Chemistry is the study of matter (and energy)

more specifically,

- what is the structure of matter and how can that structure change?
- what is the structure of matter on various length scales?
- What is the time scale in which these structures can change?

Remember, science is all about discovering and quantifying "patterns" in nature.

different patterns at different length and time scales, and sometimes, ... remarkably...
the same patterns at different length & time scales.

But!, the length & time scale of human perception is severely limited

we have 5 senses - see, hear, feel, taste, smell

how fast can you detect changes in what you see, hear, feel, taste, or smell?

how far can you see, hear, $\underbrace{\text{feel, taste,}}_{\text{not far at all!}}$ smell?

Length Scales (orders of magnitude)

10^{-35} m ← Planck length ≡ smallest meaningful length in Physics

10^{-15} m ← size of a proton

10^{-10} m ← size of an atom

10^{-8} m ← size of a protein molecule

10^{-4} m ← size of an amoeba

10^{0} m ← size of a human

10^{7} m ← diameter of earth

10^{9} m ← diameter of sun

10^{13} m ← size of solar system

10^{20} m ← size of milky way galaxy

10^{26} m ← diameter of observable universe

That's over 60 orders of magnitude for length.

how many orders of magnitude difference in length can you perceive?

Time Scales (orders of magnitude)

10^{-43} s ← Planck time ≡ smallest time measurement possible.

10^{-25} s ← Top quark lifetime

10^{-16} s ← time period for one e^- orbit around nucleus

10^{-13} s ← time to break a chemical bond

10^{-12} s ← reorientational time for a water molecule

10^{-8} s ← reorientational time for protein in solution.

10^{-2} s ← time for protein to fold into active form
← time for one flap of a hummingbird wing
← time between hummingbird heart beats

10^{0} s ← time between human heart beats

10^{1} s ← time between whale heart beats

10^{3} s ← bacteria cell mitosis

10^{7} s ← earth orbit around sun

10^{15} s ← uplift of mountain range
← sun orbit around center of galaxy

10^{17} s ← age of earth (4.54 billion years)
← age of sun (4.57 billion years)
← age of universe (14.6 billion years)

In this 1st semester we're going to learn about matter by starting at the length & time scales that are familiar to your senses.

We're not going to start with the smallest length & time scales, where you have no physical intuition at all. (in contrast to textbook)

We'll start at the human scale (macroscopic world), and we'll begin with the <u>Theory</u> of <u>Thermodynamics</u>

Then we'll dive into the microscopic world, which your naked senses can never reveal to you.

We'll see how advanced technologies can augment our senses. How various types of "microscopes" can reveal patterns in the structure and dynamics of matter at small length and time scales.

To begin, we use the scale of human senses and define 3 states of matter

<u>Solid</u> - has a definite volume, a definite shape and is rigid.

<u>Liquid</u> - has a definite volume, but no definite shape

<u>Gas</u> - has no distinct volume, no distinct shape, and can be easily compressed to occupy a smaller volume

Imagine a rock in your hands.

What are some quantifiable properties we can use to describe this "piece" of matter?

- mass, volume, temperature, density, hardness, compressibility, surface area, composition, ...

Imagine a glass of water. What other quantifiable properties can you add?

- viscosity, refractive index, ...

Imagine a balloon filled with helium. Other properties?

- pressure ← Force/Area ← force of gas on surface of balloon.

Clearly, there are numerous properties. Any others?

- Charge, magnetization, ...

Are any of these properties related to others?

e.g. density = mass/volume

What is the minimum number of properties that we need to describe a sample of matter?

We will learn the answer to all these questions.

Let's examine two important adjectives for properties of matter.

<u>Extensive Property</u> => linearly dependent on amount of substance

e.g. mass, volume, energy

useful tip

take 2 identical samples with all properties identical and combine them into a single sample.

⇓

Properties that double are extensive.

<u>Intensive Property</u> => independent of amount of substance.

e.g. temperature, pressure, density

Can you think of any property that is neither extensive nor intensive?

other important adjectives...

<u>uniform phase</u> sample => each intensive property is constant throughout space in sample

<u>homogeneous</u> <u>sample</u> => intensive properties vary continuously throughout space

<u>heterogeneous</u> <u>sample</u> => intensive properties vary discontinuously throughout space

Equilibrium Thermodynamics

Definitions

System - part of universe under study

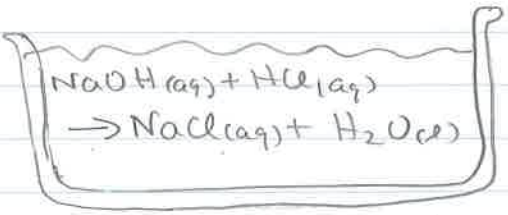
Surroundings - everything else that can interact with the system

your definition of system and surroundings depend on the problem you're considering.

e.g.

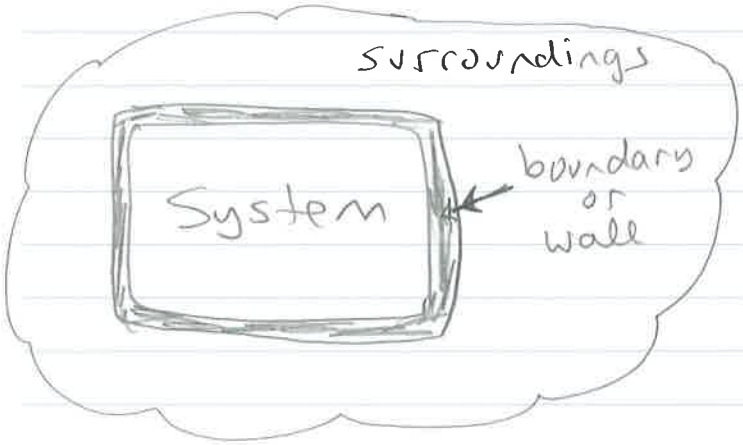
how does gas in piston behave?

System ≡ gas
Surroundings ≡ piston and all that surrounds piston



system ≡ reactants & products
surroundings ≡ beaker, could also be solvent.

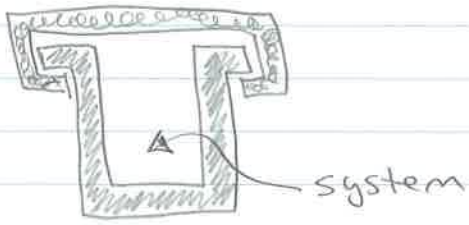
Is there any kind of boundary between the system and surroundings?



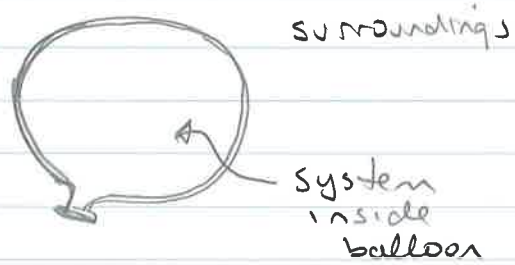
We have adjectives to define the characteristics of the boundary

The boundary (or wall) may be...

- **Rigid** or **Non Rigid**



Sealed metal container
- no volume change is possible



balloon
volume can be easily changed
(increase pressure of surroundings)

- **Adiabatic** or **Diathermal**

doesn't conduct heat

e.g. styrofoam cup to keep coffee warm

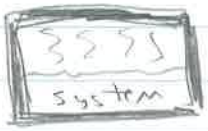
allows heat to flow between system and surroundings

e.g. Frying pan
diathermal

- **Permeable (open)** or **Impermeable (Closed)**

open flask, gas can escape into surroundings

mass cannot move between system and surroundings



An isolated system has impermeable, adiabatic, and rigid walls.

What does it mean when we say a system is at equilibrium?

