Chapter 4

The second and third laws of thermodynamics

The first law is primarily concerned with energy, and energy can be converted from one form to another. However, it doesn't give us an idea of what a reaction is (i.e., whether a reaction is spontaneous or not).

$A \rightarrow P$ **Primitive**

$A \rightleftarrows P$ **Equilibrium**

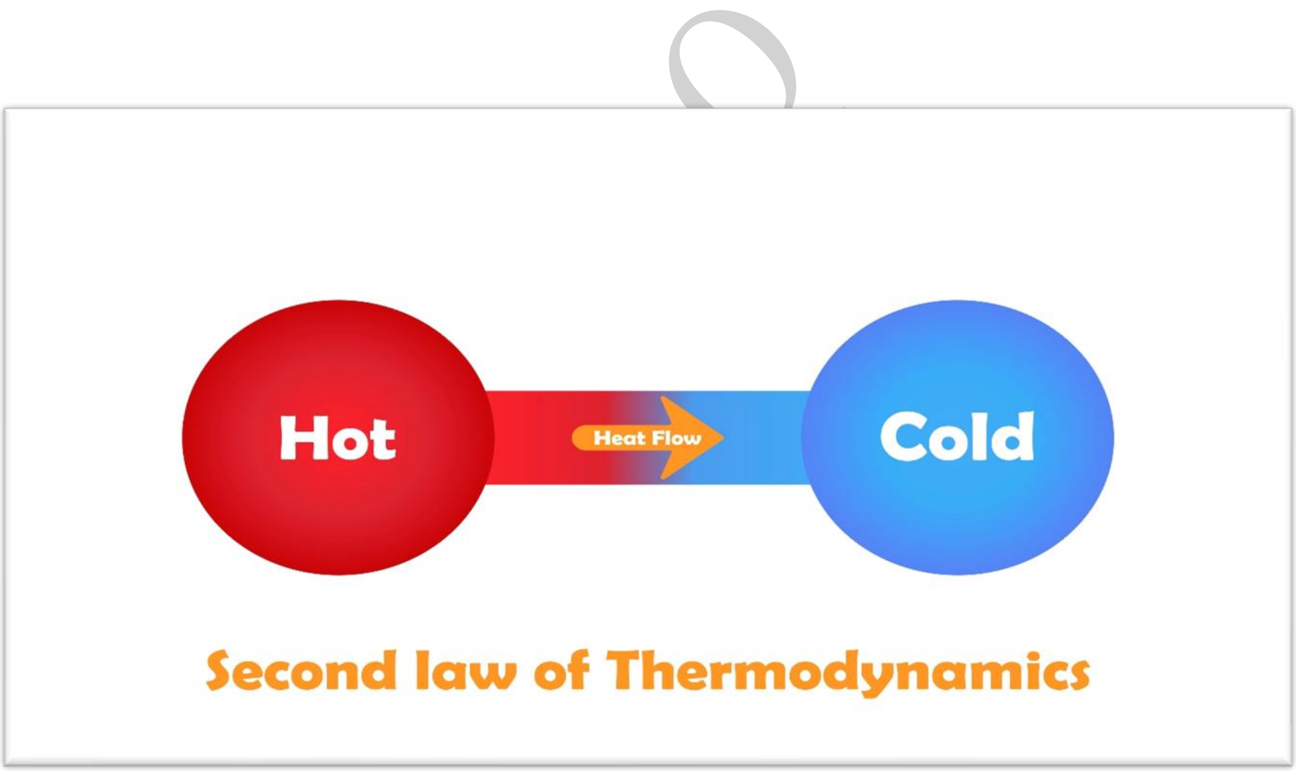
$A \xrightarrow{X} P$ **No reaction occurs**

Based on this, the second law of thermodynamics (gives us an idea of spontaneous and non-spontaneous processes) has broad applications in many fields.

Spontaneous processes: These are processes that occur automatically. Examples of these processes include the flow of water in waterfalls and the spontaneous transfer of heat from hot to cold. Spontaneous processes can be exploited to perform work, for example, generating electrical energy from waterfall water. The transfer of heat from hot to cold can also be exploited in heating machines, which is the basis of their operation and the performance of work.

** Every spontaneous reaction has a non-spontaneous reaction, such as the movement of water from bottom to top, which is a non-spontaneous process.

