# SECOND LAW OF THERMODYNAMICS

## e-content for B.Sc Physics (Honours)
## B.Sc Part-I

Paper-II

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## SECOND LAW OF THERMODYNAMICS

### INTRODUCTION

In this chapter the idea of cycle efficiency in introduced and the Second Law is then stated and distinguished from the First Law. Formal definition of a reversible process is made and its implications both for non-flow and steady-flow processes are discussed

A process is said to the reversible, it should trace the same path in the reverse direction when the process is reversed, and it is possible only when the system passes through a continuous series of equilibrium state if a system does not pass through continuous equilibrium state, then the system is said to be irreversible.

The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its potential energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses into the atoms of the floor. The reverse has never been observed to take place. The reverse, if it occurs, does not violate the1st Law as long as the energy is conserved Recall also that only a small amount of thermal energy is required to make the ball jump very high. Hence, the first Law only states that the net work cannot be produced during a cycle without some supply of heat. However, First Law never says that some proportions of heat supplied to an engine must be rejected. Hence, as per the First Law, cycle efficiency can be unity, which is impossible in practice. All that First Law states that net work cannot be produced during a cycle without some supply of heat, i.e. that a perpetual motion machine of the first kind is impossible So, the 1st Law is not enough. Something is missing! What is missing? A law that can tell us about the direction of spontaneous change. The Second Law of Thermodynamics tells us about the directionality of the process. We need it to ensure that systems we design will work. As we will see later, ENTROPY is a property that we have invented (like internal energy) that will allow us to apply the 2nd Law quantitatively.

### REVERSIBLE AND IRREVERSIBLE PROCESSES

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In the course of this development, the idea of a completely reversible process is central, and we can recall the definition, ``a process is called completely reversible if, after the process has occurred, both the system and its surroundings can be wholly restored by any means to their respective initial states''. Especially, it is to be noted that the definition does not, in this form, specify that the reverse path must be identical with the forward path. If the initial states can be restored by any means whatever, the process is by definition completely reversible. If the paths are identical, then one usually calls the process (of the system) reversible, or one may say that the state of the system follows a reversible path. In this path (between two equilibrium states 1 and 2), (i) the system passes through the path followed by the equilibrium states only, and (ii) the system will take the reversed path 2 to 1 by a simple reversal of the work done and heat added.

Reversible processes are idealizations not actually encountered. However, they are clearly useful idealizations. For a process to be completely reversible, it is necessary that it be quasi-static and that there be no dissipative influences such as friction and diffusion. The precise (necessary and sufficient) condition to be satisfied if a process is to be reversible is the second part of the Second Law.

The criterion as to whether a process is completely reversible must be based on the initial and final states. In the form presented above, the Second Law furnishes a relation between the properties defining the two states, and thereby shows whether a natural process connecting the states is possible.

**SECOND LAW OF THERMODYNAMICS**

Kelvin –Planck statement: It is impossible to construct an engine working on a cyclic process which converts all the heat energy supplied to it into equivalent amount of useful work.

Clausius statement: Heat cannot flow from cold reservoir to hot reservoir without any external aid. But heat can flow from hot reservoir to cold reservoir without any external aid.

**HEAT ENGINE, HEAT PUMP, REFRIGERATOR**

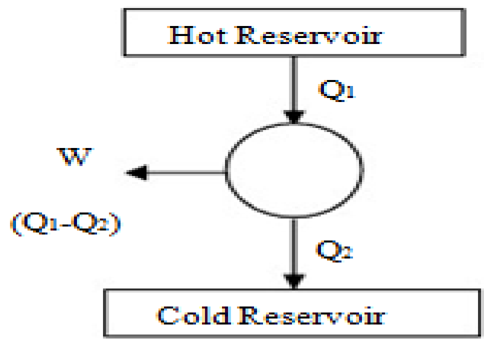
**ENERGY RESERVOIRS**: Thermal energy reservoirs (TER) is defined as a large body of infinite heat capacity, which is capable of absorbing or rejecting an unlimited quantity of heat without suffering appreciable changes in its thermodynamic coordinates.