- An isolated system is in equilibrium when its macroscopic properties remain constant in time.

- A non-isolated system is in equilibrium when

  (1.) The system's macroscopic properties remain constant with time.

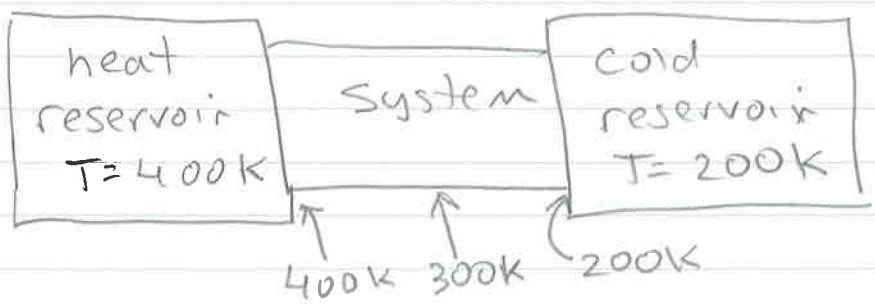
  ≡ and ≡

  (2.) Isolation of system from surroundings causes no changes in system properties.

if (1) is true, but (2) is not, then non-isolated system was in "steady-state", not equilibrium.

steady state ≡ system properties constant over time even though system exchanges matter or energy w/ surroundings

e.g.,



if we remove system from reservoirs, the temperature will change.

Types of EQUILIBRIUM

Mechanical EQUILIBRIUM - each fluid phase has same uniform pressure

Thermal EQUILIBRIUM - each phase has the same uniform temperature

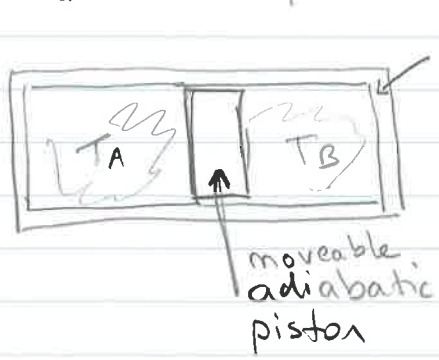
Transfer EQUILIBRIUM - The forward and backward rates of transfer of each substance between phases are equal.

Reaction EQUILIBRIUM - The forward and backward rates are equal for every elementary reaction occuring.

Transfer & Reaction equilibria are sometimes grouped together and called Materials equilibrium

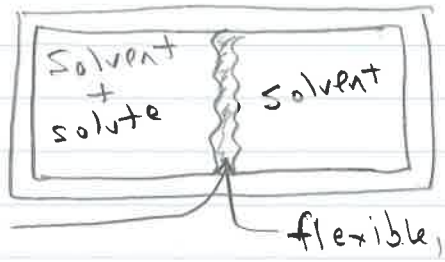
We can use boundaries to prevent systems from reaching certain types of equilibrium.

e.g.



Piston can move, so mechanical EQUILIBRIUM is reached, but adiabatic piston means Thermal EQUILIBRIUM cannot be reached.

another example



Wall is flexible & diathermal, so mechanical & Thermal equilibria are reached, but transfer equilibrium cannot be reached for solute

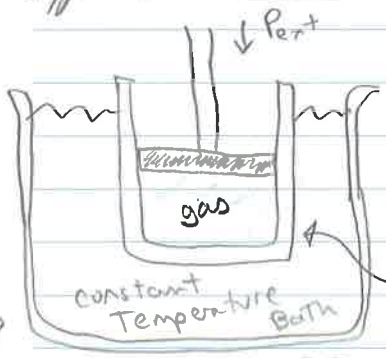
Let's go back to our question of how physical properties of matter are related.

In a uniform phase sample, such a relationship is called an <u>EQUATION OF STATE</u>

If a sample is heterogeneous, then each uniform phase will have its own Eq. of state.
- One for uniform gas phase
- one for each uniform liquid phase
- one for each uniform solid phase

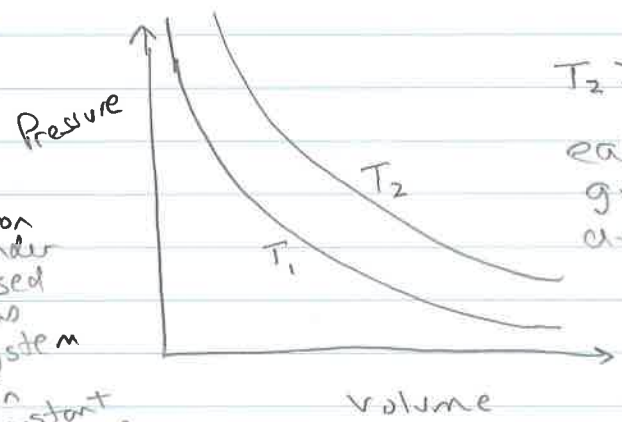
So, we will start with the easiest: <u>Gas Laws</u>

1662 <u>Boyle's Law</u> ⇒ $\boxed{pV = \text{constant}}$ at equilibrium



Piston cylinder closed gas system in constant Temperature bath

Reimagining Boyle's Experiment, Boyle's actual experiment was done in a J-tube.

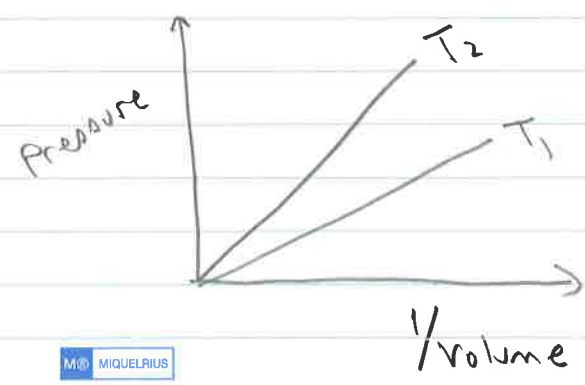


$T_2 > T_1$

each curve on graph is called an <u>isotherm</u>

↑ line of constant Temperature

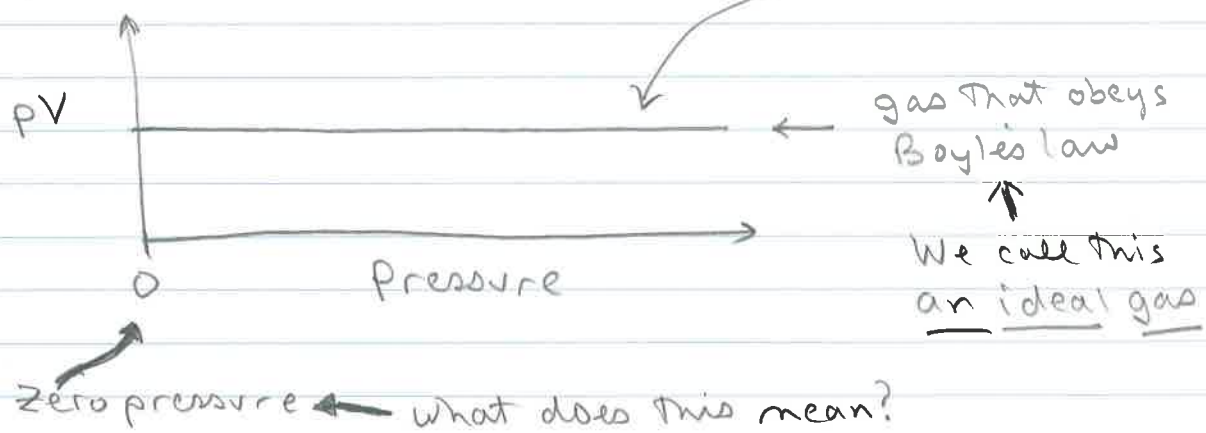
isotherms are straight lines when plotted versus $1/V$



Boyle's law is MOSTLY TRUE, with some gases obeying the law more than others.

