-}95°\ C \rightarrow CCl_2F_2(g) + 2HCl(g)$
- Freons are used in air conditioners and refrigerators, but they are destructive to the ozone layer (15-30 km layer above the earth).

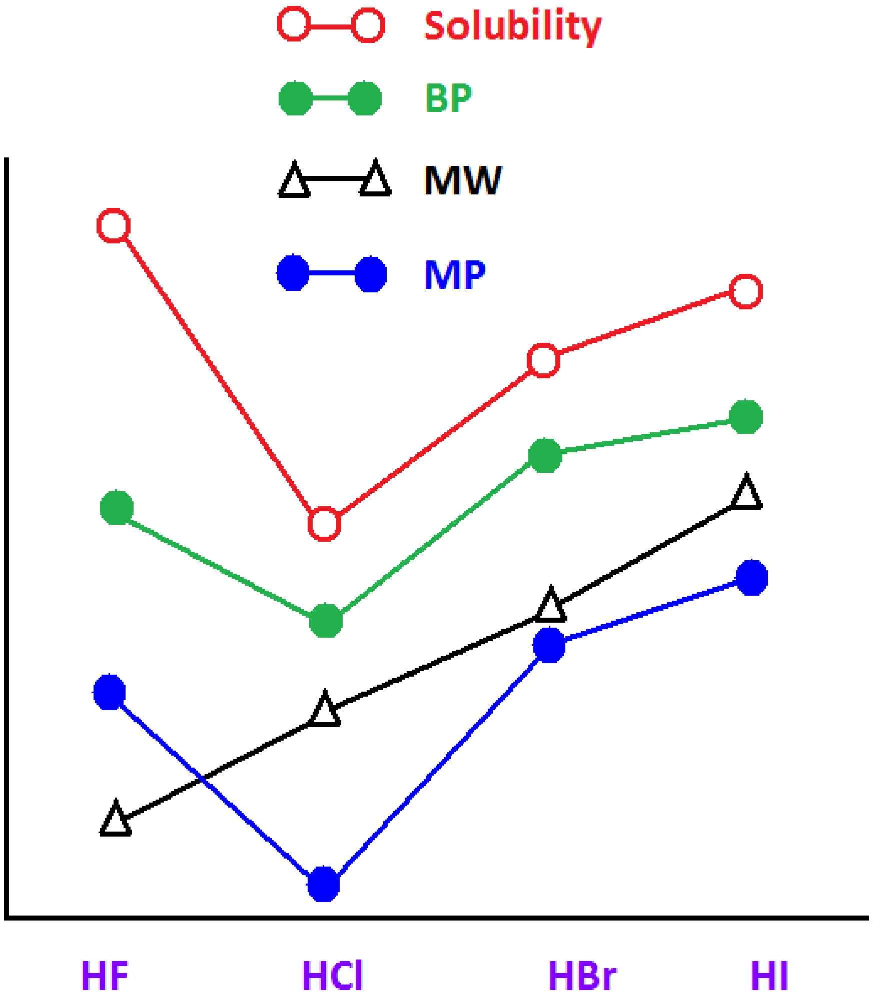
- Another $8*10^8$ pounds of HF are used per year to produce aluminum:
- $6HF(g) + Al(OH)_3(s) + 3NaOH(aq) \rightarrow Na_3AlF_6$ (synthetic cryolite) + $6H_2O(l)$
- Bauxite, the ore that contains aluminum (Al_2O_3) is the subjected to electrolysis in the cryolite solvent to form elemental aluminum.
- HF is used for glass etching and frosting bulbs. The reaction for this is:
- $SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$
- and
- $CaSiO_3(s) + 8HF(aq) \rightarrow H_2SiF_6(aq) + CaF_2(s) + 3H_2O(l)$

- HCl is produced in one of three ways and follows:
  - $CH_4(g) + Cl_2(g) + 440\,^\circ C \rightarrow CH_3Cl + HCl$
  - $H_2(g) + Cl_2(g) + h\nu \rightarrow 2HCl(g) \leftarrow$ EXPLOSIVE REACTION!
  - $2NaCl(s) + H_2SO_4(l) + \text{heat} \rightarrow 2HCl + Na_2SO_4\downarrow$
- 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 H_3PO_4 instead of H_2SO_4.

Properties of Hydrogen Halides

Hydrogen halide→	HF	HCl	HBr	HI
MW	20	36.5	80.9	127.9
Solubility in g/100 mL water	∞ @ 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

Properties of Hydrogen Halides



The Halogens Form Oxo-Acids

Hypohalous acids	**HOCl**	**HOF**	**HOBr**	**HOI**
halous acids	$HClO_2$	------	$HBrO_2$	HIO_2
halic acids	$HClO_3$	------	$HBrO_3$	HIO_3
perhalic acids	$HClO_4$	------	$HBrO_4$	HIO_4

$HClO_4$ 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:

Weakest			**Strongest**
$HClO$	**$HClO_2$**	**$HClO_3$**	**$HClO_4$**
Hypochlorous acid	**Chlorous**	**Chloric**	**Perchloric**
+1 Oxidation state	**+3 Oxidation state**	**+5 Oxidation state**	**+7 Oxidation state**

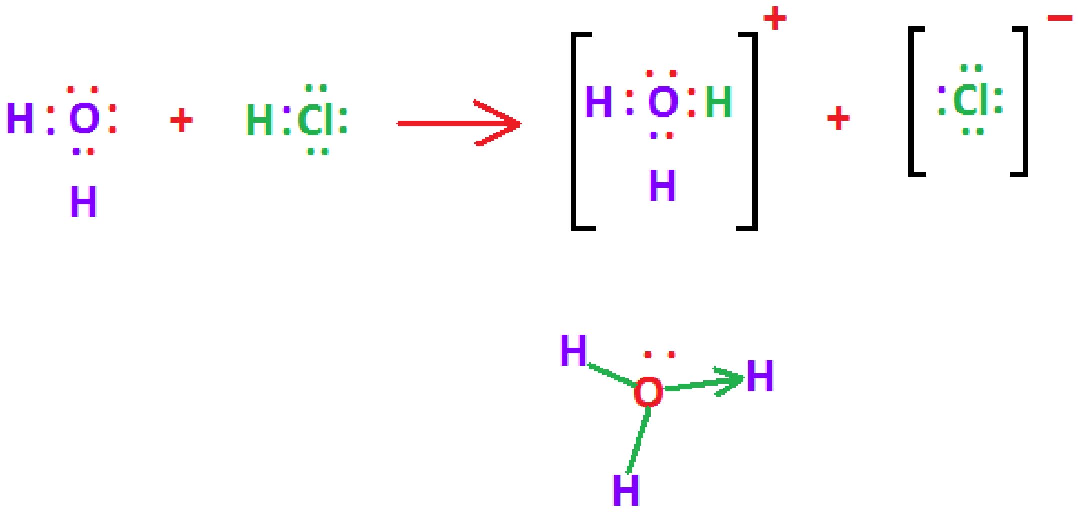
Base Formation

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

Base Mechanism	Representative Reaction
Alkali metals or alkaline earth metals react with water	$2\ K + 2\ H_2O \rightarrow 2\ K^+ + 2\ OH^- + H_2$ $Ca + 2\ H_2O \rightarrow Ca^{2+} + 2\ OH^- + H_2$ $2\ Na + 2\ H_2O \rightarrow 2\ Na^+ + 2\ OH^- + H_2$
Water reacting with oxides of alkali/alkaline earth metals	$Na_2O + H_2O \rightarrow 2\ Na^+ + 2\ OH^-$ $CaO + H_2O \rightarrow Ca^{2+} + 2\ OH^-$ $MgO + H_2O \rightarrow Mg^{2+} + 2\ OH^-$
Salts with other bases with a resulting precipitate	$2\ Na^+ + CO_3^{2-} + Ca^{2+} + 2\ OH^- \rightarrow CaCO_3\downarrow + 2\ Na^+ + 2\ OH^-$
Electrolysis	$2\ Na^+ + 2\ Cl^- + 2\ H_2O + \text{Electrolysis} \rightarrow 2\ Na^+ + 2\ OH^- + H_2 + Cl_2$
Dissolving NH_3 in water	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Lewis Definition of Acids and Bases

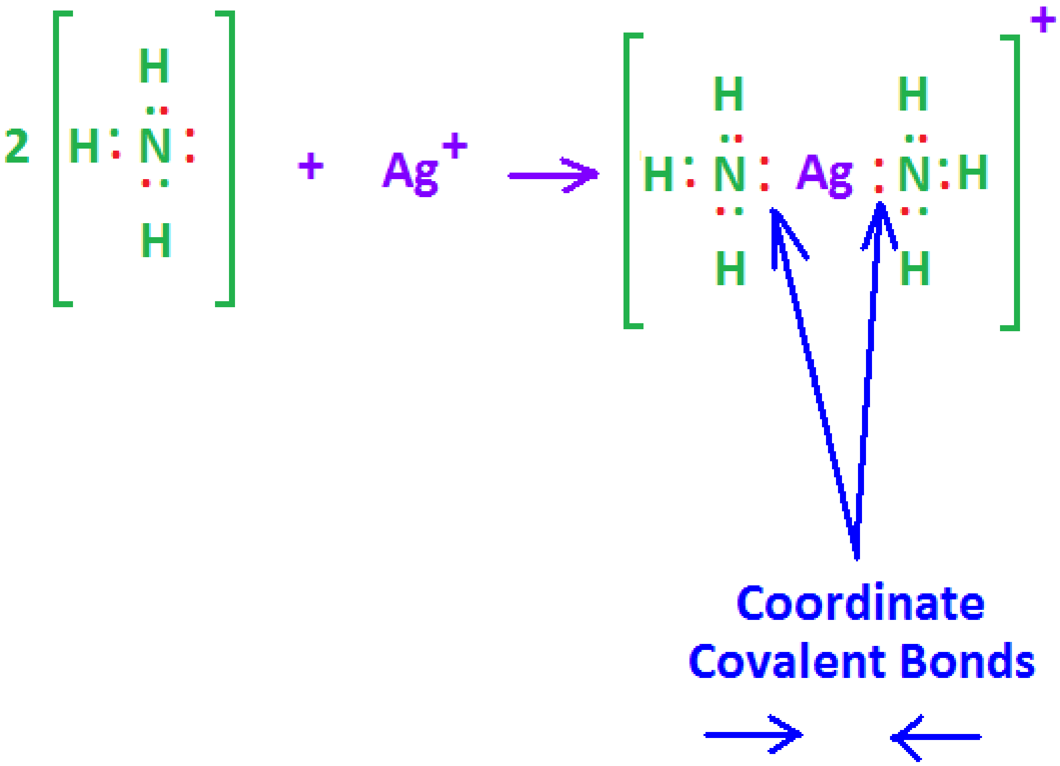
By this definition, acids are a molecule or ion which can accept a pair of electrons.



Coordinate Covalent Bond

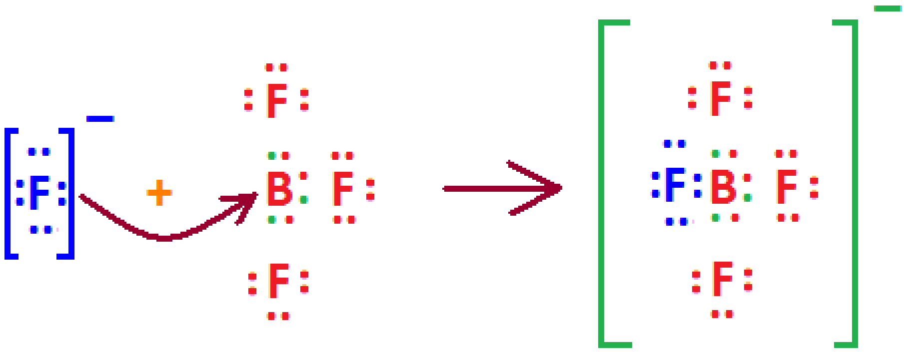
A base is a molecule or ion which can donate a pair of electrons.

