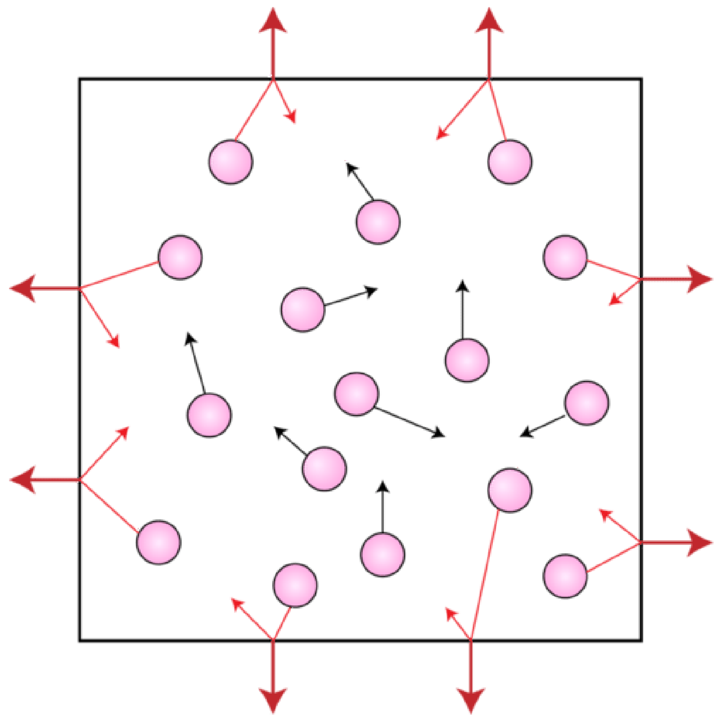
Kinetic theory of gases



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Recap of observations and important results

- State variables Pressure (P), volume (V) and temperature (T) for gases (at low pressures and high temperatures i.e. before they liquefy) satisfy a simple relation $PV = KT$
- K is constant for a given type of gas but varies with volume of the gas.
- If gas is considered to consist of atoms/molecules, then K is found to depend only on the number of atoms/molecules and not on the type of gas. In this case $K = Nk$, where k is Boltzmann constant and is (found to be) same for all the types of gases.
- If P, V and T are same then N also has to be same for all the gases. This is Avogadro's hypothesis. This amount is called one mole.
- Mass of 22.4 liters of gas is equal to its molecular weight in grams, at standard temperature & pressure (i.e. 273 K and 1 atm)
- Based on this approach we get $PV = nRT$
- Avogadro guessed the quantity of numbers based on chemical reactions. Kinetic theory of gases justifies this model based on number of particles.

Kinetic theory of gases

- Boyle's law : At constant temperature, the pressure of a given amount of gas is inversely proportional to its volume.

- Charles' law : At constant pressure, the volume occupied by a given amount of gas is directly proportional to its absolute temperature.

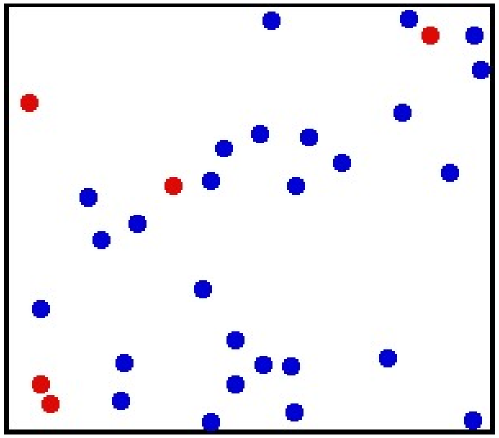
- For a system consisting of a number of non-interacting gases, the equation becomes $PV = (n_1 + n_2 + n_3 \ldots) RT$

- Therefore $P = P_1 + P_2 + P_3 \ldots$ where P_n is the pressure exerted by the n^{th} gas under the same conditions of pressure and temperature if other gases were not present (Dalton's law of partial pressure).

- The average distance a molecule can travel without colliding is called the mean free path. The mean free path, in gases, is of the order of thousands of angstroms.

Assumptions related to an ideal gas

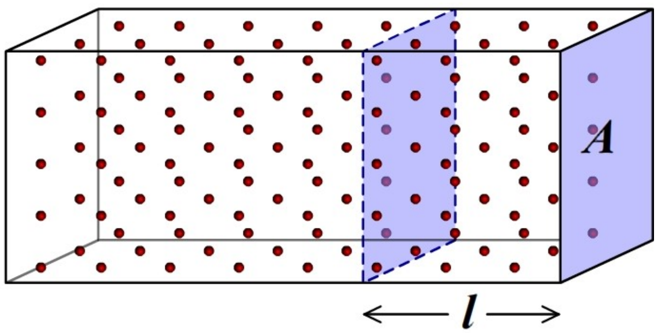
- Atoms/molecules of the ideal gas move randomly in all possible directions
- Size of atoms/molecules is much smaller than the distance of separation between them
- Interaction between the atoms/molecules is assumed to be negligible (except during the instant of collision)
- All collisions are assumed to be perfectly elastic.
- Molecules obey Newton's laws of motion
- In steady state density and distribution of atoms/molecules with different velocities is independent of their position, direction of motion and time.



