Thermodynamics

- From the Greek *thermos* meaning heat and *dynamis* meaning power is a branch of physics that studies the effects of changes in *temperature*, *pressure*, and *volume* on physical systems at the macroscopic scale by analyzing the collective motion of their particles using statistics.
  - Temperature, pressure, and volume quantitatively define the *state* of a gas
  - Temperature, pressure, and volume are *state* variables
- We want to determine the relationship (i.e., find some equations) between these state variables and more importantly, relationships between changes in these state variables.

Temperature and Thermal Equilibrium

- The zeroth law of thermodynamics:
  - If two systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with one another.
  - If two thermal systems are in thermal equilibrium with one another, then they have the same temperature.

Temperature is a way of determining (measuring?) thermal equilibrium

- Two systems have the same temperature
- They are in thermal equilibrium
- Two systems have different temperatures
- They are NOT in thermal equilibrium

Temperature Scales

- Fahrenheit:
  - $t_f = 32\degree$ at freezing point of water
  - $t_f = 212\degree$ at boiling point
- Celsius:
  - $t_c = 0\degree$ at freezing point of water
  - $t_c = 100\degree$ at boiling point

  $T(\degree C) = \frac{5}{9}(T(\degree F) - 32)$
  $T(\degree F) = \frac{9}{5}T(\degree C) + 32$


Thermal Expansion

- Solids expand when temperature increases; describe by coefficient of thermal expansion ($\alpha$):
  - $\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T}$
  - $OR \quad \Delta L = L_0 \alpha \Delta T$
- For fluids, use coefficient of volume expansion ($\beta$) instead (as length is not well-defined):
  - $\beta = \frac{1}{V_0} \frac{\Delta V}{\Delta T}$
  - $OR \quad \Delta V = V_0 \beta \Delta T$
Thermal Stress

Induced stress when the material does not freely expand or contract due to a temperature change.

\[ \sigma = E \epsilon \Rightarrow \Delta L = L_o \alpha \Delta T \]

\[ \therefore \sigma = \frac{F}{A} = E \frac{L_o \alpha \Delta T}{L_o} = E \alpha \Delta T \]

Ideal Gas Law

Using moles

\[ PV = nRT \]

- \( P \) = pressure
- \( V \) = volume
- \( n \) = number of moles
- \( R \) = universal gas constant
- \( T \) = temperature

\[ R = 8.315 \text{ J/(mol-K)} \]

Using molecules

\[ PV = \frac{NkT}{n} \]

- \( P \) = pressure
- \( V \) = volume
- \( N \) = number of molecules
- \( k \) = Boltzmann’s constant
- \( T \) = temperature

\[ k = 1.38 \times 10^{-23} \text{ J/K} \]

This is called the Equation of State. Why “Ideal”?

- Dilute, Volume of Molecules is ~ Zero
- No Attraction Between Molecules
- Temperature must be in Absolute Units, K

“Real” gases do not follow the ideal gas law precisely. However, at low pressure and temperatures “not too close” to the liquefaction point, the ideal gas law is quite accurate and useful for “real” gases.

Kinetic Theory of Gases

Connect microscopic properties (kinetic energy and momentum) of molecules to macroscopic “state” properties of a gas (temperature and pressure).

\[ PV = \frac{1}{3} Nm \overline{v^2} = \frac{2}{3} N \left( \frac{1}{2} \overline{v^2} \right) \]

But \[ \overline{K} = \frac{1}{2} \overline{mv^2} \] and \[ PV = NkT \]

\[ \therefore \overline{K} = \frac{1}{2} \overline{mv^2} = \frac{3}{2} kT \]

Temperature is a measure of the average kinetic energy (internal energy?) of the gas.

Real Gasses - Better Approximations

- Ideal Gas

- First Order
  - Clausius Equation of State (EoS)

\[ P = \frac{nRT}{V - n} \]

- Second Order
  - Van der Waals

\[ P = \frac{nRT}{V - n} - \frac{a}{V^2} - \frac{b}{n} \]
What is heat?
- Heat (Q) is the “flow” or “transfer” of energy from one system to another
- Often referred to as “heat flow” or “heat transfer”
- Requires that one system must be at a higher temperature than the other
  - Heat will only flow from the system with the higher temperature to the system with the lower temperature
  - Heat will only flow from the system with the higher average internal energy to the system with the lower average internal energy
  - Total internal energy does not matter.

