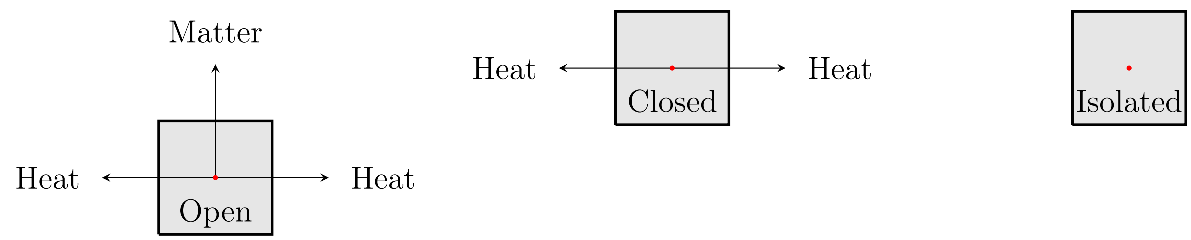
Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore.

What is a System?

A *thermodynamic system* consists of all the materials involved in the process under study. The rest of the universe is referred to as the surroundings. We can classify the following systems as follows:

- Open: Matter and energy exchange.
- Closed: Only energy exchange.
- Isolated: No matter or energy exchanged.

Below is a free body diagram that describes the three systems.



Recall that a *homogeneous reaction* is a property that remains uniform throughout, and a *heterogeneous reaction* is a property that contains multiple phases.

Question: What kind of system are cells? For example, an animal cell or a plant cell.

(a) Open Systems (b) Closed Systems (c) Isolated Systems

State Function

A function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state. For example, pressure P, volume V and temperature T are all examples of state functions.

On a *macroscopic level*, we focus on the large scale properties, including the three quantities mentioned above. But on a *microscopic level*, we focus on the concept of molecules, including the structure, dynamics and intermolecular forces, i.e. position x_i, velocity v_i, and mass m_i.

Our aim is to look at the relationship between the macroscopic properties of a gas and end up with the gas laws.

Properties of Gases

- Gases are easy to expand.
- Gases are easy to compress.
- Gases have much lower densities than liquids and solids.
- Gases expand to fill a container (diffusion).
- Hot gas leaks through small holes faster than cold gas (effusion).
- Gas molecules attract each other weakly.
- Gas molecules are far apart.
- Gas molecules are far apart compared to those in liquids and solids.
- Gas molecules are constantly in motion.
- Gas molecules move faster (greater kinetic energy) at higher temperatures.
- Mostly empty space.
- Gases molecules are in constant motion.
- Gases are disordered.
- Assume negligible interactions between gas molecules.
- Average motion of gas molecules increases with temperature.
- Distribution of speeds of gas molecules becomes broader at higher temperature.
- Volume of molecules is negligible compared to their average separation.
- Pressure is the manifestation of the molecules hitting the wall of a wall.
- Unlike solids.
- An ideal gas.
- $K = \dfrac{3RT}{2N_A}$
- Maxwell-Boltzmann distribution.

Forms of Energy

How can a material store energy? On a molecular scale, we can think in terms of

- Thermal Energy: Kinetic energy of molecular motion (translational, rotational, and vibrational). Measured by finding the *temperature*.
- Chemical Bond Energy: Potential energy stored in molecular bonds.

Properties of Matter

Properties of Matter →

- Intensive Properties: Do not depend on amount
  Density, color, boiling point
- Extensive Properties: Do depend on amount
  Mass, volume

Temperature Scale

Temperature is an abstract quantity. But how do we define it? Hot or hold. For example, using the ideal gas law

$$T = \frac{P}{\rho R}$$

Then there are three different cases that we can look at.

- When $\rho_1 = \rho_2$, then the temperature remains cold.
- When $P_1 \neq P_2$, then the temperature remains hot.
- When $T_1 \neq T_2$, then the temperature remains cold.

Two systems with rigid walls and the same molar density have different temperatures. Temperature is measured indirectly. For example,

- Measuring the volume of mercury confined to a narrow capillary.
- Measuring electrical resistance of a platinum wire.

What is Equilibrium?

Equilibrium refers to exchange of matter or energy across a boundary. Equilibrium for a variable established when variable does not change in time.

$$Var_{sys} = Var_{sur}$$

Boundary characteristics required for equilibrium:

- Are walls permeable in both directions to all species?
- Are walls moveable?

Thermal Equilibrium

Thermal equilibrium between systems exists if $P_1 = P_2$ for gaseous systems with the same molar density.

- The two systems are brought together so that the walls are in intimate contact. Even after a long time has passed, the temperature in each system is unchanged.
  - The walls are *adiabatic*. An adiabatic system does not permit the passage of energy *as heat* through its boundary even if there is a temperature difference between the system and its surroundings.
  - Isolated System $\Rightarrow$

- The two systems are brought together so that the walls are in intimate contact, but in this case after a long time has passed, the pressures are equal.
  - The walls are *diathermal*. A diathermal system permits the passage of energy *as heat* through its boundary.
  - Open/Closed System $\Rightarrow$

Question: Real walls are never totally adiabatic. Order the following walls in increasing order with respect to being diathermal:

(i) 1-cm thick concrete.

(ii) 1-cm thick vacuum.

(iii) 1-cm thick copper.

(iv) 1-cm thick cork.

(a) Concrete < Vacuum < Copper < Cork

(b) Vacuum < Copper < Cork < Concrete

(c) Copper < Concrete < Cork < Vacuum

(d) Vacuum < Cork < Concrete < Copper

(e) Copper < Vacuum < Concrete < Cork

Zeroth Law of Thermodynamics

Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.

In the gas phase, we have quantities P, n, T, and V. For pressure, P:

$$P = \frac{F}{A} = \frac{ma}{A}$$

The SI unit of the pressure is the Pascal. Other units would include the bar, mm Hg, Torr, and atm. But how do we measure pressure?

Barometer (Atmospheric Pressure)

The weight of Hg causes level in tube to drop until

$$P_{\text{Hg}} = P_{\text{atm}}$$

The average pressure at sea level will support a column of 760 mm Hg. Pressure of units of "atmospheres"

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ Torr}$$

Kinetic Molecular Theory

In this section, we want to look at the kinetic molecular theory that explains the gas laws. The kinetic molecular theory has five postulates:

P1. Gas consists of tiny particles (atoms or molecules) moving completely randomly.

P2. Volume of particles is negligible compared to total volume occupied by gas (i.e. large separation between individual gas molecules)

P3. No attractive or repulsive forces between particles.

P4. Gas molecules collide with one another (and other things) without energy loss (elastic collisions)

P5. The average kinetic energy of gas molecules is proportional to temperature. Note that

$$K = \frac{1}{2}mv^2$$

Temperature and Molecular Velocity

The average kinetic energy of a molecule is

$$K = \frac{1}{2}m\bar{v}^2$$

where $\bar{u}^2$ is the average of the squares of the particle velocities. The kinetic energy of a mole of molecules is

$$K = \frac{1}{2}N_A m\mathbf{v}^2$$

But since the kinetic energy is directly proportional to the temperature. In particular,

$$K = \frac{3}{2}RT$$

Then

$$\frac{1}{2}N_A\mathbf{v}^2 = \frac{3}{2}RT \Rightarrow \bar{v}^2 = \frac{3RT}{N_A m} = \frac{3RT}{M}$$

where M is the molar mass. Recall that the root mean square velocity is defined by

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}}$$