Chapter 2: Kinetic Theory of Gases

2.1 Macroscopic Description of An Ideal Gas.

★ Ideal gas- approximation to real gases.
★ The variables that describe the behaviour of a given quantity (mass) of gas are pressure, volume, and temperature (p, V, and T).
★ The combined gas law can re-stated as an equation of state using the gram mole.
★ At T constant: \( pV = \text{constant} \Rightarrow p_1V_1 = p_2V_2 \) (Boyle’s law)
★ At P constant: \( \frac{V}{T} = \text{constant} \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} \) (Charle’s law)
★ Ideal gas law: \( \frac{pV}{T} = \text{constant} \Rightarrow \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \)
★ Equation of state of an ideal gas law:

\[
\frac{pV}{T} = nR \Rightarrow pV = nRT
\]

\[
\frac{pV}{T} = Nk_B \Rightarrow pV = Nk_B T
\]

Equation of state of an ideal gas law: (in terms of the no. of moles in a gas)

\[
PV = nRT = \frac{m}{M}RT
\]  

...(2.1)

where \( n = \frac{m}{M} = \frac{\text{actual mass of gas}}{\text{Molar mass}} \)  

...(2.2)

\( R = 8.314 \text{ J. mol}^{-1}\text{.K}^{-1} \) is the Universal Gas Constant (SI unit: J/(mol.K))

Equation of state of an ideal gas law: (in terms no. of molecules in a gas)

\[
\frac{pV}{T} = Nk_B \Rightarrow pV = Nk_B T
\]

where \( N = nN_A \), \( N = \text{no. of molecules} \), \( n = \text{no. of moles} \),
\( N_A = \text{Avogadro’s no, } N_A = 6.022 \times 10^{23} \text{ molecules/mole (SI unit: mol}^{-1}\) 
\( k = 1.38 \times 10^{-23} \text{ J/K is the Boltzmann constant (SI unit: J/K) } \)
\( T = \text{Temperature (unit: Kelvin)} \)
Example 2.1
Find the volume occupied by 1 g mol of an ideal gas at Standard Temperature and Pressure (STP is 273K and 101.3kPa).

Solution:
\[ pV = nRT \]
\[ V = \frac{nRT}{P} = \frac{1 \times 8.314 \times 273}{101.3 \times 10^3} = 2.24 \times 10^{-2} m^3 \]

Example 2.2
Gas is contained in an 8.0 L vessel at a temperature of 20°C and at pressure of 9 atm.
   a) Determine the number of moles of gas in the container
   b) How many molecules in the vessels?

Solution:
\[ n = \frac{PV}{RT} \]
\[ = \frac{(9.0 \text{ atm})(1.013 \times 10^5 \text{ Pa/atm})(8.0 \times 10^{-3} \text{ m}^3)}{(8.31 \text{ Nm/mol K})(293 \text{ K})} \]
\[ = 3.0 \text{ moles} \]

(b) \[ N = nN_A = (3.0 \text{ moles})(6.02 \times 10^{23} \text{ molecules/mol}) \]
\[ = 1.8 \times 10^{24} \text{ molecules} \]

2.2 Avogadro’s Number And the Ideal Gas Law.

Avogadro’s Principle (1811)

★ Equal volumes of different gases at the same temperature and pressure contain the same numbers of molecules.
★ Avogadro’s number:
\[ N_A = 6.02 \times 10^{23} \text{ molecules/mol} \] ... (2.3)
Corollary to Avogadro’s hypothesis is as follows:

- Single moles quantities of any gases at standard temperature and pressure contain the same numbers of molecules.

- Alternative method for calculating the number of moles of any gas in a container is to divide the total number of molecules present, \( N \) by Avogadro’s number.

\[
n = \frac{\text{total number of molecules}}{\text{Avogadro’s number}} = \frac{N}{N_A} \quad \cdots (2.4)
\]

- Rewrite the ideal gas law in the alternative form:

\[
PV = nRT = \frac{N}{N_A}RT
\]

\[
PV = Nk_B T \quad \cdots (2.5)
\]

where \( k_B \) is Boltzmann’s constant and has a value

\[
k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} \quad \cdots (2.6)
\]

**Example 2.3**
Find the number of molecules in 1 cm³ of any gas at standard temperature and pressure.

**Solution:**

\[
PV = \frac{N}{N_A}RT
\]

\[
N = \frac{pVN_A}{RT} = \frac{101.3 \times 10^3 \times 10^{-6} \times 6.022 \times 10^{23}}{8.314 \times 273} = 2.69 \times 10^{19}
\]

- It is an absolute number in that it does not depend on the size of the mole like Avogadro’s number.
Example 2.4
One mole of hydrogen atoms has a mass of $1.0078 \times 10^{-3}$ kg. In the early twentieth century, it was found that the mass of a hydrogen atom is approximately $1.673 \times 10^{-27}$ kg. Use these values to find Avogadro's number.

