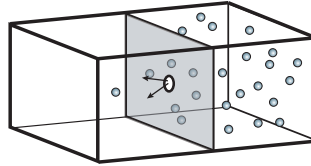


## Applications Of Kinetic Theory

### Effusion

Effusion occurs when a gas escapes into a vacuum through a small hole, of area  $a$ . The diameter of the hole is smaller than the mean free path in the gas, so that no collisions occur as the particles pass through the hole. The rate of escape of the particles is then just the rate at which they strike the hole.



$$\text{Rate} = \frac{dN}{dt} = z_{\text{wall}}a = \frac{pa}{(2\pi m k_B T)^{1/2}}$$

Note that the rate of effusion is inversely proportional to the square root of the molecular mass. As the gas leaks out of the container, the pressure decreases, so the rate of effusion will be time dependent. The rate of change of pressure with time is

$$\frac{dp}{dt} = \frac{d}{dt} \left( \frac{N k_B T}{V} \right) = \frac{k_B T}{V} \frac{dN}{dt}$$

Substituting for  $dN/dt$  and integrating gives

$$p = p_0 \exp -t/\tau \quad \text{where} \quad \tau = \left( \frac{2\pi m}{k_B T} \right)^{1/2} \frac{V}{a}$$

If we plot  $\ln(p)$  inside our chamber against  $t$ , we can determine  $p_0$  and  $\tau$ . For constant temperature and volume, measurement of  $\tau$  provides a simple way of determining the molecular mass,  $m$ .

### Transport Properties Of An Ideal Gas

A transport property of a substance describes its ability to transport matter or energy from one location to another. Examples include thermal conductivity (the transport of energy down a temperature gradient), electrical conductivity (transport of charge down a potential gradient), and diffusion (transport of matter down a concentration gradient).

When dealing with transport properties, we are generally interested in the rate at a property is transported. The **flux** describes the amount of matter, energy, charge etc. passing through a unit area per unit time.

Transport of some property generally occurs in response to a gradient in a related property, and the flux is generally proportional to the gradient. Note that both the flux and the gradient are vector properties. For example, if there is a concentration gradient in some direction  $z$ , there will be a component of mass flux,  $J_z$ , in the same direction.

$$J_z \propto \frac{d\rho_N}{dz}$$

Here,  $\rho_N = N/V$ , the number density.

Fortunately for us, many transport properties can be dealt with using essentially the same mathematical treatment.

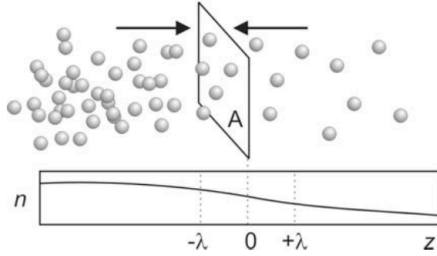
### Diffusion

The relation between matter flux and the concentration gradient is often referred to as **Fick's first law of diffusion**. The constant of proportionality is called the diffusion coefficient, and is usually given the symbol  $D$ .

$$J_z = -D \frac{d\rho_N}{dz}$$

Note the negative sign; matter diffuses down a concentration gradient from higher to lower concentration. We can use kinetic theory to show the molecular origins of Fick's first law of diffusion, and to determine a value for the diffusion coefficient,  $D$ .

Consider the flux of particles arriving from the left and from the right at an imaginary 'window' within a gas along the  $z$  axis. There is a decreasing concentration gradient from left to right.



Since the motion of the gas particles is randomised on each collision, the furthest a given particle is able to travel in a particular direction is on average equal to a distance of one mean free path,  $\lambda$ .

To a first approximation, we can assume that all of the particles arriving at the imaginary window over a time interval  $\Delta t$  have arrived there from a distance  $\lambda$  to the left or right, and the number densities of particles arriving from the left and right will therefore reflect the number densities at  $z = -\lambda$  and  $z = +\lambda$ , respectively.

If we approximate our concentration gradient to be linear between these two points with a gradient equal to that at the location of our imaginary window ( $z=0$ ). We can then write these two number densities as

$$\rho_N(-\lambda) = \rho_N(0) - \lambda \left( \frac{d\rho_N}{dz} \right)_0 \quad \text{and} \quad \rho_N(+\lambda) = \rho_N(0) + \lambda \left( \frac{d\rho_N}{dz} \right)_0$$

from the left and right respectively.

