SECOND LAW OF THERMODYNAMICS

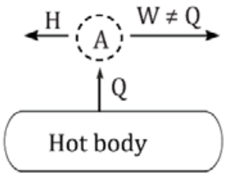
The second law of thermodynamics is a guiding principle that tells us which way energy moves.

Clausius statement

A machine can't move heat from something cold to something hot by itself—it needs help from an outside force.

Kelvin-Plank's statement

It's not possible to create an engine that takes heat and turns it all into useful work without causing any other changes.
So, the amount of work the system gets (W) will always be lower than the amount of heat given to it (Q).



Note

- The first law of thermodynamics says we can turn all work into heat and all heat into work, but the second law says otherwise.
- Work is a powerful energy, so it can become heat completely (a weaker energy).
- Heat is a weaker energy, so it can't fully become work (a powerful energy). To turn all heat into work, the heat taken from the source has to be released to something cooler.

Entropy (S)

This describes the level of chaos in how molecules move within a system.

Example:

$$S_{solid} < S_{liquid} < S_{gas}$$

The change in the entropy of a system is defined as:

$$\Delta S = \frac{\Delta Q}{T}$$

Alternative statement of second law of thermodynamics
The overall disorder in an isolated system never decreases over time and remains constant only if all processes are reversible.

Note

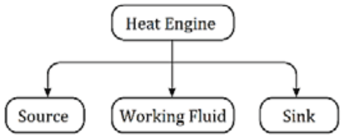
- In a natural event, the increase in disorder, known as entropy, is consistently on the positive side, meaning ΔS is never less than zero.
- The total disorder within the universe is continuously on the rise.

Heat engine

A heat engine is a contraption that turns heat into motion, proving the second law of thermodynamics.

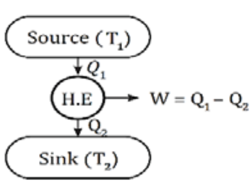
Parts of a heat engine

- **Thermal reservoir:** It is a thermodynamic system with a very large (ideally infinite) heat capacity.
- **Source:** It is a thermal reservoir at a high temperature T_1.
- **Working fluid:** Steam, petrol, etc.
- **Sink:** It is a thermal reservoir at a low temperature T_2 ($T_1 \gg T_2$).



Working of a heat engine (H.E.)

The substance in motion takes in heat (Q_1) from the hot source at a high temperature T_1 (where T_1 is much higher than T_2). As it expands, the substance does work (W). During this phase, some of the heat (Q_2) is released to a colder body (sink) at a lower temperature.



Efficiency of heat engine

It's described as the proportion of helpful work (W) gained from the engine compared to the heat provided (Q_1) to the engine.

By applying the energy conservation on the working fluid, we get,

$$Q_1 = Q_2 + W$$
$$W = Q_1 - Q_2$$

The thermal efficiency of the heat engine is given by

$$\eta = \frac{\text{Work done}}{\text{Heat supplied}}$$
$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$
$$\eta = 1 - \frac{Q_2}{Q_1}$$

The percentage of thermal efficiency of a heat engine is given by

$$\eta = \left(1 - \frac{Q_2}{Q_1}\right) \times 100\%$$

Carnot cycle and efficiency

In 1824, a French mechanical engineer named Nicolas Léonard Sadi Carnot created a perfect pattern for how a heat engine should work. This pattern is called the Carnot cycle.

The device employed to achieve the perfect sequence of tasks is called the ideal heat engine or the Carnot heat engine.

Parts of the Carnot engine

Source

A reservoir of heat at a high temperature and infinite thermal capacity

Sink

A reservoir of heat at a low temperature and infinite thermal capacity.

Cylinder

A cylinder with perfectly non-conducting walls and a non-conducting frictionless piston.

Working fluid

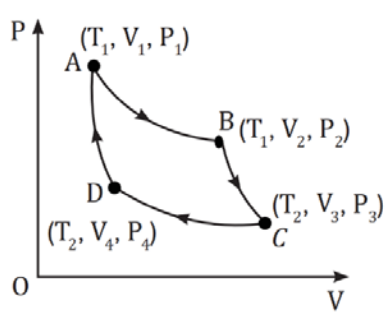
An ideal fluid that undergoes all processes reversibly

Carnot Cycle

The Carnot engine is made up of a setup with a piston and cylinder containing a gas initially at temperature T_1, pressure P_1, and volume V_1. The bottom of the container efficiently conducts heat. During operation, the substance in the engine goes through a repeating process called the Carnot cycle.