Solution:

$$N_A = \frac{N}{n} = \frac{NM}{n} = \frac{1.0078 \times 10^{-3} \text{kg/mol}}{1.673 \times 10^{-27} \text{kg/atom}}$$

$$= 6.024 \times 10^{23} \text{ atoms/mol (N=1)}$$

2.3 The Kinetic Theory of Gases.

We can readily measure the pressure and temperature of a gas using a pressure gauge and thermometer (macroscopic quantities).

It is not so easy, however, to measure microscopic quantities, such as the position or velocity of an individual molecule.

The connection between the macroscopic level and microscopic level is described by the kinetic theory of gases.

A microscopic model of an ideal gas is based on the Kinetic Theory assumptions:

1. The number of molecules is large, and the average separation between them is large compared with their dimensions. Therefore, the molecules occupy a negligible volume of the container.

2. The molecules obey Newton's laws of motion, but the individual molecules move in a random fashion. By 'randomly' we mean that the molecules move in all directions with equal probability and with various speeds.

3. The molecules undergo elastic collisions with each other and with the walls of the container. Thus, in the collisions kinetic energy is constant. In the collisions both KE and momentum are conserved.
4. The forces between molecules are negligible, except during a collision. The forces between the molecules are short-range, so the molecules interact with each other only during collisions.

5. The gas under consideration is a pure gas. That is, all molecules are identical.

-Kinetic Theory of gases use statistical methods to derive the ideal gas law from mechanical principles.

-Important conclusions:
1. Temperature is a measure of the average Kinetic Energy of the molecules.
   \[ \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T \]
2. The ideal gas law can be expressed in terms of rms speed of the molecules.
   \[ pV = \frac{1}{3} N m v_{\text{rms}}^2 \]
3. The total internal energy of an ideal monatomic gas is given
   \[ E = \frac{3}{2} N k_B T = \frac{3}{2} nRT \]

How to proof all the above three equations?
-For a molecule moving in a container, with a velocity of \( v_x \) (x direction) and mass of \( m \). As the molecule collide elastically with any wall, its velocity is reversed.
-The magnitude of the force exerted on the wall of the container by a gas molecule colliding with it
   \[ F = \frac{\Delta p}{\Delta t} \]
-The change in momentum, \( \Delta p = m v_f - m v_i = m v_x - (-m v_x) = 2m v_x \)
-So, \( F = \frac{\Delta p}{\Delta t} = \frac{2m v_x}{\Delta t} \)

-In order for the molecule to make another collision with the same wall, it must travel a distance of 2d, and
   \[ \Delta t = \frac{2d}{v_x} \]
The substitution will result:

\[ F_1 = \frac{2mv_x}{\Delta t} = \frac{2mv_x^2}{2d} = \frac{mv_x^2}{d} \]

The total force exerted on the wall by all molecules:

\[ F = \frac{m}{d} (v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots + v_{xN}^2) \]

\( (v_{x1}^2, v_{x2}^2, v_{x3}^2, v_{xN}^2 \text{ refer to individual molecules}) \)

\[ v_x^2 = \frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots + v_{xN}^2}{N} \]

\((N=\text{no. of molecules in the container})\)

-Hence, the total force on the wall can be written as

\[ F = \frac{m}{d} \ N \ v_x^2 \]

For component \( x, y \) dan \( z \),

\[ \bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 \]

The molecules' motions occur with equal frequency along any one of the 3 axes,

\[ \bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 \]

all velocity component are equivalent,

\[ \bar{v}^2 = 3 \ \bar{v}_x^2 \rightarrow \bar{v}_x^2 = \frac{1}{3} \bar{v}^2 \]

So from the equation:

\[ F = \frac{m}{d} \ N \ v_x^2 \]

The pressure exerted on the wall is:

\[ P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{d^2} \left( \frac{m}{d} \ N \frac{1}{3 \bar{v}^2} \right) \]
\[
\frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m \overline{v^2} \right)
\]

So the pressure of an ideal gas,

\[
P = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m \overline{v^2} \right) \quad \text{...(2.7)}
\]

Molecular Interpretation of Temperature

Compare above equation with empirical perfect gas law:

\[
PV = \frac{2}{3} \left( N \right) \left( \frac{1}{2} m \overline{v^2} \right) \text{ and}
\]

\[
PV = N k_B T
\]

- By equating the right sides of these expressions,

\[
T = \frac{2}{3k_B} \left( \frac{1}{2} m \overline{v^2} \right) \quad \text{...(2.8)}
\]

- This shows that the temperature is a direct measure of average molecular KE or temperature is proportional to average KE.