Generally, all gases follow Boyle's Law when the gas pressure is low enough

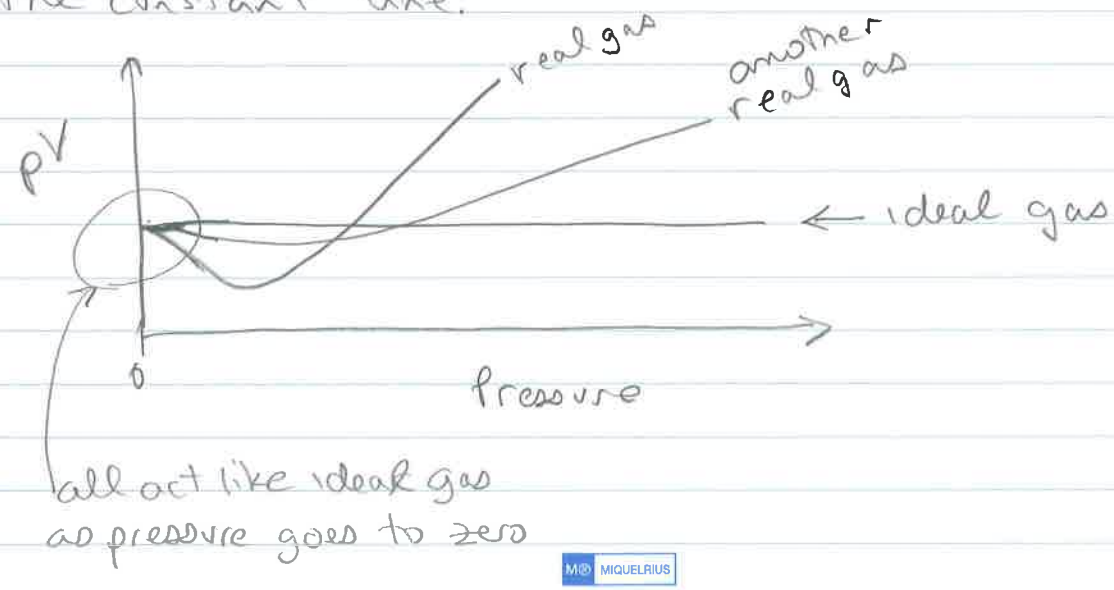
Boyle found pV = constant
so if we plot pV versus pressure we expect to see a constant line



what does this mean?

True zero pressure is total vacuum. In other words, no gas molecules present.

Real gases do not follow a constant line, but as the pressure goes towards zero, they approach the constant line.



How can we explain these deviations from Boyle's law?

1st What's happening as the pressure goes to zero? Why do all gases obey Boyle's law then?

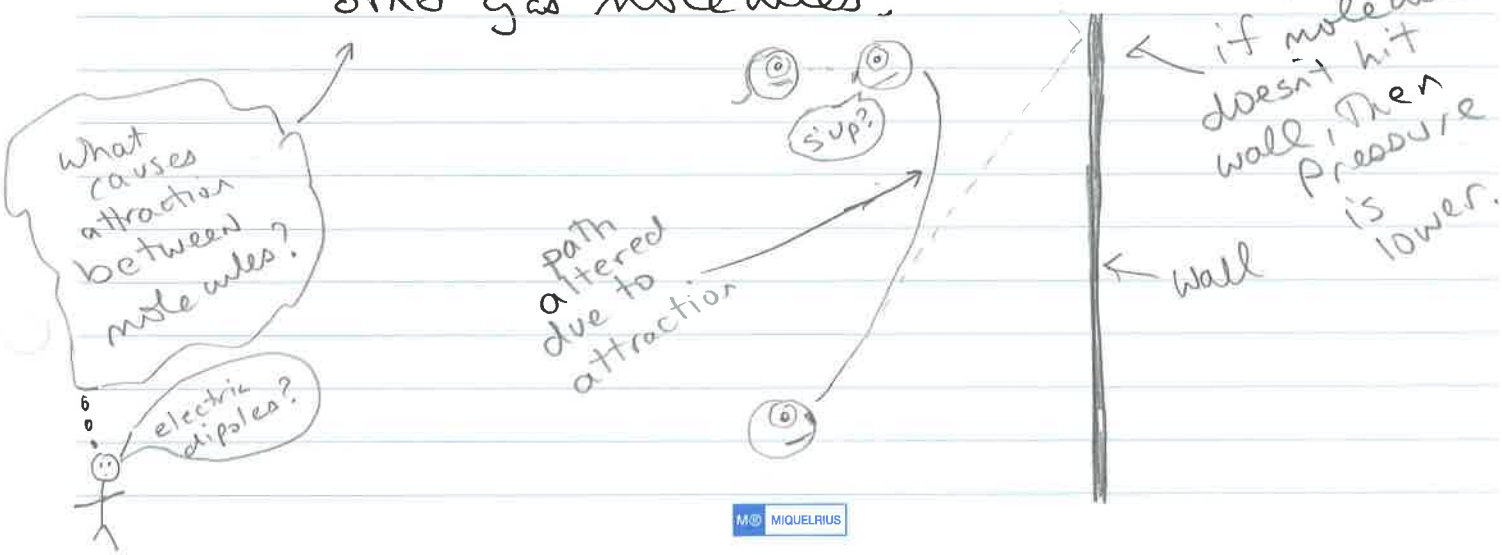
- at low pressures the density of the gas is low. So, it becomes a rare event for gas molecules to collide.

So, perhaps Boyle's law only works for molecules that never interact with other molecules.

That is, in an ideal gas, molecules hit the container walls, but never hit other molecules.

2nd Then, what causes the pV product to be smaller than the ideal value as the pressure initially increases.

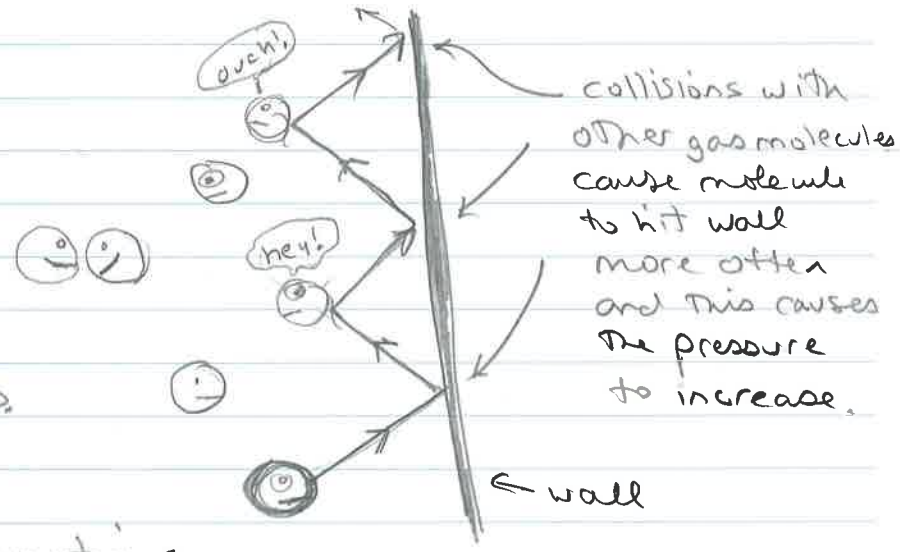
- gas molecules could be attracted to other gas molecules.



3rd Then, what causes the pV product to be larger than the ideal value as the pressure get much higher?

