

## SUMMARY OF CHAPTER 5 – Part I

### P-V-T Behavior of Ideal Gases and their Mixtures

After studying phase diagrams in chapter 4, we focused on the on vapor or gaseous portion of a phase diagram. In many engineering applications, we deal with pure gas or gas mixtures, for example, in air conditioning, or in natural gas industries. We wanted to know the PVT behavior of pure gas and gas mixture.

First we considered gases at low density (low pressure and high temperature). Most gases at low pressure follow a simple equation of state, called ideal gas (IG) equation of state (EOS):

$$Pv = nRT$$

$P$  = absolute pressure,  $v$  = volume,  $n$  = amount of substance in mole,  $T$   
= absolute temperature (K),  $R$  = gas constant

$$R = 8.314 \frac{\text{kJ}}{\text{kmol.K}} = 8.314 \frac{\text{J}}{\text{mol.K}} = 0.08205 \frac{\text{litre.atm}}{\text{mol.K}} = 0.08205 \frac{\text{m}^3.\text{atm}}{\text{kmol.K}}$$

#### **Application of IG EOS:**

We can apply the IG EOS,  $Pv = nRT$  for any of the four variables ( $P$ ,  $v$ ,  $n$ ,  $T$ ) directly if others are known. Indirectly, we can also calculate the following quantities from IG EOS

$\text{molar density, } \rho_m = \frac{n}{v}$	$\text{molar volume, } V_m = \frac{v}{n} = \frac{1}{\rho_m}$	$\text{mass of the gas, } m = nM, \text{ where, } M = \text{Molar mass}$
$\text{Specific density, } \rho = \frac{m}{v}$	$\text{specific volume, } V = \frac{v}{m} = \frac{1}{\rho}$	Also, for a fixed quantity of gas, between two states, $\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$

#### **Ideal gas mixture (IGM):**

The relationship of molar volume of an ideal gas mixture with temperature and pressure is similar to the pure component ideal gas equation. However, quantities now refer to the mixture.

$$Pv = nRT$$

$P$  = absolute pressure of the mixture,  $v$  = volume of the mixture,  
 $n$  = amount of substances in mole =  $n_A + n_B + \dots$ ,  
 $T$  = absolute temperature (K) of the mixture,

#### **Application of IGM EOS** (similar to the application of single ideal gas)

We can solve the IGM EOS  $Pv = nRT$  for any of the four variables ( $P$ ,  $v$ ,  $n$ ,  $T$  of mixture) if other three are known. Indirectly, we can also compute: molar density, molar volume, specific density, and specific volume of the mixture as before. Note that the calculation of mass which require average molecular weight.

$\text{mass of the gas mixture, } m = nM_{avg}, \text{ where, } M_{avg} = \text{Average Molar mass}$

$$M_{avg} = \sum_{i=1}^{all\ component} y_i M_i$$

$y_i$  = mole fraction of component  $i$  in the vapor phase

Partial pressure: Imagine a gas mixture in a piston-cylinder system. Then remove all other gases except A, but keep the volume and temperature same, then observe the new pressure. This pressure given by A is equal to the partial pressure of A in the mixture.

*In general,  $\bar{p}_i = y_i P$*

*Dalton's law: total pressure = sum of all partial pressures.*

Partial volume: Imagine a gas mixture in a piston-cylinder system. Then remove all other gases except A, and adjust the volume so that the temperature and pressure remains same as was in the mixture. This volume is equal to the partial volume of A in the mixture.

*Partial volume of A in mixture =  $\bar{v}_A = v_A$ , (at mixture  $T$  and  $P$ )*

*Amagat's law: total volume = sum of partial volumes*

**Flow of ideal gas or ideal gas mixture:**

$$P\dot{v} = \dot{n}RT$$

$$\dot{v} = \text{volumetric flow rate} \left( \frac{m^3}{s} \right), \dot{n} = \text{flow rate} \left( \frac{mol}{s} \right)$$

The above equation is useful when the gas is flowing through a pipe, or duct. Also note that,

Mass flow rate = density \* volumetric flow rate = density \* cross-sectional area \* average velocity.