Heat Capacity
- Heat capacity connects heat flow to temperature change:
  \[ Q = C \Delta T \]
- Heat capacity \( C \) depends on material, and also on the quantity of material present. Eliminate quantity dependence by introducing specific heat \( c \) and molar heat capacity \( c' \):
  \[ Q = mc \Delta T \quad Q = nc' \Delta T \]

Latent Heat
- A phase change occurs when a solid melts to a liquid, a liquid boils to a gas, a gas condenses to a liquid, and a liquid freezes to a solid.
- Each of these phase changes requires a certain amount of heat, although the temperature does not change.
- If a solid becomes liquid, or vice versa, the amount of heat per gram is the latent heat of fusion.
- If a liquid becomes gas, or vice versa, the amount of heat per gram is the latent heat of vaporization.

Measuring Heat Capacities
- Calorimeter
  - System is adiabatically isolated from the environment
  - Net \( Q = 0 \) from or into the device
  - Heat lost = heat gained
  - Conservation of energy
**Conduction**

- Time rate of heat transfer depends on:
  - The material
    - Specifically $k = \text{thermal conductivity}$
  - Area
  - Temperature difference
  - Thickness or length

$$Q = \frac{\Delta T}{\Delta t} = \frac{T_2 - T_1}{l}$$

Differential form

$$\frac{dQ}{dt} = -kA \frac{dT}{dx}$$

*Given $k$ and material or R-Value, Thermal Resistance Value*

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature (K)</th>
<th>Latent Heat of Fusion (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>14</td>
<td>0.12</td>
</tr>
<tr>
<td>O</td>
<td>30</td>
<td>0.44</td>
</tr>
<tr>
<td>Water (H2O)</td>
<td>217</td>
<td>0.9</td>
</tr>
<tr>
<td>Ethyl alcohol (C2H5OH)</td>
<td>239</td>
<td>4.8</td>
</tr>
<tr>
<td>Mercury</td>
<td>254</td>
<td>2.5</td>
</tr>
<tr>
<td>Lead</td>
<td>600</td>
<td>4.8</td>
</tr>
<tr>
<td>Copper</td>
<td>1337</td>
<td>15</td>
</tr>
</tbody>
</table>

**Heat Transfer**

- **Conduction**
  - Results from molecular interactions
  - Collisions?
  - Energy is transferred through interaction

- **Convection**
  - Results from the mass transfer of material
  - Think fluid flow

- **Radiation**
  - Energy transferred by electromagnetic radiation (waves)
  - Does not require a “medium”

Your refrigerator can be thought of as a box with six sides of total area 2.5 m². The effective R value of the walls is 1.5 m²–K/W. The temperature inside is 5.0°C, while the temperature outside is 25°C. Calculate the rate of heat loss.
If 18.75 mol of helium gas is at 10.0°C and a gauge pressure of 0.350 atm, calculate
a) the volume of the helium gas under these conditions, and
b) the temperature if the gas is compressed to precisely half the volume at a gauge pressure of 1.00 atm.

\[ PV = nRT \]
\[ (1.0 \text{ mol}) \times 0.350 \text{ atm} \times 8.314 \text{ J/(mol K)} \times (283 \text{ K}) \]
\[ V = 14.7 \text{ mL} \]  
\[ 1 \text{ at} \]

\[ \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \]
\[ \left( \frac{1.0 \text{ atm}}{2.0 \text{ atm}} \right) \left( \frac{V_1}{V_2} \right) = \frac{T_2}{T_1} \]
\[ \left( \frac{1.0 \text{ atm}}{2.0 \text{ atm}} \right) = \left( \frac{V_1}{2 V_1} \right) \]
\[ T_2 = 210 \text{ K} = -63°C \]