Rate of Molecular Collisions with the Container Walls

The number of collisions with container walls per unit area of the walls is

$$\rho_N \frac{\bar{c}}{4}.$$ Where

ρ_N = number density, and
$\bar{C}$ = average speed of the molecules.

5.6 Transport Properties of Gases

There are four properties that are used to describe the transport processes. These properties are:

Viscosity -> for transport of momentum
Thermal Conductivity -> for transport of heat
Diffusivity -> for transport of mass
Electrical conductivity -> for transport of electricity

We will examine the first three in this part. Electrical conductivity will be discussed only for solids in chapter 9.

5.6.1 Viscosity - Transfer of Momentum

Viscosity of a fluid is an indicator of its resistance to deformation or flow. A low viscosity fluid flows easily while a high viscosity fluid requires more effort to move. Compared to water, honey flows very reluctantly and has much higher viscosity. Gases flow even more effortlessly than water and have smaller viscosity.

Newton's Law of Viscosity
Imagine a fluid contained between two parallel horizontal plates, the bottom one being stationary while the top one is moving at a constant velocity 'U' in x direction.

To hold the bottom plate stationary, a certain force F will be required. The relationship between this force and the velocity U is given by Newton's Law of Viscosity.

$$\frac{F}{A} = \mu \frac{U}{h} = \mu \frac{du}{dy}$$

Where,

A = area of the bottom plate
h = distance between the plates
μ = viscosity of the fluid
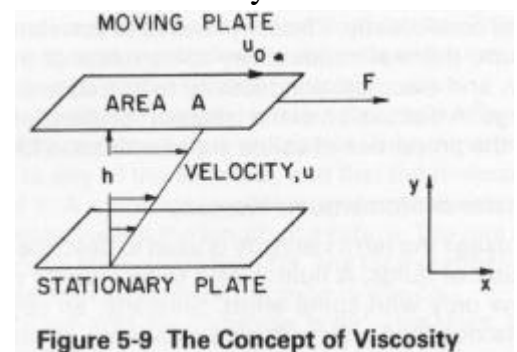u = velocity of the fluid at distance y from the stationary plate

Figure 5-9 The Concept of Viscosity

Now we will derive an expression of the value of viscosity for an ideal gas.

Visualize that an ideal gas is filling the space between the two plates. Now visualize the gas to consist of a large number of imaginary layers. The layer in contact with the stationary plate will be moving at a velocity close to zero. The layer next to the top plate will be moving at a velocity equal to U. For a specific layer, y distance away from the bottom plate, the velocity is u. The molecules, which are one free path distance away toward the top, can enter this layer from top without colliding with other molecules. Similarly the molecules, which are one mean free path distance below the layer, can enter the layer from below.

The velocity of the molecules coming from top
$$= u + l\,\frac{du}{dy}$$
The velocity of the molecules coming from bottom
$$= u - l\,\frac{du}{dy}$$
To calculate the net change in momentum due to this exchange of molecules, we need to know the rate at which the molecules are entering the layer. If you imagine that this layer is a boundary separating the gas into two compartments, then the number of molecules coming from either direction per unit area will be equal to the number of molecular collisions with the walls of a container. We have already derived the expression for number of collisions per unit area of wall as $P_N\,\dfrac{\overline{c}}{4}$.

Mass of each molecule = m

Then the momentum rate of molecules from below y-plane
$$= m\,\frac{P_N\overline{c}}{4}\,A\left[u - l\,\frac{du}{dy}\right]$$
The momentum rate of molecules from above the y-plane
$$= m\,\frac{P_N\overline{c}}{4}\,A\left[u + l\,\frac{du}{dy}\right]$$
The net force on the plane is given by the net change of momentum
$$F = m\,\frac{P_N\overline{c}}{4}\,A\left[u + l\,\frac{du}{dy}\right] - m\,\frac{P_N\overline{c}}{4}\,A\left[u - l\,\frac{du}{dy}\right] = m\,\frac{P_N\overline{c}}{2}\,A l\,\frac{du}{dy}$$
Comparing this with Newton's Law of Viscosity
$$\frac{F}{A} = \textbf{\textit{m}}\,\frac{U}{h} = \textbf{\textit{m}}\,\frac{du}{dy}$$
$$\textbf{\textit{m}} = \frac{P_N\overline{c}\,l\,m}{2}$$