Example 2

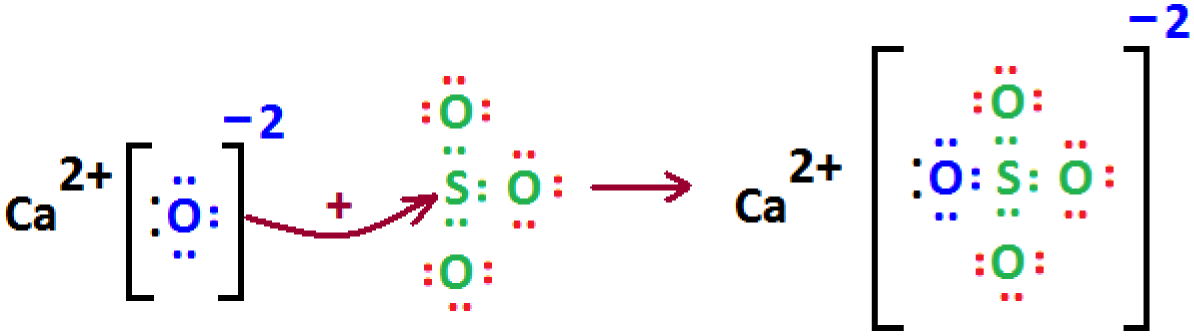


Coordinate Covalent Bonds

Example 3



Example 4



Salts

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

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

Some common salts are summarized in the table, below:

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

The formation of salts necessarily depend on their solubility -- or the lack thereof -- in water. Solubility rules that actually help make chemical reactions make sense are tabulated, following slide:

Rule	Exceptions
Alkali metal and NH_4^+ salts are all soluble.	Some cations in analytical group 5 are moderately insoluble
Nitrates and acetates are all soluble.	AgOAc is moderately insoluble
Chlorides, bromides and iodides are all soluble.	Those salts of Pb^{2+}, Ag^+, Hg_2^{2+} ; BiOCl and SbOCl
Sulfates are soluble.	Those salts of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Pb^{2+}, Hg_2^{2+}
Carbonate and sulfite salts are generally insoluble.	Those of the alkali metals and NH_4^+
Sulfides are generally insoluble.	Those of the alkali metals and NH_4^+; alkaline earth sulfides and Cr_2S_3 and Al_2S_3 are decomposed by water
Hydroxides are generally insoluble.	Alkali metals and 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 $HgCl_2$; occasionally, the following are listed without general agreement: $Hg(CN)_2$, $CdCl_2$, $CdBr_2$, CdI_2 and $Pb(OAc)_2$**

Preparation of Salts

Mechanism	Representative Reactions
Direct union of their elements.	$2Na + Cl_2 \rightarrow 2NaCl$ $Fe + S \rightarrow FeS$
Reactions of acids with metals, metal hydroxides or metal oxides.	$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ $Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$ $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
Reactions of basic anhydrides with acid anhydrides.	$BaO + SO_3 \rightarrow BaSO_4$ $CaO + CO_2 \rightarrow CaCO_3$
Reaction of acids with salts.	$BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O + CO_2$ $BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$
Reaction of salts with other salts.	$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ $ZnCl_2 + Na_2S \rightarrow ZnS + 2NaCl$

Auto-ionization of Water

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

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

The reaction is NOT favored as written, although the ratio of protons to hydroxide ions is unity.

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

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

H_3O^+ is acidic.

OH^- is alkaline.

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

In NEUTRAL solutions, they are equal to each other.

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

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

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

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

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

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:

$$K[H_2O]^2 = [H_3O^+] * [OH^-]$$

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 $[H_2O]$ are equal to the K_w and the equation takes on the following look:

$$K_w = [H_3O^+] * [OH^-]$$

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:

$K_w = [H_3O^+] * [OH^-]$, 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:
$14 = pH + pOH$, where $[H^+] = [H_3O^+]$

Another way to look at this is that:

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

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

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

Acids and Bases Dissociate in Water

Fortunately for us, acids and bases dissociate in water:

$HA + H_2O \rightarrow H_3O^+ + A^-$

Where HA is any acid and A^- 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:

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

The water concentration doesn't change as we saw in the K_w determination, so we'll rearrange the equation as follows:

$$K*[H_2O] = K_a = \frac{[H_3O^+]*[A^-]}{[HA]}$$

Where K_a is the acid dissociation constant.

We can do the same for a base:

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

The equilibrium expression is as follows:

$$K = \frac{[NH_4^{\ +}]*[OH^-]}{[NH_3]*[H_2O]}$$

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

$$K*[H_2O] = K_b = \frac{[NH_4^{\ +}]*[OH^-]}{[NH_3]}$$

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.

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

$$K_w = [H_3O^+]*[OH^-]$$

and that:

$$K_a = \frac{[H_3O^+]*[OH^-]}{[HA]}$$

and that:

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

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

$$K_a * K_b = \frac{[H_3O^+]*[HA]*[A^-]*[OH^-]}{[HA]*[A^-]}$$

Note that all we're left with after canceling is:

$$[H_3O^+]*[OH^-] = K_a K_b = K_w$$

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 $K_aK_b = 1*10^{-14}$, 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 F^- and NH_4^+ and NH_3:

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

$$K_w \overset{?}{=} \frac{[H_3O^+]*[HF]*[F^-]*[OH^-]}{[HF]*[F^-]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

and:

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

$$K_w \overset{?}{=} \frac{[H_3O^+]*[NH_3]*[NH_4^+]*[OH^-]}{[NH_3]*[NH_4^+]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

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?

Determining the pH of A Solution

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.

Determining the pH of A Solution Method 2

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 $1.8*10^{-5}$
Solution: Always write out the equation, first, in these types of questions as laid out below:

	HOAc	**+**	**H_2O**	**$\rightarrow$**	**H_3O^+**	**+**	**OAc^-**
[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:

$$K_a = \frac{[H_3O^+]*[OAc^-]}{[HOAc]} = \frac{X*X}{0.3-X} = \frac{X^2}{0.3-X} \approx \frac{X^2}{0.3}$$

$$(K_a)*(0.3) = X^2$$

$$\sqrt{(1.8*10^{-5})*(0.3)} = X = 0.0023M$$

$$X = 0.0023M = [H_3O^+]$$

$$pH = -\log 0.0023 = 2.64$$

What is the pOH for this aqueous solution?

Since pH + 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 $NH_3 = 1.8*10^{-5}$.
Solution: Set up as before:

	NH_3	+	H_2O	$\rightarrow$	NH_4^+	+	OH^-
[Before reaction]	0.8M				0M		0M
[After reaction]	- x				+ x		+ x
Total concentration of species	0.8 - x				x		x

$$K_b = \frac{[NH_4^+]*[OH^-]}{[NH_3]} = \frac{X*X}{0.8-x} \approx \frac{X^2}{0.8}$$

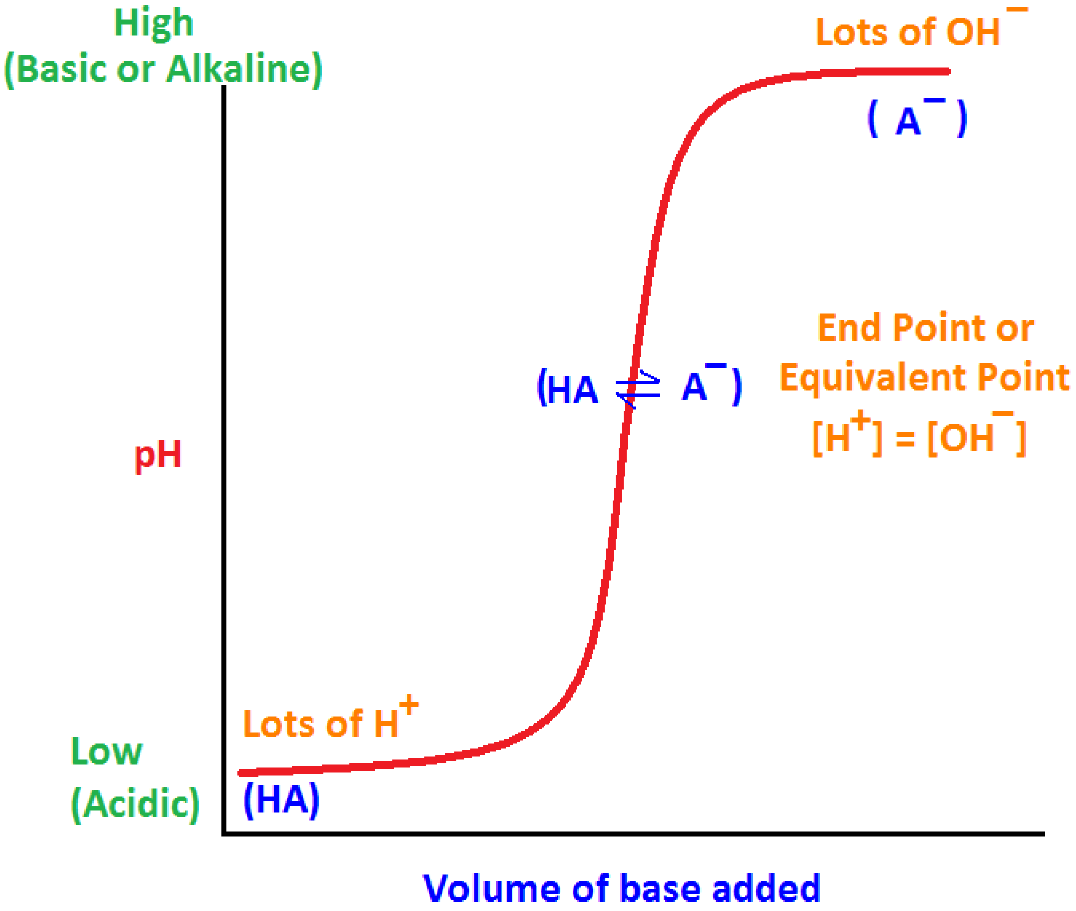
$$\sqrt{(1.8*10^{-5})*(0.8)} = X = 0.0038\,M$$

$$pOH = -\log 0.0038 = 2.42$$

$$pH = 14 - 2.42 = 11.58$$

Acid-Base Titrations: In General:

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



Acid-Base Titrations

$HA \leftrightarrow H^+ + A^-$

Or

$HA + MOH \leftrightarrow HOH + MA$

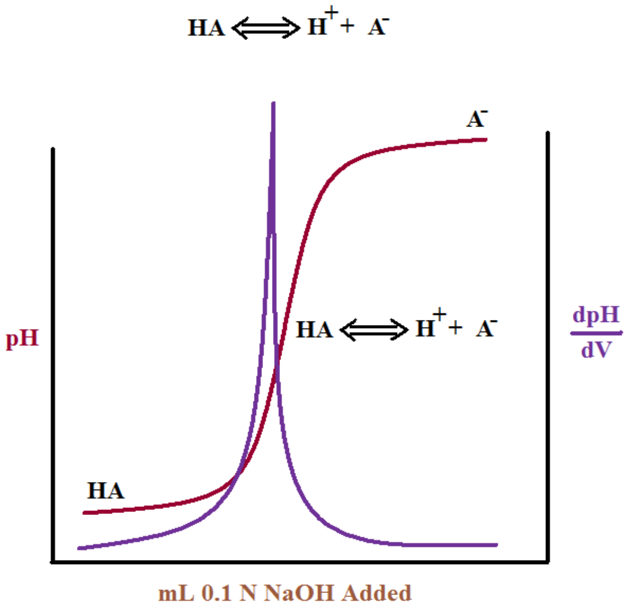
Mono-protic Acid

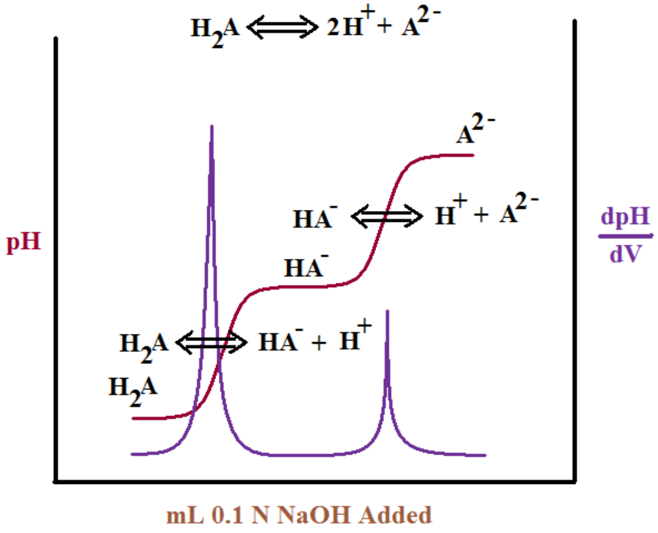
$H_2A \leftrightarrow 2H^+ + A^{-2}$

Or

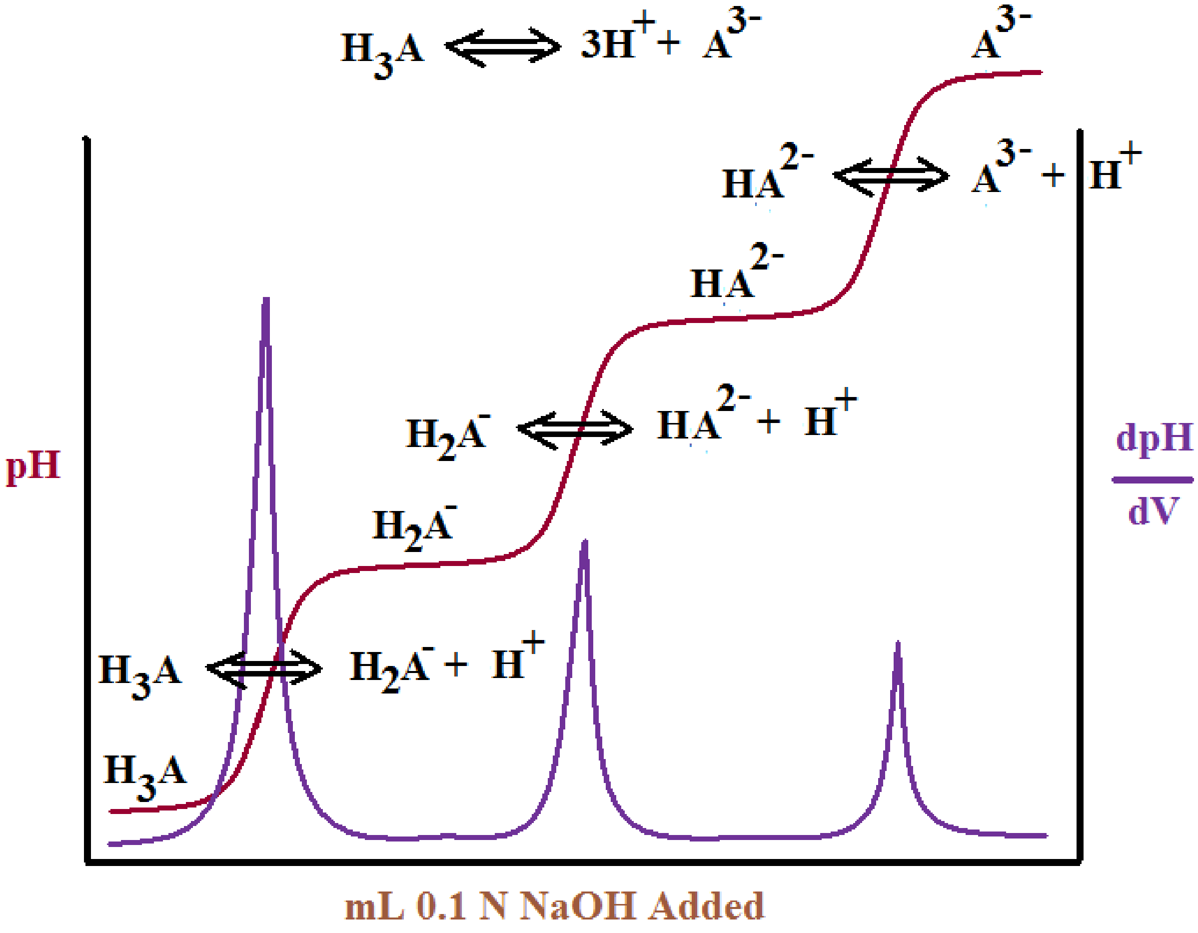
$H_2A + 2MOH \leftrightarrow 2HOH + M_2A$

Di-protic Acid

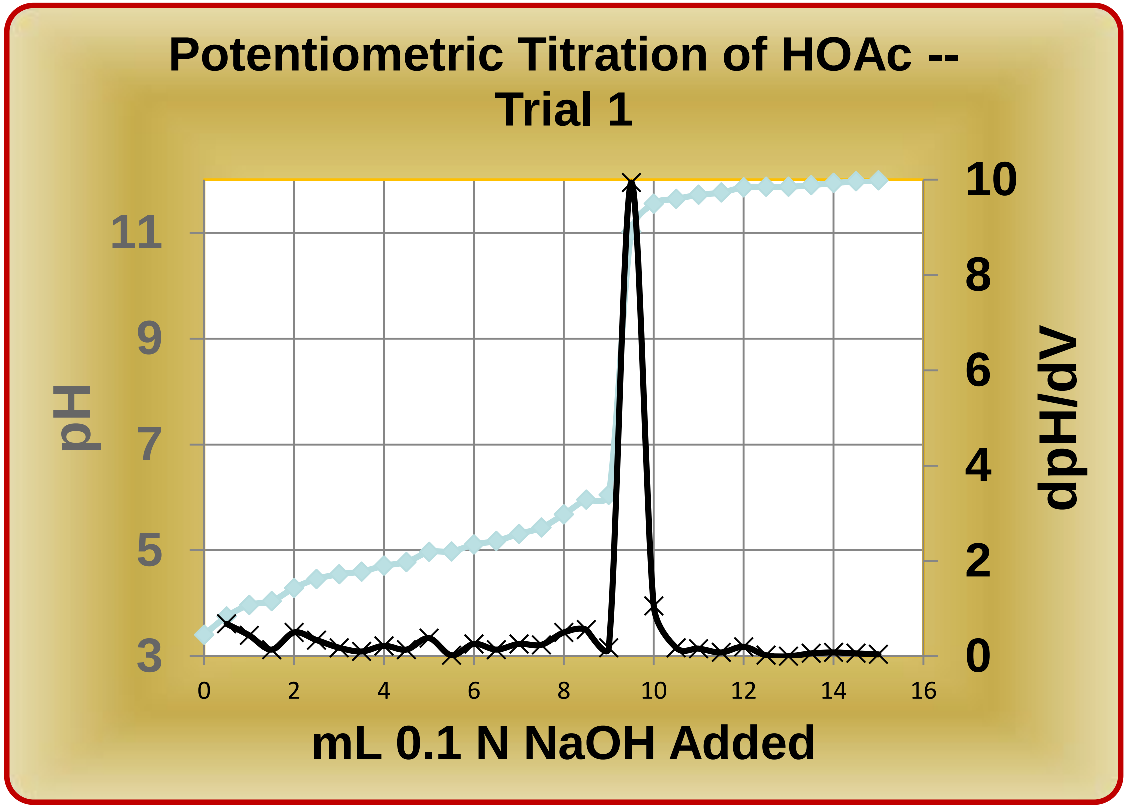




Tri-Protic Acids have THREE Endpoints

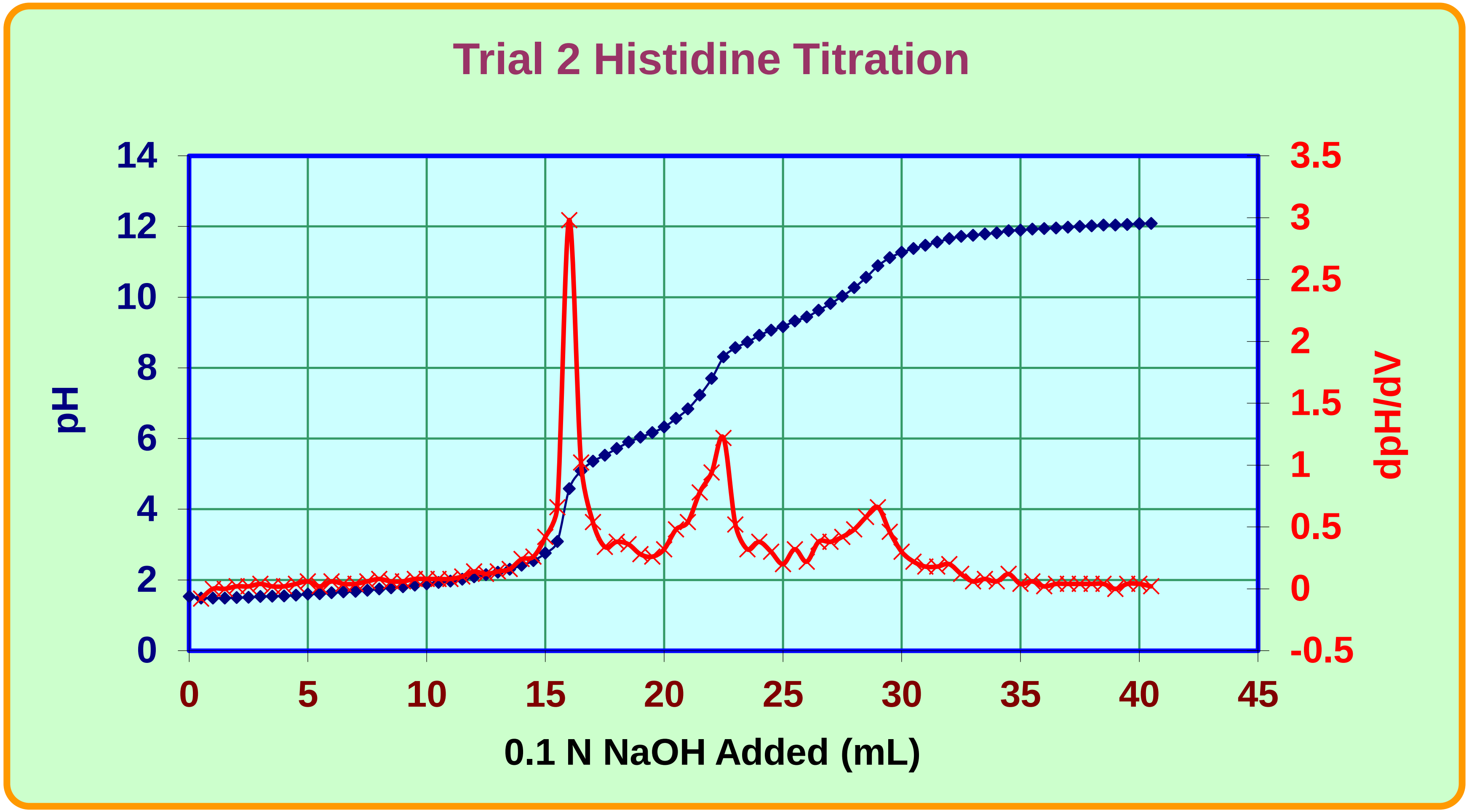


When using a pH meter to keep track of the titration, the equivalent point/end point are not obvious. Typically a technique called "taking the first derivative" of the pH curve (the sigmoid shaped curve) is used to determine these points. Without going into detail, this involves manipulating the sigmoid 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



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

$HA \Leftrightarrow H^+ + A^-$

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

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

Acids like H_2A and H_3A have multiple dissociation steps.

