

## Transport Phenomenon

The molecules in motion always possess three physical quantities, namely mass, momentum and energy. We know if the gas is in an equilibrium state, there is no net transport of these quantities but, while moving from one part to another in any specified region, the molecules can be considered as a carrier of these three physical quantities. When the gas in totality or partially is moving any three of the following cases, singly or jointly, may occur.

1. The different parts of the gas may be moving with different velocities resulting in a relative motion between adjacent layers of the gas. In such a case the faster moving layers will lose *momentum* to the slower moving layers. Therefore, across the imaginary plane there will be a net *transport of momentum*. This give rise to the phenomenon of *viscosity*.
2. The different parts of a gas may be at different temperatures. The molecules of the gas will carry *thermal energy* from regions of higher to lower temperature to attain thermal equilibrium. Therefore, across the imaginary plane there will be a net *transport of energy*. This give rise to the phenomenon of *thermal conduction*.
3. The different parts of a gas may have different *concentrations*. The molecules from regions of higher concentration will go to regions of lower concentration resulting in the *transport of mass* (matter). This gives rise to the phenomenon of *diffusion*.

We thus find that viscosity, thermal conduction and diffusion, respectively represent the transport of momentum, energy and mass. Therefore, they are called *transport phenomenon* and are irreversible in the thermodynamic sense.

### Transport of Momentum: Coefficient of Viscosity

The coefficient of viscosity of the gas,  $\eta$ , is defined as the tangential force per unit area when a unit velocity gradient exists in a perpendicular direction of flow, i.e.,

$$\frac{F}{A} = -\eta \frac{du}{dx} \quad (12)$$

where  $A$  is the area of either plate and  $du/dx$  is the velocity gradient at right angles to the plates. The negative sign signifies that viscous force acts in opposition to velocity gradient.

Viscosity of a gas arises not from any frictional forces between its molecules, but from the fact that they carry momentum across a surface as a result of their random motion.

**Expression for  $\eta$ ;** Consider a gas enclosed between two plates  $a-a'$  and  $b-b'$ , and gas moves from left to the right. Suppose the layer of the gas in contact with the lower plate is at rest. Imagine a plane  $y-y'$  within the gas at a distance  $x$  above the plate  $a-a'$  and parallel to the direction of motion.

Let the velocity gradient at  $y-y'$  be  $du/dx$  and velocity of flow be  $u$ . If the mean free path of a molecule is  $\lambda$ , then the distance for the first collision to occur above and below the plane  $y-y'$  is also equal to  $\lambda$ , but from the plate  $a-a'$  these distances are  $x + \lambda$  and  $x - \lambda$ , respectively. The average velocity of molecules at these distances are, therefore,  $(x + \lambda)du/dx$  and  $(x - \lambda)du/dx$ , respectively (shown in figure 7).

**Figure 7** A representation of different layers in fluid.

The molecules are moving at random in all directions. In three dimensional space, we consider six such direction along each axis. Approximately,  $1/6^{\text{th}}$  molecule can be assumed to be moving in one direction and other  $1/6^{\text{th}}$  in the opposite direction along each axis. Let  $\bar{u}$  be the average velocity of the molecules,  $n$  the number of molecules per unit volume and  $m$  the mass of each identical molecules.

Then the number of molecules crossing unit area in one direction in unit time =  $\frac{1}{6} n \bar{u}$

and, the mass of molecules crossing the plane  $y-y'$  per unit area per unit time =  $\frac{1}{6} mn \bar{u}$  .

Hence the net momentum  $G \downarrow$  in the direction of flow, carried across the surface per unit area per unit time by all the molecules crossing the plane  $y-y'$  from above in downward direction, is the product of mass and average velocity of the molecules crossing the plane  $y-y'$  from above:

$$G \downarrow = \frac{1}{6} mn \bar{u} \left[ (x + \lambda) \frac{du}{dx} \right] \quad (13)$$

Similarly, the momentum carried across the surface by the molecules crossing from below in upward direction is,

$$G \uparrow = \frac{1}{6} mn \bar{u} \left[ (x - \lambda) \frac{du}{dx} \right] \quad (14)$$

The net rate of transport of momentum in the upward direction, per unit area per unit time is the difference between these quantities, or

$$G = G \uparrow - G \downarrow = -\frac{1}{3} mn \bar{u} \lambda \frac{du}{dx} \quad (15)$$

and from *Newton's second law* this equals the viscous force per unit area. Hence, by comparison with the definition of the coefficient of viscosity in eq. (12), we have

$$\eta = \frac{1}{3} mn \bar{u} \lambda = \frac{1}{3} \rho \bar{u} \lambda \quad (16)$$

where  $\rho$  is the density of gas. Substituting the expression for mean free path  $\lambda$  from eq. (9), we get

$$\eta = \frac{1}{3\sqrt{2}} \frac{m \bar{u}}{\sigma} \quad (17)$$

**Dependence on Pressure and Temperature;** An unexpected conclusion from this equation is that the viscosity of a gas is *independent of the pressure* or density, and is a function of temperature alone through the

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dependence of  $\bar{u}$  on  $T$ . However, experiments does not agree with this conclusion, except at very low pressure.

