"A" students work (without solutions manual)
~ 10 problems/night.

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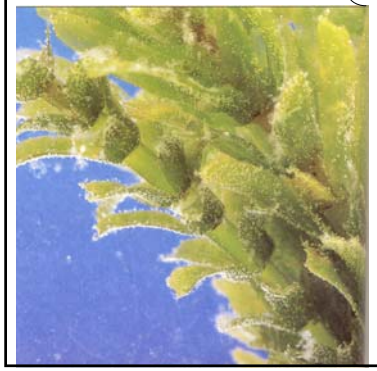
Gas Phase Reactions

Will need to define some New measurement systems

- Ideal Gas Law
- Stoichiometry of Gaseous Reactions
- Partial Pressures and Mole Fractions
- Kinetic Theory of Gases
- Real Gases



FITCH Rules

General

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings
G5. Chemists are Lazy

Chemistry

C1. It's all about charge
C2. Everybody wants to "be like Mike"
C3. Size Matters
C4. Still Waters Run Deep
C5. Alpha Dogs eat first

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Properties and Measurements

Property	Unit	Reference State
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^oC, K	boiling, freezing of water (specified Pressur
$1.66053873x10^{-24}g$	amu	mass of 1C12 atom/12
$6.022x10^{23}$	mole	atomic mass of an element in **grams**

Why specify "at sea Level?"

Because it relates to a standard Pressure

Properties and Measurements

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1.66053873x10^{-24}g	amu	mass of 1C12 atom/12
6.022x10^{23}	mole	atomic mass of an element in **grams**
Pressure	**mm Hg, bar, atm**	**sea level**

Pressure

force/unit area like psi (pounds per square inch) used in inflating our tires

$$P = \frac{F}{A}$$

Example, Sea Level Pressure exerted by Earth's atmosphere?

$$P = \frac{F}{A}$$

Force = mass x acceleration due to gravity, a

$$F = ma \qquad a = 9.8\frac{m}{s^2}$$

$$m = \left[f_{N_2} \frac{g_{N_2}}{mol_{N_2}} + f_{O_2} \frac{g_{O_2}}{mol_{O_2}} \right] mole_{gas}$$

f_{N_2} = fraction of N_2 in earth atmosphere at sea level $\quad f_{N_2} = 0.78$

f_{O_2} = fraction of O_2 in earth atmosphere at sea level $\quad f_{O_2} = 0.21$

$$m = \left[0.78_{sealevel} \left(\frac{(14+14)g_{N_2}}{mol_{N_2}} \right) + 0.21_{sealevel} \frac{(16+16)g_{O_2}}{mol_{O_2}} \right] mole_{gas,sealevel}$$

$$m = [28.56] mole_{gas,sealevel}$$

Measured Ground level air = 2.5x10^{19} particles/cm^3

Example, Sea Level Pressure exerted by Earth's atmosphere?

$$P = \frac{F}{A} \qquad F = ma$$

We have calculated the Effect of 1 m of air Pressing down on us when We stand at sea level

$$F = \left([28.56] mole_{gas,sealevel} \right) \left(9.8 \frac{m}{s^2} \right)$$

$$\left(\frac{2.9x10^{19}\ particles}{cm^3} \right) \left(\frac{100cm}{m} \right)^3 \left(\frac{1mole}{6.02x10^{23}\ particles} \right) = \frac{48.17 mole_{gas}}{m^3}$$

$$\left(\frac{28.56g}{mole_{gas}} \right) \left(\frac{48.17 mole_{gas}}{m^3} \right) = \frac{1{,}375g}{m^3}\bigg|_{sealevel} = \frac{1.375kg}{m^3}\bigg|_{sealevel}$$

Is this the number we want for our reference?

If not what do we need to do to adjust for a reference number?

1. Take into account the total air above us (distance)
2. Take into account that the composition of air varies with height

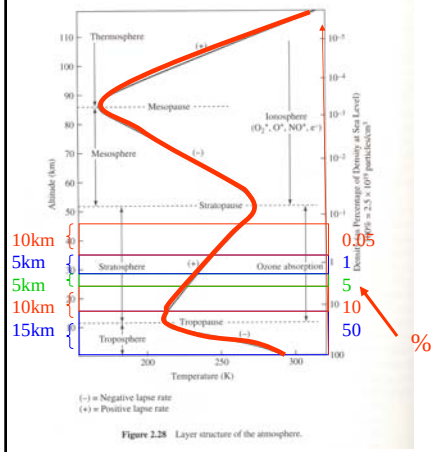
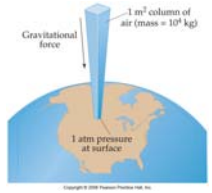


Figure 2.28 Layer structure of the atmosphere.

Take a 1 m^3 column of air through the earth's atmosphere from 0 to ~110 km and account for density changes.



% of sea level density

$$\frac{1.375kg}{m^3}\bigg|_{sealevel}$$

Composition varies with height above earth: need to take into account

% of sea level density

$$\frac{1.375kg}{m^3}\Big|_{sealevel}$$

$$total\ mass\ in\ sq\ m = \sum_i (km_i)\left(\frac{10^3 m}{km}\right)\left(\frac{\%density_i}{100}\right)(density_{sea\ level})(1m^2) =$$

$$total\ mass = \sum_i (km_i)\left(\frac{10\ m}{km}\right)(\%density_i)\left(\frac{1.375kg}{m^3}\right)(1m^2)$$

$$total\ mass = \left(\frac{10^3 m}{km}\right)\left(\frac{1.375kg}{m^3}\right)\sum_i (km_i)(\%density_i)$$

$$total\ mass = 13.75\left[(15)(50) + (10)(10) + (5)(5) + (5)(1) + 10(0.5)\right] =$$

$$total\ mass = 13.75(750 + 100 + 25 + 5 + 5.\ldots.) = 13.75(885)$$

$$total\ mass = 12{,}168kg$$

Example, Sea Level Pressure exerted by Earth's atmosphere?

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{(12{,}168kg)\left(9.8\frac{m}{s^2}\right)}{1m^2}$$

N=Newton

Sir Isaac Newton
English
Mathematician
1643-1727

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{119246\frac{kg \cdot m}{s^2}}{m^2}$$

$$P = \frac{F}{A} = \frac{ma}{A} = 1x10^5\frac{N}{m^2}$$

Round to 1 sig fig
Because estimation of
The mass of air was
Pretty crude

$$P = \frac{F}{A} = \frac{ma}{A} = 1x10^5\ Pa = 1bar$$

Pa = Pascal

Blaise Pascal, French mathematician
1623-1662

I got one of my worst grades ever in my life the first time I ever Encountered Chemistry because of these #@$% changes in units

Will You have to memorize life span of Newton?

Why put these guys in? (Which Fitch Rule applies?)

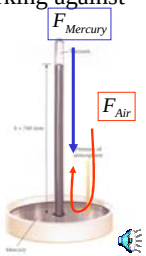
How do we measure pressure?

1. Weather glass – not scaled
2. Effect of external gas pressure working against a vacuum (mercury barometer)

$$P = \frac{F}{A} = \frac{ma}{A}$$

$$PA = F$$

$$P_{air} A_{area} = F_{air} = F_{mercury}$$



Evangelista Torricelli:
Italian scientist (1608-1647)
Entered a Jesuit School 1624
1600s invented the barometer

I have already called attention to certain philosophical experiments that are in progress ... relating to vacuum, designed not just to make a vacuum but to make an instrument which will exhibit changes in the atmosphere, which is sometimes heavier and denser and at other times lighter and thinner. Many have argued that a vacuum does not exist, others claim it exists only with difficulty in spite of the repugnance of nature; I know of no one who claims it easily exists without any resistance from nature.