Each step is represented by its own K_a or K_b:

$H_2A \Leftrightarrow HA^- + H^+$

$HA^- \Leftrightarrow A^- + H^+$

where

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]} \qquad K_{a2} = \frac{[A^-][H^+]}{[HA^-]}$$

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

$$K_{a1} \bullet K_{a2} = \frac{[HA^-][H^+][A^-][H^+]}{[H_2A][HA^-]}$$

and

$$K_{a-TOTAL} = \frac{[H^+]^2[A^-]}{[H_2A]}$$

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.

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- pair:

$$OAc^- + H^+ \Leftrightarrow HOAc$$

$$HOAc + OH^- \Leftrightarrow OAc^- + H_2O$$

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:

$$H_2O + CO_2 \Leftrightarrow H_2CO_3$$

$$HCO_3^- + H^+ \Leftrightarrow H_2CO_3$$

$$H_2CO_3 + OH^- \Leftrightarrow HCO_3^- + H_2O$$

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.

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.

$$HA \Leftrightarrow H^{+} + A^{-}$$

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

Rearranging, sequentially:

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

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

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

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

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

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 $4.4*10^{-7}$.

Solution: First get the pK_a

$$pK_a = -\log(4.4*10^{-7}) = 6.357$$

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

$$pH = pK_a + \log\left(\frac{[salt]}{[acid]}\right) \Leftrightarrow pK_a + \log\left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$pH = 6.357 + \log\left(\frac{0.025}{0.05}\right) = 6.357 + \log 0.5$$

$$pH = 6.357 - 0.301 = 6.056$$

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:

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$pH - pKa = \log\left(\frac{[HCO_3^-]}{H_2CO_3}\right)$$

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

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

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

$$anti\log(7.35 - 6.357 + (\log 0.03)) = [HCO_3^-]$$

$$anti\log(-0.530) = [HCO_3^-] = 0.295M$$

Redox Reactions

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

Oxidation-Reduction

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	$4Fe + 3O_2 \rightarrow 2Fe_2O_3$	**The product is Iron (III) oxide or ferric oxide.**
Charcoal burning	$C + O_2 \rightarrow CO_2$	**This is what happens on your charcoal grill.**
Burning sulfur	$S + O_2 \rightarrow SO_2$	**This is one process that occurs in catalytic converters.**
Automobile engines at high temperatures	$N_2 + O_2 \rightarrow 2NO$	**Another wonderful thing that came from catalytic converters.**
Burning methane (natural gas)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	**Just like in the winter time when you run your gas furnace.**
Burning off hydrogen sulfide	$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$	
Oxidizing carbon disulfide	$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$	

Three Definitions of Oxidation

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

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):
- $Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$
- $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$

- 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 Rainey nickel -- his name was Rainey) 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.:
- $2H_2 + O_2 \rightarrow 2\ H_2O$ (requires a "spark" to catalyze this reaction)
- Hydrogen reacts with cupric oxide, e.g.,
- $CuO + H_2 \rightarrow Cu + H_2O$
- Hydrogen reacts with lead (II) oxide, e.g.:
- $PbO + H_2 \rightarrow Pb + H_2O$

Three Definitions of Reduction

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

Summary Thus Far

- 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.

The table, below, summarizes oxidation and reduction definitions:

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

- The combination of substances with hydrogen is the classic definition of reduction.
- When hydrogen has combined with substances, they are said to have been REDUCED.

Redox Reactions -- More Terms

- When a redox reaction occurs, one substance is reduced and another oxidized.
  - The substance that is reduced is the OXIDIZING AGENT.
  - The substance that is oxidized is the REDUCING AGENT, e.g.:

$$CuO + H_2 \rightarrow Cu + H_2O$$

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

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

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

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

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

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
* $8H^+ + Cr_2O_7^{2-}$ (orange) + $3C_2H_5OH \rightarrow 2Cr^{3+}$ (green) + $3C_2H_4O + 7H_2O$	# $C_6H_4(OH)_2$ (hydroquinone -- "developer") + $2Ag^+ \rightarrow C_6H_4O_2$ + 2Ag (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 ($H_2C_2O_4$): $5H_2C_2O_4 + 2MnO_4^-$ (purple) $+ 6H^+ \rightarrow 10\ CO_2 + 2Mn^{2+}$ (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 (brown) $+ 2Na_2S_2O_3 \rightarrow 2NaI$ (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 Ba^{2+}, Na^+, S^{2-} and for elements such as N_2, 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.

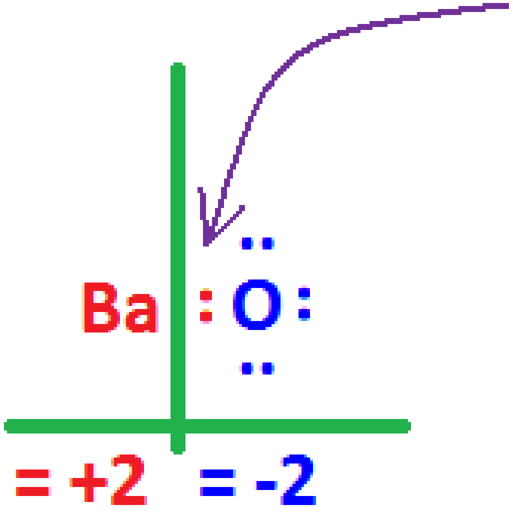
1. electrons shared between 2 unlike atoms are counted with the more electronegative atom and
2. electrons shared between 2 like atoms are divided between the sharing atoms.

E.g., determine the oxidation number of 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 N_2 is zero (0).

E.g., determine the oxidation numbers of Ba and O in 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_2	O_2	N_2	Ca
Oxidation Number	0	0	0	0

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

E.g.	Na^+	K^+	Sr^{2+}	F^-
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^+	Ba^{2+}	K^+	Mg^{2+}
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^+	H^-
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, its oxidation number is then -1:

E.g.	O^0	H_2O	H_2O_2 (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.	$KMnO_4$	K^+	Mn^{+7}	O^{-2}
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.	$Cr_2O_7^{-2}$	Cr^{+6}	O^{-2}
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(ox # of Cr^{+6}) + 7(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:
- $Cr_2O_7^{2-} + HNO_2 + H^+ \rightarrow Cr^{3+} + NO_3^- + H_2O$

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.

$$(Cr_2O_7)^{-2} = 2Cr + 7O$$

$$-2 = 2x + -14 \quad (7 \cdot -2)$$

$$\frac{-2+14}{2} = x = +6$$

$$HNO_2 = 1H + 1N + 2O$$

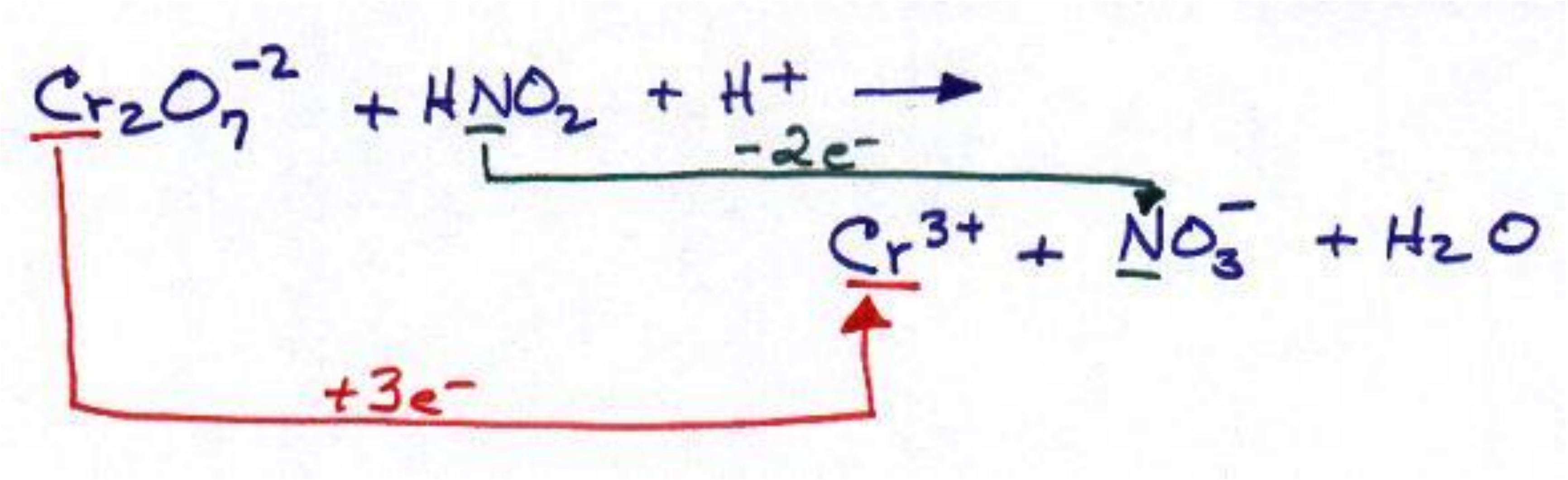
$$0 = (1 \cdot 1) + x + (2 \cdot -2)$$

$$0 = 1 + x + (-4)$$

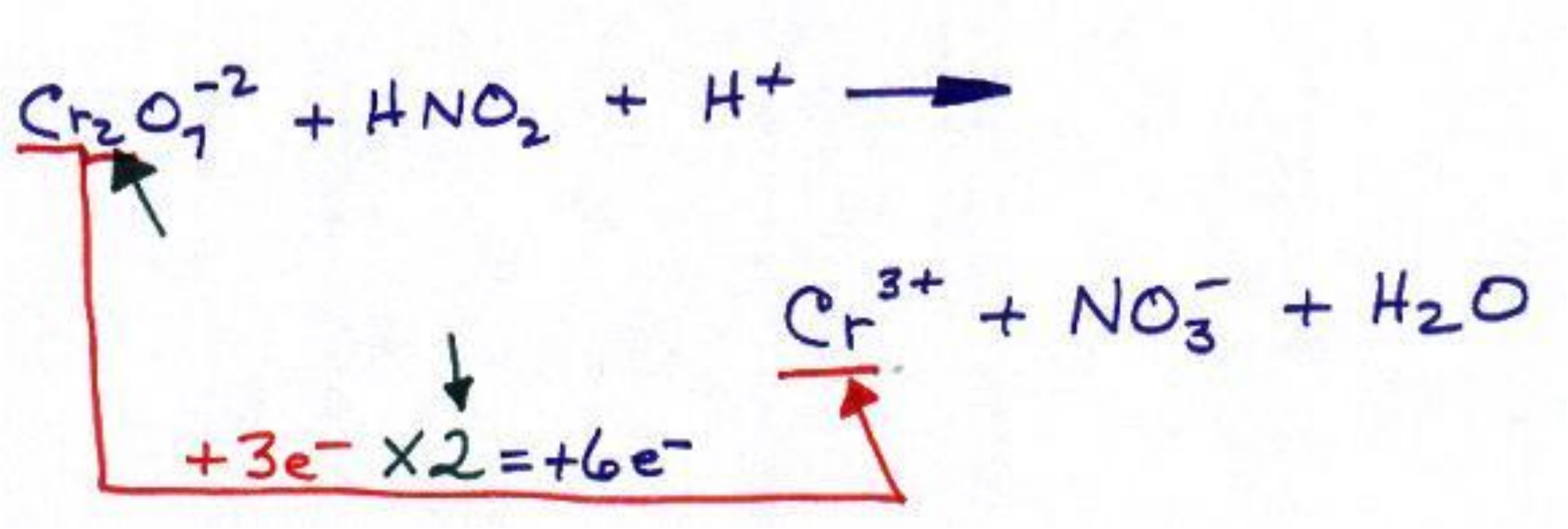
$$0 - 1 + 4 = x = +3$$

$$\overset{+6}{Cr_2}\overset{-2}{O_7}{}^{2-} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O_2} + H^+ \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O_3}{}^{-} + \overset{+1}{H_2}\overset{-2}{O}$$

- 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 ($Cr_2O_7^{2-}$) 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.

