Spring, 2016

<u>Osher Five Lecture Series</u>

Russell Doolittle

Lecture 1: Avogadro's Number

Lecture 2: The Discovery of X-Rays

Lecture 3: Nature of the Atomic Nucleus

Lecture 4: Sickle Cell Anemia: a Molecular Disease

Lecture 5: Unraveling the Genetic Code

Osher Lecture 1

Avogadro's Number

Russell Doolittle

April 6, 2016

What *is* Avogadro's number?

The number of atoms or molecules in one gram-atomic or gram-molecular weight.

A gram-atomic or gram-molecular weight is how much a defined amount of an element or compound weighs in grams.

But what is the value of the number?

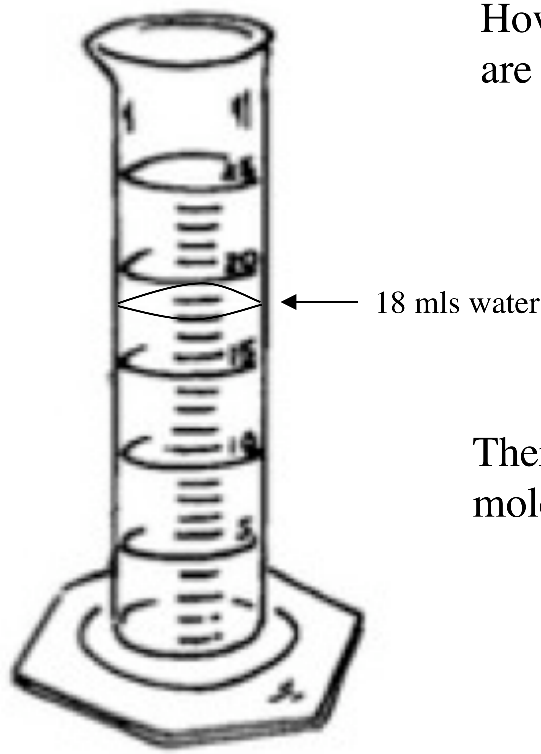
6.02×10^{23}

6,020,000,000,000,000,000,000,000

Six hundred and two thousand billion billion

Avogadro's number is one of the most important entities in all of science. It can be considered a *unifying* constant, uniting the counting of all natural substances.

Consider a cylinder with 18 mls of water.



How many molecules of water are there in the cylinder?

The gram-mol-wt of water is 18 (two hydrogens @ 1, one oxygen @ 16).

The density of water is 1.00 g/ml.

There are approximately 6×10^{23} molecules of water in the cylinder.

Some 19th century chemists

John Dalton (English)

Joseph Gay-Lussac (French)

Amadeo Avogadro (Italian)

Berzelius (Swedish)

Michael Faraday (English)

James Maxwell (English)

Ludwig Boltzmann (Austrian)

Stanislao Canizzaro (Italian)

Josef Loschmidt (Austrian)

What did they know and when did they know it?

Avogadro didn't know his number.

What he *did* know was that there *must be* such a number.

In 1808 the French chemist Joseph Gay-Lussac announced the Law of Combining Volumes for gases.

Stated simply, when two gaseous substances are combined in a chemical reaction, they react in ratios of small numbers.

300 volumes of hydrogen plus 100 volumes of nitrogen gave rise to 200 volumes of ammonia gas.

(Hmmm. Where did the missing volumes go?)

today we would write: $3H_2$ (g) + N_2(g)-----> $2NH_3$(g)

100 volumes of ammonia plus 100 volumes of gaseous HCl gave rise to solid ammonium chloride *with no gas left over*!

today we would write: NH_3 (g) + HCl (g) -----> NH_4Cl (s)

At the start of the 19th century the notion of atoms as elementary particles was in a state of confusion.

In discussions about the smallest units of matter, the terms "particles", "atoms" and "molecules" were being used interchangeably.

There were frequent discussions about "atoms" of water and air.

Electricity and magnetism were beginning to be understood.

It was appreciated that opposite charges attract and similar ones repel.

However, protons and electrons (and neutrons) were stll unknown.

Much of the confusion had to do with several elemental gases being *diatomic*.

Today we know that hydrogen, nitrogen, oxygen and chlorine, all of which were available in the early 19th century and were being used in experiments, are diatomic gases.

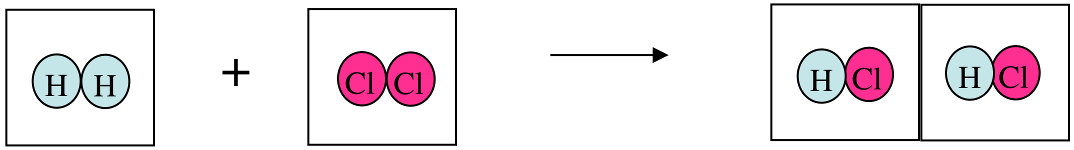
H_2 N_2 O_2 Cl_2

H-H N-N O-O Cl-Cl

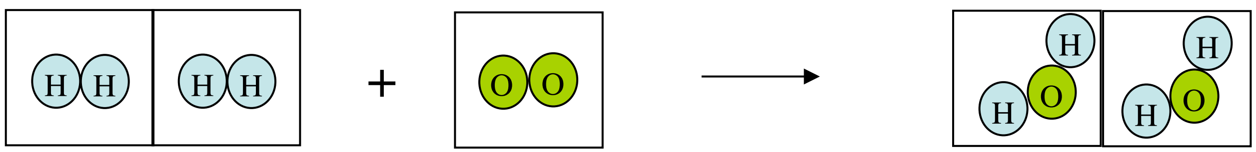
The notion of atoms being associated by having opposite electrical charges was just taking hold, and the thought of identical atoms being joined didn't seem plausible at the time.