10^5Pa = 1 bar
1.013 bar = 1 atm
760 mm Hg = 760 torr = 1 atm=1.013 bar=1.013 Pa

Sea Level
760 mm Hg
1 atm.
Torr = 1 mm Hg
Vacuum
0 mm
0 atm

Psi – 1 column 1 inch square
Rising to outerspace = 14.69
Psi = 1 atm

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Pressure	**mm Hg, bar, atm**	**sea level**

Example problem: A balloon with a volume (V) of $2.36x10^4$ m^3 contains 4.68×10^6 g of helium at 18°C and 1.20 bar. Express the volume of the balloon in liters, the amount in moles (*n*), the temperature (T) in K, and the pressure (*P* in both millimeter mercury and atmospheres

$$\frac{1L}{10^{-3}m^3} \quad \frac{1moleHe}{4.003gHe} \quad \frac{760mmHg}{1.013bar} \quad \frac{1atm}{1.013bar}$$

$$\left[2.36x10^4 m^3\right]\left[\frac{1L}{10^{-3}m^3}\right] = 2.37x10^7 L$$

$$\left[4.68x10^6 gHe\right]\left[\frac{1moleHe}{4.003gHe}\right] = 1.17x10^6 molHe$$

$$T_K = t_{^oC} + 273.15 \qquad T_K = 18 + 273.15 = 291K$$

Example problem: A balloon with a volume (V) of $2.36x10^4$ m^3 contains 4.68×10^6 g of helium at 18°C and 1.20 bar. Express the volume of the balloon in liters, the amount in moles (*n*), the temperature (T) in K, and the pressure (*P* in both millimeter mercury and atmospheres

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$2.37x10^7 L$

$1.17x10^6 molHe$

$291K$

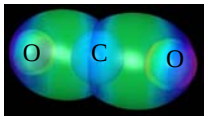
$$[1.20bar]\left[\frac{760mmHg}{1.013bar}\right] = 9.00x10^2 mmHg$$

$$[1.20bar]\left[\frac{1atm}{1.013bar}\right] = 1.18atm$$

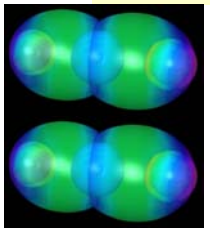
IDEAL gas law

1. Assumes that gases are infinitesimally small
2. Assumes that gases don't interact with each other (**don't see each other's charge**)

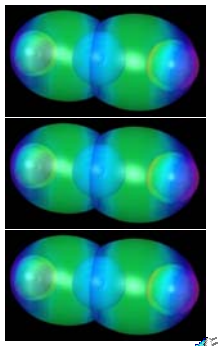
Fitch Rule C1: It's all about Charge!



1 CO_2 occupies V

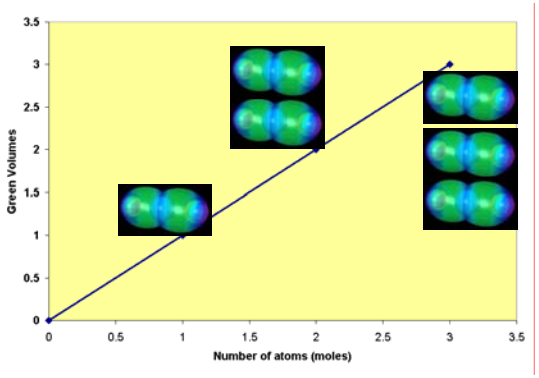


2 CO_2 occupies 2V

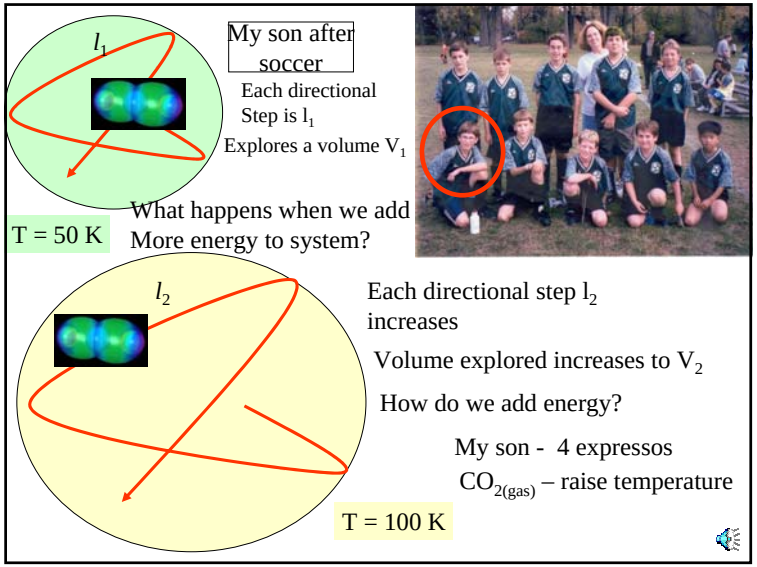


3 CO_2 occupies ?V

CO_2 charge density modelhttp://www.blacklightpower.com/theory/animations.shtml



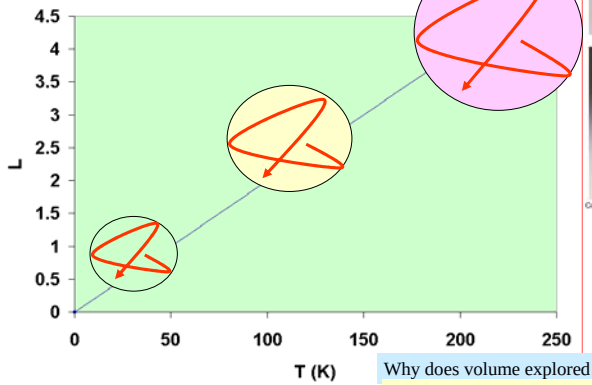
$$V = k_1 n$$



Jacques Charles, 1778-1850
Charles's law

$$V = k_2 T$$

French chemist, physicist, and aeronaut



Why does volume explored get larger with T?
Or: Why does step taken, l, get larger

more energy = more speed for constant weight

$$u_{rms} = \frac{\ell}{time}$$

rms= root mean square
-A way of getting rid of the Direction effect

Increase in Temperature provides energy

$$u_{rms} = \frac{\ell}{time} \propto T$$

Heavier guys are slower, velocity deceases with increasing mass

$$u_{rms} = \frac{\ell}{time} \propto \frac{1}{m}$$

A "constant" of proportionality

$$u_{rms} = \frac{\ell}{time} = \sqrt{\frac{3kT}{g_{molecule}}}$$

$$\ell = (u_{rms})t_{constant} = \sqrt{\frac{3kT}{g_{molecule}}}$$

Measure distance traveled for a fixed amount of tie

$$\ell_{t_{200}} > \ell_{t_{25}}$$

Kinetic Theory of Gases

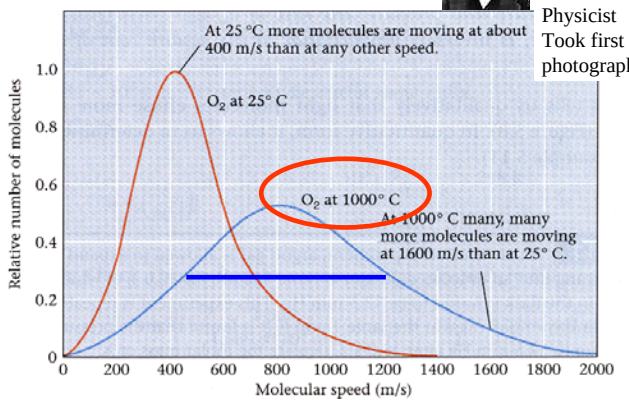
Average velocity larger at higher T

Spread (standard deviation) increases also

1831-1879

Scottish Mathematical Physicist

Took first color photograph



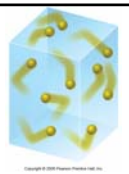
1860 James Maxwell: Maxwell's Distribution

Math Phobic

Can sleep through the next slide

Effect of Volume

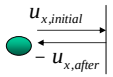
$F = ma$ $\quad \vec{F} = m\frac{du_x}{dt}$



Change in velocity, u_x

$\Delta u = u_{x,initial} - u_{x,final}$

$|u_{x,initial}| = |u_{x,final}|$

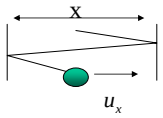


For an "elastic" collision, velocity remains constant

$\Delta u = u_{x,initial} - (-u_{x,initial}) = 2u_x$

Time for a round trip

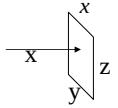
$\Delta t = \frac{2x}{u_x}$



Average Force in x direction

$\bar{\bar{F}} = \frac{2mu_x}{\left(\frac{2x}{u_x}\right)}$ $\quad \bar{\bar{F}} = \frac{2m(u_x)^2}{2x}$ $\quad \bar{\bar{F}} = \frac{m(u_x)^2}{x}$

$\bar{P} = \frac{\bar{\bar{F}}}{Area} = \frac{\bar{\bar{F}}}{yz}$



$\bar{P} = \frac{\left[m(u_x)^2\right]/x}{yz} = \frac{\left[m(u_x)^2\right]}{xyz}$ $\quad \bar{P} = \frac{m(u_x)^2}{V}$