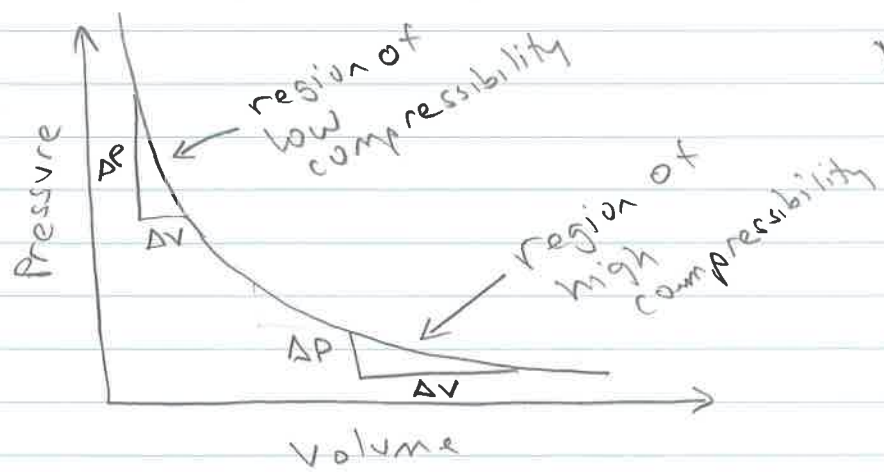
- at high pressures the density of the gas is higher, so collisions between gas molecules are much more common.

also, molecules with larger "volumes" have greater chances to collide, so this effect becomes stronger as molecular size increases.



We'll look at these deviations from ideal gas behavior in more detail later.

Compressibility of Gases

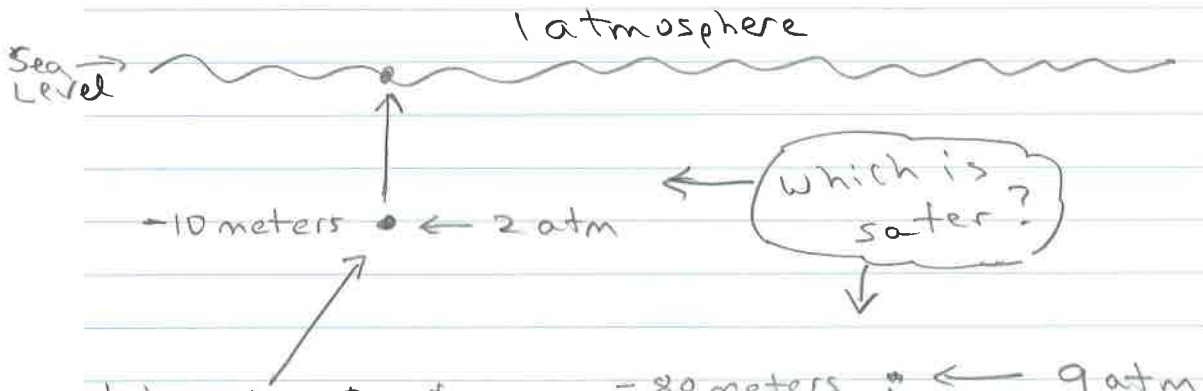


$$K = -\frac{1}{V}\left(\frac{\Delta V}{\Delta P}\right)$$

compressibility

underwater diving - Lessons from Boyle's Law

when you hold your breath you create a closed gas system in your Lungs. Let's assume Boyle's Law holds.



take a breath of air at -10 meters & rise to surface.

Pressure decreases 50% from 2 to 1 atm.

If your lungs expand by this factor they would be damaged.

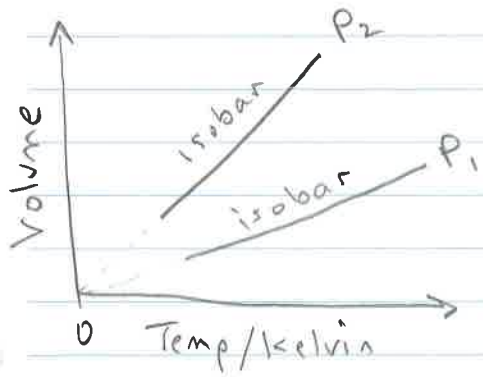
take a breath of air at -90 meters & rise to -80 meters.

Pressure decreases 10%, so volume of lung increases 10%

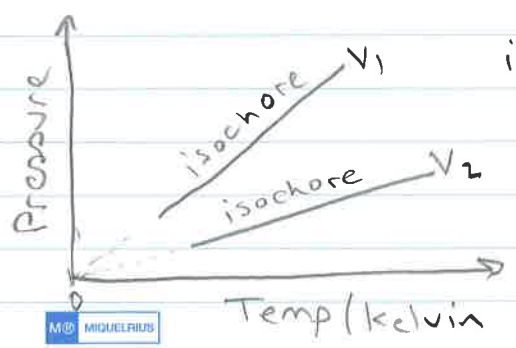
1780s

Charles Law

$$V/T = \text{constant}$$
$$P/T = \text{constant}$$



isobar ≡ constant pressure curve.



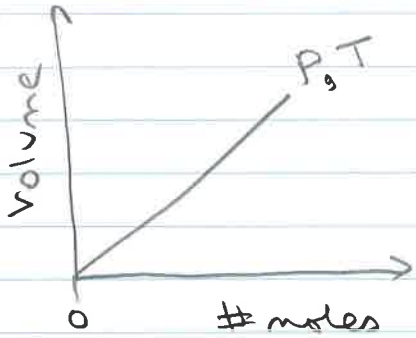
isochore ≡ constant volume curve

Avogadro's Law

$$\boxed{V/n = \text{constant}}$$

n ← # moles

1811



Émile Clapeyron combined all 3 laws into the ideal gas equation of state

1834

$$PV = nRT$$

R ← Proportionality constant

$$R = 0.08206 \frac{L\text{-}atm}{mol\text{-}K}$$

We define standard Temperature as $T = 273\,K$ and standard Pressure as $P = 1\,atm$ } STP

what is the volume of 1 mole of an ideal gas at standard temperature and pressure?

$$V = \frac{nRT}{P} = \frac{(1\,mole)(0.08206\,L\text{-}atm/mol\text{-}K)(273\,K)}{1\,atm}$$

$$= 22.4\,L$$

2.96g Mercuric Chloride is vaporized in a 1.0 L bulb at 680K and 453 Torr. Assuming ideal gas behavior, what is its molar mass?

We know everything except n, number of moles, we can find n by

$$n = \frac{PV}{RT} = \frac{453\,\text{Torr}}{} \cdot \frac{1\,\text{atm}}{760\,\text{torr}} \cdot \frac{1.0\,\text{L}}{} \cdot \frac{\text{K-mol}}{0.08206\,\text{L-atm}} \cdot \frac{}{680\,\text{K}}$$

P conversion V 1/R 1/T

$n = 0.011$ moles

Next calculate molar mass

molar mass = 2.96g / 0.011 mol = 277 g/mol

We can also use the ideal gas law as a way of converting volume into moles when calculating stoichiometric quantities in chemical reactions.

A sample of $CH_{4(g)}$ having a volume of 2.80 liters at 25°c and 1.65 atm, was ignited with a sample of oxygen gas having a volume of 35.0 liters at 31°C and 1.25 atm to produce CO_2 and H_2O vapor. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125°c.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

(1st) Find the limiting reagent

For solids, liquids, gases, we can always calculate the number of moles from the mass and the molecular weight.
For an ideal gas, however, we can also convert volume to moles using $PV = nRT$

$$n_{CH_4} = \frac{PV}{RT} = \frac{1.65\,atm \mid 2.80\,L \mid K\text{-}mol}{\mid 0.08206\,L\text{-}atm \mid 298\,K} = 0.189\ moles$$

$$n_{O_2} = \frac{PV}{RT} = \frac{1.25\,atm \mid 35.0\,L \mid K\text{-}mol}{\mid 0.08206\,L\text{-}atm \mid 304\,K} = 1.75\ moles$$

Since

$$\frac{0.189\ moles \mid 2\ mole\ O_2}{\mid 1\ mole\ CH_4} = 0.378\ O_2 < 1.75\ moles$$

chem. Eq. stoichiometry

Then O_2 is in excess, and CH_4 is the limiting reagent.

