

2106NSC

Physical & Analytical Chemistry

Thermodynamics 13

Transport properties

Motion

When considering the motion of particles/properties, one can observe the transfer of

- matter
- energy
- any other property.

Four important instances of such **transport properties** of substances are:

Diffusion	migration of matter along a concentration gradient
Thermal conduction	migration of energy along a temperature gradient
Electric conduction	migration of charges along an electric potential gradient
Viscosity	migration of a linear momentum along a velocity gradient

The kinetic theory of gases

In the kinetic theory of gases, we only consider the energy contributions from the kinetic energies of the gas molecules.

Assumptions:

- The gas consists of molecules of mass m in random motion.
- The molecules have negligible size.
- The molecules interact only through brief, infrequent, elastic collisions.

Elastic collisions:

The total translational kinetic energy of molecules is conserved.

The kinetic theory of gases: pressure, speed

From the kinetic theory, one can derive an equation that relates pressure and volume of an ideal gas with the speed of the individual gas molecules:

$$p \cdot V = \frac{1}{3} \cdot n \cdot M \cdot c^2$$

with c being the root mean square speed of the molecules, i.e. a speed averaged over the entire population of gas molecules:

$$c = \sqrt{\langle v^2 \rangle}$$

So if the root mean square speed only depends on the temperature, then the product $p \cdot V$ is constant at constant temperature (**Boyle's Law**).

The kinetic theory of gases: pressure, speed

Since we are considering an ideal gas:

$$p \cdot V = \frac{1}{3} \cdot n \cdot M \cdot c^2 = n \cdot R \cdot T$$

From this equation, we can derive an expression for the speed of the gas molecules:

$$c = \sqrt{\frac{3 \cdot R \cdot T}{M}}$$

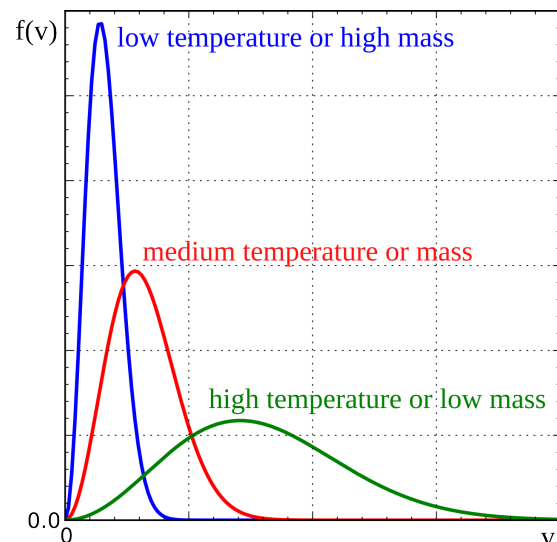
i.e.: the higher the temperature, the higher the speed of the molecules, and heavy molecules travel slower than light molecules.

The Maxwell-Boltzmann distribution

In reality, the velocity of individual gas molecules varies and spans a range of different values. A molecule may be travelling rapidly, but then collide and travel slower. It may then accelerate again, only to be slowed down by the next collision.

This distribution of velocities has been precisely formulated by Maxwell who developed a distribution from the Boltzmann distribution:

$$f(v) = 4\pi \cdot \sqrt{\left(\frac{M}{2\pi \cdot R \cdot T}\right)^3} \cdot v^2 \cdot e^{-\frac{M \cdot v^2}{2 \cdot R \cdot T}}$$



Boltzmann: $e^{-\frac{E}{k_B \cdot T}}$

[Maxwell distribution at Davidson College](#)

Transport properties

Phenomenologically, we can describe the migration of a property by its flux:

$$\text{Flux } J = \frac{\text{quantity of property}}{\text{area passed} \cdot \text{time interval}}$$

Property migrating	Process	Flow
Matter	Diffusion	No of molecules per m ² per s
Energy	Thermal conduction	Joules per m ² per s

In order to calculate the total quantity of each property migrating, one needs to calculate

$$J \cdot A \cdot \Delta t$$

Diffusion

Commonly, it turns out that the flux of a property is proportional to the first derivative of another property.

The flux of matter migrating by diffusion parallel to a particular direction x is proportional to the first derivative of the concentration along that direction:

$$J \sim \frac{dc}{dx} \quad \text{Fick's first law of diffusion}$$

Since matter migrates from areas of high concentration to low concentration, the concentration gradient along x is negative.

In order to obtain a positive flux (i.e. migration occurring in that direction), the equation needs to be set up as

$$J = -\text{const.} \cdot \frac{dc}{dx}$$

Diffusion: flux of matter

$$J = -\text{const.} \cdot \frac{dc}{dx} = -\text{const.} \cdot \frac{d\left(\frac{n}{V}\right)}{dx} = -\text{const.} \cdot \frac{1}{N_A} \cdot \frac{d\left(\frac{N}{V}\right)}{dx} = -\text{const.} \cdot \frac{1}{N_A} \cdot \frac{dN}{dx}$$

$$J = -D \cdot \frac{dN}{dx} \quad D \text{ is the } \textbf{diffusion coefficient}$$

Units:

$$\left[\frac{d(N)}{dx}\right] = \frac{\frac{1}{\text{m}^3}}{\text{m}} = \frac{1}{\text{m}^4} \quad \text{Number of molecules per volume / distance}$$

$$[J] = \frac{1}{\text{m}^2 \cdot \text{s}} \quad \text{Number of molecules passing an area per time interval}$$

Therefore:

$$[D] = 1 \frac{\text{m}^2}{\text{s}}$$

Thermal conduction: flux of energy

Energy migrates along a temperature gradient. Similar to diffusion, the energy migrates from high to low temperature, i.e. opposite the gradient.

