2. Kinetic Theory of Matter

In this case, we want to consider the motion of one molecule, out of millions of molecules, in a box of gas. Assuming the molecule is moving along the positive x-direction with a velocity u_1, the momentum of the molecule would be mu_1.

If the molecule moves across the length, l, of the box in time t, the velocity of the molecule would be $u_1 = \frac{l}{t}$.

The rate of change of momentum of the molecule is given as: $F = \frac{mu_1}{t}$, from Newton's 2nd law.

But $= \frac{l}{u_1}$, therefore, the rate of change of momentum of the molecule $F = \frac{mu_1}{\frac{l}{u_1}} = \frac{mu_1^2}{l}$

You will notice that this rate of change of momentum of the molecule is also the force with which the molecule hits the wall of the box.

From Force, $pressure = \frac{F}{area}$, and the area of the box = l^2, the pressure of the molecule on the wall is: $pressure = \left(\frac{mu_1^2}{l}\right)\left(\frac{1}{l^2}\right) = \frac{mu_1^2}{l^3}$

Knowing that there could be N molecules in the box, we compute the total pressure on the wall of the box as follows:

$$Total\, pressure = \frac{m}{l^3}(u_1^2 + u_2^2 + u_3^2 + \cdots + u_N^2)$$

From experimental data, it has been found that, on average, only one-third of all the molecules in the box will travel along the positive x-axis. This now gives us the following:

$$Total\ pressure = \frac{m}{3l^3}(u_1^2 + u_2^2 + u_3^2 + \cdots + u_N^2)$$

We can represent all the individual velocities of all the N molecules in the box with symbol $\bar{c}^2$ which is the mean square velocity of all the molecules in the box.

$$\bar{c}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \cdots + u_N^2}{N}$$

Therefore, $N\bar{c}^2 = u_1^2 + u_2^2 + u_3^2 + \cdots + u_N^2$

Hence, the $Total\ pressure = \frac{mN\bar{c}^2}{3l^3}$

You will notice that the $l^3 = volume, V$, therefore, $Total\ pressure = \frac{mN\bar{c}^2}{3V}$

writing in compact form, we have $PV = \frac{1}{3}mN\bar{c}^2$ ….this is the **Kinetic Theory of Matter**

We can go further by saying that the total mass of all the particles in the box is $M = mN$, then we have $PV = \frac{1}{3}M\bar{c}^2$. Again, we can see that density, $\rho = \frac{M}{V}$, therefore $P = \frac{1}{3}\rho\bar{c}^2$. This is another way of writing the Kinetic Theory of Matter.

Instead of using the mean square velocity of molecules in a box of gas, we often use the *root mean square velocity* of all the molecules in a box of gas.

The *root mean square velocity* = $\sqrt{\bar{c}^2} = \sqrt{\frac{u_1^2+u_2^2+u_3^2+\cdots+u_N^2}{N}}$

3. Prove of Gas Laws using the Kinetic Theory of Matter

We now use the just derived equation for the Kinetic Theory of Matter to prove the five gas laws:

- Boyle’s Law (In a gas system, Pressure is inversely proportional to the Volume, $P \propto \frac{1}{V}$, $P = \frac{k}{V}$)

From $= \frac{1}{3}mN\bar{c}^2,\ P = \frac{\left(\frac{1}{3}mN\bar{c}^2\right)}{V}$, where our constant $k = \frac{1}{3}mN\bar{c}^2$

For instance, in a mole of gas, $N \equiv L$, where $L =$ Avogadro's constant. In this case where $L =$ Avogadro's constant, $PV = nRT$ which gives

$$PV = \frac{1}{3}mL\bar{c}^2 = nRT$$

$\frac{1}{3}m\bar{c}^2 = \frac{nRT}{L}$, this is the equation of Kinetic Theory of Matter for one molecule and $n = 1$

In this case, $\frac{R}{L} =$ Boltzmann's constant.

