THE SECOND LAW OF THERMODYNAMICS

According to the First Law of Thermodynamics, the energy of the universe remains constant in any change. Energy may be transformed from one form into another, but the energy of the universe cannot be changed.

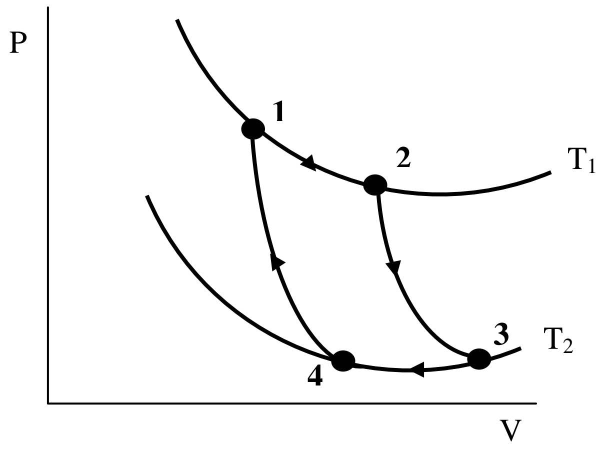
However, all real changes have a natural direction. The transformation in the opposite direction is unnatural. In nature, rivers run from the mountains to the sea, never in the opposite way. An insulated metal rod initially hot at one end and cold at the other comes to a uniform temperature. The first law does not give us any information regarding the natural direction. As long as the energy of the universe remains constant, the change may occur in either direction and satisfy the first law. The property that indicates the natural direction is ***"entropy"*** which is defined by the Second Law of Thermodynamics.

The Second Law of Thermodynamics

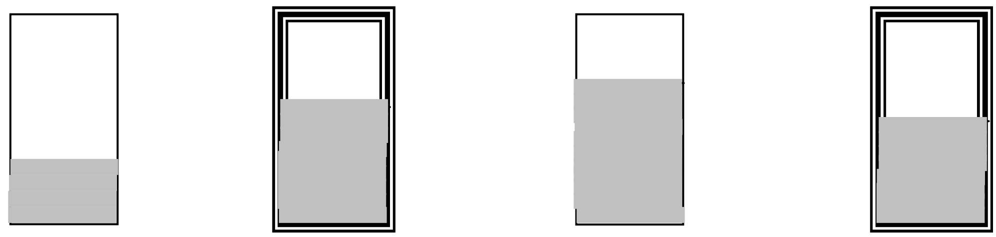
The development of the Second Law is based on the studies on heat engines. A ***heat engine*** transforms thermal energy into mechanical energy. The Second Law states that it is impossible for an engine to extract heat from the surroundings and completely transform this energy to mechanical energy. The principals governing the transformation of thermal energy into mechanical energy have been investigated by French engineer Sadi Carnot. All these principals are based on a reversible cycle called ***"Carnot Cycle"***.

Carnot Cycle

If there are two heat reservoirs at different temperatures, thermal energy may partially be transformed into mechanical energy by a cyclic operation of a fluid, when heat is flowing from one reservoir to the other. Since a cyclic operation brings the system back to its initial condition, $\Delta E = \Delta H = 0$.



The Carnot Cycle consists of 4 reversible steps;



T_1, P_1, V_1 T_1, P_2, V_2 T_2, P_3, V_3 T_2, P_4, V_4

1. **Reversible Isothermal Expansion:** The gas is confined in a cylinder. The cylinder is immersed in a heat reservoir at T_1 and expands isothermally from V_1 to V_2.

$$(T_1, P_1, V_1) \rightarrow (T_1, P_2, V_2)$$

$$\Delta E_1 = Q_1 - W_1$$

2. **Reversible Adiabatic Expansion:** The cylinder is taken out of the reservoir, insulated and the gas expands adiabatically from V_2 to V_3. In this step, the temperature of the gas drops from T_1 to T_2.

$$(T_1, P_2, V_2) \rightarrow (T_2, P_3, V_3)$$

$$\Delta E_2 = -W_2$$

3. **Reversible Isothermal Compression:** The insulation is removed and the cylinder is immersed into a heat reservoir at T_2 . The gas is compressed isothermally from V_3 to V_4 at.

$$(T_2, P_3, V_3) \rightarrow (T_2, P_4, V_4)$$

$$\Delta E_3 = Q_2 - W_3$$

4. **Reversible Adiabatic Compression:** The cylinder is taken out of the reservoir, insulated and the gas is compressed adiabatically to the original state. In this step, temperature rises from T_2 to T_1.

$$(T_2, P_4, V_4) \rightarrow (T_1, P_1, V_1)$$

$$\Delta E_4 = -W_4$$

For the cycle;

$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 = 0$

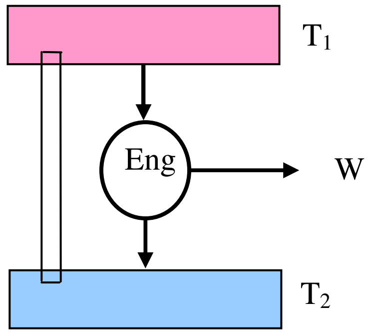
$Q_1 + Q_2 = W_1 + W_2 + W_3 + W_4$

$\Downarrow$ $\Downarrow$

Q_{cyc} W_{cyc}

Carnot engine operates according to this cycle. It is the simplest heat engine. In order to obtain work from the cycle there must be two heat reservoirs. It is impossible for a system operating in a cycle and connected to a single heat reservoir to produce work in the surroundings.