But Avogadro reasoned that it must be so.

1 vol hydrogen 1 vol chlorine 2 vols HCl



2 vols hydrogen 1 vol oxygen 2 vols water (gas)



(all in gaseous state)

Each box = 1 volume
contains one molecule.

Avogadro saw something in these results that was eluding others.

If there really were no gases remaining when equal volumes of ammonia and hydrochloric acid were reacted, then there must have been the same number of *molecules* in each of the original equal volumes.

The important matter was the number of *molecules,* which he clearly distinguished from the number of atoms.

In 1811 he published his now famous hypothesis:
equal volumes of gases under the same conditions have equal numbers of molecules.

Indeed, it was Avogadro who introduced the concept of the molecule as being a discrete unit of clustered atoms.

But it was a time of great confusion in chemistry, especially raging around the elemental nature of atoms.

It would take 50 years before chemists became convinced that Avogadro was correct, by which time he was dead.

Although it was clear to Avogadro, and later Cannizzaro, that equal volumes of gases had the same number of molecules, it needs to be appreciated that these equal volumes had different weights.

Weights* of some gases (gms/liter)

hydrogen	0.0899
nitrogen	1.2568
oxygen	1.429
chlorine	3.214
methane	0.715
ammonia	0.771
carbon monoxide	1.25
carbon dioxide	1.977

*(really densities if given in weight/volume.)

So, how does one weigh a gas?

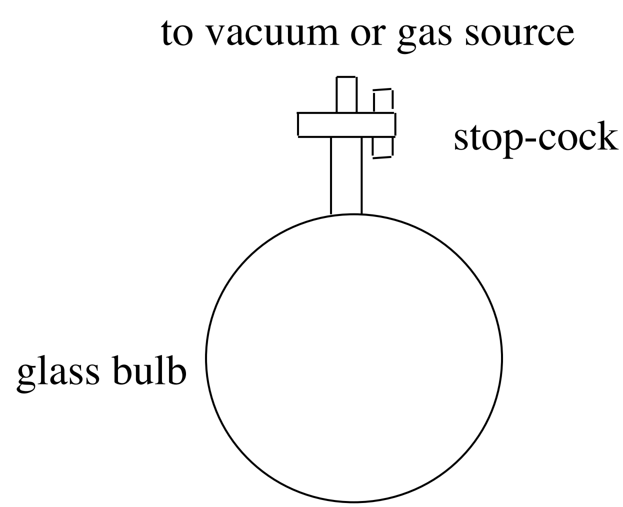
1. Remove air from a bulb of known volume with a vacuum pump.

2. Carefully weigh the empty bulb.

3. Fill the bulb with some pure gas.

4. Re-weigh the bulb with gas and subtract the weight of the empty bulb.

5. The weight of the gas divided by the volume of the bulb is the gas density.



The key is that these weights are proportional to the weight of the atoms that constitute the molecules themselves.

"weights" of gases (gms/liter)		ratio to hydrogen	
hydrogen	0.0899	0.0899/0.0899 = 1	correct
nitrogen	1.2568	1.2568/0.0899 = 14	
oxygen	1.429	1.429/0.0899 = 16	
chlorine	3.214	3.214/0.0899 = 35	
methane	0.715	0.715/.0089 = 8	incorrect
ammonia	0.771	0.771/.0089 = 8.5	
carbon monoxide	1.25	1.25/.0089 = 14	
carbon dioxide	1.977	1.977/.0899 = 22	

So, although the relative weights for *elemental* gases seemed correct, the results for gaseous *compounds* were all off by a factor of 2.

The reason was, of course, that hydrogen gas has a molecular weight of 2! It is a diatomic gas, as are nitrogen, oxygen and chlorine.

Knowing that fact, we see that the molecular weight of CO is 28 (not 14), CO_2 is 44 (not 22) and ammonia is 17 (not 8.5).

The key is that these weights are proportional to the weight of the atoms that constitute the molecules themselves.

"weights" of gases (gms/liter)		ratio to hydrogen	molecular weight
hydrogen	0.0899	0.0899/0.0899 = 1	(2 x 1 = 2)
nitrogen	1.2568	1.2568/0.0899 = 14	(2 x 14 = 28)
oxygen	1.429	1.429/0.0899 = 16	(2 x 16 = 32)
chlorine	3.214	3.214/0.0899 = 35	(2 x 35.5 = 71)
methane	0.715	0.715/.0089 = 8	(CH_4 = 16)
ammonia	0.771	0.771/.0089 = 8.5	(NH_3 = 17)
carbon monoxide	1.25	1.25/.0089 = 14	(CO = 28)
carbon dioxide	1.977	1.977/.0899 = 22	(CO_2 = 44)

If we correct for the relative molecular weights we find that the volumes of one mole of the gases are all the same!

densities of gases (gms/liter)		mol weight	gm-mol-wt/density	
hydrogen	0.0899	2	2/0.0899 =	22.24 liters
nitrogen	1.2568	28	28/1.2568 =	22.78
oxygen	1.429	32	32/1.429 =	22.38
chlorine	3.214	71	71/3.214 =	22.09
methane	0.715	16	16/0.715 =	22.38
ammonia	0.771	17	17/0.771 =	22.05
carbon monoxide	1.25	28	28/1.25 =	22. 40
carbon dioxide	1.977	44	44/1.977 =	22.26

22.4 is another well-remembered number related to Avogadro's hypothesis.