**SOURCE:** TER from which heat is transferred to the system operating in a heat engine cycle.

**SINK**: TER in which heat is rejected from the cycle during a cycle.

**HEAT ENGINE**

A heat engine is a device which is used to convert the thermal energy into mechanical energy. Heat supplied is input work done is the output. Hence efficiency of the engine



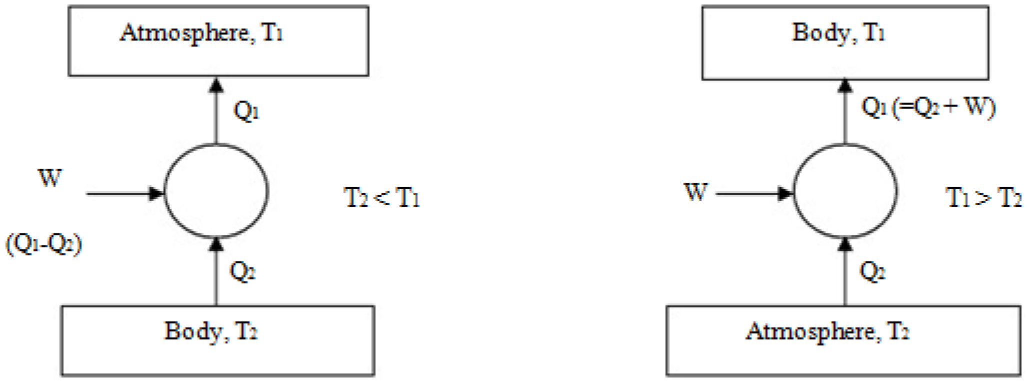

Heat engine

$$\text{Efficiency of the engine} = \frac{\text{Work output}}{\text{Heat supplied}}$$

€=(T1-T2)/T1

**REFRIGERATOR**: A device which operating in a cycle maintains a body at a temperature lower than the temperature of the surroundings

**HEAT PUMP**: Heat pump is a device which operating in a cycle process maintains the temperature of a hot body at a temperature of a hot body at a temperature higher that the temperature of surrounding. Different between heat pump and refrigeration states that heat pump is a device which operating in a cycle process maintains the temperature of a hot body at a temperature of a hot body at a temperature higher that the temperature of surrounding.




Refrigerator

Heat pump

Coefficient of performance is defined as the ratio of heat of heat extracted of rejected to work input.

$$COP = \frac{\text{Heat extracted or rejected}}{\text{Work input.}}$$

Expression for COP of heat pump and a refrigerator.

COP for heat pump:

$$COPHP = \frac{\text{Heat rejected}}{\text{Work Input}} = \frac{T2}{T2-T1}$$

COP for refrigerator:

$$COP\ Ref = \frac{\text{Heat Extracted}}{\text{Work Input}} = \frac{T2}{T2-T1}$$

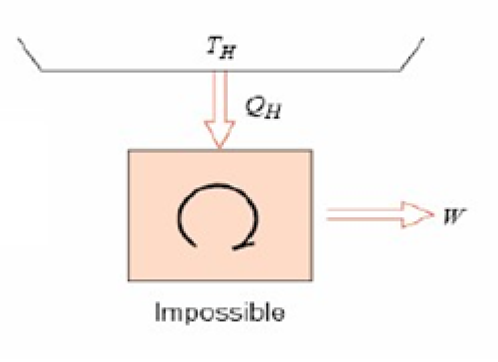
The Second Law states that some heat must be rejected during the cycle and hence, the cycle efficiency is always less than unity Thus the First Law states that net work cannot be greater than heat supplied, while the Second Law goes further and states that it must be less than heat supplied. If energy is to be supplied to a system in the form of heat, the system must be in contact with a reservoir whose temperature is higher than that of the fluid at some point in the cycle. Similarly, if heat is to be rejected, the system must be at some time be in contact with a reservoir of lower temperature than the fluid. Thus Second Law implies that if a system is to undergo a cycle and produce work, it must operate between two reservoirs of different temperatures. A machine which will work continuously, while exchanging heat with only single reservoirs, is known as a perpetual motion machine of the second kind (PMM II); such a machine contradicts Second Law. It is now possible to see why a ship could not be driven by an engine using the ocean as a source of heat, or why a power station could not be run using the atmosphere as a source of heat. They are impossible because there is no natural sink of heat at a lower temperature than the atmosphere or ocean, and they would therefore be PMM II.