We have calculated the number of collisions with a wall before, and for unit area and unit time:

$$z_{\text{wall}} = \frac{N}{V} \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{N}{V} \frac{\langle v \rangle}{4}$$

so the fluxes from the left and right are therefore

$$J_{\text{left}} = \frac{\langle v \rangle \rho_N(-\lambda)}{4} = \frac{\langle v \rangle}{4} \left( \rho_N(0) - \lambda \left( \frac{d\rho_N}{dz} \right)_0 \right)$$

and

$$J_{\text{right}} = \frac{\langle v \rangle \rho_N(+\lambda)}{4} = \frac{\langle v \rangle}{4} \left( \rho_N(0) + \lambda \left( \frac{d\rho_N}{dz} \right)_0 \right)$$

The net flux in the  $z$  direction is therefore

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \left( \frac{d\rho_N}{dz} \right)_0 \lambda \langle v \rangle$$

This shows that the flux is proportional to the concentration gradient, and hence proves Fick's first law. It would appear that the diffusion coefficient is given by

$$D = \frac{1}{2} \lambda \langle v \rangle$$

Although this is almost right, the approximations we have made are not exact. For example, within a distance  $\lambda$  from our window, some particles are lost through collisions before they can contribute to our matter flux, and this effect must be corrected for.

A more rigorous treatment yields

$$D = \frac{1}{3} \lambda \langle v \rangle$$

We can use this result to predict the way in which the rate of diffusion will respond to changes in temperature and pressure. Increasing the temperature will increase  $\langle v \rangle$ , and therefore increase the diffusion rate, while increasing the pressure will reduce  $\lambda$ , leading to a reduction in the diffusion rate.

#### An Example: Noble Gas Diffusion

By what factor would you expect the diffusion coefficients of Helium and Neon to vary if the atomic radii are 31 and 38 pm and atomic masses 4.002 and 20.17 amu, respectively?

From the above equation, and the previous expressions for  $\lambda$  and  $\langle v \rangle$ , we can deduce that the diffusion coefficient is proportional to  $r^{-2}$  and  $m^{-1/2}$ . Therefore upon going from He to Ne we can expect an increase in diffusion coefficient of 3.37 times.

#### Thermal Conductivity

Similarly to mass transport, if there is a temperature gradient along  $z$ , there will be a component of **energy flux** along  $z$ , which will determine the rate of thermal diffusion (or thermal conductivity). Again, since energy flows down a temperature gradient, the constant of proportionality,  $\kappa$  (kappa) takes a negative sign.  $\kappa$  is known as the coefficient of thermal conductivity.

$$J_z = -\kappa \frac{dT}{dz}$$

We can derive this equation and obtain a value for the coefficient of thermal conductivity,  $\kappa$ , using almost an identical approach to that used above for diffusion:

Again consider the flux of particles upon an imaginary window from the left and right, but this time we will assume that the gas has a uniform number density (i.e. there is no concentration gradient). Instead let us assume there is a temperature gradient, with the temperature decreasing from left to right. We will assume that the

average energy of a particle is  $\varepsilon = \alpha k_B T$ , where  $\alpha$  is the appropriate fraction given by the equipartition theorem (for example, a monatomic gas has  $\varepsilon = 3/2 k_B T$ ).

Using almost identical arguments to those above for diffusion, namely that particles are on average reaching the window from a distance of one mean free path away, from regions in which their energies are  $\varepsilon(-\lambda)$  and  $\varepsilon(+\lambda)$ , we obtain expressions for the energy fluxes from left and right, and again calculate the net flux.