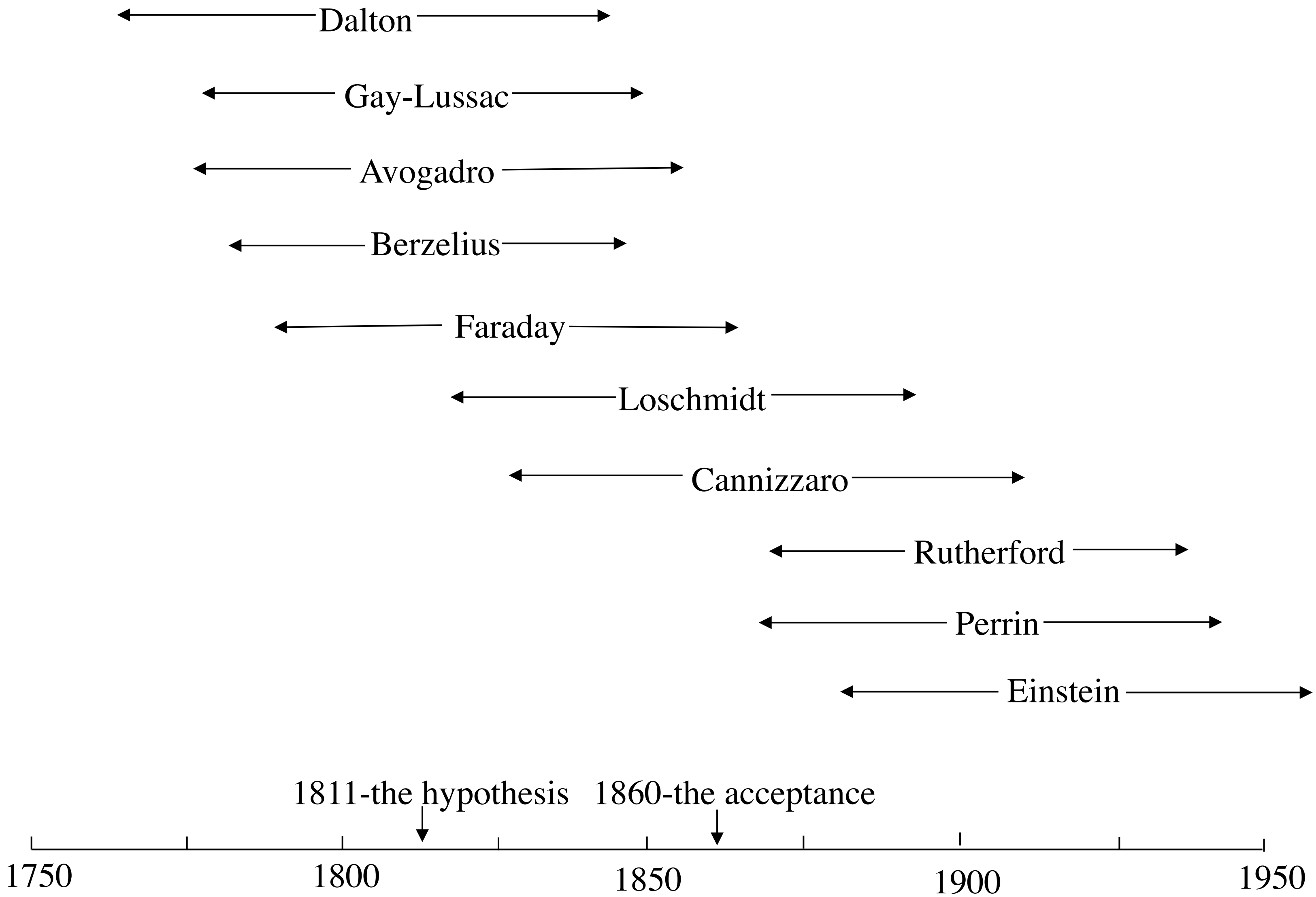
Under standard conditions (P = 1 atmosphere, T = 298 deg K), one gram-molecular weight ("1 mole") of an ideal gas occupies 22.4 liters.

22.4 liters is equivalent to about 3.5 basketball volumes.

One mole of water vapor (or steam) amounts to 3.5 basketballs, but one mole of liquid water is only about a cupful!

Obviously, the molecules in a gas must be much further apart than they are in a liquid.

It took 50 years for Avogadro's hypothesis to be generally accepted.


Dalton
Gay-Lussac
Avogadro
Berzelius
Faraday
Loschmidt
Cannizzaro
Rutherford
Perrin
Einstein
1811-the hypothesis
1860-the acceptance
1750
1800
1850
1900
1950

The acceptance came in the wake of a conference of chemists held in Karlsruhe, Germany, in1860. A fellow Italian, Stanislao Cannizzaro, convinced some of the assembled scientists that Avogadro had gotten it right with his 1811 hypothesis. Eventually the number itself was named in his honor.