$\bar{P} \propto \frac{1}{V}$ $\quad V = \frac{k_2}{P}$

Robert Boyle, 1660; Boyle's Law

1627-1691

Irish born chemist

Math phobic wake up

Putting this all together: Ideal Gas Law

$$V = k_1 n$$

Chem 101 thought Experiment

$$V = k_2 T$$

Charles' Law

$$V = \frac{k_3}{P}$$

Boyle's Law

ZZZZZZ

Math Phobic
Can sleep

$$u_{rms} = \sqrt{\frac{3kT}{g_{molecule}}}$$

$$\overline{P} = \frac{m(u_x)^2}{V}$$

$$u_{rms\,molecule} = \sqrt{\frac{3kT}{g_{molecule}}}$$

ZZZZZZ

$$\left[\frac{g}{molecule}\right]\frac{N_a\,molecules}{mole} = M$$

$$\left[\frac{g}{molecule}\right] = \frac{M}{N_a}$$

$$u_{rms\,mole} = \sqrt{\frac{3kT}{\left[\frac{M}{N_A}\right]}} \qquad u_{rms\,mole} = \sqrt{\frac{3\left[kN_A\right]T}{M}}$$

$$R \equiv \left[kN_A\right]$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{M}}$$

$$\overline{P}_x = \frac{m(u_x)^2}{V}$$

$$\overline{P}_x = \frac{m\left(\sqrt{\frac{3RT}{MM}}\right)^2}{V}$$

$$\overline{P}_x = \frac{m}{V}\left(\frac{3RT}{MM}\right)$$

$$nMM = m$$

$$n = \frac{m}{MM}$$

ZZZZZZ

$$\overline{P}_x = \frac{3nRT}{V}$$

$$\text{Pressure}_{anydirection} = \frac{3nRT}{3V}$$

$$P = \frac{nRT}{V} \qquad V = \frac{RTn}{P}$$

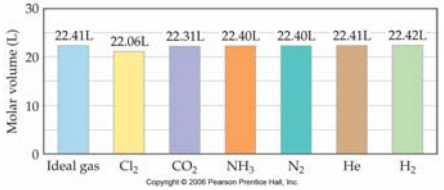
$$V = \frac{nRT}{P}$$

$$V = k_1 n$$

$$V = k_2 T$$

$$V = \frac{k_3}{P}$$

At 0 °C, 1 atm, 1 mol of nearly all gases occupies 22.4L



$$R = \frac{PV}{nT}$$

$$R = \frac{(1atm)(22.4L)}{(1mol)(273K)}$$

$$R = 0.0821\frac{L \cdot atm}{mol \cdot K}$$

R is the Natural Gas Constant

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K} \qquad R = \left(\frac{0.0821}{mol\ K}\right)(L\ atm)$$

$$R = \left(\frac{0.0821}{mol\ K}\right)\left(\frac{1000 cm^3}{L}\right)\left(\frac{1m}{100cm}\right)\left(\frac{1.01325x10^5 Pa}{atm}\right)\left(\frac{\left(\frac{kg}{m\,s^2}\right)}{Pa}\right)$$

ZZZZZZ

$$R = \left(\frac{0.0821}{mol\ K}\right)\left(\frac{1000 m^3}{1000000}\right)1.01325x10^5\left(\frac{kg}{m\,s^2}\right)$$

$$R = \left(\frac{8.31}{mol\ K}\right)\left(\frac{kg\ m^2}{s^2}\right)$$

$$R = \left(\frac{8.31}{mol\ K}\right)\left(\frac{kg\ m^2}{s^2}\right)\left(\frac{J}{\left(\frac{kg\ m^2}{s^2}\right)}\right)$$

$$R = \left(\frac{8.31}{mol\ K}\right)\left(\frac{kg\ m^2}{s^2}\right)\left(\frac{10^3 g}{kg}\right)$$

$$R = \left(\frac{8.31\ J}{mol\ K}\right)$$

$$R = 8.31x10^3\left(\frac{g\ m^2}{mol\ K\ s^2}\right)$$

$$PV = nRT$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{M}}$$

Snork,
Bst, huh? Math
Phobic wake up
here

The three to memorize

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

$$R = 8.31 \frac{J}{mol \cdot K}$$

$$R = 8.31x10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$$

$PV = nRT$ Calculations using the Ideal Gas Law

1. **Vary two parameters hold others constant**
2. Calculate P, V, n, or T
3. Calculate M (molar mass)
   Calculate g/Vol

$$P_1V_1 = n_1RT_1$$

$$P_2V_2 = n_2RT_2$$

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

Constant n, P

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

Constant T, P

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

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

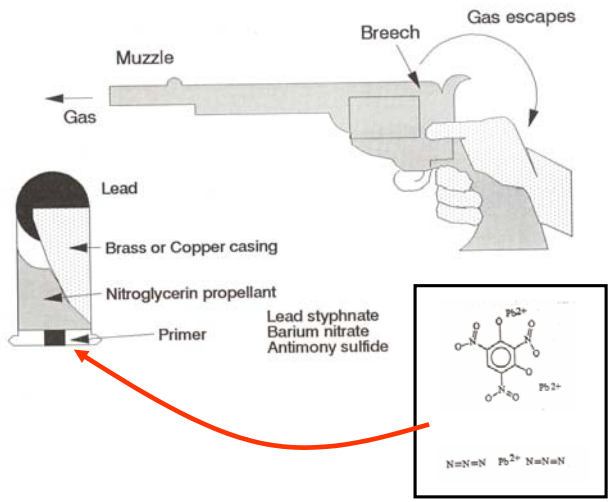
Constant T, V

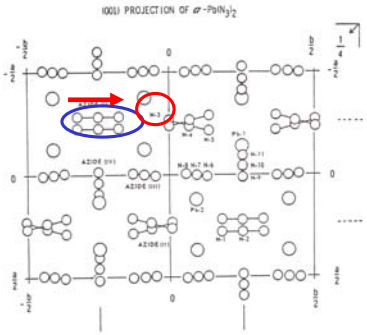
$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Constant V, n

$$\frac{n_2}{n_1} = \frac{T_1}{T_2}$$

Constant PV= open vessel experiments





Perturbation of the lead azide crystal; occurs because of the "linear" slippage of the molecules.

The perturbation of the molecule brings the **oxidizing reagent** Pb^{2+} closer to the **reducing reagent** azide

a reaction occurs producing an increase in moles, n, of gas in the pocket.

$$Pb(N_3)_{2(s)} \rightarrow Pb^{2+} + 2N_3^-$$

$$Pb^{2+} + 2e \rightarrow Pb_s$$

$$2N_3^- \rightarrow 3N_{2(g)} + 2e$$

$$Pb(N_3)_{2(s)} \rightarrow Pb_{(s)} + 3N_{2(g)}$$

Temperature rises from 25°C to 1200°C

How did the pressure change?

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

V, n constant once crystal decomposes

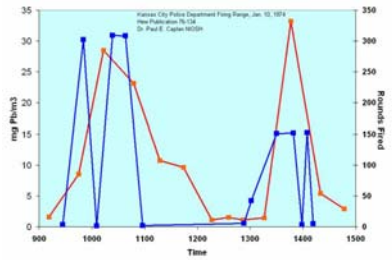
Initial Pressure not stated, assume standard conditions

(We do this assumption a lot!)

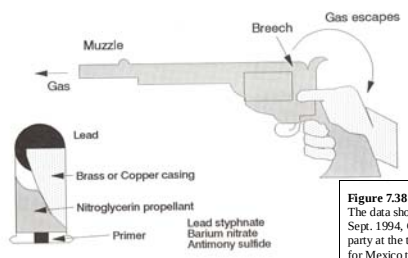
$$\frac{1atm}{P_2} = \frac{(25+273)}{(1200+273)}$$

$$P_2 = \frac{1atm(1200+273)K}{(25+273)K}$$

$$P_2 = 4.92atm$$



Indoor firing ranges have a high lead content that tracks the number of rounds fired. Those using the firing ranges are at risk for lead poisoning. Puppies attending dog training at indoor ranges also become lead poisoned.