Therefore, our constant $k\ in\ (\frac{1}{3}mN\bar{c}^2)$ is a function of the Boltzmann's constant.

- Charles' Law (Volume is directly proportional to absolute temperature at constant pressure: $\frac{PV_1}{PV_2} = \frac{T_1}{T_2}$)

  From $PV = \frac{1}{3}M\bar{c}^2$, we can write the same for two gas systems as follows:

  $PV_1 = \frac{1}{3}M\bar{c}_1^2$ and $PV_2 = \frac{1}{3}M\bar{c}_2^2$

  Please note that the expressions for the mean square velocity for system 1, $\bar{c}_1^2$, and mean square velocity for system 2, $\bar{c}_2^2$ can be written as:

  $\bar{c}_1^2 = \frac{u_{1.1}^2+u_{2,1}^2+u_{3,1}^2+\cdots+u_{N,1}^2}{N}$ and $\bar{c}_2^2 = \frac{u_{1.2}^2+u_{2,2}^2+u_{3,2}^2+\cdots+u_{N,2}^2}{N}$

  According to Charles' law, we have: $\frac{PV_1\ (=\frac{1}{3}M\bar{c}_1^2)}{PV_2\ (=\frac{1}{3}M\bar{c}_2^2)} = \frac{T_1}{T_2}$

  If we are to write in terms of the molecules' kinetic energies we have

  $ke = \frac{1}{2}Mv^2$, therefore, $PV_1 = \frac{1}{3}M\bar{c}_1^2 = \frac{2}{3}ke_1$

  Reason is because, $\frac{2}{3}ke_1 = \frac{2}{3}\left(\frac{1}{2}Mv^2\right) = \frac{1}{3}M\bar{c}_1^2$, where we have assumed that $v^2 \equiv \bar{c}_1^2$

  Therefore, $\frac{PV_1\ (=\frac{1}{3}M\bar{c}_1^2)}{PV_2\ (=\frac{1}{3}M\bar{c}_2^2)} = \frac{T_1}{T_2}$ becomes $\frac{PV_1\ (=\frac{2}{3}ke_1)}{PV_2\ (=\frac{2}{3}ke_2)} = \frac{T_1}{T_2}$

- Avogadro's Law (Any 2 gas systems at same volume, temperature and pressure will contain the same number of molecules)

From $PV = \frac{1}{3}mN\bar{c}^2$, we can write the same for two gas systems as follows:
$P_1V_1 = \frac{1}{3}mN_1\bar{c}_1^2$ and $P_2V_2 = \frac{1}{3}mN_2\bar{c}_2^2$
If $P_1V_1 = P_2V_2$, then $N_1 = N_2$

- Dalton's La of Partial Pressure (In a mixture of gases, the sum of all their partial pressures is equal to the total pressure of the entire gas occupying a given volume)

  From $PV = \frac{1}{3}mN\bar{c}^2$, we can write the separate partial pressure as:

$$\frac{PV}{V} = \frac{\frac{1}{3}m_1N_1\bar{c}_1^2}{V_1} + \frac{\frac{1}{3}m_2N_2\bar{c}_2^2}{V_2} + \cdots + \frac{\frac{1}{3}m_NN_N\bar{c}_N^2}{V_N}$$

$$\frac{PV}{V} = \frac{P_1V_1}{V_1} + \frac{P_2V_2}{V_2} + \cdots + \frac{P_NV_N}{V_N}$$

$$P = P_1 + P_2 + \cdots + P_N$$

- Graham's Law of Diffusion (The rate of diffusion of a gas is directly proportional to the mean velocity of the gas molecules OR the rate of diffusion of a gas is inversely proportional to the square root of the density of the gas)

  First, let's derive a mathematical expression for the "rate of diffusion". From the word *rate*, we know it has to do with time. Also from the word *diffusion*, we know it means *mixing* which involves the movement of gas molecules from point A to point B. Therefore, we can write

$$rate\ of\ diffusion = \frac{distance\ moved\ by\ the\ gas\ molecules}{time\ taken} = velocity$$