Freshman seminar: October, 2015 (17 students)

What is Avogadro's number?

all correct	4 students wrote	6.022×10^{23}
	6 students wrote	6.02×10^{23}
	1 student wrote	6×10^{23}
	1 student wrote	6.02242061239999942069
	1 student wrote	6.022×10^{-14}
	1 student wrote	6.0023×10^{-6}
	1 student wrote	2.64×10^{28}
	1 student wrote	2.036497×10^{-23}
	1 student wrote	"a number discovered by Avogadro."

In most of Europe, the metric system took hold in the wake of the French Revolution (1789). In 1791 the French Academy of Science appointed a committee to measure and define the meter as one-ten millionth of the distance between the Earth's equator and a pole.

	Metric	English
distance	meter, kilometer	yard (foot, inch)
volume	liter, ml, etc.	pint, quart, gallon
mass (weight)	gram, kilogram	ounce, pound
temperature scale	Centigrade	Fahrenheit
heat energy	calories	BTU's
time	seconds, etc.	seconds, etc.

Supposing the English system had prevailed in Europe:

Avogadro's number would likely have corresponded to
1.0 *ounce*-molecular weight.

1 kilo = 2.2 lbs = 35.2 ounces. 1.0 gm = 35.2/1000 oz

1.0 ounce = 28.5 gms.

Avogadro's number would have been $28.5 \times 6.2 \times 10^{23}$

$= 1.8 \times 10^{25}$

In America, in 1792, Thomas Jefferson tried to convince the Congress that the USA should go decimal and adopt the metric system.

Congress approved the idea for money (dollars, cents) but refused to go along for weights, distances, etc., because too much land had already been apportioned using feet and square miles.

In 1800 James Watt (of steam engine fame) reported that 1 cubic inch of water was transformed by heating into 1 cubic foot of steam, calculated to be a volume increase of about 1684-fold (12 x 12 x 12 = 1684).

As such, the particles (called atom-associations at the time, but now called molecules) must be much further apart in steam than they are in the liquid.

Today we would note that 18 mls of water are transformed into 22.4 liters of steam, an increase of 1244-fold.

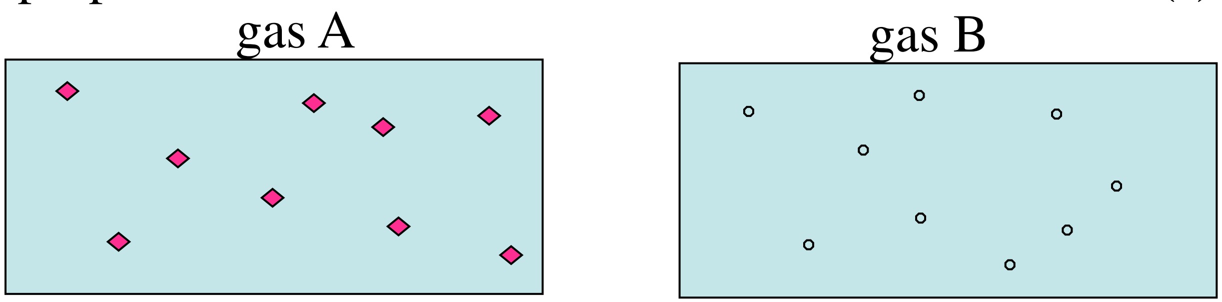
If there had been 11 inches per foot, Watt would have come closer to the truth (11" x 11" x 11" = 1331-fold).

But, *why* should equal volumes of gases have the same number of molecules?

The key is "under the same conditions of pressure and temperature."

The parameters are pressure (P), volume (V), temperature (T) and number of molecules (n). V and n are fixed by the hypothesis.

P is proportional to the number of collisions with the wall(s) per minute.



(a situation where both boxes have the same number of molecules)

larger and slower

smaller and faster

fewer collisions with more impact

more collisions with less impact

P [fewer collisions with more impact] = P [more collisions with less impact]

The argument for $T_A = T_B$ follows a similar course.

Temperature (T) is a measure of molecular motion, or, more accurately, a measure of the kinetic energy of the moving particles (molecules).

$E_{kinetic} = 1/2\ mv^2$, where m = mass and v = velocity.

The smaller m of the molecules in gas B is offset by the greater velocity (v^2).

T [larger mass but slower] = T [smaller mass but faster]

So, even without experiment, the Kinetic Theory (Boltzmann, 1860) provides the logic for the same volumes of two gases having the same number of molecules.

But, what is that number?

Some Ways of Determining Avogadro's Number

1. Kinetic Theory: Measure average speed of molecules in gas, count collisions, estimate size.

2. Brownian Motion. Particles in liquid behave like molecules in gas.

3. Electrolysis and anodal deposition. Measure current and weigh deposit.

4. X-Ray Diffraction through crystals gives distances between atoms or molecules in a solid.

5. Oil and water: surface spreading measurements.

6. Radioactivity. Measure volume of helium produced during decay.

It must be clear that Avogadro's number is not restricted to gases! It has to do with everything: solid, liquid and gas.

Today we will briefly describe only a bit of one of the six methods ("oil and water").

Some of the others will be described briefly in subsequent lectures.

An important aspect having to do with Avogadro’s number has to do with the size of the molecules.

How big is a molecule? Or, better, how small is a molecule?

Not visible to the naked eye. Not visible with a (light) microscope.

Pretty small.

Long before Avogadro’s hypothesis, Benjamin Franklin almost came up with an answer.

It had to do with “oil and water do not mix.”