The lead in the primer
Can be used for
Forensic investigations

Figure 7.38: Guilty or Not?
The data shown here was taken from a suspect in a drive-by murder attempt, Sept. 1994, Chicago. The defendant had 12 witnesses that placed him at a party at the time of the shooting. His brother, a gang member, left Chicago for Mexico the day following the shooting. The lawyer wanted to know if the time between the hand sampling in September and the actual test for metals in December could compromise the measurement.

rb = right hand, back
rp = right hand, palm
lb = left hand, back
lp = left hand, palm

location	Amount metal measured, micrograms			
	Ba	Sb	Pb	Ba/Sb
rb	0.43	0.0229	0.58	14.8
rp	0.67	0.05	1.08	13.0
lb	0.21	0.009	0.45	23.8
lp	0.54	0.026	1.97	20.6
cartridge				5.4

The lab said that the results were consistent with firing the gun. Do you agree?

$$PV = nRT$$

Calculations using the Ideal Gas Law

1. Vary temperature or pressure hold V, moles, constant:
2. **Calculate P, V, n, or T; when all but one is known**
3. **Calculate M (molar mass)**
   Calculate g/Vol (density)

$$m = nM$$

$$P = \frac{nRT}{V} \qquad V = \frac{nRT}{P} \qquad n = \frac{m}{M}$$

$$\frac{PV}{RT} = n \qquad \frac{PV}{nR} = T \qquad \frac{m}{V}\frac{RT}{P} = M$$

$$\frac{m}{V}\frac{RT}{P} = MM$$

What is the gas phase density of O_2 vs CO_2 at 0.75 atm and 100 ^oC?.

$$\frac{m}{V} = \frac{P(MM)}{RT} \qquad R = 0.0821\frac{L\cdot atm}{mol\cdot K}$$

$$\frac{m}{V} = \frac{(0.75atm)\left(\frac{2(16)g}{mol_{O_2}}\right)}{\left(\frac{0.0821L\cdot atm}{mol\cdot K}\right)(100+273K)} = \frac{0.784g_{O_2}}{L}$$

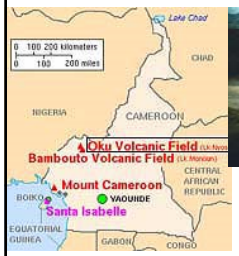
CO_2 is denser than O_2

$$\frac{m}{V} = \frac{(0.75atm)\left(\frac{2(16)+12g}{mol_{O_2}}\right)}{\left(\frac{0.0821L\cdot atm}{mol\cdot K}\right)(100+273K)} = \frac{1.0776g_{CO_2}}{L}$$

Context for this is on Next slide.

http://www.geology.sdsu.edu/how_volcanoes_work/Nyos.html

Lake Nyos, 9:30 p.m. August 12, 1986

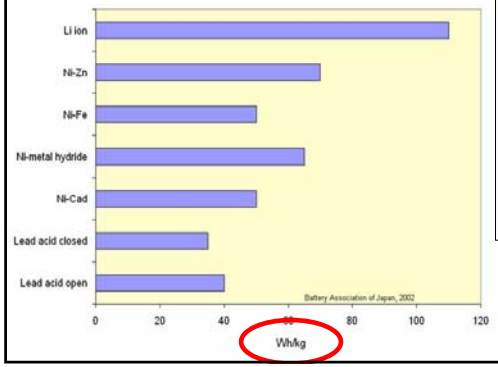


Dissolved CO_2 displaced From lake by disruption Of water layers (rain or Mudslide)

1700 human deaths
Thousands of cattle

CO_2 is denser than O_2
Settles over villages
And asphixiated villagers

Electric cars were thought to be a dead end in the early 1990s because they were based on the lead acid battery.
The weight of these batteries would preclude their serious use, unlike that of the hydrogen based fuel cell. One way that automotive engineers account for this is by the energy density: **energy per kg weight** of the fuel system.



If a hydrogen fuel cell based car fuel source is a 50.0 L container of H_2 at 225 bar, what additional kg weight would this give to the car at 25 ^oC?

$$PV = nRT \qquad m = nM$$

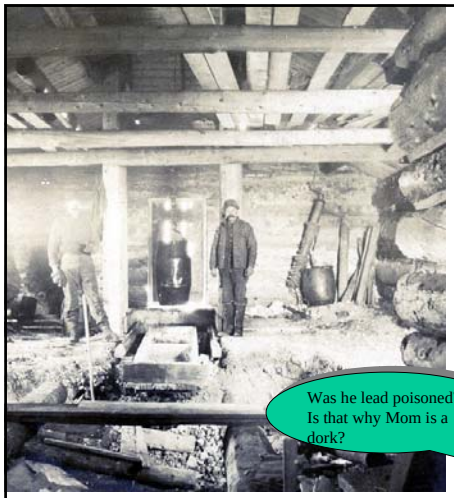
Chemists are Lazy
I can remember these 2
So I usually derive what I need

$$n = \frac{m}{M} \qquad m = \frac{PVM}{RT}$$

$$PV = \left[\frac{m}{M}\right]RT$$

If a hydrogen fuel cell based car fuel source is a 50.0 L container of H_2 at 225 bar, what additional weight would this give to the car at 25C?

$$m = \frac{\left[225bar\right]\left[\frac{1atm}{1.013bar}\right]\left[50.0L\right]\left[\frac{2(1.01)g}{mole}\right]}{\left[0.0821\frac{L\cdot atm}{mol\cdot K}\right](25+273.15)K} = 916.9g = 0.917kg$$



My Great-grandpa, Stewart Zwingli Schenk at his silver/lead mine digging in the 1890s, Colorado. He hauled his wife and kids around from one failed site to another. Eventually ran off with a dance hall girl and parked cars in Chicago.

Was he lead poisoned? Is that why Mom is a dork?

Example: My son is paranoid about lead and refuses to tour the old lead mines at Galena, Ill for fear that he will breath in galena gas vapors. He assumes that the following reaction will produce sufficient vapor to poison him:

$$PbS_{(s)} \xrightarrow{sublimes} PbS_{(g)}$$

The reaction produces a vapor pressure of PbS of $1.131x10^{-21}$torr at room temperature (~25°C). The OSHA (Office of Safety and Health Administration) sets a limit of breathable lead at 50microgPb/m^3. Is my son paranoid or simply appropriately cautious?

$$1.131x10^{-21}\,torrPbS_{(g)}$$

$$\frac{50\mu gPb}{m^3} = \lim it$$

$$1.131x10^{-21}\,torrPbS_{(g)} \geq \frac{50\mu gPb}{m^3}?$$

I have no brain cells so I am going to derive my equation rather than memorize it.

$$PV = nRT$$

ug/m^3 is a "conc." → Moles/L

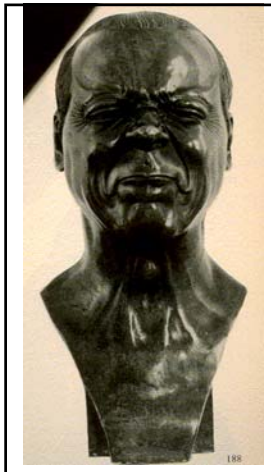
$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{\left(1.131x10^{-21}\,torr_{PbS}\right)\left(\frac{1mmHg}{torr}\right)\left(\frac{1atm}{760mmHg}\right)}{\left[0.0821\frac{L\cdot atm}{mol\cdot K}\right][25+273]K} = 6.0826x10^{-26}\frac{mol}{L}$$

$$\left[6.0826x10^{-24}\frac{molPbS}{L}\right]\left[\frac{10^3\,L}{m^3}\right]\left[\frac{1molPb}{molPbS}\right]\left[\frac{207.2gPb}{molPb}\right]\left[\frac{10^6\,\mu g}{g}\right] = \frac{1.26x10^{-14}\,\mu gPb}{m^3}$$

$$1.26x10^{-14}\frac{\mu g}{m^3}Pb \leq \frac{50\mu gPb}{m^3}$$

Son is paranoid



Messerschmidt's self portrait in lead Entitled: "Peevish Old Man"

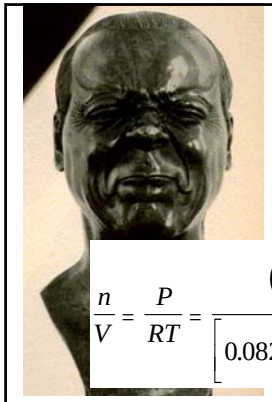
Example 2. The sculptor Messerschmidt in the 1700s got a very nice job at the Vienna academy of arts in his late 20s early 30s, but shortly after become totally unreasonable, paranoid, and offended all his colleagues. He eventually locked himself up in his home and did not leave for 15 years before dying delusional. He worked exclusively in lead metal casting. Was he poisoned from the fumes of the lead? Assume he worked lead at 483 °C.