$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow Cr^{3+} + NO_3^- + H_2O$$

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

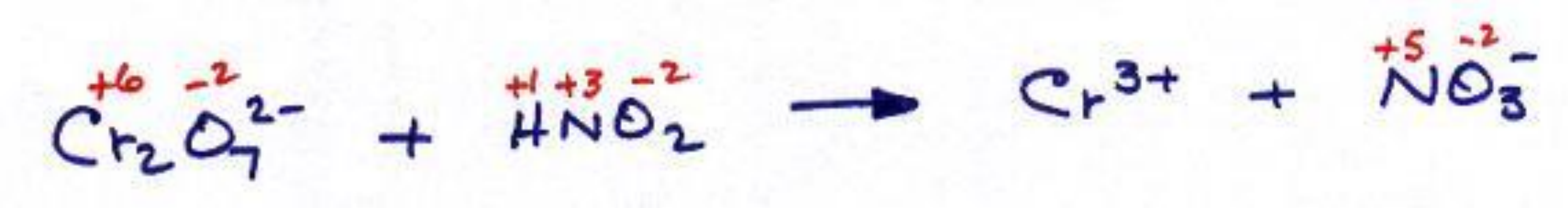
$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + H_2O$$

- 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.

$$Cr_2O_7^{-2} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

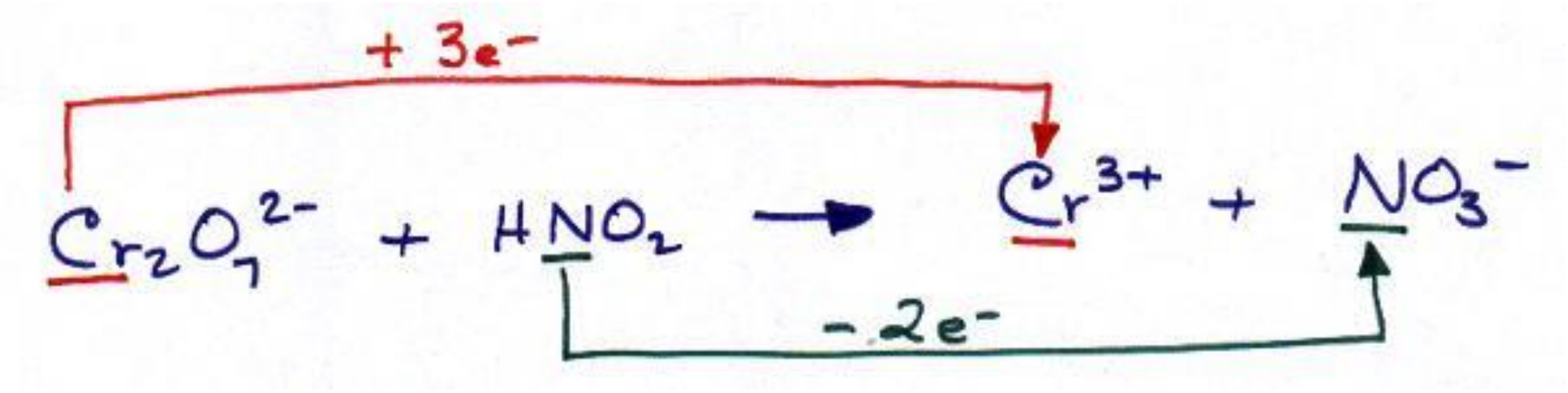
Method 2: Oxidation Number Method for Aqueous Solutions

- 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.



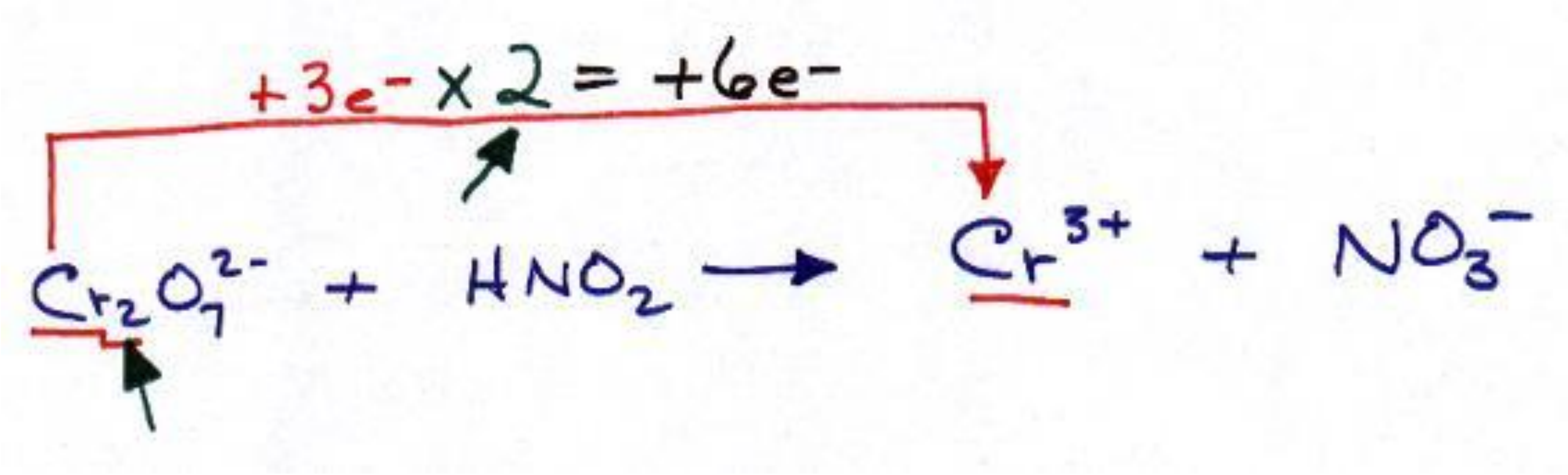
$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O}_2 \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O}_3^{-}$$

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



$$Cr_2O_7^{2-} + HNO_2 \rightarrow Cr^{3+} + NO_3^{-}$$

- Step Number Four: determine the loss and gain of electrons per formula unit -- this reaction is a great example: dichromate ion ($Cr_2O_7^{2-}$) 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.

$$Cr_2O_7^{2-} + 3HNO_2 \rightarrow Cr^{3+} + NO_3^-$$

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

$$Cr_2O_7^{2-} + 3HNO_2 \rightarrow 2Cr^{3+} + 3NO_3^-$$

- Step Number Seven: balance all but oxygen and hydrogen.
- Step Number Eight: Add up the charges on both sides of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^{-}$$

$$-2 + 0 = -2 \qquad\qquad +3 = +6 - 3$$

- Step Number Nine: balance the charges by adding H^+ for positive charges or OH^- for negative charges. Make sure the chemistry matches, e.g., H^+ for acidic reactions.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \rightarrow$$
$$2Cr^{3+} + 3NO_3^-$$

- Step Number Ten: Balance the oxygens by putting water (H_2O) on the side deficient in oxygen or the side opposite the hydroxide ions.
- Step Number Eleven: hydrogens ought to balance.
- Step Number Twelve: Write the balanced reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

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.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e^-$$

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

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3(HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e^-)$$

- 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 H^+;
  - 2) in BASE with 1 H_2O per needed hydrogen with an equal number of 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.

$$Cr_2O_7^{2-} + \overset{5}{\cancel{14}}H^+ + \cancel{6e^-} \longrightarrow 2Cr^{3+} + \overset{4}{\cancel{7}}H_2O$$

$$3\,HNO_2 + \cancel{3H_2O} \longrightarrow 3NO_3^- + \cancel{9H^+} + \cancel{6e^-}$$

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

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

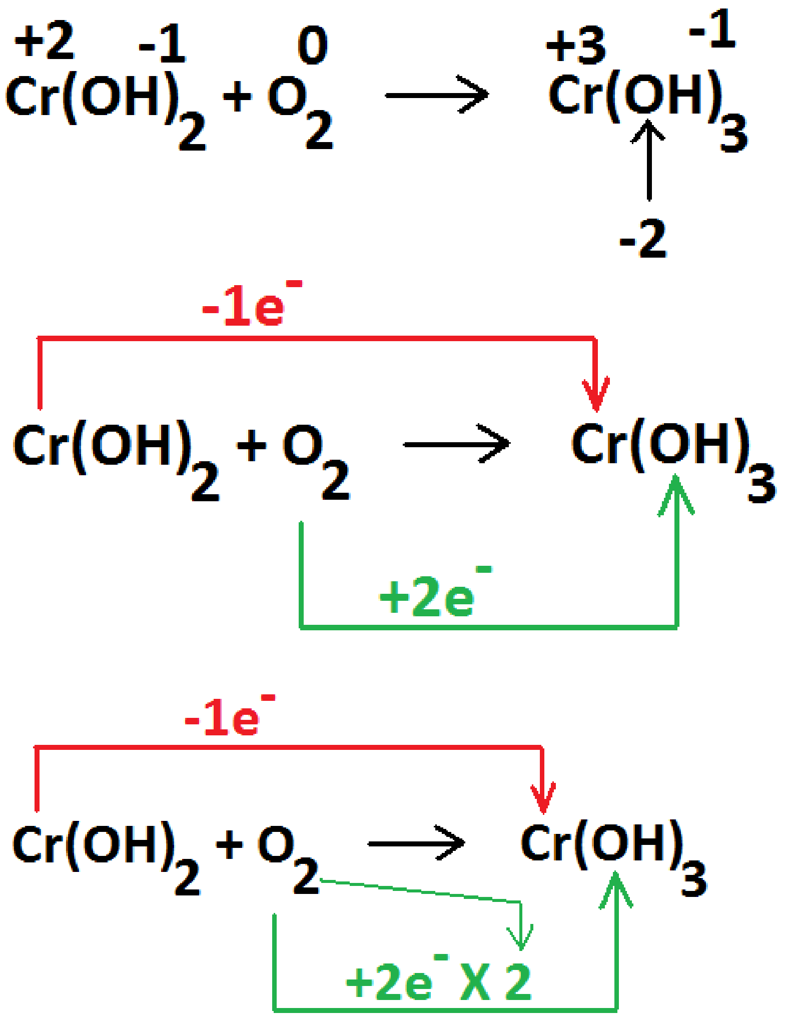
- One key concept to keep in mind is that if you've balanced the same reaction by each method above, and you don't get the same answer each time, then there is an error in the balancing.
- Go back and find it -- it usually jumps right out at you.