It should be noted that Second Law does not restrict that work cannot be continuously and completely converted to heat. In fact, a fluid in a closed vessel may have work done on it and the heat thus generated is allowed to cross the boundary. The rates of work and heat may be made equal and the internal energy of the system remaining constant. An important consequence of Second law is work is a more valuable form of energy transfer than heat as heat can never be transformed continuously and completely to work, whereas work can always be transformed continuously and completely to heat.

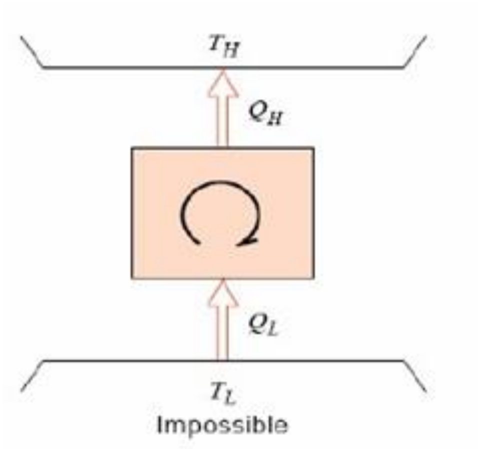
The following statements summarise the obvious consequences of the Second Law:
a) If a system is taken through a cycle and produces work, it must be exchanging heat with at least two reservoirs at different temperatures,
b) If a system is taken through a cycle while exchanging heat with one reservoir, the work done must be zero or negative,
c) Since heat can never be continuously and completely converted into work whereas work can always be continuously and completely converted into heat, work is more valuable form of energy transfer than heat.

**THE KEIVIN-PLANK'S STATEMENT OF THE SECOND LAW**

It is impossible to construct a system, It is impossible to construct a system, which will operate in a cycle, extract heat from a reservoir and do an equivalent