Lead melts at 327.502 °C. Assuming that Messerschmidt worked at a temperature of 483 °C, the vapor pressure is 10^{-5} mm Hg.

$$10^{-5}\,mmHgPb_{(g)} \geq \frac{50\mu gPb}{m^3}?$$

This is the Same as The last problem

Data source: CRC handbook



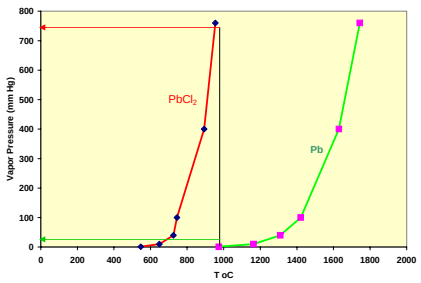
Lead melts at 327.502 °C. Assuming that Messerschmidt worked at a temperature of 483 °C, the vapor pressure is 10^{-5} mm Hg.

$$10^{-5} mmHg \geq \frac{50 \mu gPb}{m^3} ?$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{\left(10^{-5} mm\right)\left(\frac{1 atm}{760 mm}\right)}{\left[0.0821 \frac{L \cdot atm}{mol \cdot K}.\right][483 + 273] K} = 2.1199 x 10^{-10} \frac{mol}{L}$$

$$\left[2.1199 x 10^{-10} \frac{molPb}{L}\right]\left[\frac{10^3 L}{m^3}\right]\left[\frac{207.2 gPb}{molPb}\right]\left[\frac{10^6 \mu g}{g}\right] = \frac{43.9 \mu gPb}{m^3}$$

Very close to exceeding modern day limits!!!



To repair radiators solder is used. Solder consists of lead with some aluminum chloride. The aluminum Chloride is used to create a "clean" surface.

At 954 °C lead chloride results in 760 mm gas pressure $PbCl_2$
At a similar temperature (973 °C) lead results in 1 mm gas pressure Pb

What might you conclude about occupations requiring use of solder?

ZZZZZZ

A pathetic attempt to
Be relevant – i.e. slides
On context are coming

How To Make Nitric Acid

1. Cut down a tree
2. Burn tree and collect ashes

What is it about a tree that is different than a small plant?
What kind element might a tree access compared to a small plant?

3. Buy some pigs
4. Collect the soil under the pig pen
5. Filter the soil and collect the filtrate

What chemical are we collecting here?
Why from the soil and not straight from the pig?

6. Add the ashes to filtrate
7. Dry then collect the crystals

What compound have we made?

8. Put small table in small pot of water
9. Put crystals on table
10. Put pot plus table in an oven and heat
11. Collect vapor and cool = nitric acid

In the Civil War
The South urged
Ladies to collect their
"night" water

That's amazing!

How To Make Nitric Acid

1. Cut down a tree
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What compound have we made?

8. Put small table in small pot of water
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10. Put pot plus table in an oven and heat
11. Collect vapor and cool = nitric acid

Spectator ions Which are Soluble are Removed from Top of soil

K^+

Pot ash=potassium

In the Civil War The South urged Ladies to collect their "night" water

$Ca(NO_3)_2$

$$Ca(NO_3)_{2(aq)} + 2K^+_{aq} \xrightarrow{dry} 2KNO_{3,ppt}$$

Can't use calcium nitrate because it sucks up water

$$Ca(NO_3)_{2(aq)} + 2(H_2O) \xrightarrow{dry} Ca(H_2O)_2(NO_3)_{2,ppt}$$

$$6KNO_{3(s)} \xrightarrow{400^oC} 6KNO_{2(s)} + 3O_{2(g)}$$

$$6KNO_{2(s)} + \frac{3}{2}O_{2(g)} \xrightarrow{>440^oC} 3K_2O_{(s)} + 6NO_{2(g)}$$

$$6NO_{2(g)} + 2H_2O_{(g)} \rightarrow 4HNO_{3(g)} + 2NO_{(g)}$$

$$4HNO_{3(g)} \xrightarrow{bp\,83^oC} 4HNO_{3(l)}$$

Similar reactions Involved in Smog

$$6KNO_{3(s)} + 2H_2O_{(g)} \rightarrow \frac{3}{2}O_{2(g)} + 3K_2O_{(s)} + 4HNO_{3(l)} + 2NO_{(g)}$$

Requires ability to distil. Technology invented ~1100 A.D. in the Arabic countries

"De Re Metallic" by Agricola

What mass of niter is required to produce 2.00 Liters of oxygen at 25.0C and 1.00 atm?

Old fashioned word for potassium nitrate

$$6KNO_{3(s)} + 2H_2O_{(g)} \rightarrow \frac{3}{2}O_{2(g)} + 3K_2O_{(s)} + 4HNO_{3(l)} + 2NO_{(g)}$$

$PV = nRT$ $\quad n = \frac{PV}{RT}$

Know everything necessary

$$n = \frac{[1.00atm][2L]}{\left[0.0821\frac{L\cdot atm}{mol\cdot K}\right][25+273]K} = 8.174x10^{-2}molO_2$$

33.1g KNO_3

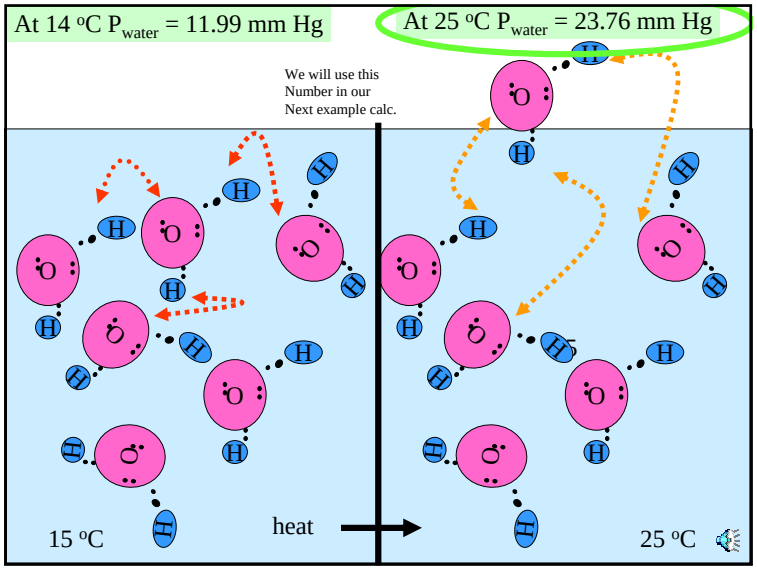
$$[8.174x10^{-2}molO_2]\left[\frac{6molKNO_3}{\frac{3}{2}molO_2}\right]\left[\frac{39.10+14.01+3(16.00)gKNO_3}{molKNO_3}\right]$$

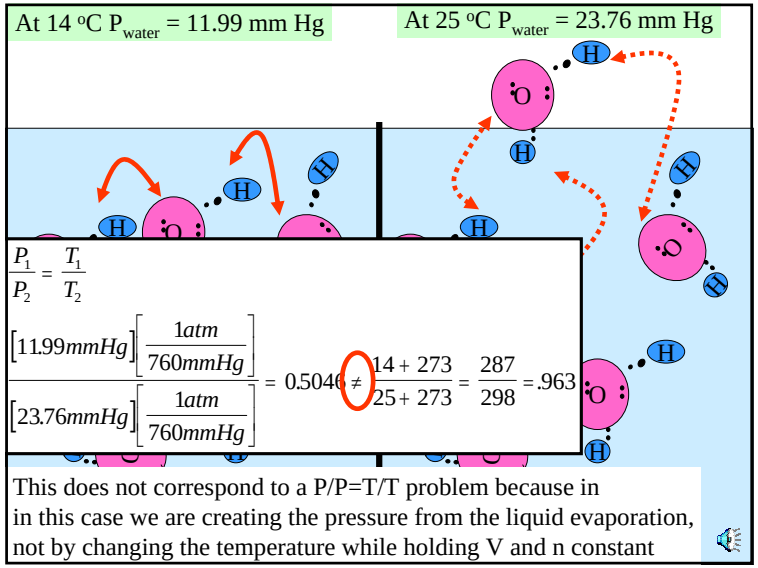
$$[8.174x10^{-2}molO_2]\left[\frac{4molKNO_3}{molO_2}\right]\left[\frac{101.1gKNO_3}{molKNO_3}\right] = 33.055gKNO_3$$

Vapor Pressure of water depends on the temperature and the strength of charge interactions of water as a liquid

