Distribution of Molecular Speeds

All speeds are possible but not equally likely. There will be a distribution of speeds. Those would be

- v_m: the most probable speed.

- v_{avg}: the average speed.

- v_{rms} the root mean square.

I. Variation in Speed with Molar Mass

Lighter molar mass gases have the distribution shifted towards higher speeds and it broadens.

II. Variation in Speed with Temperature

As the temperature increases, the average velocity increases and the distribution broadens.

Kinetic Molecular Theory and the Ideal Gas Law

The molecular vector velocity $\mathbf{v}$ is resolved into three Cartesian components v_x, v_y and v_z:

$$|\mathbf{v}|^2 = \mathbf{v} \cdot \mathbf{v} = v_x^2 + v_y^2 + v_z^2$$

The particle kinetic energy which corresponds to its translational energy is then given by

$$\epsilon = \frac{1}{2}m|\mathbf{v}|^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \epsilon_x + \epsilon_y + \epsilon_z$$

The pressure on a wall of the container by the particles inside it is given by

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

Also
$$F = ma$$

where m is the mass of the particle and a is its acceleration as it changes direction of travel due to the collision. Pressure depends on

- How many molecules hit the wall.

- How hard the molecules hit the wall.

Claim: The collisions are elastic.

The acceleration for each collision is the change in velocity dv by time dt, so the force of each collision in the x, y or z direction is

$$F = ma_i = m\frac{dv_i}{dt} = \frac{2mv_i}{\Delta t}$$

If a particle collides elastically with the wall, for a straight line collision,

$$\Delta v = v - (-v) = 2v$$

Only particles within a distance of $v\Delta t$ can reach the wall within the time Δt. Particles that can collide with the wall of surface area A will occupy the volume $v\Delta t A$. If we consider the x-direction, where Δx is the length of the box,

$$\Delta x = v_x \Delta t \qquad V = A\Delta x$$

But, the pressure results from the collisions of a collection of particles, not just a single particle. We need to use an average to describe the collection of the particles.

The total number of collisions is proportional to this volume multiplied by the density of the particles in the container. That is

number of collisions = number of particles within $v\Delta t$ travelling in x-direction

or

$$N = \tilde{N} \times Av_X\Delta t \times \frac{1}{2} = \frac{nN_A}{V}Av_x\Delta t\frac{1}{2}$$

only half are travelling towards the wall. Then the total force is computed by

$$F = \frac{nN_A}{V}Am\mathbb{E}(V_x^2)^1$$

where $\mathbb{E}$ is the average value (expected value).

The pressure on the wall is equal to the total force divided by the surface area of the wall:

$$P = \frac{\sum F}{A} = \frac{nN_A}{V}m\mathbb{E}(V_x^2)$$

The kinetic assumption we considered with the kinetic molecular theory was that the average kinetic energy is proportional to the temperature in Kelvin and actually equals to

$$\frac{1}{2}m\mathbb{E}(V_x^2) = \frac{k_BT}{2}$$

Combining the expressions

$$P = \frac{nN_A}{V}m\mathbb{E}(V_x^2) = \frac{nN_A}{V}k_BT = \frac{nRT}{V}$$

and therefore, $PV = nRT$.

Gas Laws

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[1]Note that here, V_x is the random variable representing the Maxwell-Boltzmann Distribution.

The aim is to determine the relationship between the gas observables (pressure, volume, mass, temperature).

I. Boyle's Law

Boyle found that pressure and volume were inversely proportional. The molecular interpretation is as follows: As the volume of a gas decreases
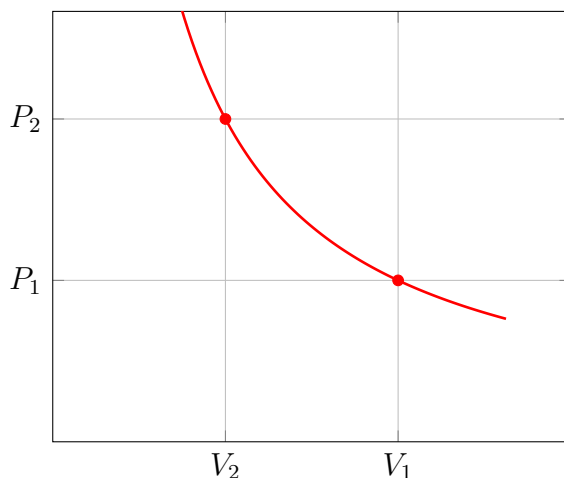
- Space between gas particles and walls decreases.

- Gas molecules collide with surrounding surfaces more frequently.

- Pressure increases.