(2nd) Volume of CO_2 produced is

$$\frac{0.189\ mol \mid 1\ mole\ CO_2}{\mid 1\ mole\ CH_4} = 0.189\ mole\ CO_2$$

$$V = \frac{nRT}{P} = \frac{0.189\ mol\ CO_2 \mid 0.08206\ L\text{-}atm \mid 298\,K \mid}{\mid mol\text{-}K \mid 2.50\,atm}$$

$$V = 2.47\ L$$

so 2.47 liters of CO_2 are produced.

Mixtures of Gases

For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone (assuming they don't chemically react).

$$P_{TOTAL} = P_1 + P_2 + P_3 + \cdots = \sum_{i=1}^{N_{gases}} P_i$$

Partial Pressure of Gas 1 — Partial Pressure of Gas 2

This is called Dalton's Law

if each gas behaves ideally then we can write

$$P_{TOTAL} = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \cdots$$

$$= (n_1 + n_2 + n_3 + \cdots)\frac{RT}{V}$$

$$= n_{TOTAL}\frac{RT}{V} \quad \text{where } n_{TOTAL} = \sum_{i=1}^{N_{gases}} n_i$$

we can also define the mole fraction of the ith component of the gas

$$x_i = \frac{n_i}{n_{TOTAL}} \quad \text{so} \quad \sum_{i=1}^{N_{gases}} x_i = 1$$

mole fraction

A common use of partial pressures is when a gas is collected over a liquid which has an appreciable vapor pressure.

For example, if oxygen is collected by displacement of H_2O, and you want to know how much oxygen is present, we need to know that the oxygen is saturated with H_2O vapor.

The total pressure is the sum of the pressure of oxygen plus that of H_2O.

$$P_{TOTAL} = P_{H_2O} + P_{O_2}$$

O_2 gas can be collected over water by decomposing $KClO_3$ according to the reaction

$$2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2$$

if 0.044 liters of O_2 saturated with H_2O vapor at 0.020 atmospheres and a temperature of 18.6°C are collected, what volume would the O_2 gas occupy at STP if it was dry (i.e., without water vapor)?

The vapor pressure of H_2O at 18.6°C is 0.020 atm. The experiment was performed on a day when the atmosphere pressure of 0.983 atm.

1st We need to calculate the partial pressure of O_2 according to

$$P_{O_2} = P_{TOTAL} - P_{H_2O}$$

which gives

$$P_{O_2} = 0.983\ \text{atm} - 0.020\ \text{atm} = 0.963\ \text{atm}$$

Under our experimental conditions we then calculate

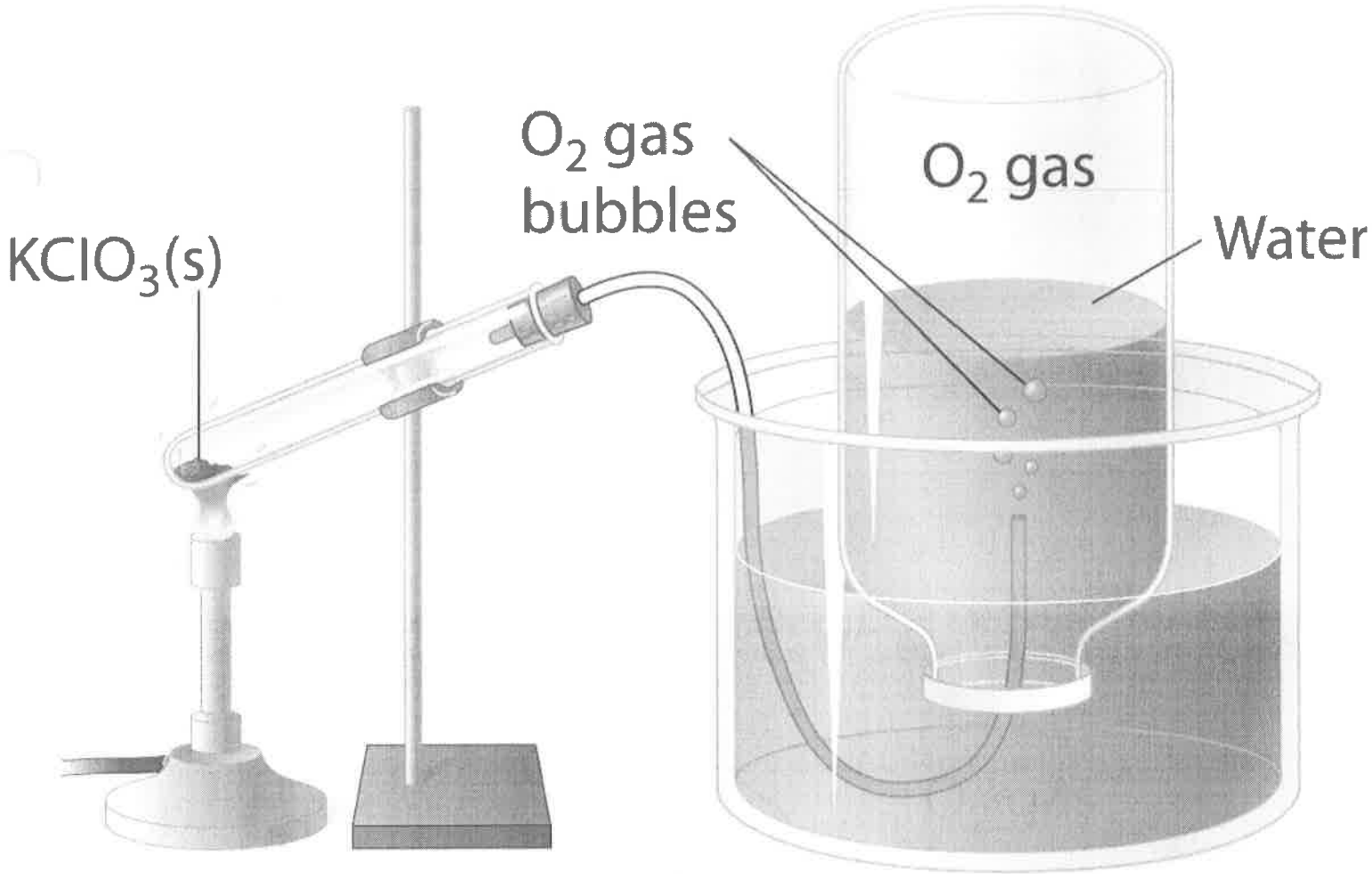
$$n_{O_2} = \frac{PV}{RT} = \frac{0.963\ \text{atm} \mid 0.044\ \text{L} \mid \text{K-mol}}{\mid 0.08206\ \text{L-atm} \mid 292\ \text{K}}$$