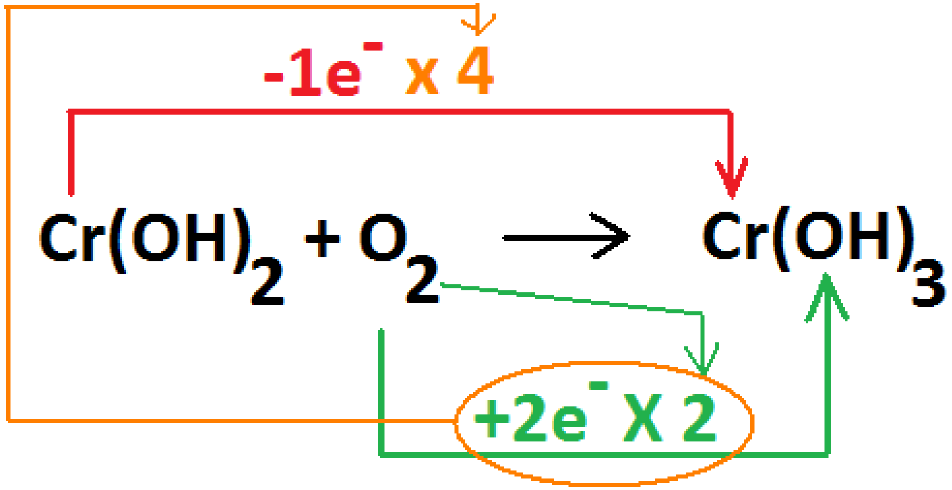
Redox Reactions with OH^-—Containing Reactions

- 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:

$$Cr(OH)_2 + O_2 \rightarrow Cr(OH)_3$$





$-1e^- \times 4$

$$Cr(OH)_2 + O_2 \longrightarrow Cr(OH)_3$$

$+2e^- \times 2$

$$4\,Cr(OH)_2 + O_2 \longrightarrow 4\,Cr(OH)_3$$

$$2H_2O + 4\,Cr(OH)_2 + O_2 \longrightarrow 4\,Cr(OH)_3$$

Non-Traditional Approach to The Same Reaction Considering Actual Chemistry

1. Write out the half-reaction for the redox pair – NOT the half reaction in the Tables of Electrochemical Potential
    1. This comes from working with redox pairs so you can identify them
    2. Do you see the “extra” OH^- in the top half reaction?
2. Balance all but H and O: DONE

$$Cr(OH)_2 \longrightarrow Cr(OH)_3$$

$$O_2 \longrightarrow OH^-$$

3. Balance O with water (H_2O)

$$H_2O + Cr(OH)_2 \longrightarrow Cr(OH)_3$$

$$O_2 \longrightarrow OH^- + H_2O$$

4. Balance H with H^+ as needed

$$H_2O + Cr(OH)_2 \longrightarrow Cr(OH)_3 + H^+$$

$$3\,H^+ + O_2 \longrightarrow OH^- + H_2O$$

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

$$H_2O + Cr(OH)_2 \longrightarrow Cr(OH)_3 + H^+ + 1e^-$$

$$4\,e^- + 3\,H^+ + O_2 \longrightarrow OH^- + H_2O$$

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

$$4\,H_2O + 4\,Cr(OH)_2 \longrightarrow 4Cr(OH)_3 + 4\,H^+ + 4e^-$$

$$4\,e^- + 3\,H^+ + O_2 \longrightarrow OH^- + H_2O$$

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

$$\overset{3}{\cancel{4}}H_2O + 4Cr(OH)_2 \longrightarrow 4Cr(OH)_3 + \overset{1}{\cancel{4}}H^+ + \cancel{4}e^-$$

$$4\cancel{e^-} + \cancel{3H^+} + O_2 \longrightarrow OH^- + \cancel{H_2O}$$

$$3H_2O + 4Cr(OH)_2 + O_2 \longrightarrow 4Cr(OH)_3 + OH^- + \underset{\uparrow}{H^+}$$

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:

$$\mathrm{OH^- + 3\,H_2O + 4\,Cr(OH)_2 + O_2 \longrightarrow 4Cr(OH)_3 + OH^- + H^+ + OH^-}$$

9. Combine and remove:

$$\mathrm{\cancel{OH^-} + 3\,H_2O + 4\,Cr(OH)_2 + O_2 \longrightarrow 4Cr(OH)_3 + \cancel{OH^-} + HOH}$$

10. Write the final balanced reaction:

$$\mathrm{3\,H_2O + 4\,Cr(OH)_2 + O_2 \longrightarrow 4Cr(OH)_3 + HOH}$$

$$\mathrm{\longrightarrow 2\,H_2O + 4\,Cr(OH)_2 + O_2 \longrightarrow 4Cr(OH)_3}$$

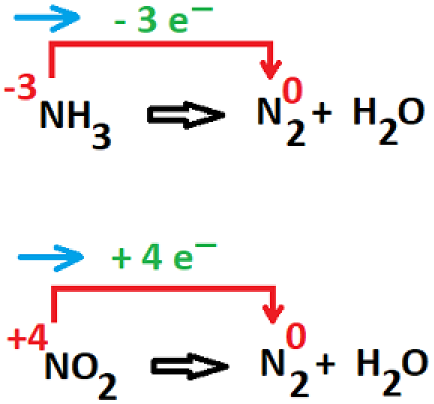
Out of The Box Redox Balancing

Heavy Critical Thinking and Knowledge-Based Creativity

$NH_3 + NO_2 \Rightarrow N_2 + H_2O$

Worksheet 28, 6 d

Requires a "different" kind of half reaction and critical thinking:



$- 3\ e^-$

$\overset{-3}{N}H_3 \Rightarrow \overset{0}{N}_2 + H_2O$

$+ 4\ e^-$

$\overset{+4}{N}O_2 \Rightarrow \overset{0}{N}_2 + H_2O$

A Very Different Redox Balancing Problem

A loss of 3 electrons does not equal a gain of 4 electrons, hence, since 12 is common between the two "different" kind of half reaction, quadruple the first and triple the second:

$$\overbrace{\overset{-3}{NH_3} \Rightarrow \overset{0}{N_2}}^{4(-3\,e^-)} + H_2O$$

$$\overbrace{\overset{+4}{NO_2} \Rightarrow \overset{0}{N_2}}^{3(+4\,e^-)} + H_2O$$

Add Coefficients for nitrogen ONLY

$$\overbrace{4\,NH_3 \Rightarrow 4\,N_2}^{4(-3\,e^-)} + H_2O$$

$$\overbrace{3\,NO_2 \Rightarrow 3\,N_2}^{3(+4\,e^-)} + H_2O$$

Balance hydrogen ONLY

$$\overbrace{4\,NH_3 \Rightarrow 4\,N_2}^{4(-3\,e^-)} + 6\,H_2O$$

Balance oxygen ONLY

$$\overbrace{3\,NO_2 \Rightarrow 3\,N_2}^{3(+4\,e^-)} + 6\,H_2O$$

Now, Add up the two "half" reactions

$$\begin{array}{rcl} 4\,NH_3 & \Rightarrow & 4\,N_2 + 6\,H_2O \\ 3\,NO_2 & \Rightarrow & 3\,N_2 + 6\,H_2O \\ \hline 4\,NH_3 + 3\,NO_2 & \Rightarrow & 7\,N_2 + 12\,H_2O \end{array}$$

Do you note that the N on the left is half that on the right?

Do you note that the H on the left is half that on the right?

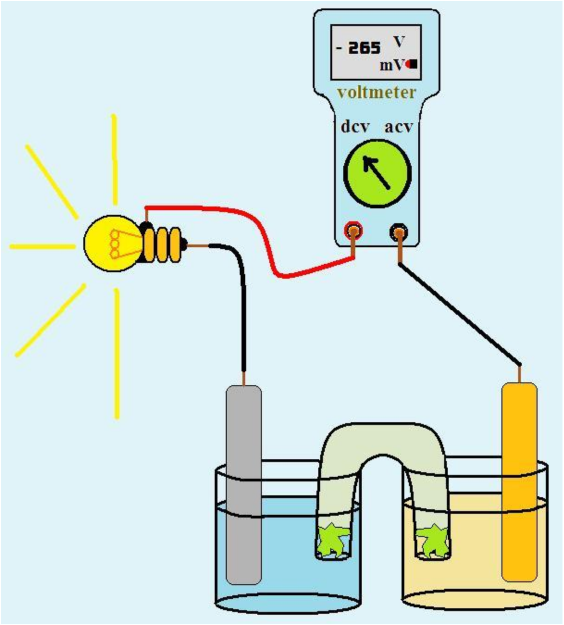
Do you note that the O in the left is half that on the right?

Simply double the ammonia and the nitrogen dioxide:

$$8\,NH_3 + 6\,NO_2 \Rightarrow 7\,N_2 + 12\,H_2O$$

And, it's balanced!

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.

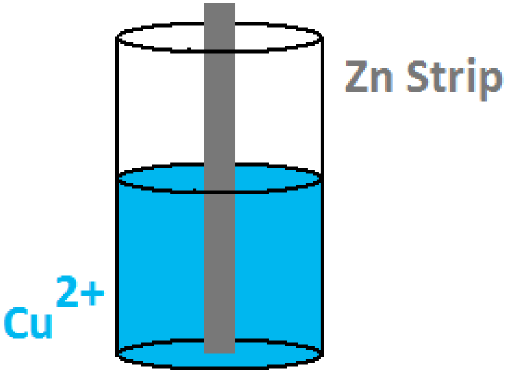
A very simple battery may be constructed by simply placing a zinc strip in an aqueous solution of copper (II) sulfate.

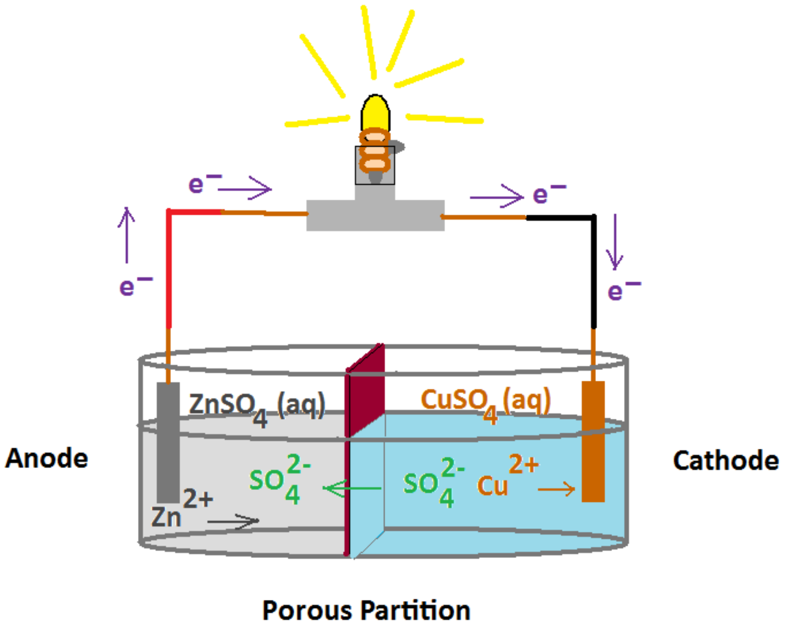
Over time, the zinc strip disappears and elemental copper precipitates.