Therefore, coming up with the formula

$$P \propto \frac{1}{V} \Rightarrow P = c\frac{1}{V}$$
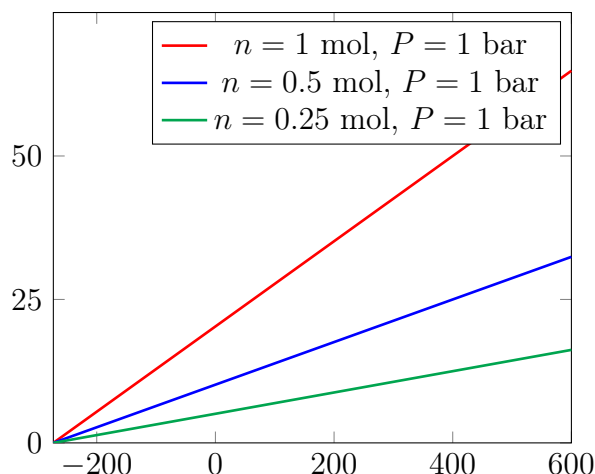
or for a two-point form

$$P_1 V_1 = P_2 V_2$$

II. Charles's Law

Charles's made the conditions clear that the pressure and the mass must stay constant. He studied the relationship between V and T. He found that the volume is directly proportional to the temperature of a gas, if the quantity and pressure of the gas are kept constant. That is,

$$V \propto T \Rightarrow V = cT$$

or for a two-point form,

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

Question: What happens if the gas in a container that can't expand or contract?

Example 1: At atmospheric pressure of 1 bar, dry ice, CO_2, sublimates at $-78.5°C$. Assume you are in a coastal town and you have an empty container with a movable piston and you put a 3.25 cm^3 chunk of dry ice into that container and you leave it at room temperature for a few hours ensuring that all of it has sublimated. What is the final volume of the container? The density of dry ice is 1.6 g/cm^3.

Solution: Let $P(CO_2) = 1$ bar, $T = -78.5°C = 199.5$ K, $V_i(CO_2) = 3.25$ cm^3, and $\delta(CO_2) = 1.6$ g/cm^3. We want to determine the final volume of the container V.

Let $m(CO_2)$ represent the mass of the dry ice. Then

$$\delta(CO_2) = \frac{m(CO_2)}{V_i(CO_2)} \Rightarrow m(CO_2) = \delta(CO_2) \times V_i(CO_2) = (1.6 \text{ g/cm}^3)(3.25 \text{ cm}^3) = 5.2 \text{ g}$$

Next, let $n(CO_2)$ represent the amount of dry ice. Then

$$n(CO_2) = \frac{m(CO_2)}{M(CO_2)} = \frac{5.2 \text{ g}}{44.01 \text{ g/mol}} = 0.1182 \text{ mol}$$

Lastly, to find the volume, we use the ideal gas law.

$$V = \frac{nRT}{P} = \frac{(0.1182 \text{ mol})(0.08314 \text{ L bar/mol K})(298.5 \text{ K})}{1 \text{ bar}} = 2.93 \text{ L}$$

Question: Which of the lines on the figure below is the best representation of the relationship between the volume of a gas and its Celsius temperature, other factors remaining constant. (x-axis is Temperature in °C, and y-axis is Volume in L)
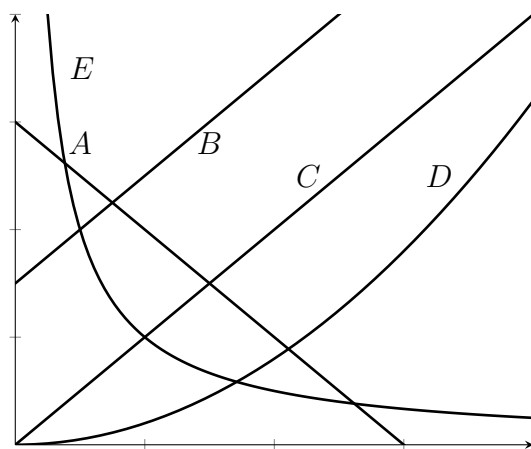
(a) A (b) B (c) C (d) D (e) E

III. Avogadro's Law

Avogadro's law requires two specific conditions: pressure and temperature are constant. Avogadro studied the relationship between V and n, and states, at fixed temperature and pressure, the volume of a gas is directly proportional to the quantity of the gas. That is,

$$V \propto n \Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2} = k$$

IV. The Ideal Gas Law (Combined)

Now let's combine Boyle's law, Charles's law and Avogadro's law to develop a general expression that relates P, T, n and V.

Since

$$V \propto \frac{1}{P} \Leftrightarrow V \propto T \Leftrightarrow V \propto n$$

Then

$$V \propto \frac{nT}{P} \qquad PV = nkT$$

The constants have been combined to form the gas constant R where

$$PV = nRT$$

Recall that the following are equivalent forms of R, but the units are different:

- Standard: 8.314 J/mol K

- In bar: 0.08314 L bar/mol K

- In atm: 0.08206 L atm/mol K

The ideal gas law can be written in terms of molecules or moles. When the ideal gas law is written in terms of moles,

$$PV = nRT$$

and when the ideal gas law is in terms of the number of molecules,

$$PV = Nk_BT$$

where $n = \dfrac{N(molecules)}{N_A}$ and $k_B = \dfrac{R}{N_A}$ is the Boltzmann constant.

Recall the two conditions for temperature and pressure:

- STP: Standard Temperature and Pressure $(T = 0°C$ and $P = 1$ bar$)$

- SATP: Standard Ambient Temperature and Pressure $(T = 25°C$ and $P = 1$ bar$)$