The second law of thermodynamics

Although the mathematical and conceptual tools provided by the zeroth and first laws of thermodynamics are very useful, we need more. There is a major question that these laws cannot answer: Will a given process occur spontaneously?

Thermodynamics helps to understand the spontaneity of processes—but only once we add more of its tools. These tools are called the **second** and **third** laws of **thermodynamics**.

A statement about which processes **occur** and which do **not**.

There are many ways to state the second law; here is one:

-**Heat** can flow **spontaneously** from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.

-A gas expands to fill the available volume.

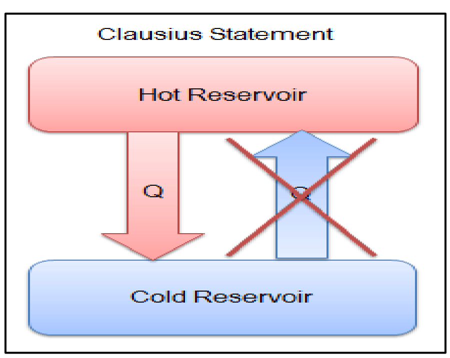
-A chemical reaction runs in one direction rather than another.

- **There are Two statement of second law of thermodyanmic**

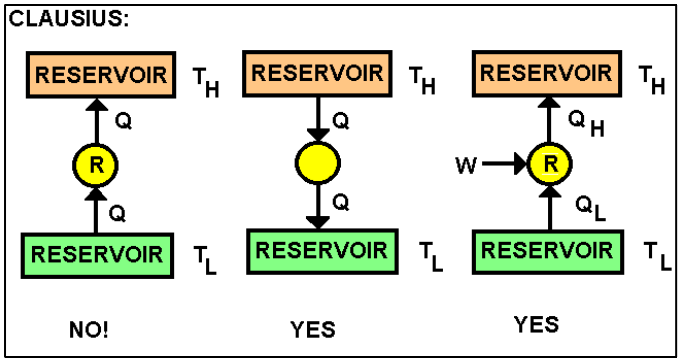
1- Clausius Statement:

It is impossible to construct a device which operates on a cycle and whose sole effect is the transfer of heat from a cooler body to a hotter body".

In simpler terms, energy does not flow spontaneously from a cold object to a hot object.

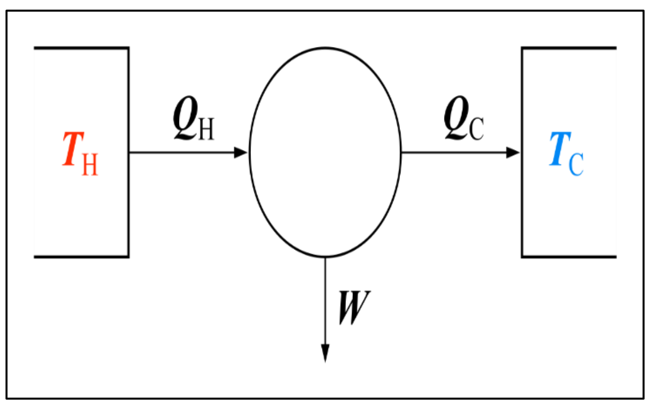


Heat cannot spontaneously flow from cold system to hot system without **external work** being performed on the system. This is exactly what **refrigerators** accomplish.



2- Kevin-Planck Statement:

It is impossible by cyclic process to take heat from a reservoir and convert it into work without at the same time transferring heat from a hot to cold reservoir. For an example operating of heat engine.



By another words, it is impossible to construct this type of Heat engine that operates on cyclic process and converts all the heat supplied to it into equivalent amount of work.

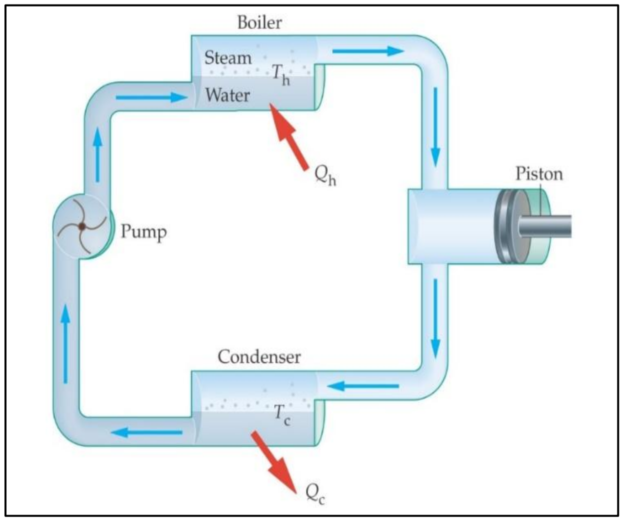
The **conclusions** stated below can be made from statement

1. No cyclic engine can converts whole heat into **equivalent** work.

2. There is degradation of **energy** in a cyclic heat engine as **some** of the heat has to be rejected.

Heat engine

A heat engine is a device that converts heat into work. A classic example is the steam engine. Fuel heats the water; the vapor expands and does work against the piston; the vapor condenses back into water again and the cycle repeats.