The value of mean free path, λ, is given by $\mathbf{l} = \dfrac{1}{\sqrt{2}\boldsymbol{p}\boldsymbol{s}^2 P_N}$

Therefore

$$\boldsymbol{m} = P_N \bar{c}\, \frac{m}{2}\, \frac{1}{\sqrt{2}\boldsymbol{p}\boldsymbol{s}^2 P_N} = \frac{m\bar{c}}{2\sqrt{2}\boldsymbol{p}\boldsymbol{s}^2} = 0.1125 \frac{m\bar{c}}{\boldsymbol{s}^2}$$

It shows that viscosity is proportional to the mass of the molecule (or molar mass) and the average velocity but inversely proportional to the square of molecular diameter. It should also be noted that the viscosity is not a function of pressure, according to the kinetic theory.

Figure 5-10 shows that the viscosity of air at room temperature is nearly independent of pressure from 1 kPa to 1000 kPa. At very low and very high pressures, some of the assumptions are not valid.

At very low pressures, the mean free paths are very large, hence molecules collide with walls more frequently than with each other. The picture of one mean-free-path is not quite valid.
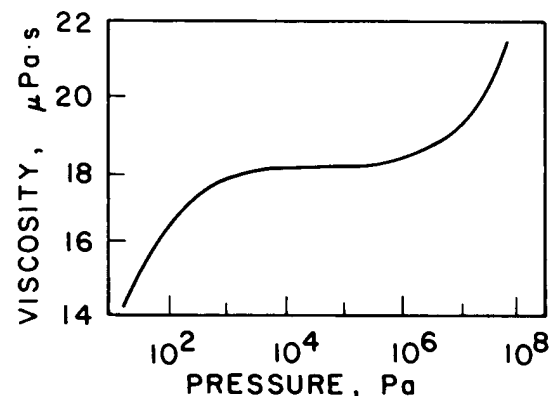

Figure 5-10 Viscosity of Air at Different Pressures T = 288 K

At high pressures, the separation distance becomes small, hence intermolecular forces become important. The molecules no longer move totally independent of each other.

We derived an expression for the average velocity in terms of temperature.

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

Substituting this into the expression for viscosity gives

$$\boldsymbol{m} = \frac{m}{2\sqrt{2}\boldsymbol{p}\boldsymbol{s}^2}\sqrt{\frac{8RT}{\boldsymbol{p}M}} = \frac{M}{N_A \boldsymbol{p}\boldsymbol{s}^2}\sqrt{\frac{8RT}{\boldsymbol{p}M}}$$

We have substituted M/N_A for m, the mass of one molecule.

This shows that the viscosity is proportional to square root of temperature.
Let us look at an example problem from the text, Example Problem 5-5.

Example Problem 5-5

The viscosity of a gas at 2 atm and 25°C is 1.78 x 10^{-5} Pa s. If the molar mass of the gas is 28.02 kg/kmol, estimate the collision diameter.

Solution

Consider 1 kmol of the gas which contains 6.023 x 10^{26} molecules. The mass of one molecule, m, is

$$\frac{28.02}{6.023 \times 10^{26}} \text{ kg.}$$

The viscosity of the gas, μ, is given as 1.78 x 10^{-5} Pa s and the temperature is 25°C or 298.15 K. The gas constant is 8.314 kJ/kmol K. From Equation **5.71**, the collision diameter may be evaluated. That is,

$$\sigma^2 = \frac{1}{2^{3/2}} \frac{m}{\pi\mu} \sqrt{\frac{8RT}{\pi M}}.$$

On substitution and solving, the collision diameter σ is found to be

$$\sigma = 3.74 \times 10^{-10} \text{ m.}$$

5.6.2 Conduction of Heat; Thermal Conductivity

To understand heat conduction (which is transfer of energy from one point to another) in gases you have to first understand how heat energy is stored in gases and how it travels from point A to Point B. We know that the temperature is a measure of kinetic energy of gases. For the purpose of this discussion, it would be sufficient to recall that when a gas is heated at constant volume, all of the heat energy goes toward increasing the kinetic energy of molecules. So we can say that the energy is stored as kinetic energy of the molecules.