## Kinetic Theory of Gases

*EPISODE 1: Molecules collides with wall. Link pressure with temperature through average molecular kinetic energy.*

We picture ideal gas as a collection of vast number of very tiny particles (molecules) moving freely in all direction in an apparently random, chaotic manner. First, we considered just two properties of these particles: their mass and speed. We tried to relate these two mechanical properties with the pressure of a gas that we can experimentally determine. Realize here that the pressure of a gas is the result of interaction of ALL molecules with the wall. All molecules? Assume we have N molecules in a closed container of volume v. Then we determined the rate of change of momentum of all N molecules with all the inner walls of the container, and obtained an expression of gas pressure:

$$Pv = \frac{1}{3} m N \overline{c^2}$$

The above equation relates the product **pressure times volume** to mass of one molecule (m), number of molecules (N), and the quantity,  $\overline{c^2}$ , mean of squared velocity, is defined as

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + \cdots \dots \dots + c_N^2}{N}$$

And  $c_1, c_2$ , etc. are the individual speed of molecule 1, molecule 2, etc. The overbar over something indicates average, for example,  $\bar{x}$ , read as x-bar, is average value of x.

We know that product pressure\*volume has dimension of work or energy. Let's see the right hand side in terms of kinetic energy.

$$Pv = \frac{1}{3} m N \overline{c^2} = \left(\frac{2}{3} N\right) * \left(\frac{1}{2} m \overline{c^2}\right)$$

But,  $\frac{1}{2} m \overline{c^2} = \left(\frac{1}{2} m \overline{c^2}\right)$  = average kinetic energy of one molecule.

So,

$$Pv = \left(\frac{2}{3} N\right) * \text{average kinetic energy of one molecule}$$

We have not yet got the ideal gas equation  $Pv = nRT$ . We need to bring **temperature** of the gas in to picture. We assumed that hotter molecules, will have, on average, more kinetic energy. Mathematically, *we next assumed*,

***Average kinetic energy per molecule  $\propto$  temperature***

$$\Rightarrow \frac{1}{2} m \overline{c^2} \propto T$$

To make it an equality, we introduced a proportionality constant k in the following manner

$$\Rightarrow \frac{1}{2} m \overline{c^2} = \frac{3}{2} k T$$

Using the above relation, we can eliminate kinetic energy term, and obtain a direct relationship between pressure, volume and temperature.

$$Pv = \left(\frac{2}{3} N\right) * \left(\frac{1}{2} m \overline{c^2}\right) = \left(\frac{2}{3} N\right) * \left(\frac{3}{2} k T\right) = N k T$$

$$\Rightarrow Pv = N k T$$

If we consider 1 mole of gas, then the volume is equivalent to molar volume and the number of molecules, N, is equal to Avogadro's number of molecules,  $N_A$ . Then,

$$Pv_m = N_A k T$$

Comparing the above equation with the ideal gas law,  $Pv_m = R T$ , we see how constant, k, is related to Avogadro's number and gas constant:  $N_A k = R$

Therefore, ***we accept our constant k as  $R/N_A$ , and call it Boltzmann's constant.*** Then, our pressure equation becomes identical to the ideal gas equation of state:

$$Pv_m = R T$$

At last, our very simple picture of ideal gas was able to produce the ideal gas equation of state when we agree with the very few assumptions of kinetic theory.

### **Two more useful relations:**

We can also obtain two more useful relations by going back to our assumption:

$$\frac{1}{2} m \overline{c^2} = \frac{3}{2} kT$$

(1) Multiplying the above equation by 2\*Avogadro's number,

$$m \overline{c^2} * N_A = 3 kT * N_A$$

$$\Rightarrow M \overline{c^2} = 3RT$$

$$\Rightarrow \overline{c^2} = \frac{3RT}{M}$$

$\overline{c^2}$  has units of  $m^2/s^2$ , so next, we defined, root-mean-squared velocity =  $C_{rms} = \sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}}$

(2) Going back again to the velocity-temperature assumption,

$$\frac{1}{2} m \overline{c^2} = \frac{3}{2} kT = \text{average kinetic energy of 1 molecule}$$

And multiplying by Avogadro's number,

$$\frac{1}{2} m N_A \overline{c^2} = \frac{1}{2} M \overline{c^2} = \frac{3}{2} k N_A T = \frac{3}{2} RT = E_{k,m}$$

$$= \text{average kinetic energy of 1 mol of molecules}$$

At that point the ideal gas story seemed complete. However, we have not YET talked about **collision between molecules themselves**. Let's do this in EPISODE II.

## *EPISODE II: Molecules collide with themselves. Linking pressure with temperature through average molecular kinetic energy.*

Frequency of collisions of an object with other objects depends on size (if you occupy more space, you may collide more frequently), speed (more speed, chance of more collision), and probability of finding another molecule on the way (high number density, more collision, as in a busy supermarket). Therefore, we brought into picture **three new parameters**: (i) the collision diameter,  $\sigma$ . We imagined molecules to be of spherical shape, but of different sizes, so of different diameters, (ii) Average speed (not the rms velocity), defined as

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

And (iii) the number density is simply the number of molecules divided by the volume,

$$\rho_N = \frac{N}{V} = \frac{N_A}{V_m} = \frac{P}{kT}$$

Using these quantities, we estimated the mean free path, the average path a molecule travel before it collides.

