Example Ideal Gas Law Problem:
32 g of liquid methane (CH₄, molecular weight = 16) are condensed in a 500 mL flask at low temperature. Should we let it warm up? Calculate the pressure at 25ºC.

\[
P = \frac{nRT}{V} = \frac{(32/16 \text{ mol})\cdot(0.082 \text{ L\cdot atm\cdot mol}^{-1}\cdot \text{K}^{-1})\cdot(298 \text{ K})}{(0.500 \text{ L})}
\]

\[P = 97.7 \text{ atm at 25ºC} \quad \text{No!} \quad (1436 \text{ lbs/in}^2).
\]

Next:

Dalton’s Law of Partial Pressures:
For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each would exert if it were there alone.

\[P_{\text{total}} = P_1 + P_2 + P_3 \quad \text{(where } P_1, P_2, \text{ and } P_3 \text{ are partial pressures).}
\]

e.g.: n moles of He(g) & n moles of Ar(g) – each initially in volume V at 1 atm individual pressure. Both gases at the same temperature T. The partition is removed – gases mix at same temperature in total volume 2V.

\[
\begin{align*}
\text{Initial:} & \quad n \text{ moles of He(g) in V at 1 atm.} \\
& \quad n \text{ moles of Ar(g) in V at 1 atm.}
\end{align*}
\]

\[
\begin{align*}
\text{Final:} & \quad n \text{ moles of He(g) in 2V at 0.5 atm. (Boyle)} \\
& \quad n \text{ moles of Ar(g) in 2V at 0.5 atm. (Boyle)}
\end{align*}
\]

\[P_{\text{total}} = P_{\text{He}} + P_{\text{Ar}} = 0.5 \text{ atm} + 0.5 \text{ atm} = 1 \text{ atm}
\]
• Mole Fraction (χ (chi)):
  Ratio of the number of moles of the component of a mixture to the total number of moles of everything in mixture.

\[
\chi_A = \frac{n_A}{n_{\text{total}}} \quad \text{&} \quad \frac{n_A}{n_{\text{total}}} = \frac{P_A}{P_{\text{total}}} \quad \text{(they both scale in the same way)}.
\]

For the example above of (He(g) & Ar(g)) – in the final state:

\[
\chi_{\text{He,f}} = \frac{n}{2n} = 0.5 = \frac{P_{\text{He,f}}}{P_{\text{total,f}}} = \frac{0.5 \text{ atm}}{1 \text{ atm}} = 0.5
\]

⇒ \( P_A = \chi_A \cdot P_{\text{total}} \)

[Also in Section 5.5 – vapor pressure of H\(_2\)O & collecting a gas over water. In recitation.]

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**Kinetic Theory of Gases** – an atomistic model to rationalize ideal gas behavior and the ideal gas equation of state (PV = nRT).

**Four (4) postulates** (assumptions) for an ideal gas:

1. Particles are so small compared to the distances between them, their volume can be assumed to be zero.
2. Particles are in constant motion. Collisions with the walls of the container cause pressure.
3. Particles exert no forces on each other. [Long distances – weak forces]
4. Average kinetic energy of a collection of gas particles is directly proportional to the kelvin temperature. Collisions with container walls are assumed to be elastic (no loss of kinetic energy).

**Goal:** Calculate pressure exerted on the container wall.

⇒ Need the collision frequency = \( \frac{\text{collisions}}{\text{unit time}} \) & Impact (force) of collision.

Consider a box (cube – for simplicity - of edge length \( L \)). Note that the shape does not affect the outcome.

• \( A = \text{area of one wall} = L^2 \quad \text{&} \quad V = \text{volume of box} = L^3 \)

• **Particles:** each of mass \( m \).

• **Velocity** = \( u = (u_x, u_y, u_z) \).
We begin easy. Focus on 1 particle of mass \( m \) – moving only along the “x” direction.

- This particle hits one (1) specific wall every \( 2L \) distance.
- This particle undergoes one (1) collision with a specific wall every 
  \[ \frac{2L}{u_x} = \Delta t \] 
  seconds.
- Force \((F)\) exerted on that wall = mass \( \cdot \) acceleration \( \text{ (Newton’s 2nd Law)} \)

Noting that acceleration is the change in velocity per unit time = \( \frac{\Delta u_x}{\Delta t} \), here.

