The Ideal Gas Law: A Derivation

Dr. Ethan’s Chem. 11 Class

Assumptions of the ideal gas law:

1. The molecules in the gas can be considered small hard spheres.
2. All collisions between gas molecules are elastic and all motion is frictionless (no energy is lost in collisions or in motion).
3. Newton’s laws apply.
4. The distance between molecules on average is much larger than the size of the molecules.
5. The gas molecules are constantly moving in random directions with a distribution of speeds.
6. There are no attractive or repulsive forces between the molecules or the surroundings.

Suppose there is a single gas particle of mass $m$ in a two-dimensional box of length $L_x$ traveling with velocity $u_x$.

![Diagram of gas particle in a box]

When the particle collides with the wall the force, $F$, defined by Newton’s laws is given as the mass times the acceleration (the change in velocity with time):

$$ F = ma = m \left( \frac{\Delta u}{\Delta t} \right) = \frac{\Delta (mu)}{\Delta t} = \frac{\Delta p}{\Delta t} $$

The quantity $mu$ is the momentum, $p$, of the particle (momentum is mass times velocity):

$$ p = mu $$

Because the system involves no external forces, friction, or forces of attraction or repulsion between particles; no force is exerted on a particle until it collides with the wall or another gas molecule. When a particle hits a wall perpendicular to the x-axis, an elastic collision results in an exact reversal of the x component of its velocity. That is the sign, or direction, of $u_x$ reverses. Thus the final momentum (after the collision) is negative (or has the opposite sign) of the initial momentum (before the collision with a wall). Remember that an elastic collision means there is no change in the magnitude of
the velocity, only the direction or sign. Thus $\Delta (mu)$, the change in momentum along the x-axis, is:

\[
\Delta p = \Delta (mu) = \text{final momentum} - \text{initial momentum} = (-mu) - (mu)
\]

\[= -2mu
\]

But we are interested in the force the gas particle exerts on the walls of the box. Since we know that every action produces an equal but opposite reaction, the change in momentum with respect to the wall on impact is:

\[
\Delta p_{\text{wall}} = -(-2mu) = 2mu.
\]

Since force is the change in momentum per unit time, the force on one wall following a collision can now be expressed as:

\[
F_{\text{wall}} = \frac{2mu}{\Delta t}
\]

The time between collisions with one wall of the container, $\Delta t$, can be found since the time that it takes to travel a given distance may be expressed as the distance over the velocity:

\[
\Delta t = \frac{d}{u}
\]

In this case the distance traveled is $2L$ (L is doubled since the particle must travel to the far wall and back between collisions). Thus:

\[
\Delta t = \frac{2L}{u}
\]
Plugging this value for $\Delta t$ into our expression for the force on one wall yields:

$$F_{wall} = (2mu_x) \frac{u_x}{2L} = \frac{mu_x^2}{L}$$

Suppose now that a large number of molecules, $N$, of mass $m$ are moving independently in the box with $x$ components of velocity $u_{x1}$, $u_{x2}$, $u_{x3}$, and so forth. Then the total force exerted on the wall by the $N$ molecules is the sum of the forces exerted by the individual molecules:

$$F_{wall} = \frac{mu_{x1}^2}{L} + \frac{mu_{x2}^2}{L} + \cdots + \frac{mu_{xN}^2}{L}$$

$$= \frac{m}{L} \left( u_{x1}^2 + u_{x2}^2 + \cdots + u_{xN}^2 \right)$$

Using a line above a symbol to represent the average, that is:

$$\bar{x} = \frac{x_1 + x_2 + \cdots + x_N}{N}$$

We see that:

$$\overline{u^2} = \frac{1}{N} \left( u_{x1}^2 + u_{x2}^2 + \cdots + u_{xN}^2 \right) \quad \text{or} \quad Nu^2 = u_{x1}^2 + u_{x2}^2 + \cdots + u_{xN}^2$$

Substituting this into the equation for the force on the wall we get:

$$F_{wall} = \frac{Nm\overline{u^2}}{L}$$

Pressure is defined as force over area:

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

Thus:

$$P = \frac{Nm}{AL} \overline{(u_x^2)}$$
But since \( A \) times \( L \) is the volume, \( V \), of the box, we get:

\[
P = \frac{Nm}{V}(\overline{u_x}) \quad \text{or} \quad PV = Nm(\overline{u_x}^2)
\]

So far we have only considered particles moving along the x-axis. Now we want to consider the problem in three dimensions.

In two dimensions the Pythagorean theorem states that for a right triangle the length of the hypotenuse is:

\[
u_{xy}^2 = u_x^2 + u_y^2
\]

Extending this into three dimensions we get:

\[
u_{xy}^2 \text{ (dashed line)} = u_x^2 + u_y^2
\]

and

\[
u^2 = u_{xy}^2 + u_z^2
\]

combining these we get:

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

in 3D.
The gas molecules have no preferred direction of motion, and so the average velocities in x, y, and z should all be equal or:

\[ \overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \]

Using the three dimensional Pythagorean theorem:

\[ \overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} = 3\overline{u_x^2} \quad \text{or} \quad \frac{1}{3}\overline{u^2} = \overline{u_x^2} \]

Putting this result back into the equation for pressure we get an expression for the pressure of the gas in three dimensions:

\[ PV = \frac{1}{3} N m (\overline{u^2}) \]

Remembering that the number of particles, \( N \), is equal to the number of moles, \( n \), multiplied by Avagadro's number (\( N_a = 6.022 \times 10^{23} \)).

\[ N = n \cdot N_a \]

We get:

\[ PV = \frac{1}{3} n N_a m (\overline{u^2}) \]

From physics we know that the kinetic energy of a moving particle is:

\[ E = \frac{1}{2} m u^2 \]

Using calculus and statistics, it is possible to derive that the kinetic energy of a moving particle in one dimension can also be related to its temperature, \( T \), by the expression:

\[ E = \frac{1}{2} k T \quad \text{ (one dimension)} \]

and in three dimensions this is three times the energy of one dimension (3E) or:

\[ E = \frac{1}{2} k T \quad \text{ (three dimensions)} \]

where \( k \) is the Boltzman Constant (\( k = 1.3807 \times 10^{-23} \) \( \text{J/K} \)).
The energy of one mole of particles is just $E$ multiplied by $N_a$ or:

$$E = \frac{1}{2} k N_a T = \frac{1}{2} RT$$

Where $R$ (the gas constant) is defined as $k$ times $N_a$: $R = k N_a$ ($R = 8.314 \text{ J/mol·K}$)

Multiplying the physics equation for kinetic energy ($E=\frac{1}{2}mu^2$) by Avagadro's number to describe the kinetic energy of a mole of particles, and setting this equal to the energy expression above we find that:

$$N_a \frac{1}{2} m u^2 = \frac{3}{2} RT \quad \text{or} \quad \frac{2}{3} \frac{1}{2} N_a m u^2 = RT \quad \text{or} \quad \frac{1}{3} N_a m u^2 = RT$$

Now using our previous result that:

$$PV = \frac{1}{3} n N_a m u^2$$

And substituting in this new expression, we finally arrive at:

$$PV = nRT$$

*The ideal gas law!*