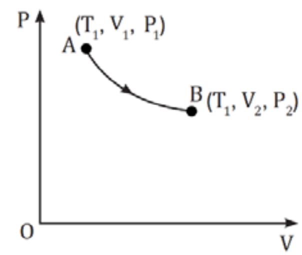
Processes in Carnot cycle

1. **Isothermal expansion (process AB)**
2. **Adiabatic expansion (process BC)**
3. **Isothermal compression (process CD)**
4. **Adiabatic compression (process DA)**



Isothermal expansion from A to B

In this part of the cycle, the system (cylinder) is placed on the source at temperature T_1, due to which heat is added to the system and the gas is allowed to expand by a slow, outward motion of the piston. It absorbs Q_1 amount of heat from the source for the required work, W_1. Therefore, the temperature remains constant (i.e., $\Delta T = 0$). Hence, the gas expands isothermally, the pressure changes to P_2 from P_1 and the volume changes to V_2 from V_1.



From the first law of thermodynamics,

$$Q = W + \Delta U$$

$$Q_1 = W_1 (\text{ Since } \Delta T = 0 \Rightarrow \Delta U = 0)$$

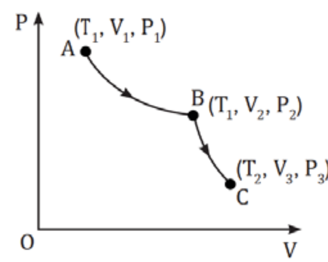
Work done is given as follows:

$$W_1 = \int_{V_1}^{V_2} PdV$$

$$Q_1 = W_1 = RT_1 \log_e \frac{V_2}{V_1}$$

Adiabatic expansion from B to C

Now, the cylinder is taken away from the heat source and put on an insulating pad. The gas inside is allowed to expand more. This means the system is completely insulated from heat on all sides, so no heat is transferred (which means $\Delta Q = 0$). As a result, the system's temperature decreases from T_1 to T_2. During this process, the gas expands without any heat exchange (adiabatically), causing the pressure to change from P_2 to P_3 and the volume to change from V_2 to V_3.



From the first law of thermodynamics,

$Q = W + \Delta U$

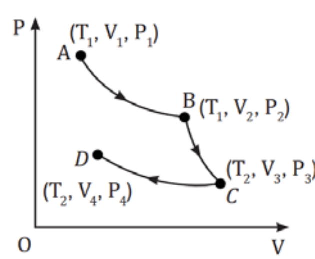
$$W_2 = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$$W_2 = \frac{R(T_1 - T_2)}{\gamma - 1}$$

Isothermal compression from C to D

Now, the cylinder is taken off the insulating pad and placed on the sink. At temperature T_2, the piston is gently pushed inward until the pressure changes from P_3 to P_4 and the volume changes from V_3 to V_4. Since the system is on the sink and the base conducts heat, the heat generated during compression, Q_2, will flow to the sink. Thus, the temperature stays the same (meaning $\Delta T = 0$).

From the first law of thermodynamics,



$$Q = W + \Delta U$$

$$Q_2 = W_3 (\text{ Since } \Delta T = 0 \Rightarrow \Delta U = 0)$$

Work done is given as follows

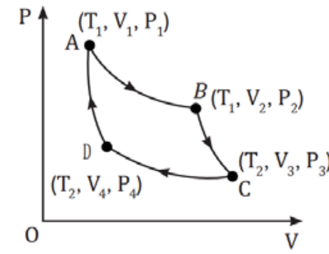
$$W_3 = \int_{V_3}^{V_4} PdV$$

$$Q_2 = W_3 = -RT_2 \log_e \frac{V_3}{V_4}$$

Adiabatic compression from D to A

Now, the system (cylinder) is removed from the sink and again placed on an insulating pad, and the piston is further moved downward. Since the system is thermally insulated from all the sides, there is no heat transfer (i.e., $\Delta Q = 0$) taking place. Therefore, the gas is compressed adiabatically, and the heat produced in the compression raises the temperature of the system from T_2 to T_1.

Hence, the gas is compressed adiabatically, the pressure changes to P_1 from P_4, and the volume changes to V_1 from V_4.



Work done is given as follows:

$$W_4 = \frac{P_4V_4 - P_1V_1}{\gamma - 1}$$

$$W_4 = \frac{R(T_2 - T_1)}{\gamma - 1} \text{ (Since } T_4 = T_2)$$

The net work done by the Carnot cycle is as follows:

$$W_{net} = W_1 + W_2 + W_3 + W_4$$

$$W_2 = \frac{R(T_1 - T_2)}{\gamma - 1}$$

$$W_2 = -\frac{R(T_2 - T_1)}{\gamma - 1} = -W_4$$

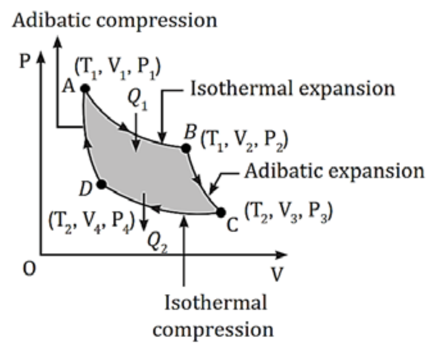
$$W_{net} = W_1 + W_3$$

$$W_{net} = Q_1 + Q_2$$

We have,

$$Q_1 = W_1 = RT_1 \log_e \frac{V_2}{V_1}$$

$$Q_2 = W_3 = -RT_2 \log_e \frac{V_3}{V_4}$$



Net heat supplied,

$$Q_1 = W_1 = RT_1 \log_e \frac{V_2}{V_1}$$

Efficiency of the cycle,

$$\eta = \frac{W_{net}}{Q}$$

$$\eta = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{RT_2 \log_e \frac{V_3}{V_4}}{RT_1 \log_e \frac{V_2}{V_1}}$$

We know,

1. Isothermal expansion from A to B, $P_1V_1 = P_2V_2$ …. (i)
2. Adiabatic expansion from B to C, $P_2V_2^{\gamma} = P_3V_3^{\gamma}$...(ii)
3. Isothermal compression from C to D, $P_3V_3 = P_4V_4$... (iii)
4. Adiabatic compression from D to A, $P_4V_4^{\gamma} = P_1V_1^{\gamma}$...(iv)

Multiplying equations (i), (ii), (iii), and (iv),

$$(P_1V_1)(P_2V_2^{\gamma})(P_3V_3)(P_4V_4^{\gamma}) = (P_2V_2)(P_3V_3^{\gamma})(P_4V_4)(P_1V_1^{\gamma})$$

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

Efficiency of the cycle,

$$\eta = 1 - \frac{RT_2 \log_e \frac{V_3}{V_4}}{RT_1 \log_e \frac{V_2}{V_1}}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

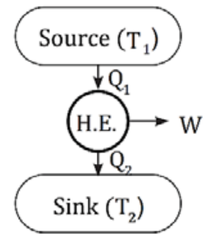
Note

- The effectiveness of a heat engine relies solely on the temperatures of its heat source and heat sink.
- Any reversible heat engines operating between identical temperatures are equally effective, and none can surpass the efficiency of a Carnot engine.
- As both T_1 and T_2 are positive and definite, with T_1 being greater than T_2, the efficiency of a heat engine is invariably less than one.

Carnot's Theorem

No heat engine operating between a set temperature difference of the source and the sink can outperform a reversible Carnot engine functioning within the same temperature range.

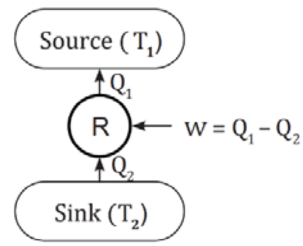
Regardless of the working fluid used, all reversible engines operating between identical temperatures have identical efficiency.



Refrigerator

It operates based on the concept of a backward heat engine. A refrigerator removes heat from its contents and releases it at a temperature higher than the surroundings. To enable these actions, the surroundings must perform work on the system.

$$Q_1 = W + Q_2$$



COP of carnot refrigerator

For a Carnot cycle,

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

$$\frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

The coefficient of performance (COP) is given as follows:

$$\beta = \frac{T_2}{T_1 - T_2}$$

Where, T_1 is temperature of surrounding and T_2 is the temperature of the cold body.

Coefficient of performance (β)

The coefficient of performance (COP) is the ratio of the desired effect to the input to the system.

$$\beta = \frac{\text{Heat extracted}}{\text{Work done}}$$

$$\beta = \frac{Q_2}{W}$$

Also, $$W = Q_1 - Q_2$$

$$\beta = \frac{Q_2}{Q_1 - Q_2}$$

Relation between COP and η

$$\beta = \frac{Q_2}{Q_1 - Q_2}$$

$$B = \frac{\frac{Q_2}{Q_1}}{1 - \frac{Q_2}{Q_1}}$$

Also, $$\eta = 1 - \frac{Q_2}{Q_1}$$

$$\frac{Q_2}{Q_1} = 1 - \eta$$

$$\beta = \frac{1 - \eta}{\eta}$$

Heat Pump

It's a contraption that operates in reverse to a heat engine. A heat pump extracts heat from a lower temperature area and releases it into the surroundings at a higher temperature.

Coefficient of performance (γ).

$$\gamma = \frac{\text{Desired effect}}{\text{Work done}}$$

$$\Rightarrow \gamma = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}$$

$$\Rightarrow \gamma = \frac{Q_1}{Q_1 - Q_2}$$