The second law of thermodynamics really consists of a number of statements that one might consider rules of reality that help explain physical observations that are not explained by the conservation of mass or conservation of energy principles. These rules of reality will help us in the following ways:

1. determining the final equilibrium state for a spontaneous process
2. providing a means of measuring the quality of energy
3. determining the reality of a process or device
4. determining the direction of change for a process
5. providing a criteria for ideal performance of a device.

### Heat Engines, Heat Pumps, and Refrigerators

Devices that operate on a cycle (a series of processes that eventually return the system to its initial state) are one of three types as summarized below.

<table>
<thead>
<tr>
<th>Device</th>
<th>Purpose</th>
<th>Performance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Engine</td>
<td>Produce Work</td>
<td>Thermal Efficiency, ( \eta_{th} = \frac{W_{net}}{Q_H} = \frac{\dot{W}_{net}}{\dot{Q}<em>H} = \frac{w</em>{net}}{w_H} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Pump</td>
<td>Supply Heat to a Body</td>
<td>Coefficient of Performance, ( (COP)<em>{HP} = \frac{Q_H}{W</em>{net}} = \frac{\dot{Q}<em>H}{\dot{W}</em>{net}} = \frac{q_H}{w_{net}} )</td>
</tr>
<tr>
<td>Refrigerator</td>
<td>Extract Heat From a Body</td>
<td>Coefficient of Performance, ( (COP)<em>{Ref} = \frac{Q_L}{W</em>{net}} = \frac{\dot{Q}<em>L}{\dot{W}</em>{net}} = \frac{q_L}{w_{net}} )</td>
</tr>
</tbody>
</table>

All of these devices operate by interacting with a low temperature heat reservoir at temperature \( T_L \) and a high temperature heat reservoir at temperature \( T_H \). The parameters \( Q_L, Q_H, \) and \( W_{net} \) indicate these interactions. These interactions are shown more clearly on the figure below.
A conservation of energy or first law analysis on these cycle devices gives

$$Q_H = W_{net} + Q_L$$

**Carnot Cycle Devices**

It has been found that if the devices discussed above operate a series of processes called the Carnot cycle, maximum performance will be achieved. The Carnot cycle consists of four processes as follows:

**Process A:** Isothermal heat addition at $T_H$
**Process B:** Isentropic and adiabatic expansion to $T_L$
**Process C:** Isothermal heat removal at $T_L$
**Process D:** Isentropic and adiabatic compression back to the initial state
The performance characteristics for a device operating on a Carnot cycle are

Heat Engine \[ \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \]

Heat Pump \[ \text{COP}_{\text{Carnot}} = \frac{1}{1 - \frac{T_L}{T_H}} \]

Refrigerator \[ \text{COP}_{\text{Carnot}} = \frac{1}{\frac{T_H}{T_L} - 1} \]

When words such as minimum, maximum, or evaluate the claim are used in a cyclic device problem, they are indicating to treat the device as a Carnot cycle device.

**Heat Transfer and Entropy**

For an isothermal, reversible process the heat transfer can be related to the entropy change by

\[ m(s_2 - s_1) = \frac{Q}{T}, \quad \dot{m}(s_2 - s_1) = \frac{\dot{Q}}{T}, \quad s_2 - s_1 = \frac{q}{T} \]

**Second Law for A Process**

The mathematical statement for the second law for a process is

\[ (\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surr}} \geq 0 \]

For a closed system we have

\[ (\Delta S)_{\text{system}} = m(s_2 - s_1) \]

and

\[ (\Delta S)_{\text{surr}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}} = -\frac{Q_{\text{system}}}{T_{\text{surr}}} \]
For a transient system we find it useful to introduce the concept of rate of entropy production, $\dot{S}_{\text{prod}}$, which is given by

$$
\dot{S}_{\text{prod}} = \frac{(m_t s_f - m_i s_i)}{\Delta t} + \sum_{\text{outlets}} \dot{m}_e s_e - \sum_{\text{inlets}} \dot{m}_i s_i - \frac{Q_{\text{sys}}}{T_{\text{surr}}} \geq 0
$$

For a control volume system we can reduce this further and write

$$
\dot{S}_{\text{prod}} = \sum_{\text{outlets}} \dot{m}_e s_e - \sum_{\text{inlets}} \dot{m}_i s_i - \frac{Q_{\text{sys}}}{T_{\text{surr}}} \geq 0
$$

**Second Law Problems**

In general there are two types of problems that apply the second law,

Process Problems: Single process where we use $\Delta S_{\text{universe}} = 0$

Cycle Device Problems: Heat Engine, Heat Pump, or Refrigerator devices where we use the Carnot cycle thermal efficiency or COP.