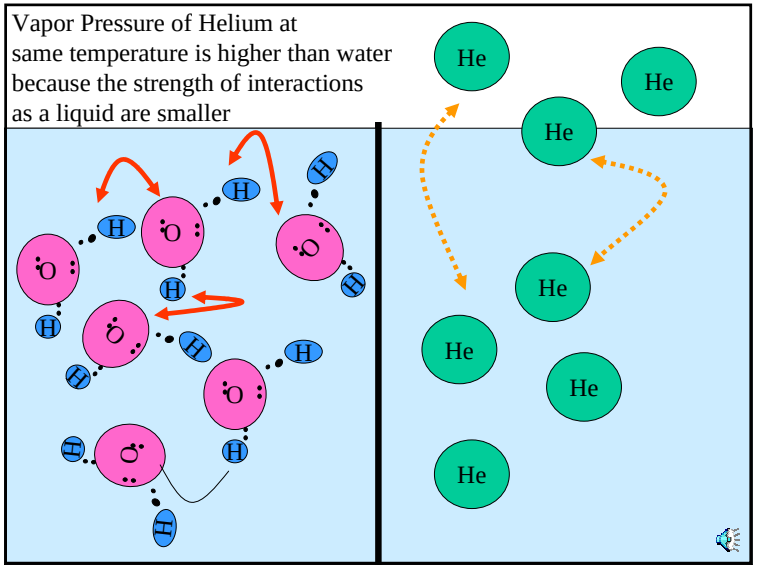
First Rule of Chemistry:
It's all about Charge
Weak charge
Interactions from dipoles
Holds liquids together

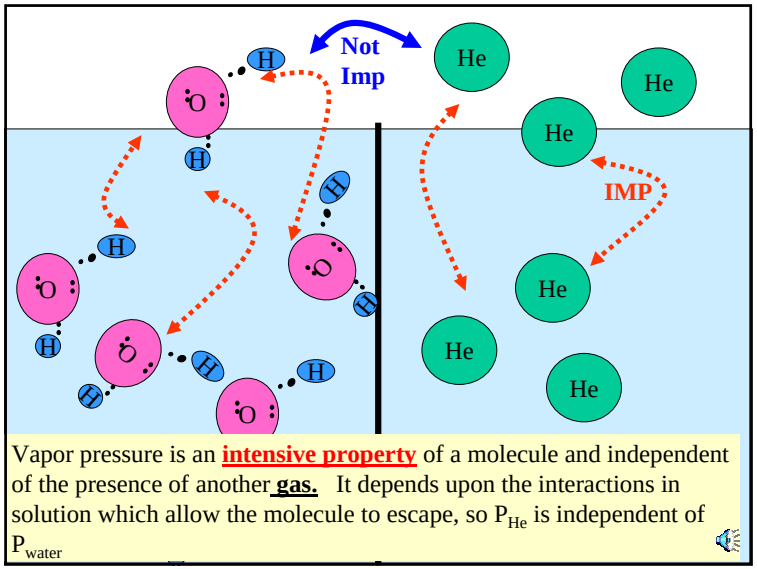
http://preparatorychemistry.com/water.htm





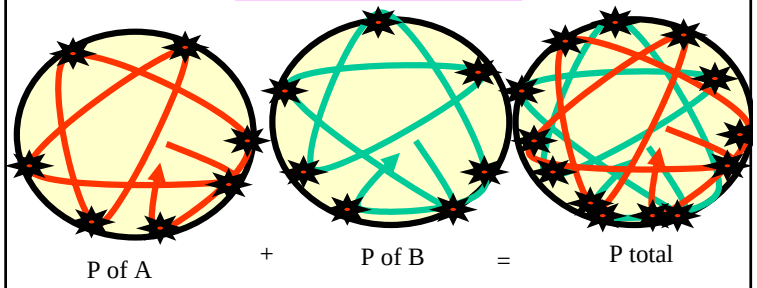
This does not correspond to a P/P=T/T problem because in in this case we are creating the pressure from the liquid evaporation, not by changing the temperature while holding V and n constant





Vapor pressure is an **intensive property** of a molecule and independent of the presence of another **gas.** It depends upon the interactions in solution which allow the molecule to escape, so P_{He} is independent of P_{water}

"Ideal" gases don't interact



P of A + P of B = P total

Ideal gases don't obey Rule C1 – It's all about charge

Partial Pressures and Mole Fractions

$$P_{Tot} = n_{Tot}\frac{RT}{V}$$

$$P_{Tot} = (n_A + n_B)\frac{RT}{V}$$

$$P_{Tot} = n_A\frac{RT}{V} + n_B\frac{RT}{V}$$

$$P_{Tot} = P_A + P_B$$

Dalton's Law (1801)

Partial Pressure B

Partial Pressure A

John Dalton

1766-1844
English (Quaker) chemist

While electrolyzing water to produce H_2 gas at 25.0°C, 152 mL of H_2 at a total pressure of 758 mm Hg are collected. Calculate the partial pressure of H_2

$$P_{Tot} = P_A + P_B$$

What are the two gases?

Water
H_2

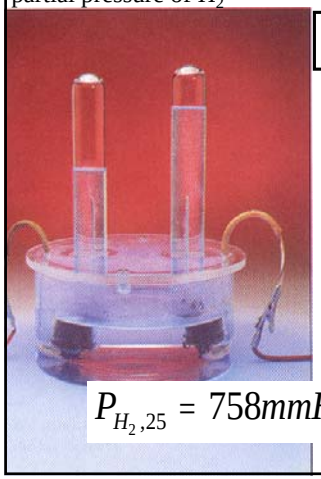
Don't know P of either, or do we?

Recall: we know what P_{water} should be from years of accumulated data.

In fact, we referred to P_{water} in the preceding slides as an intensive property

Mad scientist

While electrolyzing water to produce H_2 gas at 25.0°C, 1[illegible] L of H_2 at a total pressure of 758 mm Hg are collected. Calculate the partial pressure of H_2



$$P_{Tot} = P_A + P_B$$

$$758mmHg = P_{H_2O,25} + P_{H_2,25}$$

$$758mmHg = 23.76mmHg + P_{H_2,25}$$

$$P_{H_2,25} = 758mmHg - 23.76mmHg = 734mmHg$$

Volume was a red herring!!!!

Another related concept:

Mole fraction, X_A

$$P_{Tot} = P_A + P_B$$

$$\frac{P_A}{P_{Tot}} = \frac{\frac{n_A RT}{V}}{\frac{n_{tot} RT}{V}}$$

$$\frac{P_A}{P_{Tot}} = \frac{n_A}{n_{tot}}$$

$$\frac{n_A}{n_{tot}} \equiv \chi_A$$

$$\frac{P_A}{P_{Tot}} = \chi_A$$

$$P_A = \chi_A P_{tot}$$

Example : Chemical analysis of dry air shows that the mole fractions of nitrogen, oxygen, and argon are 0.781, 0.210, and 0.009, respectively. Calculate the partial pressure of each of these gases on a day when the barometric pressure is 747 mm Hg

$$P_A = \chi_A P_{tot}$$

$$P_{N_2} = \chi_{N_2} 747mmHg$$

$$P_{N_2} = [0.781]747mmHg$$

$$P_{N_2} = 583mmHg$$

$$P_{O_2} = \chi_{O_2} 747mmHg$$

$$P_{O_2} = [0.210]747mmHg$$

$$P_{O_2} = 157mmHg$$

$$P_{Ar} = \chi_{Ar} 747mmHg$$

$$P_{AR} = [0.009]747mmHg$$

$$P_{Ar} = 7mmHg$$

$$PV = nRT$$

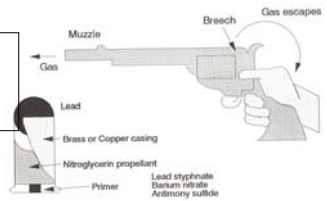
The two to memorize

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

Calculations involving Average speed, u

1. Speed vs a specific molecule or atom

What is the velocity of N_2 in the barrel of the gun if the local barrel temperature is 2,500 K?



What is the velocity of N_2 in the barrel of the gun if the local barrel temperature is 2,500 K?