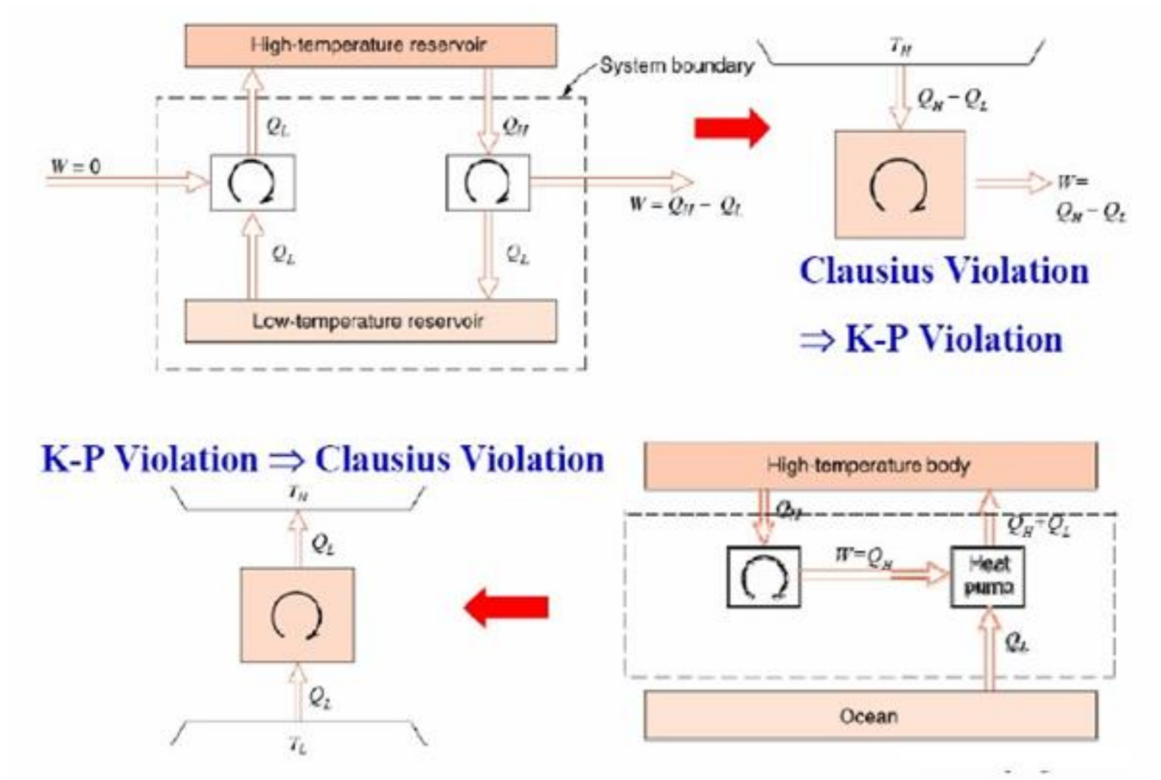



**THE CLAUSIUS STATEMENT OF THE SECOND LAW**
It is impossible to construct a system, which will operate in a cycle and transfer heat from a cooler to a hotter body without work being work done on the system by the surrounding




**EQUIVALENCE KELVIN PLANK'S AND CLAUSIUS STATEMENTS.**

Proof: Suppose the converse of the Clausius' proposition is true. The system can be represented by a heat pump for which W = 0. If it takes Q units of heat from the cold reservoir, it must deliver Q units to the hot reservoir to satisfy the First Law. A heat engine could also be operated between the two reservoirs; let it be of such a size that it delivers Q units of heat to the cold reservoir while performing W units of work. Then the First Law states that the engine must be supplied with (W + Q) units of heat from the hot reservoir. In the combined plant, the cold reservoir becomes superfluous because the heat engine could reject its heat directly to the heat pump. The combined plant represents a heat engine extracting (W + Q) – Q = W units of heat from a reservoir and delivering an equivalent amount of work. This is impossible according to Kelvin-Plank's statement of Second Law. Hence converse of Clausius' statement is not true and the original proposition must be true.



**CARNOT'S THEOREM**.

No heat engine operating in a cycle process between two fixed temperatures can be more efficient that a reversible engine operating between the same temperature limits.

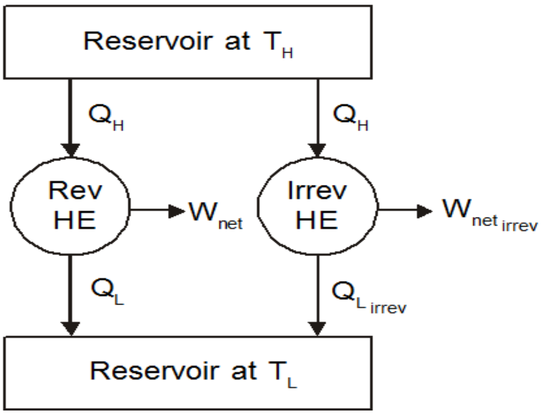
**COROLLARIES OF CORNOT THEOREM**

i. All the reversible engines operating between the two given thermal reservoir with fixed temperature have the same efficient.

ii. The efficient of any reversible heat engine operating between two reservoir is independent of the nature of the working fluid and depends only on the temperature of the reservoirs.

