1.1: The System and the Surroundings

The Zeroth Law of Thermodynamics deals with the temperature of a system. And while it may seem intuitive as to what terms like "temperature" and "system" mean, it is important to define these terms. The easiest terms to define are the ones used to describe the system of interest and the surroundings, both of which are subsets of the universe.

- **Universe** – everything
- **System** – subset of the universe that is being studied and/or measured
- **Surroundings** – every part of the universe that is not the system itself.

As it turns out, there can be several types of systems, depending on the nature of the boundary that separates the system from the surroundings, and specifically whether or not it allows to the transmittance of matter or energy across it.

- **Open System** – allows for both mass and energy transfer across its boundary
- **Closed System** – allows for energy transfer across its boundary, but not mass transfer
- **Isolated System** – allows neither mass nor energy transfer across its boundary

Further, systems can be **homogeneous** (consisting of only a single phase of matter, and with uniform concentration of all substances present throughout) or **heterogeneous** (containing multiple phases and/or varying concentrations of the constituents throughout.) A very important variable that describes a system is its composition, which can be specified by the number of moles of each component or the concentration of each component. The number of moles of a substance is given by the ratio of the number of particles to Avogadro's number

$$n = \frac{N}{N_A}$$

where n is the number of moles, N is the number of particles (atoms, molecules, or formula units) and N_A is Avogadro's number ($N_A = 6.022 \times 10^{23}$ mol^{-1}).

Other important variables that are used to describe a system include the important variables of pressure, temperature, and volume. Other variables may also be important, but can often be determined if these **state variables** are known. Oftentimes, knowing a small number of state variables is all that is required to determine all of the other properties of a system. The relationship that allows for the determination of these properties from the values of a couple of state variables is called an **equation of state**.

Variables that describe a system can be either **intensive** (independent of the amount of any given substance present in the system) or **extensive** (dependent on the amount of substance present in the system.) Temperature and color are examples of intensive variables, whereas volume and mass are examples of extensive variables. The value of intensive properties is that they can be conveniently tabulated for various substances, whereas extensive properties would be specific to individual systems.

Oftentimes it is the case that the ratio of two extensive variables results in an intensive variable (since the amount of substance cancels out.) An example of this is density, which is the ratio of mass and volume. Another example is molar volume (V_m) which is the ratio of volume and number of moles of substance. For a given substance, the molar volume is inversely proportional to the density of the substance.

In a homogeneous system, an intensive variable will describe not just the system as a whole, but also any subset of that system. However, this may not be the case in a heterogeneous system!