

LECTURE 15. MORE ADVANCED IDEAS INVOLVING GASES

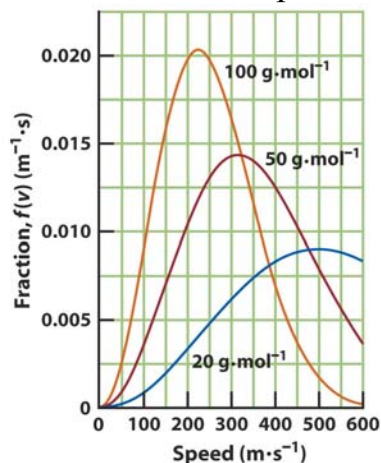
How fast are gas molecules?

From kmt, $T \propto E = \frac{1}{2} kT$ (temp term) = $\frac{1}{2} mv^2$ (velocity term)

Note that the velocity is easily determined from

$$E = \frac{1}{2} mv^2$$

Also note that the higher the temperature, the higher the velocity. Depending on the mass and T, gas molecules move at hundreds of miles per hour at room temperature!!



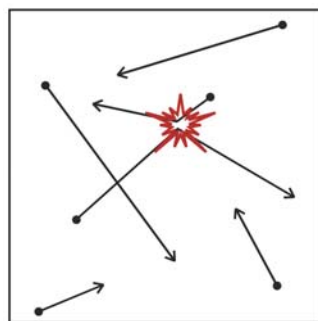
Also note that there is an inverse square relationship between molecular speed and mass that falls out of the equation.

Example: At a certain temperature, H₂ is traveling 1000 mph. how fast is O₂ moving at that temperature?

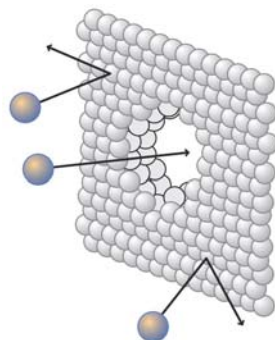
Energy is the same so $\frac{1}{2} m_{H_2} v_{H_2}^2 = \frac{1}{2} m_{O_2} v_{O_2}^2 \rightarrow 2 v_{H_2}^2 = 32 v_{O_2}^2 \rightarrow$
 $32/2 = v_{H_2}^2 / v_{O_2}^2 \rightarrow 16 = (1000 \text{ H}_2 / v_{O_2}) \rightarrow \text{square root } 4 = 1000 / v \text{ so } v = 250 \text{ mph.}$

Diffusion and Effusion

We know that gas molecules don't really move at hundreds of mph. If they did, smells would come (and go) much faster. Actually at atmospheric pressure, constant collisions occur and the actual speed is reduced many orders of magnitude at atmospheric pressure. So what do they call this collisional velocity? Diffusion. And a similar kind of velocity that has to do with the ability of gas molecules to get through a pin hole is called effusion.



diffusion



effusion

The good news from a calculation perspective is that while the math is much more difficult when looking at the same inverse square relationship.

In both cases, the rate of effusion and diffusion is the same **inverse square** relationship as speed.

So the 4- fold slower velocity of O_2 than H_2 is also a 4- fold slower diffusion and effusion.

Non-Ideality of gases

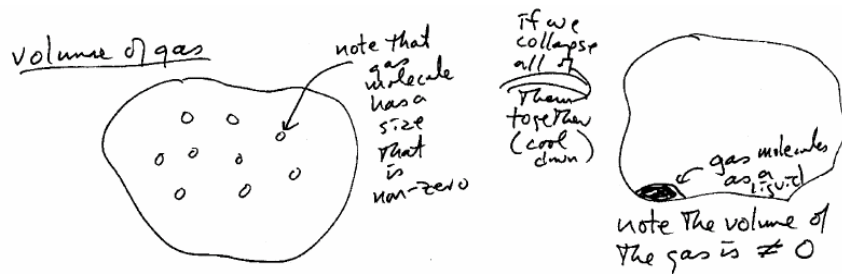
Is kmt flawed? Recall that in the introduction to gases we learned that according to kmt:

- gas molecules have no volume
- gas molecules are not attracted to each other (all collisions are elastic)

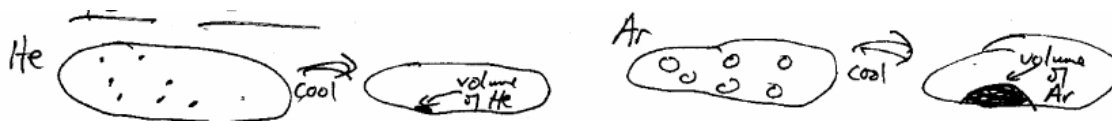
But in practice, neither statement is completely true.

Gas volume is not zero

Consider whether a gas atom or molecule takes up physical space. Of course it does and we can actually see this when we pour liquid nitrogen over a balloon and watch the gas liquefy.



Note also, bigger molecules take more space and are less ideal.



Attraction between gases occurs

Gases bump into each other and stick, not a lot, but some. So the collisions are actually somewhat inelastic—not much (or they wouldn't be gases) but some. As we will learn in Chapter 5, the bigger the molecule, the more sticking and the more polar the molecule, the more sticking.

Why does this matter? It reduces the number of particles hitting wall and consequently $P \downarrow$.



Correcting for non-ideality

How do we correct? Fudge factors fix non-ideality

$$PV \neq nRT \rightarrow (P + \text{Fudge Factor})(V + \text{Fudge Factor}) = nRT$$

P = attraction issues \uparrow equation for non-ideality

V = volume issues

There are many versions of non-ideal gas laws. The Vanderwaals equation is one:

$$(P + n^2a / v^2)(v - nb) = nRT$$

In the equation, **a** and **b** are fudge factors that are dependent on the kind of gas.

The bigger a and b, the more non-ideal.

For example: for He $a = .0034$ and $b = 0.237$ These values suggest that He is small and not attractive
for NH_3 $a = 4.17$ and $b = 3.71$. These values suggest that NH_3 is bigger and really sticky

So when is a gas more ideal?

- at high temperature and low pressure, fewer collisions occur so the gas behaves more ideally.
- for small, non-polar gases, the volume taken and the attractive forces in the collision are small and so the gas behaves more ideally.

Summarizing Trends

For small gases like He and H_2

$PV = nRT$ is a fine equation to use because the gas is more ideal due to less attraction and less volume

For large gases like CO_2 or H_2O

$(P + n^2a / v^2)(v - nb) = nRT$ is the better equation because the gas is less ideal due to stronger attraction and greater volume

Other trends:

For small gases

Faster speed –
Faster diffusion –
Faster effusion –

For larger gases

- slower speed
- slower diffusion
- slower effusion

Example: Rank ideality, speed, diffusion, effusion for He, O₂, N₂, CO₂
He > N₂ > O₂ > CO₂ for speed and ideality. The same trend applies in all cases

Example. At a certain temperature, He gas travels with a velocity of 300 mph. What is the MW of a gas which at the same temperature has a velocity of 150 mph?

- At the same temperature, the energy of the system is constant

- E system = $\frac{1}{2} mv^2$ for all gases

for He $E = \frac{1}{2} m_1 v_1^2$ and for the other gas $E = \frac{1}{2} m_2 v_2^2$

Rearranging $m_2 = m_1 v_1^2 / v_2^2$

- solving: $m_2 = (4 \text{ g / mole}) (300 \text{ mph} / 150 \text{ mph})^2 = 16 \text{ g / mole}$

Example. A ranking of ideality (or velocity)

Rank the following gases in terms of increasing non- ideality.

He, O₂, N₂, CH₄

a) He > N₂ > O₂ > CH₄

b) He > CH₄ > N₂ > O₂

c) O₂ < N₂ < CH₄ < He

d) He < CH₄ < N₂ < O₂ ← **Correct**

Explanation: In general, the bigger, the slower, and the less ideal. So O₂ is biggest, He smallest. In the class we will assume that size is proportional to molecular weight.