Thermal Conductivity of a Gas

Equation (1-11) can be used as a starting point in order to develop an approximate relation for the thermal conductivity of any substance, provided that you understand its physical structure. For example, we can apply this equation to an ideal gas where the energy carriers are the gas molecules. The number density of the energy carriers is equal to the number density of the gas (n):

$$n_{ms} = n \tag{1-12}$$

The ratio of the energy per molecule to its temperature, c_{ms} in Eq.(1-11), is proportional to c_v, the constant volume specific heat capacity of the gas (i.e., the partial derivative of internal energy with respect to temperature at constant specific volume):

$$c_{ms} \propto c_v \tag{1-13}$$

The mean velocity of the molecules, v_{ms}, can be determined from kinetic theory (Walton (1989)) and can be shown to be proportional to the square root of the absolute temperature (T):

$$v_{ms} \propto \sqrt{\frac{R_{univ}\, T}{MW}} \tag{1-14}$$

where R_{univ} is the universal gas constant (8314 J/kmol-K) and MW is the molar mass of the gas.

The distance between energy carrier interactions, L_{ms}, is the mean free path. The mean free path is defined as the average distance that a molecule of gas will move between collisions with another molecule of gas. The volume occupied by the molecules is very small relative to the total volume occupied by the gas. However, the molecules must occupy some volume or they would never collide. A typical model for a molecule is a sphere with a radius of σ. Consider a single molecule that is moving at velocity v_{ms} through a gas with number density n. If we neglect the complication associated with the motion of the other molecules, then during any given time period, Δt, the molecule will subtend a volume that is equal to the product of its frontal area, $\pi \sigma^2$, and its path length, $v_{ms}\, \Delta t$. Any molecules caught within this volume will collide with the moving molecule; the number of molecules in the volume (i.e., the number of collisions) is the product of the number density and the subtended volume.

$$\#\text{ collisions} = \pi \sigma^2 v_{ms}\, \Delta t\, n \tag{1-15}$$

On average, the molecule will move without collision until Eq. (1-15) is equal to 1; at this point, the distance traveled (the product $v_{ms}\, \Delta t$) will be equal to the mean free path:

$$1 = \pi \sigma^2 \underbrace{v_{ms}\, \Delta t}_{L_{ms}}\, n = \pi \sigma^2 L_{ms}\, n \tag{1-16}$$

Consequently, the mean free path, L_{ms}, is approximately:

$$L_{ms} \approx \frac{1}{n \pi \sigma^2} \tag{1-17}$$

Substituting Eqs. (1-12), (1-13), (1-14), and (1-17) into Eq. (1-11) results in the following scaling equation for the thermal conductivity of an ideal gas.

$$k \propto \frac{c_v}{\sigma^2} \sqrt{\frac{T}{MW}} \tag{1-18}$$

The molecular radius is determined from an analysis of intermolecular forces and can be approximated as being proportional to the cube root of the critical volume. Equation (1-18) is approximate because its development did not consider the distribution of molecular velocities and, for polyatomic molecules, energy storage effects that occur through rotation or vibration. Nevertheless, Eq. (1-18) is useful in that it correctly predicts that the thermal conductivity of an ideal gas is independent of pressure, but increases approximately according to the square root of temperature. There is no pressure dependence because increasing the pressure both increases the number density of the gas and decreases the mean free path; these changes exactly cancel for an ideal gas. The thermal conductivity of a 'real gas' (i.e., a gas at conditions where it does not obey the ideal gas law) will exhibit a dependence on pressure that increases with increased deviation from ideal gas behavior. Equation (1-18) also provides some indication of how thermal conductivity will vary with the molecular weight and radius of the gas molecules.