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

$$MM = 14.01 + 14.01 = \frac{28.02\,g}{mole}$$

$$R = 0.0821\frac{L \cdot atm}{mol \cdot K}$$

$$R = 8.31\frac{J}{mol \cdot K}$$

$$R = 8.31x10^3\frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$$

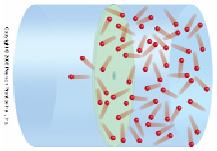
$$u_{rms\,mole} = \sqrt{\frac{3\left(8.31x10^3\frac{g \cdot m^2}{s^2 \cdot mol \cdot K}\right)2500K}{28.02\frac{g}{mol}}} = 1.4914x10^3\frac{m}{s}$$

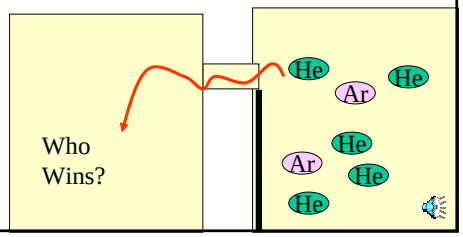
$$\left[1.4914x10^3\frac{m}{s}\right]\left[\frac{1mi}{1.609x10^3 m}\right]\left[\frac{60s}{\min}\right]\left[\frac{60\min}{hr}\right] = 3.336x10^3 mph$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

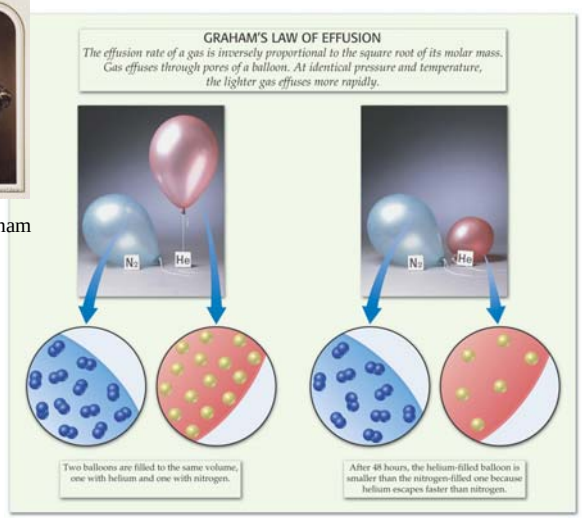
Calculations involving Average speed, u

1. Speed vs a specific molecule or atom
2. **Effusion and Diffusion**
   1. Purifying gases (Uranium enrichment)
   2. Biofractionation of isotopes – methods of studying past climates





Thomas Graham
1805-1869
Scottish
Inorganic
chemist



$$rate\,effusion_A = \frac{moles}{time} \propto P_A u_{rms,A} \propto \left(\frac{m}{s}\right)$$

$$\frac{rate\,effusion_A}{rate\,effusion_B} \propto \frac{u_{rms,A}}{u_{rms,B}}$$

If you compare the rate of effusion for two gases each with the same partial pressure

$$\frac{rate\,effusion_A}{rate\,effusion_B} = \frac{u_{rms,A}}{u_{rms,B}} = \frac{\sqrt{\frac{3RT}{MM_A}}}{\sqrt{\frac{3RT}{MM_B}}} = \frac{\sqrt{\frac{1}{MM_A}}}{\sqrt{\frac{1}{MM_b}}} = \sqrt{\frac{MM_B}{MM_A}}$$

$$\frac{rate\,effusion_A}{rate\,effusion_B} = \sqrt{\frac{MM_B}{MM_A}}$$

Uranium Enrichment

Nuclear Reactions require U-235

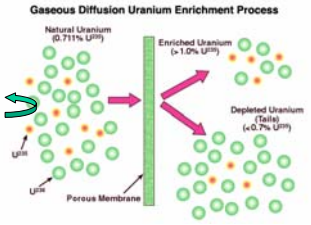
Naturally occurring ore bodies:

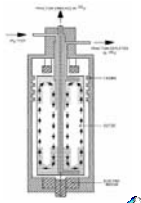
%	p	n	mass	
99.3	92	146	238	
0.7%	92	143	235	→ 5%
0.01%	92	142	234	

Need to get uranium into the gas phase: $UF_{6(g)}$

The "infamous" Centrifuge pipes

Forces gas to side
And increases
Rate of effusion





http://www.nrc.gov/materials/fuel-cycle-fac/ur-enrichment.html#3

Need enough U-235 to
Be in path of neutrons

Chain reaction

$${}^{1}_{0}n + {}^{235}_{92}U \xrightarrow{\text{very fast}} {}^{236}_{92}U \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n$$

$${}^{238}_{94}Pu \rightarrow {}^{4}_{2}He + {}^{234}_{92}U$$

$${}^{4}_{2}He + {}^{9}_{4}Be \rightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

$UO_{2(s)}$

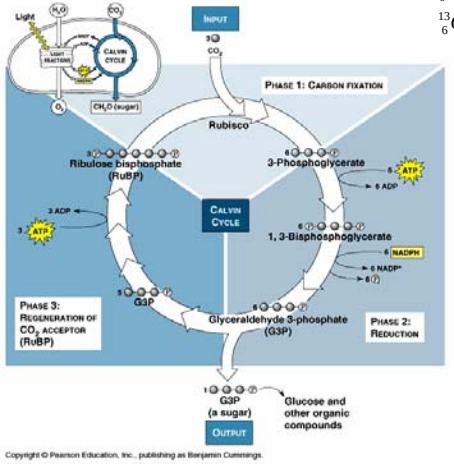
Rods control
n which controls
Rate of chain rx

Cd_s

A biological example of this process

Stable Isotopes of Carbon

	% Abundance	Mass
$^{12}_{6}C$	98.89	12.0000
$^{13}_{6}C$	1.11	13.00335



http://www.msu.edu/~smithe44/calvin_cycle_process.htm

Reaction of CO_2 with Rubisco depends upon gas phase velocity carrying the molecule to the reaction site

Will the resulting Sugars contain the Same relative abundance Of ^{12}C and ^{13}C?

Math in Green is Not on an Exam

$$MM_{^{12}CO_2} = 12 + 16 + 16 = 44$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

$$MM_{^{13}CO_2} = 13 + 16 + 16 = 45$$

$$\frac{u_{44}}{u_{45}} = \frac{\sqrt{\frac{3RT}{M_{44}}}}{\sqrt{\frac{3RT}{M_{45}}}} = \sqrt{\frac{M_{45}}{M_{44}}} = \sqrt{\frac{45}{44}} = 1.0113$$

^{12}C ↓

	$\delta^{13}C$
PeeDeeB	0
Air	-8
C4	-10 to -15
Marine Plankton	-21 to -22
C3	-20 to -30

Expect biofractionation of isotopes to result in greater 12-C Compared to Some Standard **(Rule G3: Science is Referential)**

$$R_i = \frac{[^{13}C_i]}{[^{12}C_i]}$$

$$\delta^{13}C = \left[\frac{R_{sample}}{R_{standard}} - 1\right]1000$$

$$\delta^{13}C = \left[\frac{\frac{[^{13}C_{sample}]}{[^{12}C_{sample}]}}{\frac{[^{13}C_{PDB}]}{[^{12}C_{PBD}]}} - 1\right]1000$$

Where PDB = Pee Dee Belemite A South Carolina, U.S. limestone, $CaCO_3$

Who moves to Rubisco faster?

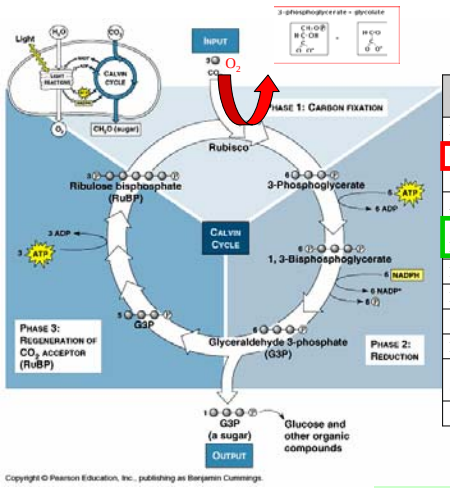


Table 7a-1: Average composition of the atmosphere up to an altitude of 25 km.

Gas Name	Chemical Formula	Percent Volume
Nitrogen	N_2	78.08%
Oxygen	O_2	20.95%
*Water	H_2O	0 to 4%
Argon	Ar	0.93%
*Carbon Dioxide	CO_2	0.0360%
Neon	Ne	0.0018%
Helium	He	0.0005%
*Methane	CH_4	0.00017%
Hydrogen	H_2	0.00005%
*Nitrous Oxide	N_2O	0.00003%
*Ozone	O_3	0.000004%