Reading reference: "Ben Franklin Stilled the Waves" (C. Tanford, 2004)

Back in the 1790's, Franklin took a teaspoon of oil (castor oil?) and tossed it on the water of a small pond on the south side of London (Clapham Common).

The oil spread around on the surface until it had covered about a half acre.

Franklin had done similar experiments before and had been thinking about this a lot.

But affairs of state must have precluded his coming up with the big answer: to wit, the size of a "molecule" (he was using the term "particle.")

What was happening was a three-dimensional problem had become two-dimensional.

1 teaspoon of oil became a half acre of oil.

Because oil and water don't mix, the half acre of oil must be only one-molecule thick!

1 teaspoonful $= 5\ cc^3$.

half an acre $=$ 2,000 square meters $= 2 \times 10^7\ cm^2$.

height = volume/area $= 5\ cm^3 / 2 \times 10^7\ cm^2 = 2.5 \times 10^{-7}$ cm
= 25 Angstroms

If we assume no space between cube-shaped molecules in a liquid,

Avogadro's number = area / height^2 $= 20 \times 10^6\ cm^2 / 6.25 \times 10^{-14}$

$= 3 \times 10^{20}$

Not a terrible result considering all the estimates involved.

Closer than some of the students in the freshman seminar.

Website for downloading a pdf of today's lecture:

http://dogfish.ucsd.edu

Go to the tab "Lectures"

The website also lists a reading suggestion for next weeks lecture:

"Going to the Synchrotron"
(contains a section on X-ray crystallography)

(the following pictures only for use in discussion)

What is the Kinetic Theory all about?

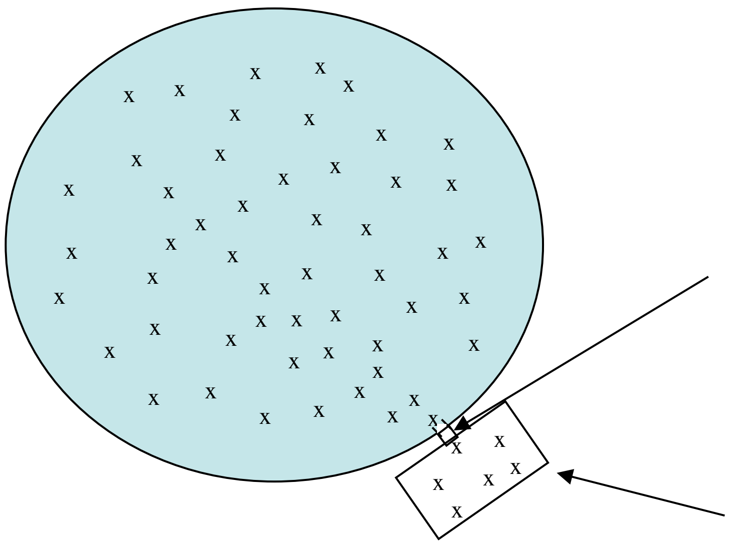
Briefly put, all atoms and molecules and other particles are in a state of perpetual motion (kinesis = motion).

$$\text{kinetic energy} = 1/2\, mv^2$$

m = mass of the particle, v = its velocity.

Finding the Speed of a Gaseous Molecule

The (average) speed of a gaseous molecule can be determined by effusion experiments in which a tiny escape hole is opened in a container of the gas. The faster the molecules are moving, the more that will escape per unit time.



very, very small hole allows molecules to escape without changing conditions in the bulk holder.

collector: rate of arrival tells average speed.

As we have already suggested, the speed of a gaseous molecule is inversely proportional to its molecular weight. Heavier molecules move slower than lighter ones.

More quantitatively, the speed of a gaseous molecule is inversely proportional to the *square root* of its molecular weight.

For example, oxygen is 16 x heavier than hydrogen. The square root of 16 is 4. Therefore, we expect hydrogen to move 4 x faster than oxygen.

Relative effusion rate of hydrogen = 3.607 (relative to air).

Relative effusion rate of oxygen = 0.950 (relative to air).

3.607 / 0.950 = 3.79. (pretty close)

The true speed of a hydrogen molecule at room temperature is approximately 1700 meters/second (about the same as a rifle bullet).

In 1865 Josef Loschmidt realized that knowing the *size* of the molecules in a gas was a key to the solution, as well as how fast they were moving (velocity).

He got these by figuring the number of inter-molecular collisions that were occurring. The more of these collisions per unit time, the bigger the molecules must be.

In the end, he was able to determine the fraction of the gas that was occupied by the molecules themselves.

He then used the known amount of volume change in going from the gas to the liquid, assuming that in the liquid the molecules themselves occupied most of the total volume.

Loschmidt's result was 2.6×10^{19} molecules/cc

($22{,}400 \times 2.6 \times 10^{19} = 5.8 \times 10^{23}$ molecules)

Brownian Motion

In 1827, the botanist Robert Brown was using a microscope to observe pollen grains suspended in water. He noticed that they were continually in motion. He thought this was an indication of an internal vital force in the pollen, but it was later found to occur even in suspensions of totally inert materials.

In 1905 Einstein published a paper theorizing that such movements were manifestations of the Kinetic Theory the same as had been proposed for gases.

In 1912 Jean Perrin reported a series of experiments proving that Einstein was correct. Indeed, these experiments were validation of the Kinetic Theory.