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \left( \frac{dT}{dz} \right)_0 \alpha k_B \rho_N \lambda \langle v \rangle$$

Again, this is an approximation, and the true flux is

$$J_z = -\frac{1}{3} \left( \frac{dT}{dz} \right)_0 \alpha k_B \rho_N \lambda \langle v \rangle$$

This shows that the energy flux is proportional to the temperature gradient, and that the coefficient of thermal conductivity,  $\kappa$ , is given by

$$\kappa = \frac{1}{3} \alpha k_B \rho_N \lambda \langle v \rangle$$

We can simplify this by recognising that for an ideal gas, the heat capacity at constant volume is given by  $C_v = \alpha k_B N_A$ . Substituting this into the above yields

$$\kappa = \frac{1}{3} \lambda \langle v \rangle C_V [X]$$

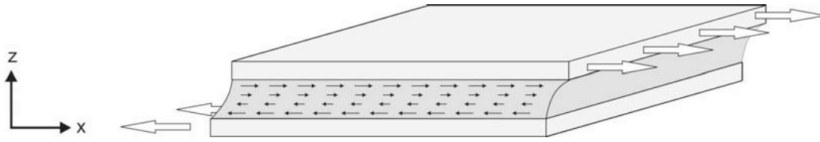
where  $[X] = Q_N/N_A = N/(N_A V)$  is the molar concentration. Note that because  $\lambda \propto 1/p$  and  $[X] \propto p$ , the thermal conductivity is essentially independent of pressure.<sup>6</sup>

<sup>6</sup> This is true at all but very low pressures. At extremely low pressures, the mean free path becomes larger than the dimensions of the container, and the container itself starts to influence the distance over which energy may be transferred.

### Viscosity

Viscosity describes a fluid's resistance to deformation when subjected to a shear stress.

When a force is applied to an object or material, the material exerts an opposing force (by Newton's third law). A shear stress is present when the force is applied parallel to a face of the material. An example of shear stress would be the stress induced in a liquid trapped between two glass plates when the plates are moved across each other.



We can also think of viscosity as a measure of the internal friction within a fluid, and hence its internal resistance to flow, as when a fluid flows, a shear stress is induced as 'layers' of fluid try to move over each other.

Shear stress results in different velocity components of the fluid (in the  $x$  direction) as we move through the depth of the fluid (in the  $z$  direction). We therefore have a gradient in  $v_x$  along the  $z$  direction, and in analogy to diffusion and thermal conductivity, this gives rise to a flux in  $v_x$  (or equivalently momentum  $p_x$ ) along  $z$ .

$$J_z = -\eta \frac{dv_x}{dz}$$

here  $\eta$  is the coefficient of viscosity (or more usually just 'the viscosity') of the fluid.

We can carry out a similar treatment to those above for diffusion and thermal conductivity: We assume that (in the  $z$  direction) particles incident on our imaginary window (in the  $xy$  plane) from the left carry momentum  $p_x(-\lambda) = mv_x(-\lambda)$  and those from the right carry momentum  $p_x(+\lambda) = mv_x(+\lambda)$ .

Our fluxes are now

$$J_{\text{left}} = \frac{1}{4} \langle v \rangle \rho_N m v_x(-\lambda) = \frac{1}{4} \langle v \rangle \rho_N \left[ m v_x(0) - m \lambda \left( \frac{dv_x}{dz} \right)_0 \right]$$

and

$$J_{\text{right}} = \frac{1}{4} \langle v \rangle \rho_N m v_x(+\lambda) = \frac{1}{4} \langle v \rangle \rho_N \left[ m v_x(0) + m \lambda \left( \frac{dv_x}{dz} \right)_0 \right]$$

The net flux of momentum  $p_x$  in the  $z$  direction is therefore

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \rho_N m \lambda \langle v \rangle \left( \frac{dv_x}{dz} \right)_0$$

Again we need to correct this expression to give

$$J_z = -\frac{1}{3} \rho_N m \lambda \langle v \rangle \left( \frac{dv_x}{dz} \right)_0$$

The flux is proportional to the velocity gradient, as required, and we see that the coefficient of viscosity for an ideal gas is given by

$$\eta = \frac{1}{3} \rho_N m \lambda \langle v \rangle = \frac{1}{3} m \lambda \langle v \rangle N_A [X]$$

As with thermal conductivity, the viscosity is independent of the pressure. However, the viscosity does have a  $T^{1/2}$  dependence on temperature, as the mean velocity  $\langle v \rangle \propto T^{1/2}$ . Note that this means that, unlike a liquid, the viscosity of a gas increases with temperature, since the increased velocity of the gas particles increases the momentum flux.

In general, for a liquid the viscosity decreases with increasing temperature, as in a liquid most of the energy goes into overcoming intermolecular forces, thereby making it easier for the particles to move past each other. In the gas phase we are able to neglect intermolecular forces to a good approximation, but in a liquid these forces have a major effect.