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \rho_N}$$

At this stage, we have two important parameters regarding collisions, (i) the average path between two successive collisions ( $\lambda$ ) and (ii) the average speed with which molecules are moving time-interval between two collisions ( $\bar{c}$ ). At this point, we anticipated that these two quantities will play a major role in TRANSPORT of energy, mass and momentum that occur due to molecular collisions. Indeed, later (please see you note – part II of summary of chapter 5) we saw that the conductivity, diffusivity and viscosity are related to these two quantities.

$$\kappa(\text{conductivity}) = \frac{\bar{c} \lambda}{2} * \rho_N \left( \frac{C_v}{N_A} \right) = \frac{C_v}{N_A \pi \sigma^2} \sqrt{\frac{RT}{\pi M}}$$

$$\mu(\text{viscosity}) = \frac{\bar{c} \lambda}{2} * \rho_N m = \frac{M \lambda m}{N_A \pi \sigma^2} \sqrt{\frac{RT}{\pi M}}$$

$$D_{AB}(\text{Diffusion coefficient}) = D = \frac{\bar{c} \lambda}{2} = \frac{RT}{P N_A \pi \sigma_A^2} \sqrt{\frac{RT}{\pi M_A}}$$

### Other actors/actresses of EPISODE I and II:

Three velocities: Apart from the two velocities (rms velocity and average velocity) that we have discussed so far, we also have an expression for a third velocity, the most probable velocity, which is the velocity of most of the molecules.

$$c_{mp} = \sqrt{\frac{2RT}{M}}$$

Three distances: Apart from the two lengths, the collision diameter, and mean free path, we also defined a length called *mean distance* between molecules of a gas,

$$\delta = \left(\frac{v}{N}\right)^{1/3} = \left(\frac{1}{\rho_N}\right)^{1/3} = \left(\frac{kT}{P}\right)^{1/3}$$

To visualize this distance, imagine you remove all the molecules from the container, divide the container into small cubes, so that each cube get equal volume,  $\frac{v}{N}$ . What is the side of a cube of volume  $\frac{v}{N}$ ? Cube root of  $\frac{v}{N}$ , which is called mean distance  $\delta$ . This is actually the center-to-center distance between two cubes along the edges. If we imagine now each molecule is sitting at the center of a cube, then we can consider delta as the mean distance between molecules. This mean distance has importance when gas transforms into vapor, and near critical temperature, delta becomes of the same order of magnitude of sigma, collision diameter. At ordinary conditions, delta is usually 10 times of sigma, and lambda is typically 100 times sigma. Remember the relationship of the three velocities, and the three distances (sigma, delta, lambda).

Cp, Cv, R: We also observed that the ideal gas constant R is related to the molar heat capacities of ideal gases. R, Cp, Cv all have same units [J/(mol.K) or kJ/(kmol.K)]. Recall that molar heat capacity represent the AMOUNT of heat needed to raise the temperature of 1 mol of ideal gas by 1 K. But HEATING is a process. How you heat matters. What happens to other process variables (P, v) when you heat a gas? When you try to change temperature by heating, gas tend to expand. You have two choices, either you let the gas expand, but keep the **pressure constant**, or you do not let the gas expand, thereby keep its **volume constant**, but then its pressure rises. The ideal gas molar heat capacity at constant pressure, Cp, is 2.5\*R, and the ideal gas heat capacity at constant volume, Cv, is 1.5\*R. So, you do not need to do an experiment to know heating requirement of ideal gases as you know their Cp and Cv values. In reality, these results are true for small monoatomic gases, but not for polyatomic molecules (because they do not conform very well to our model of spherical non-interacting molecules, e.g. table 5.2). Note that Cp > Cv, and their differences is always R.

Collision rate: The flux of molecules hitting a surface placed anywhere inside the container is given by

$$\left[\frac{\rho_N \bar{c}}{4}\right] = \frac{\text{number of molecules}}{m^3} * \frac{m}{s} = \frac{\text{number of molecules}}{m^2 \cdot s} = \text{flux}$$

Using the above equation, we can calculate number of collision on your open palm in this room in 2 seconds (flux\*area of palm\*time-interval).

This summarizes the basics of kinetic theory. PLEASE CONTINUE READING TO PART II.