Jean Perrin's 1909 Experiments

1. Prepare a uniform population of microscopically visible yellow spheres (Gamboge latex).

2. Track their movements over time by observing with a microscope and a camera lucida device.

3. Calculate mean square displacement. Plug into Einstein formula and calculate N.

4. $N = 5.9 \times 10^{23}$ (close enough!)

In 1915 X-ray diffraction (lecture number 2) was used to measure how far apart the atoms were in a salt. It was possible to compute the number of atoms per gram-mol-weight directly.

In 1918 Ernest Rutherford calculated Avogadro's number on the basis of radioactivity (lecture number 3).

Another way to calculate the number is from the spreading of oil on water. Reading reference: "Ben Franklin Stilled the Waves" (C. Tanford, 2004)

Electrolysis and Michael Faraday

In 1833 formulated his laws of electrolysis.

The mass of a substance deposited upon an electrode is proportional to the amount of electricity that is passed through the system.

But it was not until 1911 that the amount of electricity on an electron was determined (Millikan oil drop experiment).

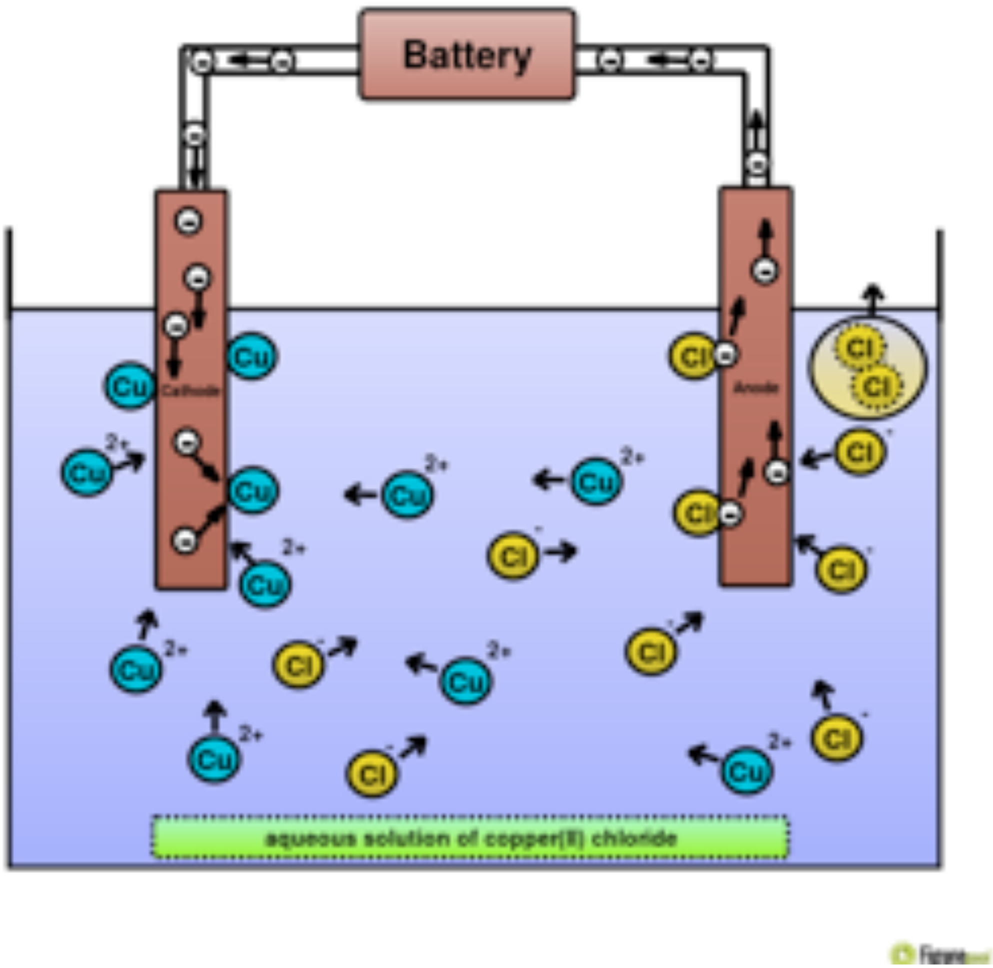
It takes 96,500 coulombs to deposit 1.0 gram-molecular-weight of a substance.

Today we refer to 96,500 coulombs as a "Faraday." It is equal to a mole of electrons.

$$6.02 \times 10^{23}$$

(1 coulomb = 1 ampere/second).