Therefore:

$$J = -\kappa \cdot \frac{dT}{dx} \quad \kappa \text{ is the } \mathbf{\text{thermal conductivity}}$$

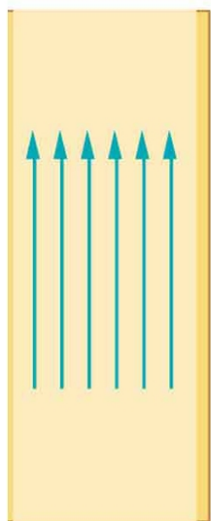
$$[\kappa] = 1 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$$

$$[J] = 1 \text{ J m}^{-2} \text{ s}^{-1}$$

Viscosity: flux of momentum

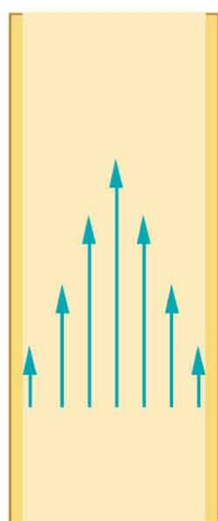
Consider a liquid stream comprising a series of layers, where each layer moves with a different velocity along one particular direction. Molecules from one layer (that moves at slow speed) can switch to a neighbouring layer that moves faster. The neighbouring layer will be retarded because of the lower momentum of the switching molecules. The opposite holds for molecules switching from a faster moving layer.

Nonviscous
 $\eta = 0$

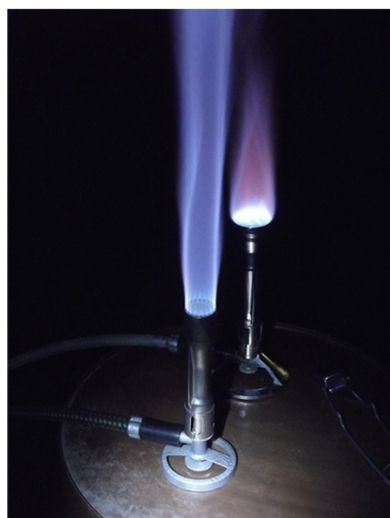


(a)

Viscous



(b)



(c)

(a) If fluid flow in a tube has negligible resistance, the speed is the same all across the tube.

(b) When a viscous fluid flows through a tube, its speed at the walls is zero, increasing steadily to its maximum at the centre of the tube.

(c) The shape of the Bunsen burner flame is due to the velocity profile across the tube.

Figure taken from:

[Viscosity and Laminar Flow \(cnx.org\)](https://cnx.org/content/col12119/1.10)

Viscosity: flux of momentum

The flux of the momentum ($m \cdot v_x$) is described by:

$$J = -\text{const.} \cdot \frac{d(m \cdot v_x)}{dx}$$

$$J = -(\text{const.} \cdot m) \cdot \frac{dv_x}{dx}$$

$$J = -\eta \cdot \frac{dv_x}{dx} \quad \eta \text{ is the } \mathbf{\text{viscosity}}$$

If all layers move at the same velocity, the gradient ($d(mv_x)/dx$) is zero, and there is no flux of momentum!

Units:

$$[\eta] = 1 \text{ kg m}^{-1} \text{ s}^{-1} = 1 \text{ N s m}^{-2} = 10 \text{ P (Poise)}$$

The transport parameters

The kinetic model of an ideal gas leads to expressions for transport parameters.

The diffusion coefficient of the ideal gas:

$$D = \frac{1}{3} \cdot \lambda \cdot \bar{c} \quad \text{with} \quad \begin{array}{l} \lambda \text{ mean free path (average distance without collisions)} \\ \bar{c} \text{ mean speed of molecules} \end{array}$$

This means:

The mean free path λ of gas molecules decreases with increasing pressure (more collisions). Therefore, the diffusion coefficient D decreases with increasing pressure. At higher pressure, molecules diffuse more slowly.

The mean speed \bar{c} increases with increasing temperature, and so does the diffusion coefficient D . At higher temperatures, molecules diffuse more quickly.

The mean free path λ (and thus D) increases when the collision cross-section of molecules decrease. Smaller molecules diffuse quicker than large molecules.

The transport parameters

The thermal conductivity of an ideal gas A:

$$\kappa = \frac{1}{3} \cdot \lambda \cdot \bar{c} \cdot C_{V,m} \cdot c(A) \quad \text{with } C_{V,m} \text{ molar heat capacity at constant volume}$$

This means:

The mean free path λ is inversely proportional to the pressure and inversely proportional to the concentration. κ is thus independent of the pressure.

The thermal conductivity is larger for gases with a larger heat capacity.

The transport parameters

The viscosity of an ideal gas A:

$$\eta = \frac{1}{3} \cdot M \cdot \lambda \cdot \bar{c} \cdot c(\text{A})$$

This means:

The mean free path λ is inversely proportional to the pressure and inversely proportional to the concentration. η is thus independent of the pressure.

The mean speed \bar{c} increases with increasing temperature, and so does the viscosity η . At higher temperatures, gases have a higher viscosity.

(In liquids, for a molecule to move, it must overcome intermolecular interactions. With increasing temperature, more molecules acquire this energy and can move; the viscosity of a liquid thus decreases with increasing temperature).

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections V.1.1-V.1.7

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Sections 20.1 – 20.4 (pp. 745-758)