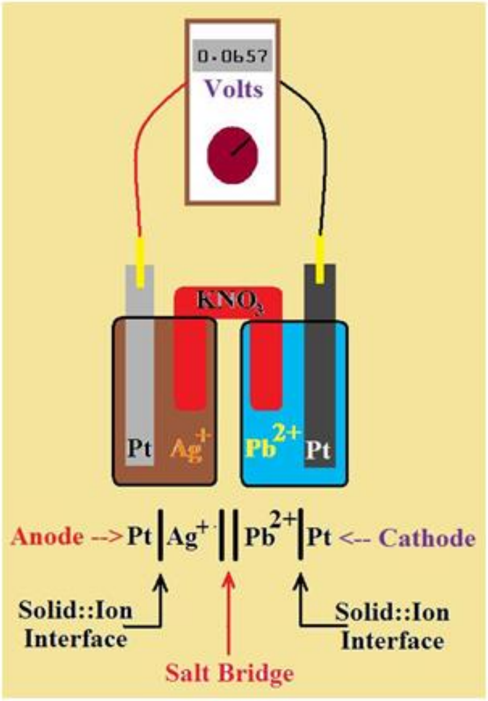
The reaction is:

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

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



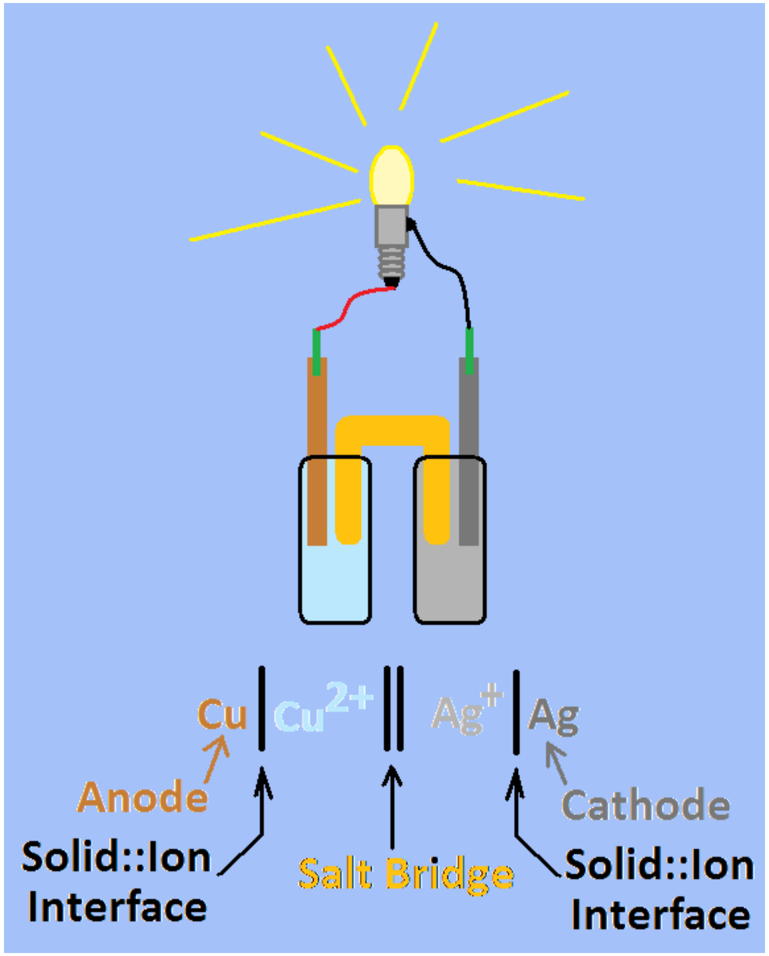




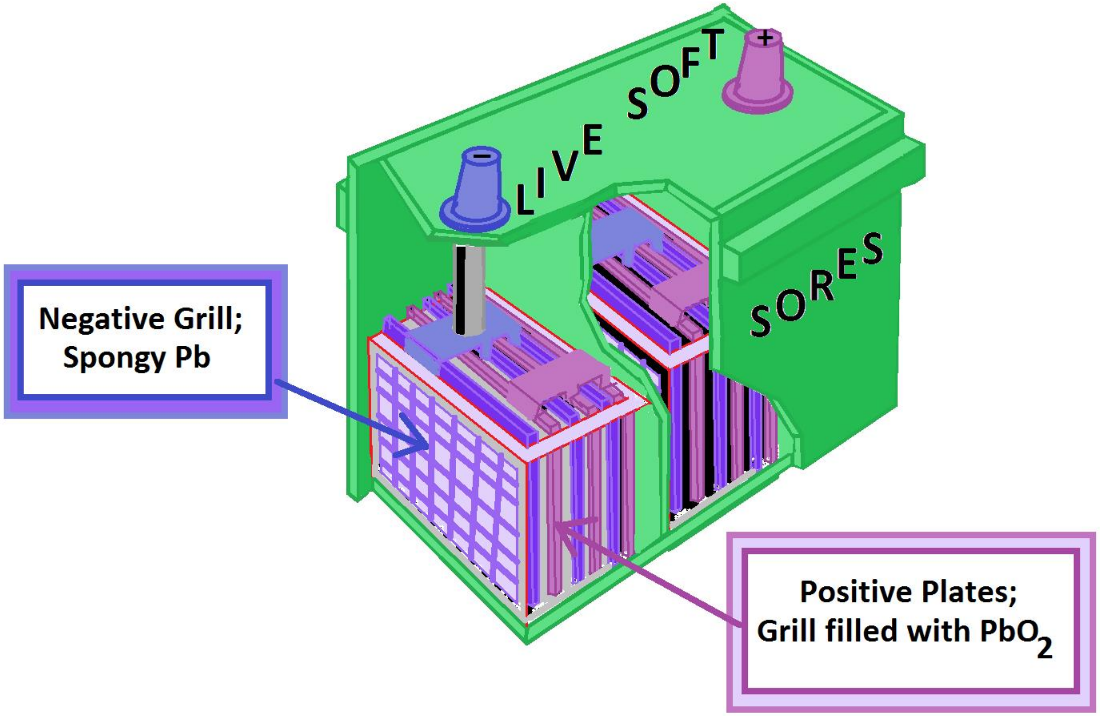
- The following graphic is an example of a fairly simple battery set up with a light in the circuit.
- Note the flow of electrons from the elemental zinc strip to the copper (II) side.
- The side of a battery that gives up electrons is the ANODE (I use the mnemonic "anoxia" -- "an" = anode and "ox" =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

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.
  - 1 solid vertical line indicates the solid::Ion interface (where you dip the metal electrode in the corresponding ionic solution)
  - 2 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)



- A car battery is a series of 6 cells wired in series. On discharge (when you start the engine), the following reaction occurs:
- $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$
- And on recharge (when your car is running and the generator or alternator is recharging it), the following reaction occurs:
- $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$



Negative Grill; Spongy Pb

Positive Plates; Grill filled with PbO_2

Used with permission from Duracell

Anode = Zinc (Zn)

Cathode = manganese dioxide (MnO_2)

Electrolyte = potassium hydroxide (KOH)

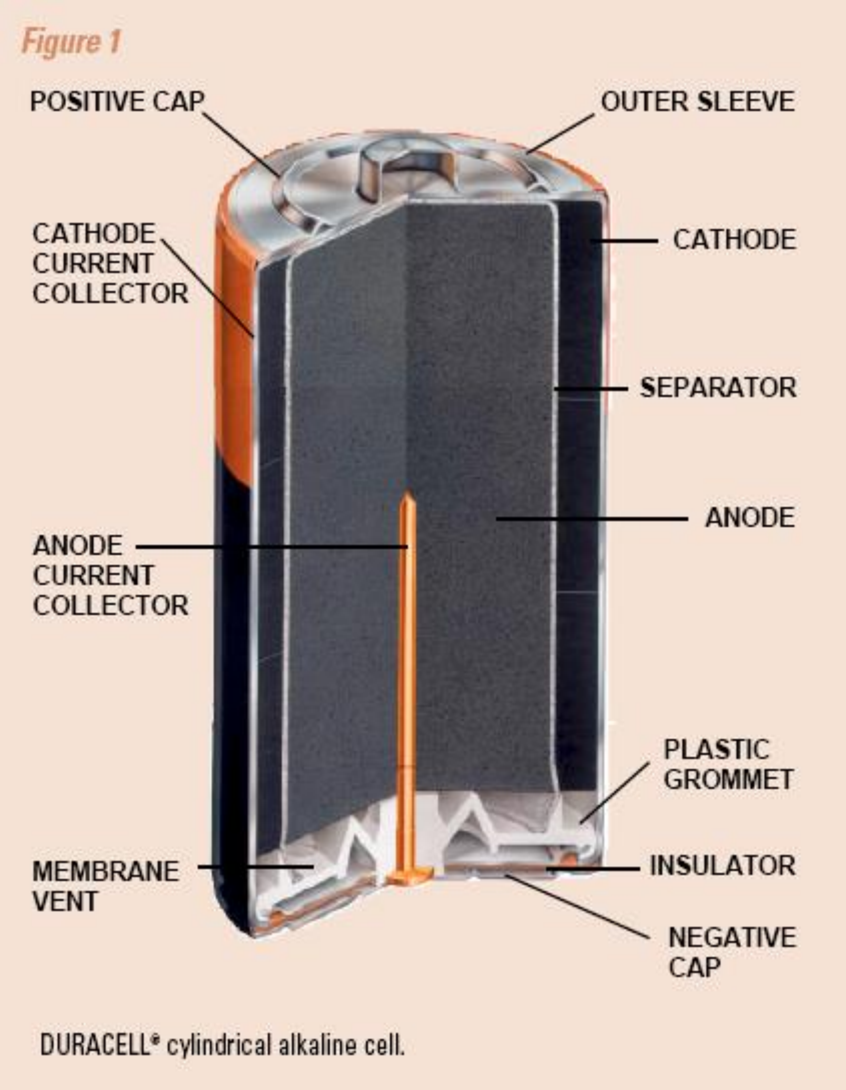
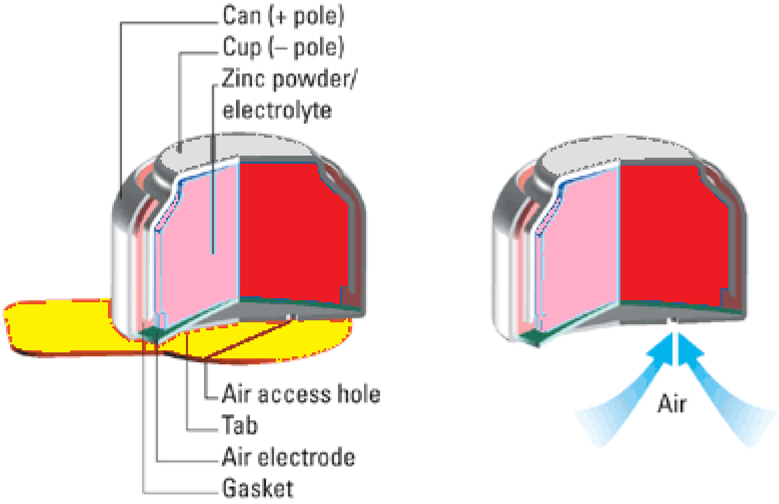


Figure 1

DURACELL® cylindrical alkaline cell.