Non-Spontaneous processes can be converted into Spontaneous processes using external sources, such as pumps to raise water from the bottom to the top, or refrigerator motors to convert hot water to cold water. There are special cases in which automatic processes are in equilibrium when the change is slight.



7.1 Formulas of the Second Law of Thermodynamics

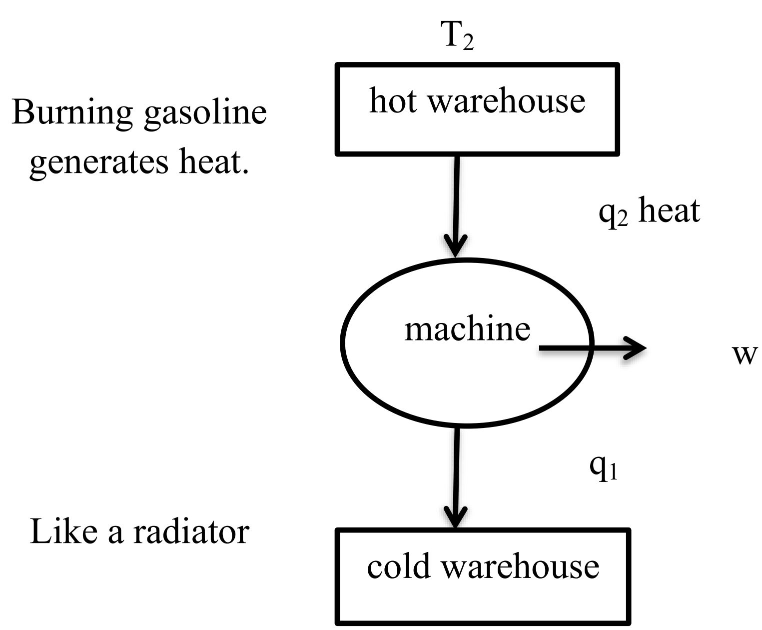
(1) Kelvin's Law (Kelvin Statement)

The scientist Kelvin used circular processes ( ) and considered the work of heating engines. Kelvin's law states that:

(In circular processes, it is impossible to transfer heat from the hot reservoir and convert it completely into work unless the heat is simultaneously transferred (lost) to the cold reservoir (such as the work of heating engines)).

In practice, no machine ever operates at 100% efficiency, as it requires cooling to lower its temperature.

The diagram below represents the Kelvin diagram.

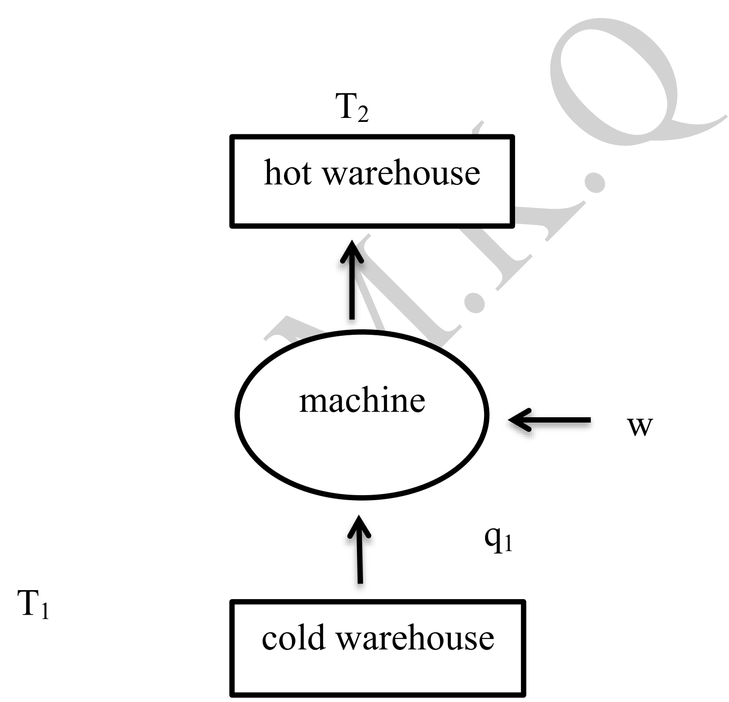


(2) Clusius's Law

Use a cold reservoir, in contrast to Kelvin's law. The law states that:

It is impossible to transfer heat from a cold reservoir to a hot reservoir in a circular process unless work is performed on the machine. It is similar to the operation of a refrigerator (and all refrigeration machines).