As we can show that the average velocity  $\bar{u}$  is given by

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$$

so that,

$$\eta = \frac{1}{3\sigma} \sqrt{\frac{4mk_B T}{\pi}} \quad (18)$$

Thus for molecules of a given species, the theory predicts that  $\eta$  is proportional to  $\sqrt{T}$  and for different species at a given temperature it is proportional to  $\sqrt{m}/\sigma$ .

### Transport of Energy: Thermal Conductivity

Let us now investigate the similar problem of thermal conductivity of a gas. In this case the temperature and hence the energy varies from layer to layer and it is the energy which is transferred from one layer to another.

The thermal conductivity of a gas is treated in the same way as its viscosity. Let the upper and lower plates in figure 6 be at rest but at different temperatures, so that there is a *temperature gradient* rather than a velocity gradient in the gas. If  $dT/dx$  is the temperature gradient normal to a surface within the gas, the thermal conductivity  $K$  is defined by the equation

$$H = -K \frac{dT}{dx} \quad (19)$$

where  $H$  is the heat flow or **heat current** per unit area and per unit time across the surface. The negative sign is included because if  $dT/dx$  is positive the heat current is downward and is negative.

**Expression for  $K$ ;** Consider heat flow across the gas moving between parallel plates  $a-a'$  and  $b-b'$  which are at rest but at different temperatures. Imagine a plane  $y-y'$  within the gas at a distance  $x$  above the plate  $a-a'$  and parallel to the direction of motion. Let  $dT/dx$  is the temperature gradient at the plane  $y-y'$  which is positive in upward direction and normal to the surface  $y-y'$ , and if  $T$  is temperature at the plane  $y-y'$ .

If the mean free path of a molecule is  $\lambda$ , then the distance for the first collision to occur above and below the plane  $y-y'$  is also equal to  $\lambda$ , but from the plate  $a-a'$  these distances are  $x + \lambda$  and  $x - \lambda$ , respectively.

The average temperature of the molecules crossing the layer  $y-y'$  from above in downward direction =  $T + \lambda \frac{dT}{dx}$  and the average temperature of the molecules crossing the layer  $y-y'$  from below in upward direction =  $T - \lambda \frac{dT}{dx}$  (shown in fig. 4.7).

The molecules are moving at random in all directions. In three dimensional space, we consider six such direction along each axis. Approximately,  $1/6^{\text{th}}$  molecule can be assumed to be moving in one direction and other  $1/6^{\text{th}}$  in the opposite direction along each axis. Let  $\bar{u}$  be the average velocity of the molecules,  $n$  the number of molecules per unit volume and  $m$  the mass of each identical molecules.

Then the number of molecules crossing unit area in one direction in unit time =  $\frac{1}{6} n \bar{u}$

and, the mass of molecules crossing the plane  $y-y'$  per unit area per unit time =  $\frac{1}{6} mn \bar{u}$ .

Then, the heat energy transported by molecules moving from above in the downward direction per unit

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area per unit time is the product of the mass of molecules, specific heat at constant volume and average temperature of the molecules crossing the layer  $y-y'$  from above, thus

$$H \downarrow = \frac{1}{6} mn \bar{u} C_V \left( T + \lambda \frac{dT}{dx} \right) \quad (20)$$

In the same way, the heat energy transported by molecules crossing from below in upward direction is

$$H \uparrow = \frac{1}{6} mn \bar{u} C_V \left( T - \lambda \frac{dT}{dx} \right) \quad (21)$$

The net rate of transport per unit area per unit time, in the upward direction, which we identify with the *heat current*  $H$ , is

$$H = H \downarrow - H \uparrow = -\frac{1}{3} mn \bar{u} C_V \lambda \frac{dT}{dx} \quad (22)$$

and by comparison with eq. (19) we see that the thermal conductivity  $K$  is

$$K = \frac{1}{3} mn \bar{u} C_V \lambda = \frac{1}{3} \rho \bar{u} C_V \lambda \quad (23)$$

where  $\rho$  is the density of the gas.

On substituting the expression for mean free path  $\lambda$  from eq. (9), we get

$$K = \frac{1}{3\sqrt{2}} \frac{m \bar{u} C_V}{\sigma} \quad (24)$$

### Interrelationship

The ratio of thermal conductivity to viscosity is

$$\frac{K}{\eta} = C_V \quad (25)$$

**Dependence on Pressure and Temperature;** Thus the thermal conductivity, like the viscosity, should be *independent of pressure* or density and is a function of temperature alone through the dependence of  $\bar{u}$  on  $T$ . This is also in good agreement with experiments down to very low pressures.