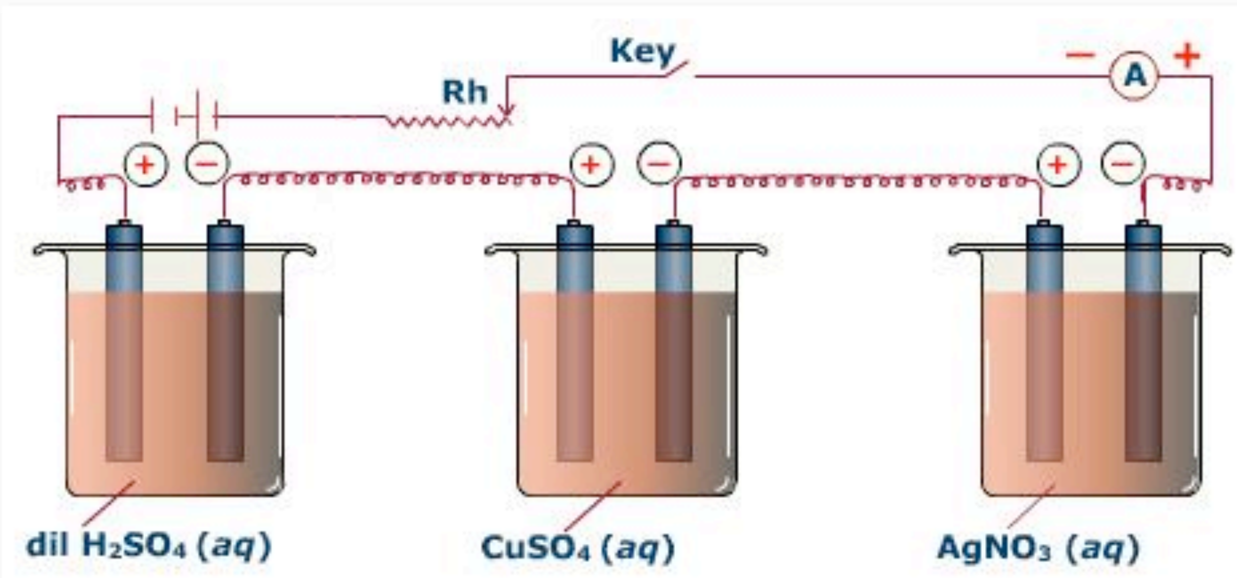
1833: Michael Faraday

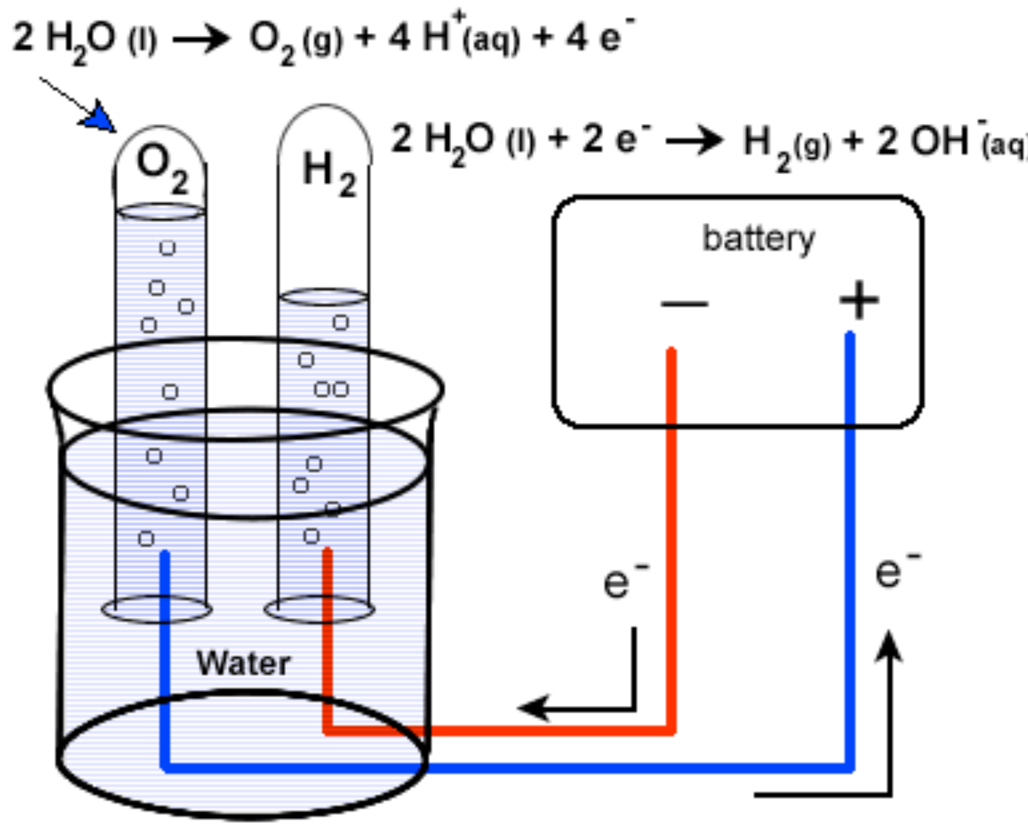


$$\frac{\text{Mass of copper deposited}}{\text{Mass of hydrogen gas liberated}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of hydrogen}}$$

and

$$\frac{\text{Mass of copper deposited}}{\text{Mass of hydrogen gas liberated}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of hydrogen}}$$





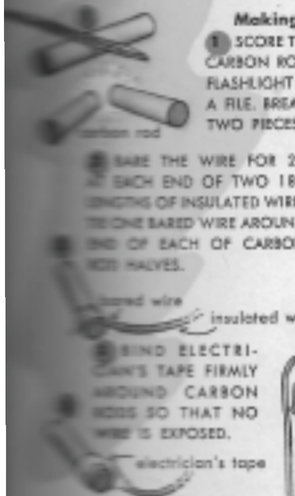
$2\,H_2O\,(l) \rightarrow O_2\,(g) + 4\,H^+(aq) + 4\,e^-$
$2\,H_2O\,(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$
O_2
H_2
battery
–
+
e^-
e^-
Water

ELECTROLYSIS OF WATER

ELECTRICITY CAN BE USED TO BREAK WATER APART INTO THE TWO ELEMENTS OF WHICH IT CONSISTS —THE GASES HYDROGEN AND OXYGEN.