The diagram below represents the Clausius diagram.



* Compare Kelvin's law and Claesius's law and draw a diagram for them.

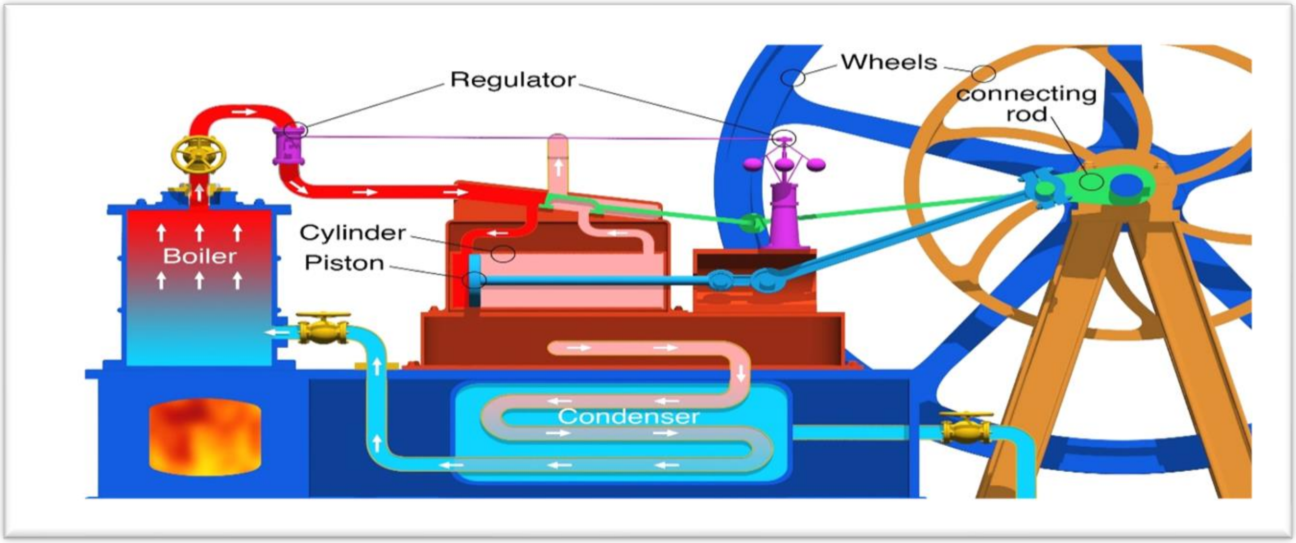
7.2 Limitations of the Second Law of Thermodynamics on the Efficiency of Heat Engines

The most important principles governing the design and operation of power systems are the Second Law of Thermodynamics. This law places natural limits on the efficiency of any heat engine, explaining why 100% efficiency is never achieved.

7.2.1 What is a heat engine?

A heat engine is a device that converts thermal energy into mechanical work. It operates by absorbing heat from a hot source (Q_H) and using some of it to perform work (W), while expelling the remainder as waste heat (Q_C) to a cold source.

Example: A conventional steam power plant. Water (the hot source) is heated to produce high-pressure steam, which passes through a turbine (the heat engine) to produce mechanical work (driving a generator). The remaining steam is then cooled (the waste heat is expelled) and converted back into water.



7.2.2 Limitations of the Second Law

The second law of thermodynamics tells us that it is impossible to convert all of the absorbed heat into useful work. Some of the heat must always be expelled to a cooler source. This means that the efficiency of any heat engine will never reach 100%.

Thermal efficiency (η) is the ratio of the work done (W) to the heat absorbed (Q_H).

$\eta = W / Q_H$

Since $W = Q_H - Q_C$

the efficiency equation can be rewritten as**:**

$\eta = 1 - Q_C / Q_H$

This equation clearly shows that the efficiency will not be 100% unless

$Q_C = 0$

, which is practically impossible according to the second law.

7.2.3 Why are these limitations present?

Imagine trying to transfer energy from one tank to another. If the two tanks are at the same level, water won't flow from one to the other. But if one is higher than the other, water will flow normally. The same applies to heat. For heat to be converted into work, it must flow from a high temperature (T_H) to a low temperature (T_C)

This temperature difference is the driving force that allows the engine to work.