  Hence, by Graham's La of Diffusion, $rate\ of\ diffusion = V_A = \sqrt{\bar{c}_A^2} = \frac{1}{\sqrt{\rho_A}}$

  In a mixture of gases, we have $\frac{rate\ of\ diffusion\ of\ gas\ A}{rate\ of\ diffusion\ of\ gas\ B} = \frac{V_A}{V_B} = \frac{\sqrt{\bar{c}_A^2}}{\sqrt{\bar{c}_B^2}} = \frac{\sqrt{\rho_B}}{\sqrt{\rho_A}}$

4. Mean Free Path of Molecules in a Gas

From the word *Free Path,* it means path of a molecule during which it makes no collision. Then the statement *Mean Free Path,* is the mean of such paths. In other words, Mean Free Path of Molecules in a Gas is the total number of distance traveled by a molecule divided by the number of collisions during that distance.

$$Mean\ Free\ Path = \frac{d_1 + d_2 + \cdots + d_N}{number\ of\ collisions}$$

In order to calculate the number of collisions, we'll assume that the gas is in a pipe of cross-sectional area πr^2 and that there are N molecules in the gas and each moving throughout the length L of the pipe.

Another assumption is that the range of possible movements of one molecule (colliding) with others is from (a) colliding and never leave length $L = 1$ and (b) colliding and reaching length $L = L$

The total number of collision is within this range and choosing $L = L$, we have $total\ number\ of\ collisions = (\pi r^2)(N)(L)$

It is interesting to note that choosing a case where the molecule collides with others and reach the other end of the pipe, the total number of distance in-between collision is approximately equal to the length of the pipe. Therefore, $d_1 + d_2 + \cdots + d_N \approx L$

Hence,

$$Mean\ Free\ Path = \frac{L}{(\pi r^2)(N)(L)} = \frac{1}{(\pi r^2)(N)}$$

5 Micro-canonical Ensemble

The word canonical (from the word canon) means a general law, rule, principle, criterion or assumptions by which something is being judged or treated. The word ensemble means to view (or treat) a list of items as a group rather than as individuals.

Let us consider an isolated system with fixed energy (i.e energy is neither leaving nor entering the system). If we assume that the system is an equilibrium system, then it means that temperature and pressure at any section of the system is exactly the same all through the system. Therefore, such isolated equilibrium system will be one whose *accessible* micro-states are statistically equally likely.

We have introduced the word *accessible* because since the system is an isolated one, it is expected that any access (or attempt to access) any of its micro-states will result in raising its temperature of pressure.

Let us define

$$\Omega(E) = number\ of\ states\ with\ energy\ E\ within\ an\ equilibrium\ ensemble$$

The probability of picking a given state in such an ensemble is

$\mathrm{p(n)} = \frac{1}{\Omega(E)}$

Since our system is an isolated equilibrium one, the probability of picking a state with energy $E' \neq E$ is zero.

Now, a Micro-canonical Ensemble is an isolated equilibrium system which is treated using probability distribution $\mathrm{p(n)} = \frac{1}{\Omega(E)}$.

Please note that $\Omega(E)$ could be ridiculously large, usually in the range of 10^{23} and for systems with 2 possibilities like quantum states spin-up and spin-down, the value could be about $2^{10^{23}}$. Therefore, there is usually no physical meaning for these states since their number is too large to mathematically deal with. This therefore, brings up the need for statistical treatment.

6 Entropy of an Equilibrium System

The Entropy of an Equilibrium System is given as $\mathrm{S}(E) = k_B \log\Omega(E)$, where $k_B = 1.38 \times 10^{-23} JK^{-1}$ (i.e the Boltzmann's constant).