$$= 1.8 \times 10^{-3}\ \text{mol}$$

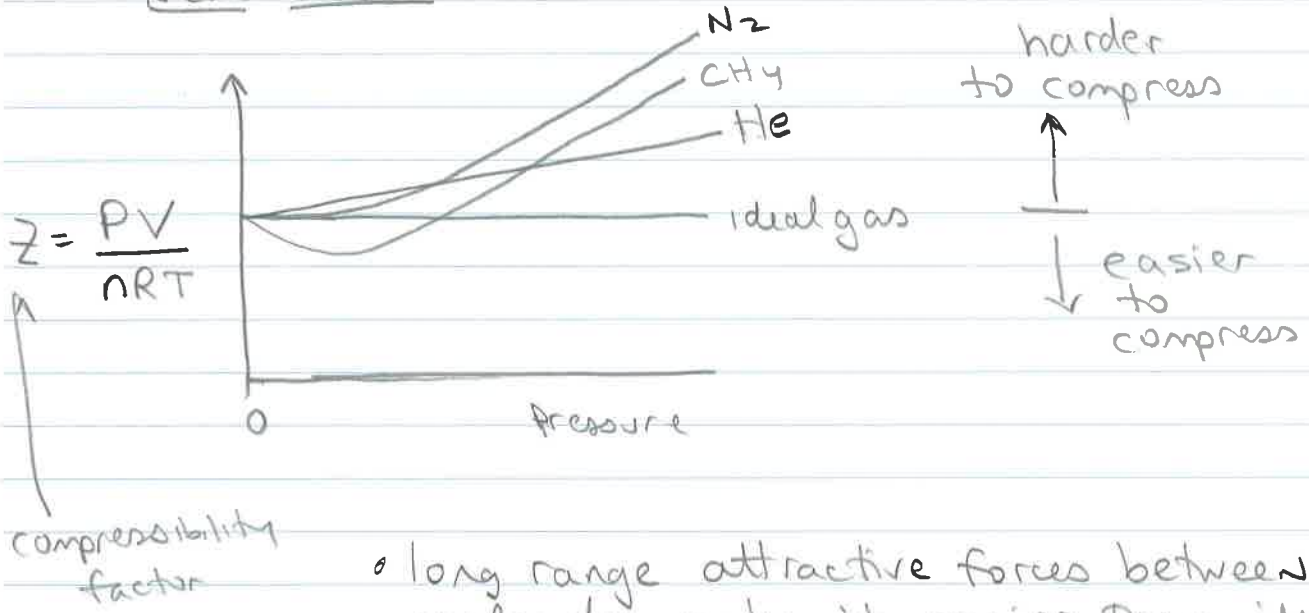
so at STP, 1.8×10^{-3} mol of O_2 will occupy

$$V = \frac{nRT}{P} = \frac{1.8 \times 10^{-3}\ \text{mol}\ O_2 \mid 0.08206\ \text{L-atm} \mid 273\ \text{K} \mid}{\text{mol-K} \mid 1\ \text{atm}}$$

$$= 0.040\ \text{L}$$


$KClO_3(s)$
O_2 gas bubbles
O_2 gas
Water

Real Gases



- long range attractive forces between molecules make it easier than ideal gas to compress at low pressure

- finite volume of molecules & short range repulsive force make it more difficult than ideal gas to compress at higher pressures.

Clearly, we need a better EQUATION OF STATE for gases.

$PV = nRT$ not so good at high pressures

Van der Waals EQUATION OF STATE

$$\underbrace{\left(P_{real} + \frac{an^2}{V_{real}^2}\right)}_{P_{ideal}} \underbrace{\left(V_{real} - nb\right)}_{V_{ideal}} = nRT$$

$$P_{real} = P_{ideal} - \frac{a n^2}{V_{real}^2}$$

actual Pressure

Pressure if there were no intermolecular attractions

reduction in pressure due to molecular attractions ⇝ depends on density of gas, the higher the density the less "ideal", i.e., more intermolecular attractions

$$a\underbrace{\left(\frac{n}{V}\right)\left(\frac{n}{V}\right)}_{\rho^2}$$

Proportionality constant

units: $\frac{atm \cdot L^2}{mol^2}$

ρ ← molecular number density

$$V_{Real} = V_{ideal} + n b$$

Volume assuming individual molecules have no volume

adds volume of molecules to total volume ⇝ b is proportional to size of molecule.

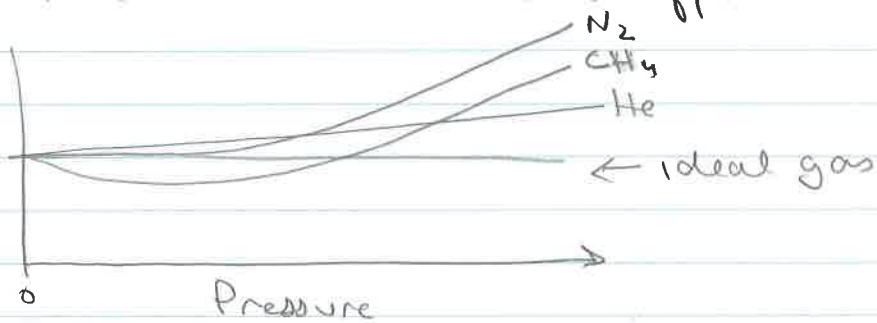
Substance	$a / atm \cdot L^2 \cdot mol^{-2}$	$b / L \cdot mol^{-1}$	$T_{b.p.}/K$	
He	0.0341	0.0237	4.2	noble gases
Ar	0.214	0.0174	27.2	
N_2	1.35	0.0386	77.4	non-polar molecules
O_2	1.34	0.0312	90.2	
CH_4	2.26	0.0430	109.2	
H_2O	5.47	0.0305	373.15	Polar molecules
NH_3	4.25	0.0379	239.8	

correlation to molecular size as expected, but not always clear.

Virial EQUATION OF STATE

take a more mathematical approach

$$Z = \frac{PV}{nRT}$$



remembering some algebra, you might see that these curves look familiar – like parabolas?

$$Z = \frac{PV}{nRT} = \underbrace{1 + B'(T)p + C'(T)p^2 + D'(T)p^3 + \cdots}_{\text{Virial Expansion}}$$

expand Z in terms of powers of p with coefficients that depend on each gas.

$B'(T)$, $C'(T)$, $D'(T)$ all called virial coefficients, and are functions of temperature, and obtained by experimental measurements and data fitting.

For many gases, can terminate expansion with B' coefficient,

$$Z = 1 + B'(T)p$$

is enough to accurately predict E.O.S. for many gases.

Can also do Virial Expansion in terms of molar volume.

molar volume $V_m = V/n$ ← volume (extensive) ← # moles (extensive)

intensive property

$$\boxed{Z = \frac{PV}{nRT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots}$$

The Virial Equation of state will work for all real gases. One just needs to know how far to go in the equation expansion and all the coefficients.

A disadvantage of the Virial E.O.S. is that the coefficients are less physically intuitive compared to Vander Waals E.O.S.

☆☆☆

Use the van der Waals equation to calculate the pressure of a sample of one mole of O_2 gas in a 22.415 L vessel at 0°C.

Go to table in text and for O_2 find

$a = 1.364\ L^2\text{-atm/mol}$
$b = 3.19 \times 10^{-2}\ L/mol$

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

$n = 1$
$V = 22.415\ L$

$$p = (1\ mol)\left(\frac{0.08206\ L\text{-atm}}{mol\text{-}K}\right)\cdot\frac{273.15\ K}{(22.415\ L - (1\ mol)(3.19\times10^{-2}\ L/mol))}$$

$$- 1.364\ \frac{L^2\text{-atm}}{mol}\left(\frac{1\ mol}{22.415\ L}\right)^2$$

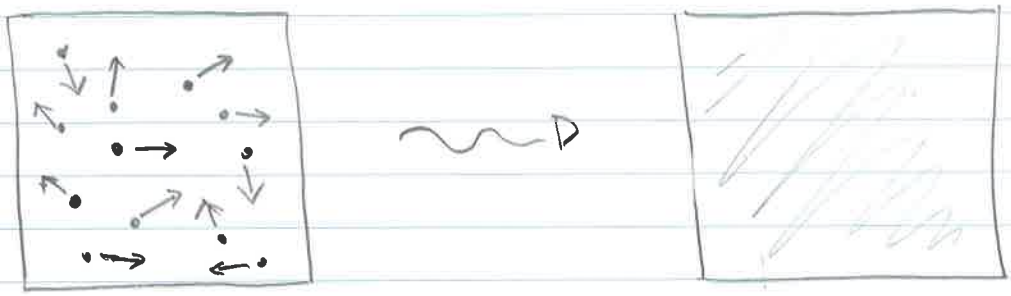
$$p = 1.0014\ atm - 0.0027\ atm$$

$$p = 0.9987\ atm$$

What would the pressure be if this was an ideal gas?