If there is a difference in temperature between two points in a gas, the kinetic energy of the molecules will be higher where the temperature is higher. However, the molecules move in random fashion and collide with each other frequently. Thus it is likely that some of the molecules from high-energy region would wander off toward the low-energy region. Secondly, when two molecules collide, there can be an exchange of kinetic energy. Both, the random physical movement of molecules and the energy exchange by collisions, tend to increase the kinetic energy of molecules in the low-temperature region at the expense of kinetic energy of molecules in the high-temperature region. This is the physical process responsible for heat conduction in gases.

The rate at which heat is transferred depends on the several factors.

a. Temperature difference between the two regions -- larger the temperature difference, faster is the rate of heat transfer.

b. Distance between the two regions -- shorter the difference, faster is the rate of heat

transfer.

c. Area for heat flow -- Larger the area, faster is the heat transfer. If the molecules must pass through a small area the rate will become smaller compared to the situation where a large area is available.

We can formalize these considerations in the form of an equation that is known as Fourier's Law of Heat Transfer.

$$Q \propto A\left(\frac{\Delta T}{L}\right)$$

Where,

Q = Rate of heat flow

A = Area for heat flow

ΔT = Temperature difference

L = Distance

The term (ΔT/L) is the temperature gradient and can be represented more accurately by (dT/dx). Denoting the constant of proportionality by k, we can write

$$Q = -kA\left(\frac{\Delta T}{L}\right)$$

The constant of proportionality, k, is called thermal conductivity. It is equal to the rate at which heat is transferred through a unit area when the temperature gradient is one degree per unit length. Its units in the SI system are (W/m.K)

A relationship between the properties of an ideal gas and its heat conductivity can be developed the same way as we saw for viscosity. I am not going to go through the derivation, but I will give you the results.

$$k = \frac{1 P_N \overline{C} C_v}{2 N_A} = \frac{1}{\sqrt{2} \boldsymbol{ps}^2 P_N} P_N \sqrt{\frac{8RT}{\boldsymbol{p}M}} \frac{C_v}{2 N_A} = \frac{C_v}{N_A \boldsymbol{ps}^2} \sqrt{\frac{RT}{\boldsymbol{p}M}}$$

It shows that $k \propto \sqrt{T}$ and independent of P or the molar volume. Experimental results support these inferences.

The numerical value of k for gases is quite low, much lower than that for liquids and solids. Gases are good insulators.

5.6.3 Molecular Diffusion; Diffusivity

Molecular diffusion can be defined as the net transport of a substance from one region to another within a single phase without any bulk movement or agitation.

The driving force for molecular diffusion is difference in concentration. Because of the fact that gas molecules enjoy complete freedom to move around, diffusion is more prominent in gases. Diffusion in liquids occurs at a slower rate and in solids it occurs at exceedingly low rate. The rate of diffusion is described by Fick's Law.

$$j_A = -D_{AB}\frac{dC_A}{dx}$$

Where,
j_A = Flux of material A (moles of material A flowing per unit area per unit time)
D_{AB}= diffusion coefficient or diffusivity (m²/s)
C_A = Concentration of material A, moles/m³

Note that for a concentration difference to exist, we must have at least two components in the system. Here we are talking about the diffusion of component A through component B. The approach for obtaining an expression from kinetic theory is similar to that for thermal conductivity, but more involved due to the presence of two components.

For diffusion of a molecule of A into another gas having molecules of same size and mass, the expression for diffusivity is

$$D_{AB} = \frac{l\overline{C}}{2} = D_{AA}$$

D_{AA} is the diffusivity for self "diffusion." Substituting the values for λ and $\overline{C}$, we get

$$D_{AA} = \frac{RT}{PN_A\boldsymbol{ps}^2}\sqrt{\frac{RT}{\boldsymbol{p}M}}$$

It shows that

$$D_{AA} \propto \frac{T^{3/2}}{P}$$

Look at Table 5-4 for some typical values.