As we can show that the average velocity  $\bar{u}$  is given by

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$$

so that,

$$K = \frac{1}{3\sigma} \sqrt{\frac{4m C_V k_B T}{\pi}} \quad (26)$$

Thus for molecules of a given species, the theory predicts that  $K$  is **proportional to**  $\sqrt{T}$  and for different species at a given temperature it is proportional to  $\sqrt{m}/\sigma$ . As in case of viscosity, the conductivity of all gases increases more rapidly than the square root of the absolute temperature.

### Transport of Mass: Coefficient of Self Diffusion

The vessel in figure 9 is initially divided by a partition, on opposite side of which are two different gases A and B at the same temperature and pressure, so that the number of molecules per unit volume is the same on both sides. If the partition is removed, there is no large scale motion of the gas in either direction, but after a sufficient long time has elapsed, one finds that both gases are uniformly distributed throughout the entire volume. This phenomenon, as a result of which each gas gradually permeates the other, is called *diffusion*.

**Figure 9** A vessel containing two different gases separated by a partition.

It is not limited to gases but occurs in the liquid and solid as well. Diffusion is a result of random molecular motion and occurs whenever there is a *concentration gradient* of any molecular species, i.e., when the number of particles of one kind per unit volume on one side of a surface differs from that on the other side. The phenomenon can be described as a *transport of mass* (of matter or molecules) across a surface.

The phenomenon of diffusion may be complicated by the fact that when more than one type of molecule is present the rates of diffusion of one into the other are not the same. We can simplify the problem and still bring out the essential ideas by considering the diffusion of molecules of a single species into others of the same species, known as *self-diffusion*.

If  $\Gamma$  represents the number of molecules crossing across the surface, per unit time and per unit area, the coefficient of self-diffusion  $D$  is defined by the equation

$$\Gamma = -D \frac{dn}{dx} \quad (27)$$

where  $dn/dx$  is the concentration gradient along  $x$ -axis. The negative sign is included since  $dn/dx$  is positive in upward direction, but the gas molecules are moving from regions of higher to lower concentration and so  $\Gamma$  is negative.

**Expression for  $D$ ;** Consider molecules are moving between parallel surfaces  $a-a'$  and  $b-b'$  which are at rest but having different concentration. Let  $n$  be the molecular concentration along a horizontal plane  $y-y'$  and let there be a positive concentration gradient  $dn/dx$  in the vertical plane.

If the mean free path of a molecule is  $\lambda$ , then the distance for the first collision to occur above and below the plane  $y-y'$  is also equal to  $\lambda$ , but from the plate  $a-a'$  these distances are  $x + \lambda$  and  $x - \lambda$ , respectively.

The average molecular concentration crossing the layer  $y-y'$  from above in downward direction =  $n + \lambda \frac{dn}{dx}$  and the average molecular concentration crossing the layer  $y-y'$  from below in upward direction =  $n - \lambda \frac{dn}{dx}$  (shown in figure 7).

The molecules are moving at random in all directions. In three dimensional space, we consider six such direction along each axis. Approximately,  $1/6^{\text{th}}$  molecule can be assumed to be moving in one direction and other  $1/6^{\text{th}}$  in the opposite direction along each axis.

Let  $\bar{u}$  be the average velocity of the molecules,  $n$  the number of molecules per unit volume and  $m$  the mass of each identical molecules.

Hence the number of molecules crossing the given surface per unit area per time from above in the

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downward direction, is the product of average velocity of the molecules and their numbers moving in downward direction, thus

$$\Gamma \downarrow = \frac{1}{6} \bar{u} \left( n + \lambda \frac{dn}{dx} \right) \quad (28)$$

In the same way, the number of molecules crossing the surface from below in upward direction is

$$\Gamma \uparrow = \frac{1}{6} \bar{u} \left( n - \lambda \frac{dn}{dx} \right) \quad (29)$$

Therefore, the net number of molecules transferred upwards across the given surface per unit area per unit time is

$$\Gamma = \Gamma \uparrow - \Gamma \downarrow = -\frac{1}{3} \bar{u} \lambda \frac{dn}{dx} \quad (30)$$

Comparison with eq. (27) shows that

$$D = \frac{1}{3} \bar{u} \lambda \quad (31)$$

On substituting the expression for mean free path  $\lambda$  from eq. (9), we get

$$D = \frac{1}{3\sqrt{2}} \frac{\bar{u}}{n\sigma} \quad (32)$$

### 4.2.3b Interrelationship

On combining the expression for viscosity, thermal conductivity and diffusion, we note that

$$\eta = \frac{K}{C_v} = mD \quad (33)$$

**4.2.3c Dependence on Pressure and Temperature;** Since from eq. (10) one can write the expression for mean free path in terms of the pressure and temperature as

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\sigma} \frac{k_B T}{p} \quad (10)$$

As we can show that the average velocity  $\bar{u}$  is given by

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$$

so, eq. (31) implies that the diffusion coefficient will vary **inversely as pressure  $p$  and directly as  $T^{3/2}$** . The predicted variation with pressure is in agreement with the observed results but the power of temperature lies between 1.75 to 2, against the predicted 1.5. This more rapid increase with temperature is due to the presence of intermolecular forces.