Kinetic Theory of Gases

Let's consider a gas of N molecules, each of mass m, in box of volume V.



microscopic world — Macroscopic World

x_i, v_i, m_i

position, velocity, mass

for every molecule in the gas

P, V, T, n

Pressure, Volume, Temperature, # moles

How are these related?

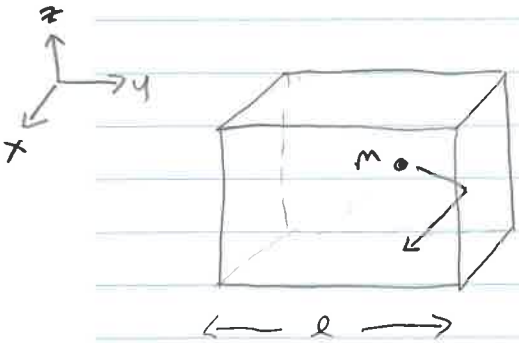
We will not derive $PV = nRT$, but instead use it to understand micro and macro relationships.

In kinetic theory of gases, one assumption is that the particles do not "see" each other or interact with one another in any way.

Our task: Derive an expression from the macroscopic pressure inside the box in terms of the microscopic coordinates and mass of the gas molecules

Pressure is defined as Force per unit area

What is the force of one molecule hitting a wall of the box?



Force is the change in momentum of a molecule hitting one wall of the box.

force along y

$$F_y = \frac{\Delta P_y}{\Delta t}$$

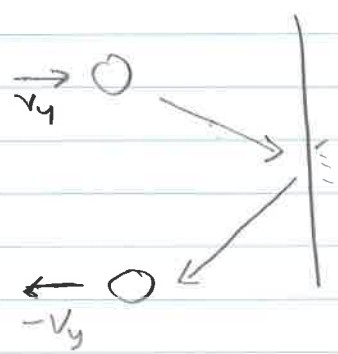
change in y component of molecule momentum

time between wall collisions

from Newton's 2nd Law of motion

recall the momentum $\vec{p} = m\vec{v}$

We assume that collision with wall is elastic, so



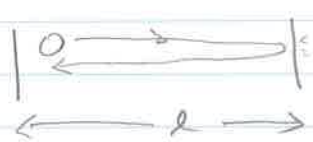
$$\Delta P_y = P_y^{final} - P_y^{initial}$$

$$= (-mV_y) - (mV_y) = -2mV_y$$

and

$$\Delta t = \frac{2l}{V_y}$$

length of box in y-direction



time to travel length of box, hit the wall, and travel back to starting point.

so

force of one molecule hitting one wall of box

$$F_{y_1} = \frac{\Delta P_y}{\Delta t} = \frac{-2mV_y}{2l/V_y} = -\frac{mV_y^2}{l}$$

Next we sum over all molecules hitting one wall

$$F_{y_N} = \frac{-m \sum_{j=1}^{N} V_{y_j}^2}{\ell}$$

recall $\sum_{i=1}^{N} x_i = x_1 + x_2 + \cdots + x_N$

Now we add together the magnitude of the forces when all molecules hit all 6 walls.

We need to sum the magnitude of forces (i.e, ignore signs)

$$F_{TOTAL} = 2 \cdot \frac{m}{\ell} \left(\sum_{j=1}^{N} V_{x_j}^2 + \sum_{j=1}^{N} V_{y_j}^2 + \sum_{j=1}^{N} V_{z_j}^2 \right)$$

$$F_{TOTAL} = 2 \frac{m}{\ell} \left[\sum_j \left(V_{x_j}^2 + V_{y_j}^2 + V_{z_j}^2 \right) \right]$$

define the magnitude of the velocity vector

$$V^2 = V_x^2 + V_y^2 + V_z^2$$

so

$$F_{TOTAL} = 2 \frac{m}{\ell} \sum_j V_j^2$$

sum over velocity for every molecule

if the mean squared velocity is given by

$$\overline{V^2} = \frac{1}{N} \sum_j V_j^2$$

Substitute

Then we can rearrange to get $N \bar{V}^2 = \sum_j V_j^2$

to get

$$F_{TOTAL} = 2\frac{m}{\ell} N \bar{v}^2$$ ← total force on all walls of box.

Next, Pressure = Force / Area
← total area of box

Total area = $6 \cdot A$
← area of one wall

so

$$P = 2\frac{m}{\ell} N \bar{v}^2 / 6A = \frac{N m \bar{v}^2}{3A\ell}$$

volume of box is $V = A\ell$

so

$$P = \frac{N m \bar{v}^2}{3V} \quad \text{or} \quad PV = \frac{1}{3} N m \bar{v}^2$$

rearrange to

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2\right)$$

average kinetic energy

$$\bar{\epsilon}_k = \frac{1}{2} m \bar{v}^2$$

← recognize this? it's the average kinetic energy of a gas molecule

so

$$PV = \frac{2}{3} N \bar{\epsilon}_k$$

if $N = N_A = 6.022 \times 10^{23}$ then

$$PV = \frac{2}{3} N_A \bar{\epsilon}_k = \frac{2}{3} E_k$$

$E_k = N_A \bar{\epsilon}_k$
← average kinetic energy of 1 mole of gas molecules

and since $PV = RT$ ($n = 1$ mole)

Then $PV = \frac{2}{3} E_k = RT$ or $\boxed{E_k = \frac{3}{2} RT}$

$$\boxed{E_k = \frac{3}{2}RT}$$

reveals the relationship between temperature and Energy, and says that if you raise the temperature of the system then you increase the energy of the system.

divide by N_A to get per molecule basis

$$\boxed{\bar{E}_k = \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}k_B T}$$

Gas Constant

$k_B = R/N_A$

Avogadro's #

Boltzmann's Constant

$R = 8.31\ J\text{-}K^{-1}\text{-}mol^{-1}$

$k_B = 1.38 \times 10^{-23}\ J\text{-}K^{-1}$

These equations also show us the absolute nature of temperature in the fact that temperature goes to zero as the energy goes to zero.

You can't have negative temperature, since you can't have negative kinetic energy.

How much <u>thermal</u> <u>energy</u> in 1 mole of gas?

at Room temperature $T = 300K$, $R \approx 8\ J\text{-}K^{-1}\text{-}mole^{-1}$

so $E \approx \frac{3}{2}(8\ J/K\text{-}mol)(300K) \approx \underline{3.5\ kJ/mole}$

Thermal Energy

Concept of Thermal Energy is important, and helps us understand whether a reaction will occur or NOT. That is, is there enough Thermal energy to break a bond and cause a rxn to occur.

From all this another interesting quantity is molecular speed

since $\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$

Then

$$C_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 RT}{M}}$$

speed is scalar, velocity is vector

(molecule) — molecular mass

(mole) — molar mass

EQUATIONS MAKE SENSE
since speed is proportional to $\sqrt{T}$ and $\sqrt{1/M}$

- as temperature increase, the energy of molecule increases, and thus velocity increases.

- as molecular mass increases, for a fixed energy, the molecular speed must decrease. That is why molecular speed is inversely proportional to molecular mass.

Maxwell Distribution Law

James Clerk Maxwell and also Ludwig Boltzmann wanted to know the full distribution of velocities and speeds in a gas, not just the average speed.