Random motion of atoms/molecules of a gas in a container

Pressure of an ideal gas

Consider a container containing certain amount of an ideal gas. Atoms of the gas would be continuously undergoing collision with the wall of the container.



Consider an atom of mass m moving with velocity v. Let v_x be the component of its velocity normal to surface of the wall. Change in momentum as it undergoes a one dimensional elastic collision with the wall of the container is

$$\Delta p = -2mv_x \quad \text{— i}$$

In a time interval Δt , the number of atoms within the reach of the wall is

$$N' = n_o A v_x \Delta t$$

n_o : number of atoms per unit volume
A : is area of wall of the container
v_x : average velocity of a particle

As the gas is isotropic, the number of atoms moving towards the wall may be assumed to be equal to the number of atoms moving away from the wall in any interval of time.

Therefore the number of atoms moving towards the wall is

$$N = \frac{n_o A v_x \Delta t}{2} \quad \text{— ii}$$

Pressure of an ideal gas (continued…)

Total change in momentum of these particles is

$$\Delta p_{total} = (-2mv_x) \times \frac{n_o A v_x \Delta t}{2}$$

$$\Delta p_{total} = -mv_x n_o A v_x \Delta t$$

Total force exerted on these molecules (by the wall) is

$$F = \frac{\Delta p_{total}}{\Delta t}$$

$$F = \frac{-mv_x n_o A v_x \Delta t}{\Delta t}$$

$$F = -n_o A m v_x^{\,2}$$

Force acting on the wall is therefore given by

$$F = n_o A m v_x^{\,2} \qquad \text{iii}$$

Using $P = F/A$ and substituting F from eq(iii) we get

$$P = \frac{n_o A m v_x^{\,2}}{A}$$

$$P = n_o m v_x^{\,2}$$

$$P = 2 n_o \frac{1}{2} m v_x^{\,2} \qquad \text{v}$$

Is the last term kinetic energy?

No. Recall that v_x is only the x-component of velocity of a specific molecule under consideration !

Pressure of an ideal gas (continued…)

Magnitude of average velocity associated with each particle is

$$v = \sqrt{\bar{v}_x^{\,2} + \bar{v}_y^{\,2} + \bar{v}_z^{\,2}}$$

For isotropic gas, all the components of velocities (on an average) may be assumed to be equal. Therefore

$$v_x = v_y = v_z$$

$$v_{\text{rms}} = \sqrt{\bar{v}_x^{\,2} + \bar{v}_x^{\,2} + \bar{v}_x^{\,2}}$$

$$v_{\text{rms}}^{\,2} = 3\bar{v}_x^{\,2}$$

$$\bar{v}_x^{\,2} = \frac{v_{\text{rms}}^{\,2}}{3}$$

Using this in eq (v)

$$P = 2n_{\text{o}}\frac{1}{2}m\frac{v_{\text{rms}}^{\,2}}{3}$$

$$P = \frac{2}{3}n_{\text{o}}\frac{1}{2}m v_{\text{rms}}^{\,2}$$

$$\boxed{P = \frac{2}{3}n_{\text{o}}\langle \text{KE}\rangle}$$

The above equation relates a macroscopic quantity (P) to a microscopic quantity (average KE of each atom/molecule)

Kinetic interpretation of temperature

Pressure exerted by an ideal gas is given by

$$P = \frac{2}{3} n_o \langle KE \rangle$$

$$P = \frac{2}{3} \frac{N}{V} \langle KE \rangle$$

$$PV = \frac{2}{3} N \langle KE \rangle$$

Using ideal gas equation we get

$$\mu RT = \frac{2}{3} N \langle KE \rangle$$

$$\frac{N}{N_A} RT = \frac{2}{3} N \langle KE \rangle$$

$$\frac{R}{N_A} T = \frac{2}{3} \langle KE \rangle$$

using $k_B = \frac{R}{N_A}$ we get

$$\boxed{\langle KE \rangle = \frac{3}{2} k_B T}$$

- Average < KE >$_{\text{particle}}$ is proportional to the absolute temperature of the system.
- < KE >$_{\text{particle}}$ is independent of P, V and nature of gas
- Microscopic parameter < KE >$_{\text{particle}}$ and macroscopic parameter (T) are connected by Boltzmann constant (k_B)

Dalton's law of partial pressure

In a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases.

Pressure exerted by the gas is given by

$$P = \frac{1}{3} n_o m v_{rms}^{2}$$

For a mixture of non-reactive ideal gases, the total pressure gets contribution from each gas in the mixture. Therefore

$$P = \frac{1}{3}\left[n_1 m_1 \overline{v}_1^{\,2} + n_2 m_2 \overline{v}_2^{\,2} + \ldots\right]$$

In equilibrium, $< KE >_{\text{particle}}$ of different gases is same as it depends only on the temperature (T) as $3/2 k_B T$. Therefore

$$\frac{1}{2} m v_{rms}^{2} = \frac{3}{2} k_B T$$

Using this in the above relation

$$P = \frac{1}{3}\left[n_1 \, 3k_B T + n_2 \, 3k_B T + \ldots\right]$$

$$P = \left[n_1 + n_2 + \ldots\right] k_B T$$

The above relation is Dalton's law of partial pressure.

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