**CLAUSIUS INEQUALITY**

Consider two heat engines operating between two reservoirs kept at temperature $T_H$ and $T_L$ as shown in the Figure. Of the two heat engines, one is reversible and the other is irreversible.




For the reversible heat engine it has already been proved that

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\oint \left(\frac{dQ}{T}\right)_{rev} = 0$$

As discussed earlier, the work output from the irreversible engine should be less than that of the reversible engine for the same heat input $Q_H$. Therefore $Q_{L,Irrev}$ will be greater than $Q_{L,Rev}$ . Let us define

$$Q_{L,Irrev} = Q_{L,Rev} + dQ$$

then

$$\oint\left(\frac{dQ}{T}\right)_{Irrev} = \frac{Q_H}{T_H} - \frac{Q_{L,Irev}}{T_L}$$

$$= \frac{Q_H}{T_H} - \frac{Q_{L,rev}}{T_L} - \frac{dQ}{T_L}$$

$$= 0 - \frac{dQ}{T_L}$$

$$< 0$$

By combining this result with that of a reversible engine we get

$$\oint\left(\frac{dQ}{T}\right)_{Irrev} \leq 0$$

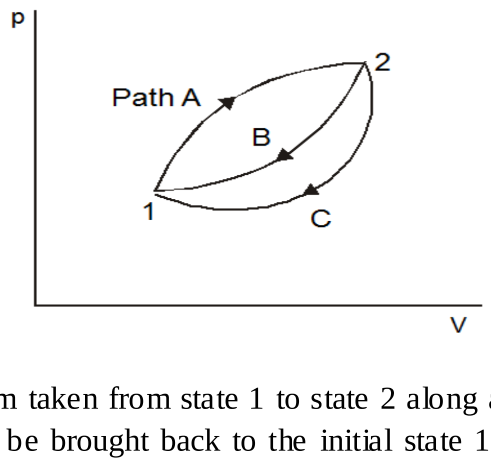
This is known as Clausius inequality.

The following conditions of clausius inequality
ƒdQ/T ≤ 0 is known as inequality of clausius.
If 1. ƒ dQ/T = 0,the cycle is reversible.
2. ƒ dQ/T < 0,the cycle is irreversible and possible.
3. ƒ dQ/T > 0,the cycle is impossible.

**ENTROPY**

The measure of irreversibility when the energy transfer takes place within the system or between system and surrounding is called as change of entropy. It is simply known as unaccounted heat loss.The change entropy of the system with respect to ambient conditions or any other standard reference conditions is known as absolute entropy.

Clausius inequality forms the basis for the definition of a new property known as entropy.




Consider a system taken from state 1 to state 2 along a reversible path A as shown in Figure. Let the system be brought back to the initial state 1 from state 2 along a reversible path B. Now the system has completed one cycle. Applying Clausius inequality we get

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

$$\int_1^2 \left(\frac{dQ}{T}\right)_A + \int_2^1 \left(\frac{dQ}{T}\right)_B = 0$$

Instead of taking the system from state2 to state1 along B, consider another reversible path C. Then for this cycle 1-A-2-C-1, applying Clausius inequality:

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

$$\int_1^2 \left(\frac{dQ}{T}\right)_A + \int_2^1 \left(\frac{dQ}{T}\right)_C = 0$$

Comparing, Hence, it can be concluded that the quantity is a point function, independent of the path followed. Therefore it is a property of the system

**Principle of increasing entropy**

Applying Clausius inequality,
For any infinitesimal process undergone by a system, change in entropy

$$dS \geq dQ/T$$

For reversible, $dQ = 0$ hence $dS = 0$
For irreversible, $dS > 0$

Consider a system interacting with its surroundings. Let the system and its surroundings are included in a boundary forming an isolated system. Since all the reactions are taking place within the combined system, whenever a process occurs entropy of the universe (System plus surroundings) will increase if it is irreversible and remain constant if it is reversible. Since all the processes in practice are irreversible, entropy of universe always increases

ie., $(\Delta s)_{universe} > 0$