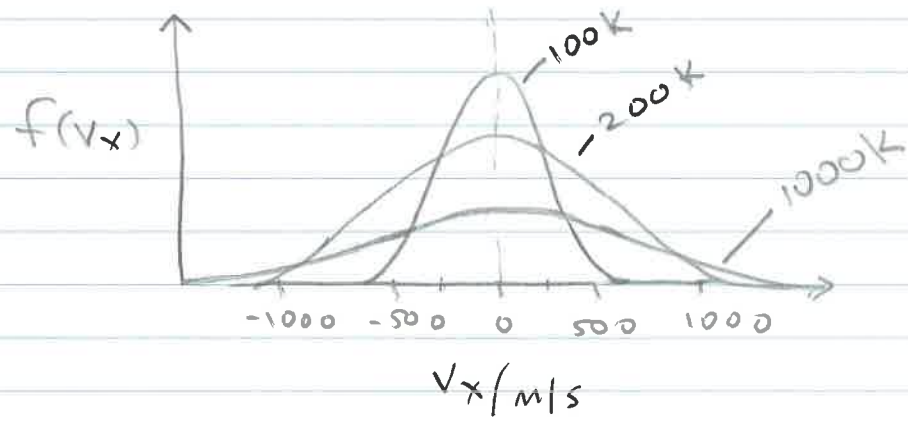
- What fraction of molecules are moving faster than a specific speed or velocity?

They derived an expression for the probability distribution of molecular velocities and speeds.

Maxwell-Boltzmann distribution of velocities in x direction

$$f(V_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mV_x^2/2k_BT}$$

This equation has the mathematical form of a Gaussian distribution aka the normal distribution aka the Bell curve



The area under each curve is 1.

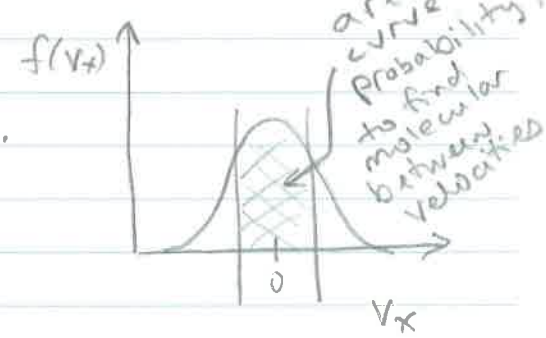
$$\int_{-\infty}^{\infty} f(V_x)\,dx = 1$$

means that the probability of finding a gas molecule between $V_x = -\infty$ m/s and $V_x = +\infty$ m/s is 100% (no surprise!)

$$\int_{-500\,m/s}^{+500\,m/s} f(V_x)\,dx = ?$$

This is how to calculate the probability of finding a gas molecule between $V_x = -500$ m/s & $V_x = +500$ m/s

You don't need to know how to calculate this integral in this course, but you should understand its physical significance.

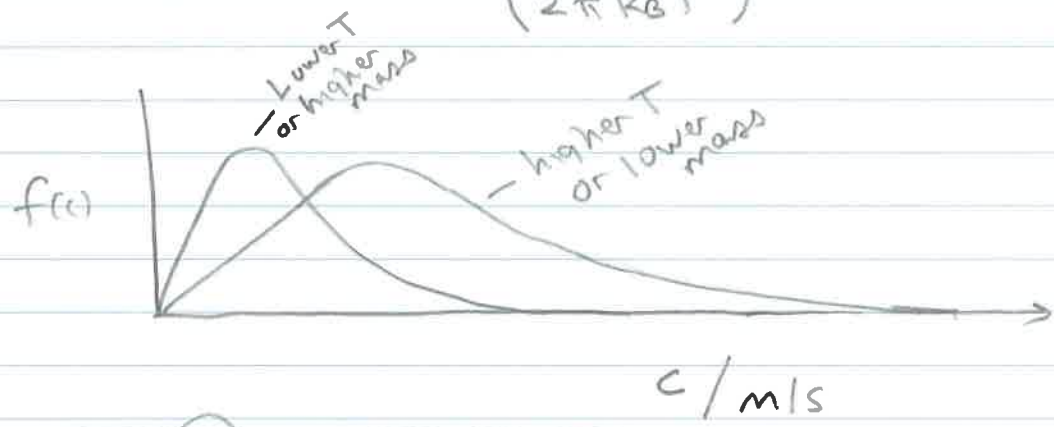


Velocity is a vector quantity and speed is magnitude of the velocity vector.

$$c = \sqrt{\vec{v}\cdot\vec{v}}$$ ← square root of the vector dot product

The Maxwell-Boltzmann distribution of speeds is

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc^2/2k_BT}$$



What is the root mean square speed for a mole of vanillin molecules at room temperature?

Vanillin ≡ $C_8H_8O_3$ (m.w. = 152.15 g/mole)

$$c_{rms} = \sqrt{\frac{3RT}{M}}$$

careful w/units!

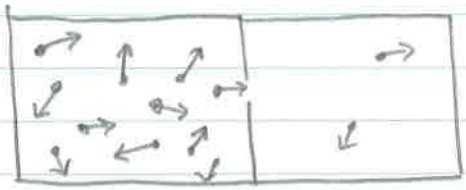
$R = 8.31\ J/K\text{-}mol = 8.31\ kg\text{-}m^2/K\text{-}mol\text{-}s^2$

$$c_{rms} = \sqrt{\frac{3(8.31\ kg\text{-}m^2/K\text{-}mol\text{-}s^2)(298\ K)}{(152.15\ g/mol)(1\ kg/1000\ g)}} = 221\ m/s$$

≈ 500 mph

if vanillin has such a high speed why does it take so long to travel across the room?

Effusion = Rate at which gas escapes through pin hole into vacuum of low pressure region.



size of pinhole is smaller than the mean free path

average distance a molecule travels between collisions in the gas phase.

Using the Maxwell-Boltzmann distribution, one can calculate the effusion rate;

$$Z_A = \frac{P}{(2\pi m k_B T)^{1/2}}$$

Temperature

using $P = nRT/V$, Z_A becomes

$$Z_A = \frac{nRT^{1/2}}{V(2\pi m k_B)^{1/2}}$$

We can compare this to Graham's experimental observation comparing two gases A & B:

$$\frac{\text{effusion rate of gas A}}{\text{effusion rate of gas B}} = \sqrt{\frac{M_B}{M_A}}$$

molar masses

Graham also observed for a given gas that

$$\frac{\text{effusion rate at } T_2}{\text{effusion rate at } T_1} = \sqrt{\frac{T_2}{T_1}}$$

Liquefaction of Gases & The Joule-Thomson Effect

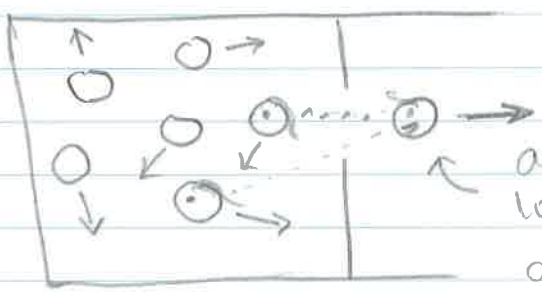
Here's an interesting trick,

We now know that the speed of gas molecules is related to the temperature of the gas:

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

So, if we can slow the molecules down, we will cool the gas.

Joule & Thompson realized that a Real gas can be cooled simply by letting the gas expand.



as real gas molecule escapes into low pressure region its attraction to molecules "behind" it cause it to slow down.

an ideal gas molecule wouldn't slow down because it experiences no intermolecular attractions.

This cooling is called the Joule-Thompson Effect, and is used to liquefy gases.