1.5 Thermal Phenomena

Thermal systems have a **temperature** and **thermal contact** allows the system to reach **thermal equilibrium**, or a common temperature. The **volume** and **pressure** of a gas are closely related to temperature.

$$T = \lim_{p \to 0} \frac{p}{p_{tp}}(273.16K)$$

p_{tp} is the pressure of water at its triple point: when ice, steam, and liquid water can coexist in equilibrium. The **ideal-gas** equation of state relates thermodynamic variables:

$$pV = nRT = NkT$$

where n is the number of moles of gas, N is the number of individual gas molecules. $n = N \times N_A$ where N_A is **Avogadro's numbers** (6.23×10^{23}). R and k are the **universal gas constant** $(8.314 \text{ J}/(\text{mol} \cdot \text{K}))$ and **Boltzmann's constant** $(R \times N_A)$.

Thermodynamic transformations occur when thermodynamic variables change under outside influences. A transformation can either by a **reversible transformation** (a piston pushed into a cylinder) or an **irreversible transformation** (gas freely escaping from a container), which are often spontaneous. There are three types of reversible transformations: isothermal, isobaric, and isochoric, in which the temperature, pressure, and volume, respectively, remain fixed.
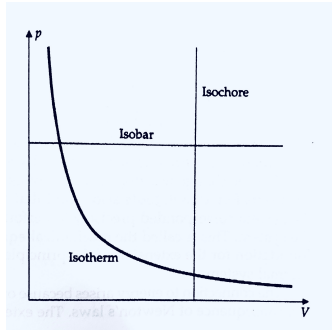
In the case of a piston being pushed into a cylinder containing gas, we can look at the work done by the gas on the piston. $dW = F\ dx = pA\ dx = p\ dV$, so

$$W = \int_{V_i}^{V_f} p\ dV$$

or the area under a curve of a p-V diagram. This is a path dependent quantity.

Temperature can also be added through thermal contact: adding heat to the system. The differential amount of heat dQ added is proportional to the temperature change dT, so that

$$dQ = C\ dT$$

where C is the **heat capacity**, a quantity that depends on how the temperature change has been made. C_V is when volume is constant. Q, heat, is also a path dependent quantity and if no external work is done then heat must be conserved. A transformation with no thermal contact is called **adiabatic**.

Thermal energy U, aka internal energy, is

$$dU = dQ - dW$$

where dQ is the heat added to the system and dW is the work done by the system. This is known as the **first law of thermodynamics**. For constant volume,

$$U(T) = \int dQ - 0 = \int^T C_V \ dT = C_V T$$

The **second law of thermodynamics** states that no engine can be perfectly efficient.

$$\text{maximum efficiency} = 1 - T_c/T_h$$

Entropy is a measure of chaos in a system. In an isolated system, entropy has the property that it increases when irreversible processes occur. The stable equilibrium state is the state of maximum entropy.

Kinetic Theory

Temperature can be understood in terms of the **kinetic theory of gases**. Consider this situation, gas is applying pressure to a wall. The internal energy of the gas is the sum of all the kinetic energies of the particles ($U = NK_{av}$). We can assume that all the particles are moving at the same speed.

Now consider a single molecule with initial velocity $\vec{v}$ bouncing elastically from the wall with area A in the yz-plane. The change in momentum of the particle is $2mv_x$.

Let $n(\vec{v})$ be the distribution function: the number of particles with velocity $\vec{v}$ per unit area. Let's look at the molecules with velocities ranging from $\vec{v} = (v_x, v_y, v_z)$ to $\vec{v} + d\vec{v} = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$. $n(\vec{v})d^3\vec{v}$ is the number of molecules within this range per unit volume since it is a uniformly random distribution.

For the particle to hit the wall it must be within $v_x dt$ of the wall and it must be in the area A. So it must be in the prism with height $v_x dt$ and base area A (the wall).

So the total change in momentum is

$$dp_{tot} = (2mv_x)n(\vec{v})d^3\vec{v}(v_x dt A) = 2mdt A v_x^2 n(\vec{v})d^3\vec{v}$$

$$dF = \frac{dp_{tot}}{dt} = 2mA v_x^2 n(\vec{v})d^3\vec{v}$$

$$dP = \frac{dF}{A} = 2mv_x^2 n(\vec{v})d^3\vec{v}$$

To find total pressure P (for all particles not only in velocity range) we must integrate through all v_y, v_z, and all $v_x > 0$ (must be going towards wall).

$$P = 2m \int v_x^2 n(\vec{v}) d^3\vec{v} \text{for all } v_x > 0 = 2m\frac{1}{2} \int v_x^2 n(\vec{v}) d^3\vec{v}$$

since $v_x > 0$ will occur about half the times since direction uniformly random.

Since all directions are uniformly distributed ($n(\vec{v}) = n(v)$),

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and $v^2 = v_x^2 + v_y^2 + v_z^2$ so on average $v_x^2 = v^2/3$. Since v is a constant for all molecules, it can be taken out of the integral.

$$\int n(\vec{v}) d^3\vec{v} = N/V$$

the number of molecules per unit volume since $n(\vec{v})$ is for the range from $\vec{v}$ to $\vec{v} + d\vec{v}$ and the integral is for all $\vec{v}$.

Using these properties,

$$P = m \int v_x^2 n(\vec{v}) d^3\vec{v} = \frac{mv^2}{3} \int n(\vec{v}) d^3\vec{v} = \frac{mv^2}{3}(\frac{N}{V}) = \frac{2}{3}K_{av}(\frac{N}{V})$$

$$PV = nRT = NkT = \frac{2}{3}K_{av}N = \frac{2}{3}U$$

$$U = \frac{3}{2}NkT \text{ and } kT = \frac{2}{3}K_{av}$$