YOU CAN GET THE REQUIRED ELECTRICITY FROM THREE OR FOUR ORDINARY FLASHLIGHT BATTERIES. YOU WILL ALSO NEED TWO PIECES OF INSULATED COPPER WIRE AND TWO "ELECTRODES" MADE FROM CARBON RODS.

Making Electrodes



1 SCORE THE MIDDLE OF THE CARBON ROD FROM AN OLD FLASHLIGHT BATTERY, USING A FILE. BREAK THE ROD INTO TWO PIECES.

2 BARE THE WIRE FOR 2" AT EACH END OF TWO 18" LENGTHS OF INSULATED WIRE. TIE ONE BARED WIRE AROUND END OF EACH OF CARBON ROD HALVES.

3 BIND ELECTRICIAN'S TAPE FIRMLY AROUND CARBON RODS SO THAT NO WIRE IS EXPOSED.

Setting up Electrolysis

WATER IS A POOR CONDUCTOR OF ELECTRICITY—SO YOU DISSOLVE 1 TABLESPOON OF WASHING SODA IN 1 PINT OF WATER AND FILL A WATER GLASS AND TWO TEST TUBES WITH THIS SOLUTION. THEN SET UP THE APPARATUS AS SHOWN AT RIGHT.

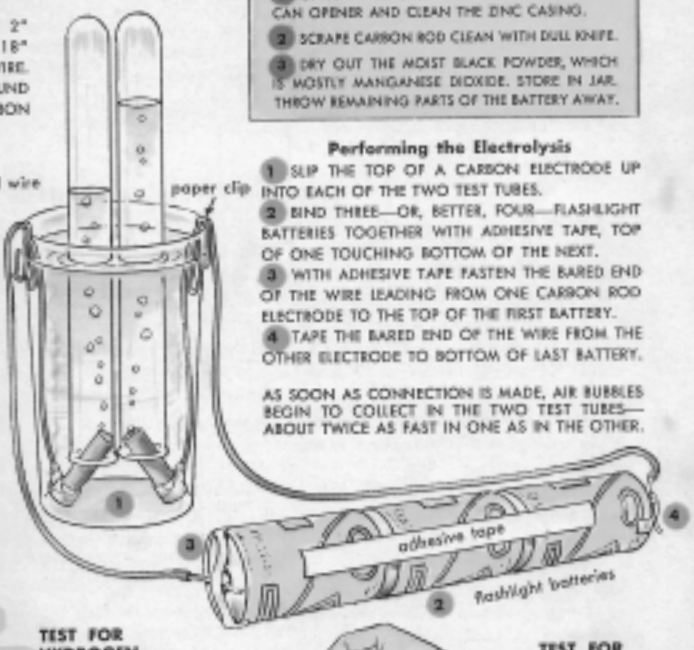
MATERIALS FOR EXPERIMENTS

AN ORDINARY FLASHLIGHT BATTERY WILL GIVE YOU MATERIALS YOU NEED FOR EXPERIMENTS ON THIS AND SEVERAL FOLLOWING PAGES.

1 OPEN UP BATTERY CASE CAREFULLY WITH A CAN OPENER AND CLEAN THE ZINC CASING.

2 SCRAPE CARBON ROD CLEAN WITH DULL KNIFE.

3 DRY OUT THE MOIST BLACK POWDER, WHICH IS MOSTLY MANGANESE DIOXIDE. STORE IN JAR. THROW REMAINING PARTS OF THE BATTERY AWAY.



Performing the Electrolysis

1 SLIP THE TOP OF A CARBON ELECTRODE UP INTO EACH OF THE TWO TEST TUBES.

2 BIND THREE—OR, BETTER, FOUR—FLASHLIGHT BATTERIES TOGETHER WITH ADHESIVE TAPE, TOP OF ONE TOUCHING BOTTOM OF THE NEXT.

3 WITH ADHESIVE TAPE FASTEN THE BARED END OF THE WIRE LEADING FROM ONE CARBON ROD ELECTRODE TO THE TOP OF THE FIRST BATTERY.

4 TAPE THE BARED END OF THE WIRE FROM THE OTHER ELECTRODE TO BOTTOM OF LAST BATTERY.

AS SOON AS CONNECTION IS MADE, AIR BUBBLES BEGIN TO COLLECT IN THE TWO TEST TUBES—ABOUT TWICE AS FAST IN ONE AS IN THE OTHER.

TEST FOR HYDROGEN

1 WITH YOUR THUMB, CLOSE THE MOUTH OF THE TEST TUBE FIRST FILLED WITH GAS. LIFT THE TUBE OUT OF THE WATER, MOUTH DOWN.

2 BRING LIGHTED MATCH TO THE MOUTH OF THE TUBE. CONTENTS BURN WITH A SOFT "POP!" THIS IS THE TEST FOR HYDROGEN.

TEST FOR OXYGEN

1 WHEN SECOND TUBE IS FULL OF GAS, CLOSE ITS MOUTH WITH YOUR THUMB. LIFT THE TUBE OUT OF THE WATER WITH MOUTH UP.

2 LIGHT A BROOMSTRAW. BLOW OUT THE FLAME. BRING THE GLOWING END DOWN IN THE TEST TUBE. GLOWING EMBER BURSTS INTO BRIGHT FLAME. THIS IS TEST FOR OXYGEN.