* variable gases

http://www.msu.edu/~smithe44/calvin_cycle_process.htm

http://www.physicalgeography.net/fundamentals/7a.html

Using Gas Phase Reactions to Understand Climate Change

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

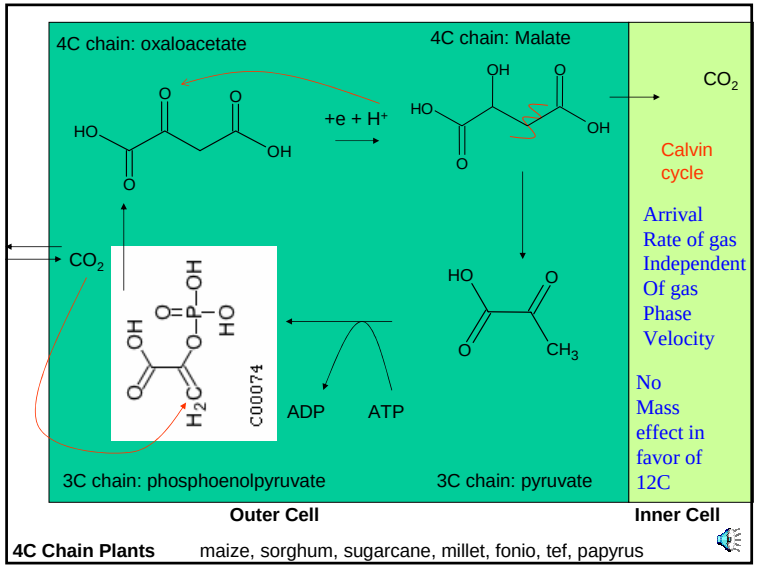
$MM_{O_2} = 16 + 16 = 32$

$MM_{CO_2} = 12 + 16 + 16 = 44$

$$\frac{u_{32}}{u_{44}} = \frac{\sqrt{\frac{3RT}{M_{32}}}}{\sqrt{\frac{3RT}{M_{44}}}} = \sqrt{\frac{M_{44}}{M_{32}}} = \sqrt{\frac{44}{32}} = 1.17$$

O_2 can swamp Rubisco reaction by

1. Concentration
2. Gas phase velocity in arriving at the reaction center



4C Chain Plants maize, sorghum, sugarcane, millet, fonio, tef, papyrus

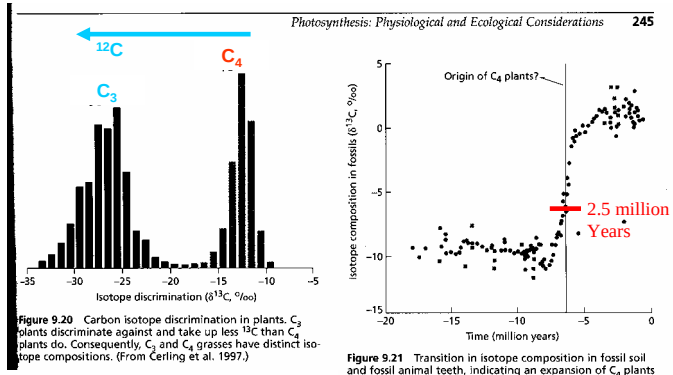
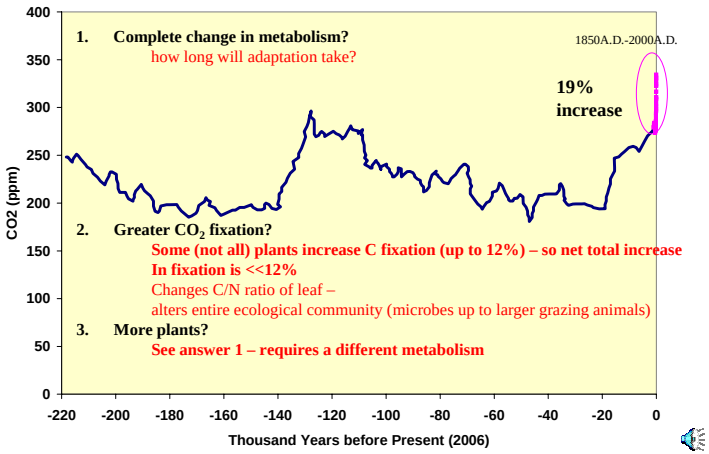


Figure 9.20 Carbon isotope discrimination in plants. C_3 plants discriminate against and take up less ^{13}C than C_4 plants do. Consequently, C_3 and C_4 grasses have distinct isotope compositions. (From Cerling et al. 1997.)

Figure 9.21 Transition in isotope composition in fossil soil and fossil animal teeth, indicating an expansion of C_4 plants in the late Miocene. Isotope values are shown for carbonates (black circles) extracted from fossil soil from Pakistan, for fossil mammalian tooth enamel from Pakistan (light green squares), and for fossil horse tooth enamel from North America (green circles). The change in isotope composition 5 to 7 million years ago suggests a shift from a flora dominated by C_3 plants to a flora dominated by C_4 plants. (After Cerling et al. 1993.)

www.fsl.orst.edu/~bond/fs561/lectures/isotope%20lecture%202005.ppt

What might be the effect of increasing CO_2 concentration
On plant survival strategies?



EXAM HINT

"Relevance" (essay) questions

- Gas phase reactions and biofractionation/climate change
- Gas phase reactions and effusion/nuclear power
- Gas phase reactions and smog
- Gas phase reactions – history of ability to control those reactions

Does the Ideal Gas Law Work Well?

$$V = k_1 n$$

$$PV = nRT$$ Ideal Gas Law

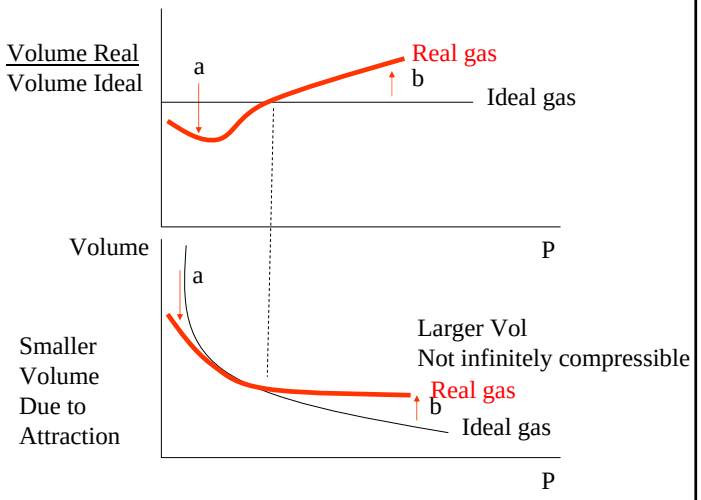
$$V_m = \frac{V}{n} = \frac{RT}{P} = constant$$ Predicts constant molar Volume (V/n)

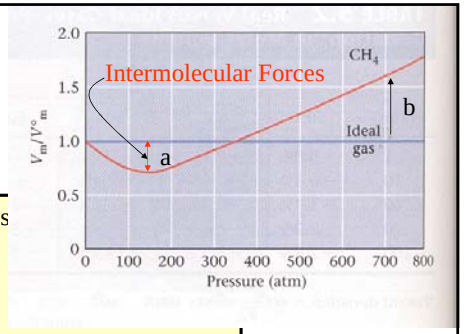
What would we expect in "real life"?

Real gases notice each other **(It's All about charge)**

a) repulsion;
volume is larger when pressure goes up

b) attraction
volume is smaller than expected at low pressure





Observed that real molecules have changes in molar volume as the pressure goes up

1. At high pressure they have **more** volume than we think - due to the "real" volume they have - they are not infinitely compressible

2. At low pressure they have **less** volume than we think -due to the fact that the molecules do notice each other and are attracted to each other.

Hmm- is this foreshadowing

Van der Waals Equation

$$P = \frac{nRT}{V}$$ Ideal gas

1837-1923
Johannes Diderik Van der Waals
Dutch
1910 Nobel Prize in Physics

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Volume of real molecules

Molecular attraction

Rule C1: (charge/vol)^2

Substance	b(volume)	a(attraction)
He	0.02370	0.0341
Ne	0.0171	0.211
Ar	0.0322	1.34
Kr	0.0398	2.32
Xe	0.0510	4.19

What do you Observe?

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Interaction "a" increases with Depth in periodic table (total number of electrons); b (size) too!

$$PV = nRT$$

$$u_{rms\,mole} = \sqrt{\frac{3RT}{MM}}$$

If you have these three memorized you can get to anything you need

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

$$R = 8.31 \frac{J}{mol \cdot K}$$

$$R = 8.31 x 10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$$

"A" students work (without solutions manual)
~ 10 problems/night.

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TABLE 5.2 Real Versus Ideal Gases; Percent Deviation* in Molar Volume

	O_2			CO_2		
P(atm)	50°C	0°C	−50°C	50°C	0°C	−50°C
1	−0.0%	−0.1%	−0.2%	−0.4%	−0.7%	−1.4%
10	−0.4%	−1.0%	−2.1%	−4.0%	−7.1%	
40	−1.4%	−3.7%	−8.5%	−17.9%		
70	−2.2%	−6.0%	−14.4%	−34.2%	Condenses to liquid	
100	−2.8%	−7.7%	−19.1%	−59.0%		

$$\text{Percent deviation} = \frac{(V_m - V_m^\circ)}{V_m^\circ} \times 100\%$$

Intermolecular Forces!