Note that the log is the natural log (i.e ln and not log to base 10). We're taking natural log in order to reduce (compress, make less messy) the value of $\Omega(E)$. In actual fact, the $\Omega{\sim}e^N$ while S~E. Hence, entropy is merely proportional to the number of molecules in the system which means that entropy is an additive quantity.

To show that the entropy is an additive quantity, consider two non-interacting systems with energies E_1 and E_2. The total number of states in them is $\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2)$.

If we bring these two non-interacting systems together with *assumption that the can exchange energy*, the entropy of the two systems will now become:

$\mathrm{S}(E_1, E_2) = k_B ln[\Omega_1(E_1)\Omega_2(E_2)]$

$\mathrm{S}(E_1, E_2) = k_B ln[\Omega_1(E_1)] + k_B ln[\Omega_2(E_2)]$

$\mathrm{S}(E_1, E_2) = \mathrm{S}_1(E_1) + \mathrm{S}_2(E_2)$ ….this therefore shows that entropy is additive

Furthermore, since the energy of the combined system is $E_{total} = E_1 + E_2$, if we let the first system to take up energy $E \leq E_{total}$, then the second system can only take the remaining energy which is $E_{total} - E$. Hence, the number of available states in the combined system is

$$\Omega(E_{total}) = \sum_{(E_i)} \Omega_1(E_i)\Omega_2(E_{total} - E_i)$$

Then, $S(E_{total}) = \sum_{(E_i)} k_B ln\big(\Omega_1(E_i)\Omega_2(E_{total} - E_i)\big)$

$$S(E_{total}) = \sum_{(E_i)} k_B ln\big(\Omega_1(E_i)\big) + k_B ln\big(\Omega_2(E_{total} - E_i)\big)$$

Letting $S_1(E_i) = k_B ln\big(\Omega_1(E_i)\big)$

$$\frac{S_1(E_i)}{k_B} = ln\big(\Omega_1(E_i)\big)$$

$$\Omega_1(E_i) = e^{\left(\frac{S_1(E_i)}{k_B}\right)}$$

Similarly, Letting $S_2(E_{total} - E_i) = k_B ln\big(\Omega_2(E_{total} - E_i)\big)$

$$\frac{S_2(E_{total} - E_i)}{k_B} = ln\big(\Omega_2(E_{total} - E_i)\big)$$

$$\Omega_2(E_{total} - E_i) = e^{\left(\frac{S_2(E_{total} - E_i)}{k_B}\right)}$$

Substituting into $\Omega_1(E_i)$ and $\Omega_2(E_{total} - E_i)$ into $\Omega(E_{total}) = \sum_{(E_i)} \Omega_1(E_i)\Omega_2(E_{total} - E_i)$

$$\Omega(E_{total}) = \sum_{(E_i)} e^{\left(\frac{S_1(E_i)}{k_B}\right)} e^{\left(\frac{S_2(E_{total} - E_i)}{k_B}\right)}$$

$$\Omega(E_{total}) = \sum_{(E_i)} e^{\left[\left(\frac{S_1(E_i)}{k_B}\right) + \left(\frac{S_2(E_{total} - E_i)}{k_B}\right)\right]}$$

$$\Omega(E_{total}) = \sum_{(E_i)} \exp\left[\left(\frac{S_1(E_i)}{k_B}\right) + \left(\frac{S_2(E_{total} - E_i)}{k_B}\right)\right]$$

Applying micro-canonical ensemble principle into this combined system, we assume that all states in the new combined system are all equally likely. The fact that all states are all equally likely means that for a combined state made up of smaller number of particles, the probability will be higher for such combined than for individual states with lower number of particles.

Therefore, $S(E_{total}) \equiv k_B ln\Omega(E_{total}) \geq S_1(E_1) + S_2(E_2)$

This simple expression is commonly seen around us everywhere in the world. In a nutshell, entropy increases when systems overlap or the restriction on system is removed. This is simply the second law of thermodynamics.

7 Temperature

8 Heat Capacity