Carnot engine can be shown schematically as in the figure. According to the Second Law Q_1 and Q_2 cannot have the same sign. If they are both positive, then



W_{cyc} is also positive. If Q_2 is positive, heat flows out of the cold reservoir. We can restore this quantity by connecting the two reservoirs with a metal rod. Heat flows from the high-temperature reservoir to the low-temperature reservoir. Finally, the reservoir at T_2 gains the energy it lost. Thus, heat engine and low-temperature reservoir behave as a composite engine connected to a single reservoir, which is impossible. So, Q_1 and Q_2 must differ in sign.

The ***efficiency*** of a heat engine is defined as the ratio of the work produced to the quantity of heat extracted from the high-temperature reservoir.

$$\varepsilon = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

- The efficiency of any engine is less than or equal to the efficiency of a reversible engine, both operating between the same two heat reservoirs.
- All reversible engines operating between the same two heat reservoirs have the same efficiency.
- The efficiency of an irreversible engine is less than the reversible engine.

Carnot Cycle of an Ideal Gas

1. Reversible Isothermal Expansion

$$\Delta E_1 = Q_1 - W_1 = Q_1 - RT_1 \ln \frac{V_2}{V_1} = 0$$

2. Reversible Adiabatic Expansion

$$\Delta E_2 = -W_2 = \int_{T_1}^{T_2} C_v dT$$

3. Reversible Isothermal Compression

$$\Delta E_3 = Q_2 - W_3 = Q_2 - RT_2 \ln \frac{V_4}{V_3}$$

4. Reversible Adiabatic Compression

$$\Delta E_4 = -W_4 = \int_{T_2}^{T_1} C_v dT$$

Total work obtained from the cycle is;

$$W = RT_1 \ln \frac{V_2}{V_1} - \int_{T_1}^{T_2} C_v dT + RT_2 \ln \frac{V_4}{V_3} - \int_{T_2}^{T_1} C_v dT$$

Interchanging the limits of the second integral we obtain;

$$W = RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_4}{V_3}$$

Since $V_2 \rightarrow V_3$ and $V_4 \rightarrow V_1$ are adiabatic changes;

$T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$

$T_1V_1^{\gamma-1} = T_2V_4^{\gamma-1}$

Dividing both sides we obtain;

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

By substituting this equation in the equation giving W, we obtain a nice equation for the work obtained from the cycle;

$$W = R(T_1 - T_2)\ln\frac{V_2}{V_1}$$

Work produced by the cycle depends upon the difference between the temperatures of the heat reservoirs and V_2/V_1 ratio. By using the first law equation for step 1 we may write Q_1 as;

$$Q_1 = RT_1 \ln\frac{V_2}{V_1}$$

The efficiency of the cycle may be found as;

$$\varepsilon = \frac{W}{Q_1} = \frac{R(T_1 - T_2)\ln\frac{V_2}{V_1}}{RT_1 \ln\frac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

The efficiency depends upon the temperature difference.

Entropy

The efficiency of the Carnot engine may be shown by the below two equations;

$$\varepsilon = 1 + \frac{Q_2}{Q_1} \qquad \text{and} \qquad \varepsilon = 1 - \frac{T_2}{T_1}$$

Subtracting these two equations yields;

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

The left-hand side of this equation is the sum of the quantity Q/T for the cycle.

$$\oint \frac{dQ}{T} = 0$$

Since cyclic integral is zero, dQ/T is a state function. The defining equation for entropy is;

$$dS = \frac{dQ_{rev}}{T}$$

Entropy is a state function. dS is an exact differential. The change in entropy does not depend upon the path. Entropy is an extensive property. For a reversible change; the change in entropy may be expressed as;

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T}$$

For all reversible cycles;

$$\oint \frac{dQ}{T} = 0$$

For all irreversible cycles;

$$\oint \frac{dQ}{T} < 0$$

Clausius Inequality

Assume that the system is transformed irreversibly from 1 to 2, and then brought back reversibly from 2 to 1. For the cycle;

$$\oint \frac{dQ}{T} = \int_1^2 \frac{dQ_{irr}}{T} + \int_2^1 \frac{dQ_{rev}}{T} < 0$$

$$\int_1^2 \frac{dQ_{irr}}{T} + \int_2^1 dS < 0 \qquad \int_1^2 dS \geq \int_1^2 \frac{dQ}{T}$$

This inequality is known as "Clausius Inequality" and simply expressed as;

$$dS \geq \frac{dQ}{T}$$

Clausius inequality is valid for all changes. If the system is isolated dQ = 0. Then the entropy change becomes;

$dS \geq 0$

Any natural change occurring in an isolated system is attended by an increase in entropy. The entropy continues to increase as long as the change occurs. Finally, the system reaches equilibrium. At equilibrium, the entropy is at its maximum value.

Entropy is a measure of disorder. Therefore, increase in entropy means increase in disorder. In the universe, the entropy increases continuously as natural changes occur within it.

Entropy is related with the probability of occurrence. If entropy increases during a change, the probability of occurrence for that change is high.