Zinc-Air Batteries

- Left: Inactivated (tab in place)
- Right: Activated (tab removed)
- Research is exploring battery development to run off of a person's blood sugar – ramifications: pacer's/defib's



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

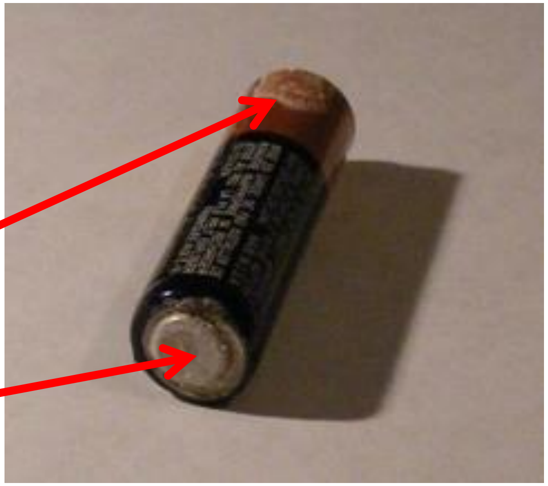
Fluid: $Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2\ OH^-$

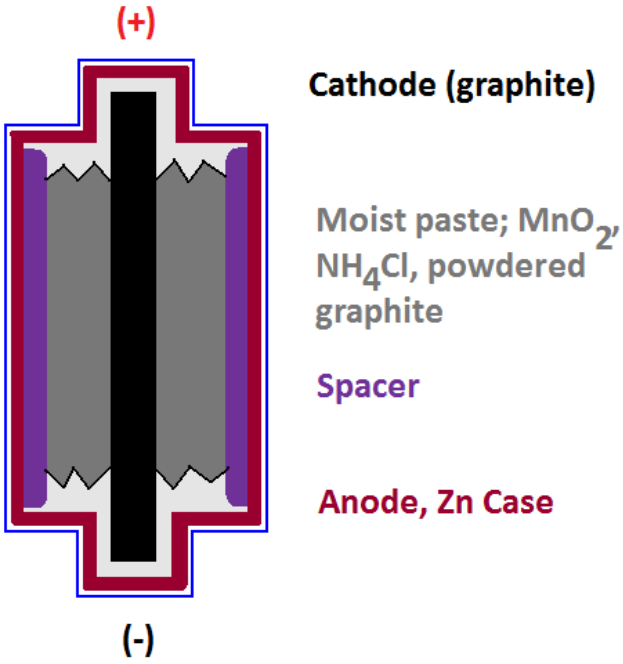
Cathode: $\frac{1}{2}\ O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-$

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

ca 1.60 V produced theoretically

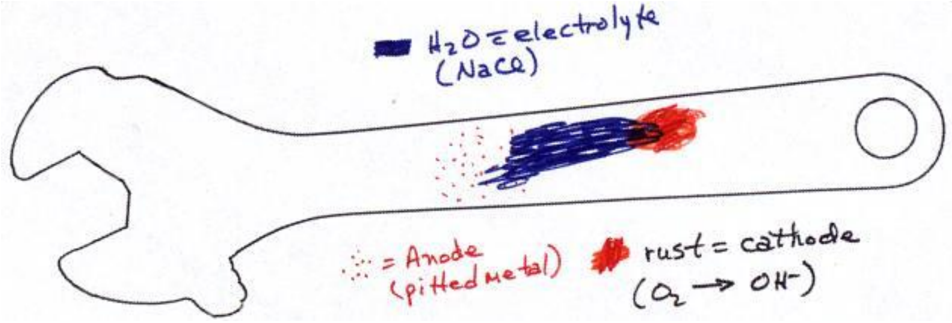
- Dry cells have been around quite a while, now.
- While each manufacturer has its own style, they all pretty much follow, in very general terms, the graphic of a generic dry cell.
- The cathode is a piece of graphite and the anode is the zinc case.
- It is the latter "disappearing" as the battery runs 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:
- $Zn + 2MnO_2 + 2H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$





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

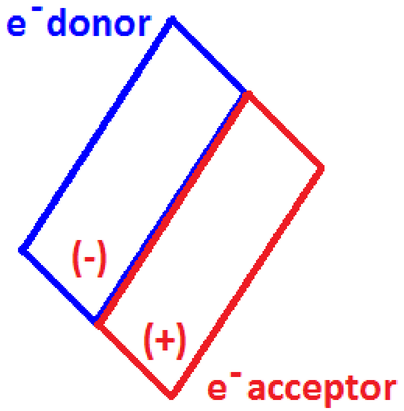
The reactions that occur on this wrench are as follow:

Location	Reaction
At anode	$Fe \rightarrow Fe^{2+} + 2e^-$
At cathode	$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
Also at cathode	$Fe(OH)_2 + O_2 \rightarrow Fe(OH)_3$; $Fe(OH)_3 + O_2 \rightarrow Fe_2O_3$

The pitting makes the wrench more chemically reactive.

Solar Batteries

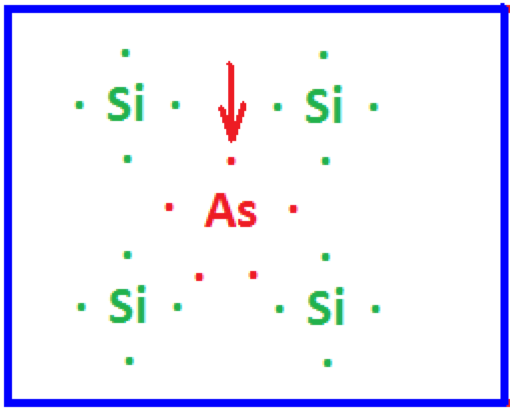
- Solar power has gone through numerous changes.
- Changes tend to be very rapid.
- Hence, this is a very generic, low-key description to give you the idea behind solar batteries.

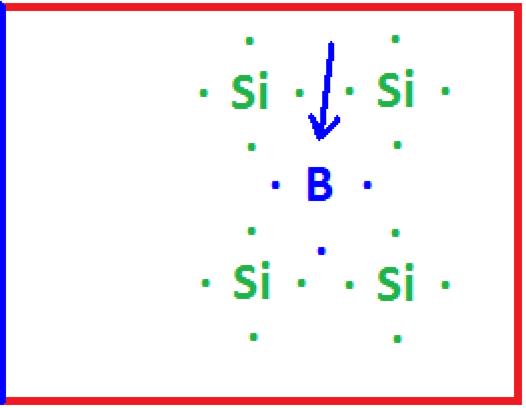


- In general, a solar battery is made up of two "wafers" of material: an electron donor wafer and an electron acceptor wafer.

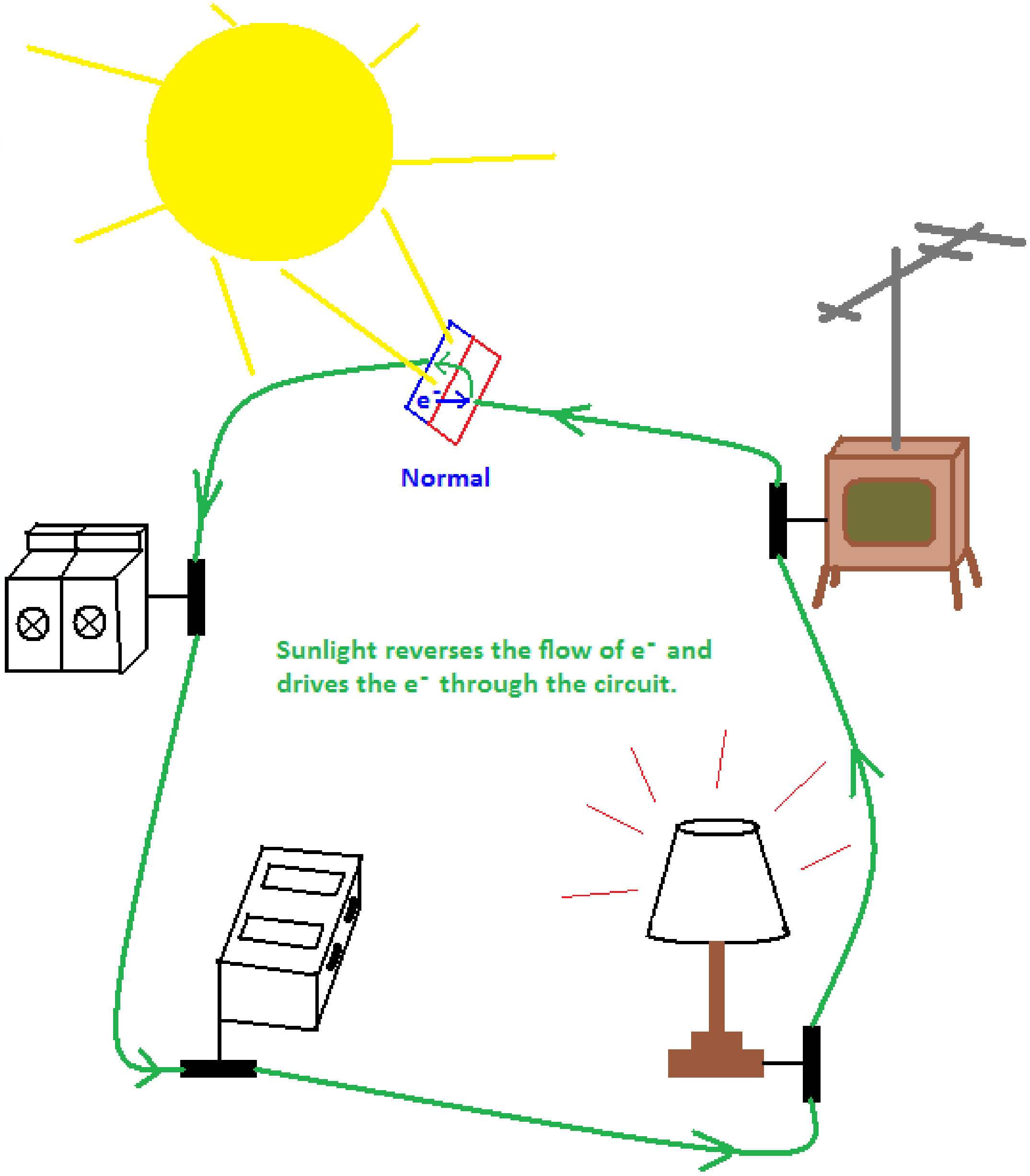
The table, below, summarizes the characteristics of the donor and acceptor wafers:

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).



- ✓At the time I put this together, solar cells were only about 10% efficient in energy conversion.
- ✓Efficiencies, now, range from 8-20% depending on the technology and manufacturer
- ✓What the 10% meant was that to operate one 100W bulb would require a series of solar cells 1m by 1m.
- ✓At that time, 5000 acres of solar cells would produce the energy equivalent to one nuclear power plant.
- ✓To give you some perspective on this, one section of land is 640 acres and is one mile by one mile.
- ✓This means that it would take (at old efficiency rates) a piece of ground that is 8 sections or 8 square miles in area (equivalent to a strip of land 4 miles long and 2 miles wide).

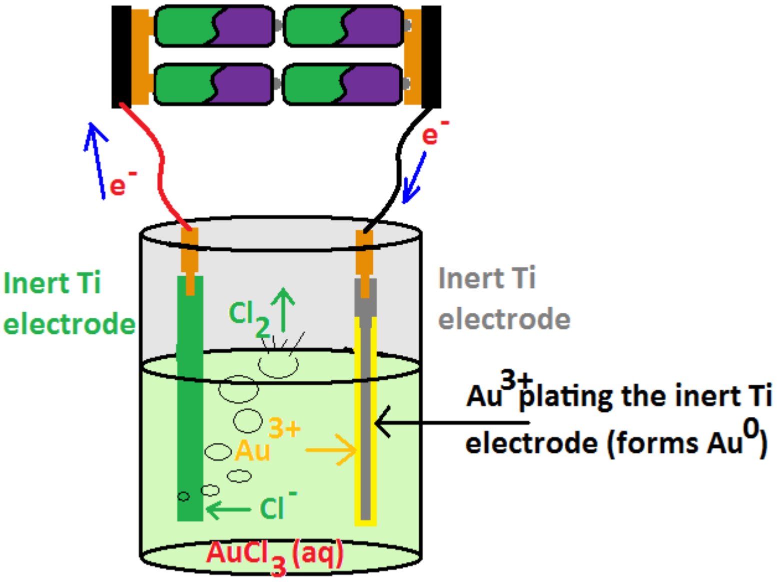
Electrolysis

Electrical energy is used to drive an otherwise "not runable" 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 are tabulated, below:

Location	Reaction
Anode	$2Cl^- \rightarrow Cl_2 + 2e^-$
Cathode	$Au^{3+} + 3e^- \rightarrow Au$

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