- \( F_x = m\left(\frac{\Delta u_x}{\Delta t}\right) = \frac{\Delta (mu_x)}{\Delta t} \); where \( \Delta (mu_x) = \text{change in momentum.} \)

**Force on wall** is due to change in momentum per unit time.

- Change in momentum for particle = final momentum – initial momentum
  \[ = m(-u_x) - m(+u_x) = -2mu_x \]

- For wall, change in momentum is equal & opposite \( \text{(Newton’s 3rd Law)} \):
  \[ F_{\text{one wall-one particle}} = \frac{+2mu_x}{\Delta t} \]
  \[ \Rightarrow F_{\text{one wall-one particle}} = \frac{mu_x^2}{L} \]
  \( \text{(Force felt by one specific wall due to one particle)} \)
For **N-particles** (each of mass **m**):

- Not all will have the same speeds – even in one particular direction! There will be a distribution of speeds – the *Boltzmann Distribution*.

- Must work with the **average** of the square of the **u_x** speeds: \( \overline{u_x^2} \).

- \( F_N = \text{(average) force for N-particles on one specific wall} = \frac{Nm \overline{u_x^2}}{L} \).

But, we have constrained particles to move in 1 (±x) direction. The general case is – of course – 3 dimensions. General case:

Velocity vector \( u \) has the 3 components \( u_x, u_y, \& u_z \) – as shown.

The **speed** (\( u \)) – the magnitude of vector \( u \) - is related to the components by:

\[
u^2 = u_x^2 + u_y^2 + u_z^2.
\]

In terms of averages, we have:

**Average of the square of the speed** = \( \overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} \).

Note that **no direction is preferred**! Thus:

\[
\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \Rightarrow \overline{u^2} = 3 \cdot \overline{u_x^2} \Rightarrow \frac{1}{3} \overline{u^2} = \overline{u_x^2}.
\]

\( F_N = \text{(average) force for N-particles on one specific wall} = \frac{1}{3} \cdot \frac{Nm \overline{u_x^2}}{L} \).

Want the **Pressure** = \( \frac{\text{Force}}{\text{Area}} \); recall that the area of a wall = \( A = L^2 \).
\[ \Rightarrow P_{\text{wall}} = \frac{\frac{1}{3} N_m \overline{u^2}}{L \cdot L^2} = \left( \text{since } V = L^3 \right) = \frac{1}{3} \cdot \frac{N_m \overline{u^2}}{V}. \]

Note that the above is the same as the pressure (P) on all walls.

\[ \Rightarrow P = \frac{1}{3} N_m \overline{u^2} \quad \text{or} \quad PV = \frac{1}{3} N_m \overline{u^2} \]

\[ N = \# \text{ of particles} \quad ; \quad N_A = \text{Avogadro’s} \# \quad ; \quad \# \text{ of moles} = \frac{N}{N_A} = n. \]

Rewriting:

\[ PV = \frac{1}{3} n N_A m \overline{u^2} \quad \text{- Kinetic Theory – Ideal Gas Law} \]

Compared to experiment: \[ PV = \frac{1}{3} n N_A m \overline{u^2} \]

\[ PV = nRT \]

Right-hand-sides (r.h.s.) must be equal.

Now, express in terms of the (average) kinetic energy:

\[ \overline{E} = \frac{1}{2} m \overline{u^2} \quad \Rightarrow \quad m \overline{u^2} = 2 \cdot \overline{E}. \]

\[ \Rightarrow PV = \frac{2}{3} n N_A \overline{E} = \frac{2}{3} n \overline{KE}_{\text{avg}} ; \quad \text{where:} \]

\[ \overline{KE}_{\text{avg}} = \text{average kinetic energy of 1 mole.} \]

\[ \Rightarrow \overline{KE}_{\text{avg}} = \text{average kinetic energy of 1 mole} = \frac{3}{2} \cdot \frac{PV}{n} = \frac{3}{2} RT \]

Note that this is consistent with \( \overline{KE}_{\text{avg}} \) proportional to kelvin temperature \( T \).

This is energy of motion or translational energy. [Translational energy: \( \frac{1}{2} RT \text{ per direction.} \)]

\[ \Rightarrow \text{Higher } T \Rightarrow \text{Greater motion} \Rightarrow \text{Greater velocity.} \]