All heat engines have:

1- A working substance (such as a water)

2- A high-temperature reservoir (T_h)

3- A low-temperature reservoir (T_c)

4- A cyclical engine

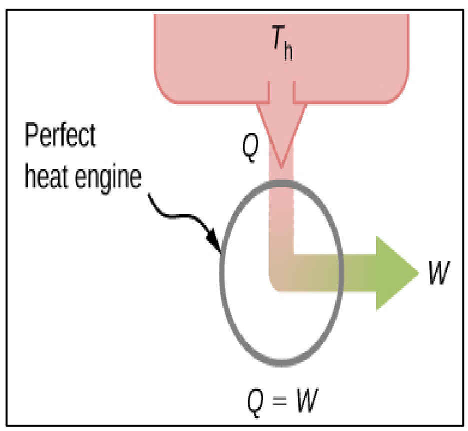
Heat engines differ considerably from one another, but all can be characterized by the following:

1. They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).

2. They convert part of this heat to work (ex. rotating shaft).

3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).

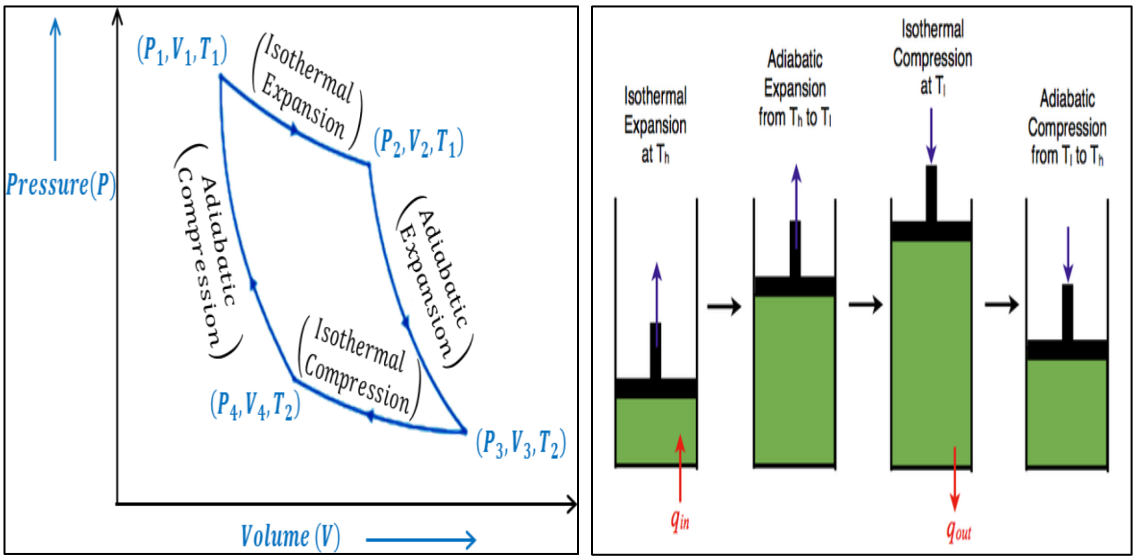
4. They operate on a cycle



Despite advancing technology, we are not able to build a **prefect heat engine** that is 100% efficient. The first law does not exclude the possibility of constructing a perfect engine, but the second law forbids it according to **Kevin-Planck Statement.**

Carnot cycle

Carnot proceeded to define the **steps** for the operation of an **engine**. These steps, collectively called the **Carnot** cycle, can be used to define how **efficient** the engine was at converting **heat** to **work**. The engine itself is defined as the **system**. The steps of a Carnot cycle are:



1. **Reversible isothermal expansion** at T_h. In order for this to occur, heat must be absorbed from the high-temperature reservoir. And the amount of work performed by the system as w1 in.