- Relation between the translational molecular KE to the temperature:

\[
\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad \text{...(2.9)}
\]

- This shows that average translational kinetic energy per molecule is \( \frac{3}{2} k_B T \).

- So, for \( x, y \) and \( z \) motion,

\[
\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T,
\]

\[
\frac{1}{2} m \overline{v_y^2} = \frac{1}{2} k_B T \quad \text{and}
\]

\[
\frac{1}{2} m \overline{v_z^2} = \frac{1}{2} k_B T
\]
\[
\frac{1}{2} m v_z^2 = \frac{1}{2} k_B T \quad \text{...(2.10)}
\]

★ This generalization result the **Theorem of Equipartition of Energy** which says:

"The energy of a system in thermal equilibrium is equally divided among all degrees of freedom."

★ The total translational kinetic energy of \( N \) molecules of gas:

\[
E = N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} nR T \quad \text{...(2.11)}
\]

★ For the root-mean-square (rms) speed of the molecule,

\[
\sqrt{\overline{v^2}} = v_{rms} \rightarrow \overline{v^2} = v_{rms}^2
\]

\[
N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} nRT = \frac{3}{2} \frac{m}{M} RT
\]

\[
\overline{v^2} = \frac{3}{MN} RT
\]

\[
V_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} \quad \text{...(2.12)}
\]

where \( M \) is the molar mass in kilograms per mole and \( N=1 \).

**Example 2.5**

A tank contains 2.0 mol of helium (\( N=1 \)) gas at 20\(^0\)C. Assume that the helium behaves as an ideal gas.

a) Find the total internal energy of the system

b) What is the average kinetic energy per molecule?

**Solution:**

a) \[
E = \frac{3}{2} nR T
\]

\[
= \frac{3}{2} (2.0 \text{ mol})(8.31 \text{ J/mol.K})(293\text{K})
\]

\[
= 7.3 \times 10^3 \text{J}
\]
b) Using \( \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{J/K})(293 \text{K}) \)

\[ = 6.1 \times 10^{-21} \text{J} \]

**Example 2.6**

In a period of 1.0s, \( 5.0 \times 10^{23} \) nitrogen molecules strike a wall of area 8.0cm\(^2\). If the molecules move at 300 m/s and strike the wall head on in a perfectly elastic collision, find the pressure exerted on the wall. (The mass of one \( \text{N}_2 \) molecule is \( 4.68 \times 10^{-26} \) kg).

**Solution:**

For one of these elastic head-on collisions, the change in momentum of one molecule of mass \( m \) is: \( \Delta mv = mv_f - mv_i = mv - (-mv) = 2mv \).

The total impulse delivered to the wall in one second is \( F(1.0 \text{ s}) = 2mvN \), where \( N \) is the number of molecules hitting the wall in the 1 second interval. Therefore,

\[ F = \frac{(2 \times 4.68 \times 10^{-26} \text{ kg} \times 300 \text{ m/s})(5 \times 10^{23})}{1.0 \text{ s}} \]

\[ = 14.0 \text{ N}, \text{ and} \]

\[ P = \frac{F}{A} = \frac{14.0 \text{ N}}{8.0 \times 10^{-4} \text{ m}^2} = 1.8 \times 10^4 \text{ Pa}. \]

**Example 2.7:**

Calculate the rms speed of a hydrogen molecule and an oxygen molecule at a temperature of 300K. (Given \( m_H=3.3\times10^{-27} \text{ kg} \) and \( m_O=5.3\times10^{-26} \text{ kg} \))

**Solution:**

From \( \frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T \)

So \( v_{rms} = \sqrt{\frac{3k_B T}{m}} \)

For Hydrogen: \( v_{rms} = \sqrt{\frac{3(1.38\times10^{-23} \text{ J/K})(300 K)}{3.3\times10^{-27} \text{ kg}}} = 1.9\times10^3 \text{ m/s} \)
For Oxygen: \( \nu_{\text{rms}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J} / \text{K})(300 \text{K})}{5.3 \times 10^{-26} \text{kg}}} = 4.8 \times 10^3 \text{ m/s} \)

More massive molecule gas gave smaller \( \nu_{\text{rms}} \).

**Vapor pressure**: is the pressure exerted by a gas when it is in equilibrium with its liquid form.

**Dew point**: is the temperature at which the air becomes saturated with water vapor.

**Boiling** begins when the vapor pressure is equal to atmospheric pressure.