$\Delta U_1 = 0$ at isothermal process

$$q_1 = -w_1 = -(nRT_h \ln\frac{V_2}{V_1}) \quad .....(1)$$

2. **Reversible adiabatic expansion** at constant heat. Because it is expansion, work is done by the engine as w_2.

$q_2 = 0$ at adiabatic process

$$w_2 = \Delta u_2 = C_V (T_h - T_c) = nC_{v,m}(T_h - T_c) \quad ....(2)$$

3. **Reversible isothermal compression** at constant T_c. In order for this step to be isothermal, heat must leave the system. The amount of work in this step will be called w3 out.

$$\Delta U = 0 \qquad \text{at isothermal process}$$

$$q_3 = -w_3 = -(-nRT_c \ln\frac{V_4}{V_3}) \qquad .....(3)$$

4. **Reversible adiabatic compression**. The system (that is, the engine) is returned to its original conditions. In this step, q is 0 again, and work is done on the system. This amount of work is termed w_4.

$$q_4 = 0 \qquad \text{at adiabatic process}$$

$$w_4 = \Delta u = C_V\,(T_c - T_h) = nC_{v,m}\,(T_c - T_h) \qquad ....(4)$$

For each **cycle** else the engine would get hotter (or colder) with every cycle

$\Delta U_{cycle} = \Delta U_2 + \Delta U_4 = 0$ net internal energy change

$w_{cycle} = w_1 + w_2 + w_3 + w_4$

$q_{cycle} = q_1 + q_3$

$\Delta U_{cycle} = q_{cycle} + w_{cycle}$

$0 = q_{cycle} + w_{cycle}$

$q_{cycle} = -w_{cycle}$

Efficiency of a Heat Engine

An amount of heat q_h is supplied from the hot reservoir to the engine during each cycle. Of that heat, some appears as work, and the rest, q_c, is given off as waste heat to the cold reservoir.

We now define efficiency (**e)** as the **negative** ratio of the work of the cycle to the heat that comes from the high-temperature reservoir:

$$e = -\frac{w_{cycle}}{q_1}$$

w_{cycle} always negative value

The efficiency can also be written:

$$e = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1}$$

q_3 always negative value

EX)) Determine the efficiency of a Carnot engine that takes in 855 J of heat, performs 225 J of work, and gives off the remaining energy as heat.

w_{cycle} = -255 J

q_1=855 J

$$e = -\frac{w_{cycle}}{q_1}$$

$$e = -\left(\frac{225J}{855J}\right) = 0.263$$

H.W) Consider the following quantities for a Carnot-type cycle:

Step 1: q = 1850 J, w= 2850 J. Step 2: q = 0, w = 2155 J.

Step 3: q = 2623 J, w = 1623 J. Step 4: q = 0, w = 1155 J.

Calculate the efficiency of the cycle.

There is another way to express efficiency in terms of the temperatures of the high- and low-temperature reservoirs, assuming an ideal gas. For the isothermal steps 1 and 3, the change in the internal energy is zero because ('Therefore, q =-w for steps 1 and 3.

$$q_1 = -w_1 = -(nRT_h \ln\frac{V_2}{V_1}) \quad .....(1)$$

$$q_3 = -w_3 = -(-nRT_c \ln\frac{V_4}{V_3}) \quad .....(2)$$

For the adiabatic steps 2 and 4, we can use equation

$$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \frac{T_c}{T_h}$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \frac{T_c}{T_h}$$

Equating the volume expressions, which both equal T_c / T_h

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

Raising both sides to the power of γ-1 and rearrage the equation, we get

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

Substituting for V_4/V_3 in the following equation

$$q_3 = -w_3 = -(-nRT_c \ln\frac{V_4}{V_3}) = nRT_c \ln\frac{V_1}{V_2} = -nRT_c \ln\frac{V_2}{V_1}$$

Equation 1 and 3 can be divided to get a new expression for the ratio q_3 / q_1

$$\frac{q_3}{q_1} = \frac{nRT_c \ln \frac{v_2}{v_1}}{-nRT_h \ln \frac{v_2}{v_1}} = -\frac{T_c}{T_h}$$

Substituting into equation ( ), we get an equation for efficiency in terms of the temperature

$$e = 1 + \frac{q_3}{q_1} = 1 - \frac{T_c}{T_h}$$

H.w) what is the temperature of the low-temperature reservoir of a process that has an efficiency of 0.440 (44.0%) and a high temperature reservoir at 150°C?

H.W) What is the efficiency of an engine whose T_h is 100°C and whose T_c is 0°C?

A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?