S. S. College, Jehanabad
B.Sc(H) Physics Part I
Topic : Second Law of Thermodynamics
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1.1 Introduction

The first law of thermodynamics is the law of conservation of energy but it does not tell anything about the direction of flow of energy in any process. The first law shows that the **perpetual motion** of the first kind is impossible i.e. production of energy without dissipation of equivalent amount of energy is not possible. The first law places no restriction on the direction of a process whereas the second law of thermodynamics is a general law which gives information about the direction of heat transfer.
The second Law of thermodynamics is probably the most fundamental physical law and there are various ways to state this law. There are two important statements of the second law. One is given by Kelvin-Plank in reference to heat engine and another one by Clausius which is in reference to refrigerator. Hundred percent efficient engines and a self-acting refrigerator are impossible. Second law shows that **perpetual motion** of the second kind i.e. production of useful energy from the internal energy of a given body is impossible. Both statements are equivalent and their consequences are identical. The second Law is the generalization of certain experiences and observations. A system has a tendency to change spontaneously in a definite direction towards equilibrium. Entropy characterizes to approach to equilibrium. Here we will restrict our discussion of second law of thermodynamics to heat engines and refrigerator only. Unattainability of absolute zero is also one of the implications of second Law of thermodynamics.

1.2 Reversible and irreversible processes

Reversible Process: A reversible process is a process that can be reversed by means of infinitesimal changes in some property of the system without dissipation of energy. Due to these infinitesimal changes, the system is in thermodynamic equilibrium throughout the process.
Reversible processes are slow processes. The changes taking place very slowly during the process will also take place by the same amount when the process is reversed but in opposite sense. The process will not be reversible if there is any loss of energy. In an actual process there is always loss of heat due to friction, conduction, convection or radiation. Thus a pure reversible process is an ideal case.
Irreversible Process: The process is said to be an irreversible process if it cannot return the system and the surroundings to their original conditions when the process is reversed.
The system cannot be brought back to its original position and the energy once lost due to dissipative effects can never be regained.
The system is not at equilibrium throughout the irreversible process.
Few examples of irreversible process are discussed below:
1. If we put a body at 1000c in contact with a similar body at 00c, after some time both acquire an equilibrium temperature of 500c.

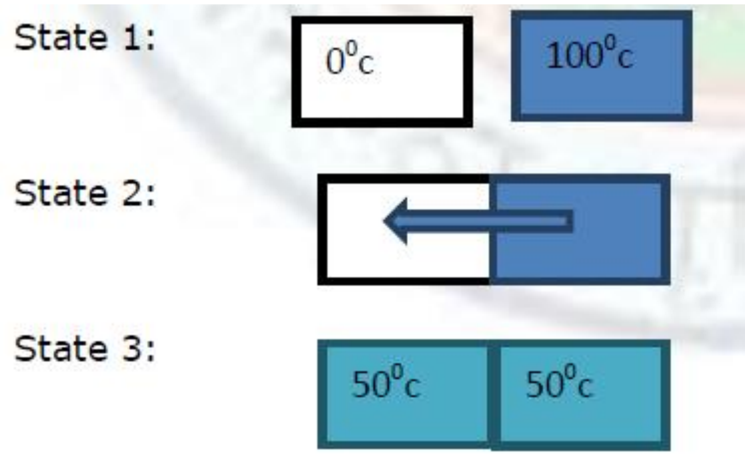


Figure 1.1: Heat transfer is an irreversible process
Is it possible that if we put two similar bodies at 500c in contact and after sometime one becomes 1000c and the other becomes 00c? The answer is NO, because this process of heat transfer from a hotter to a colder body is irreversible.

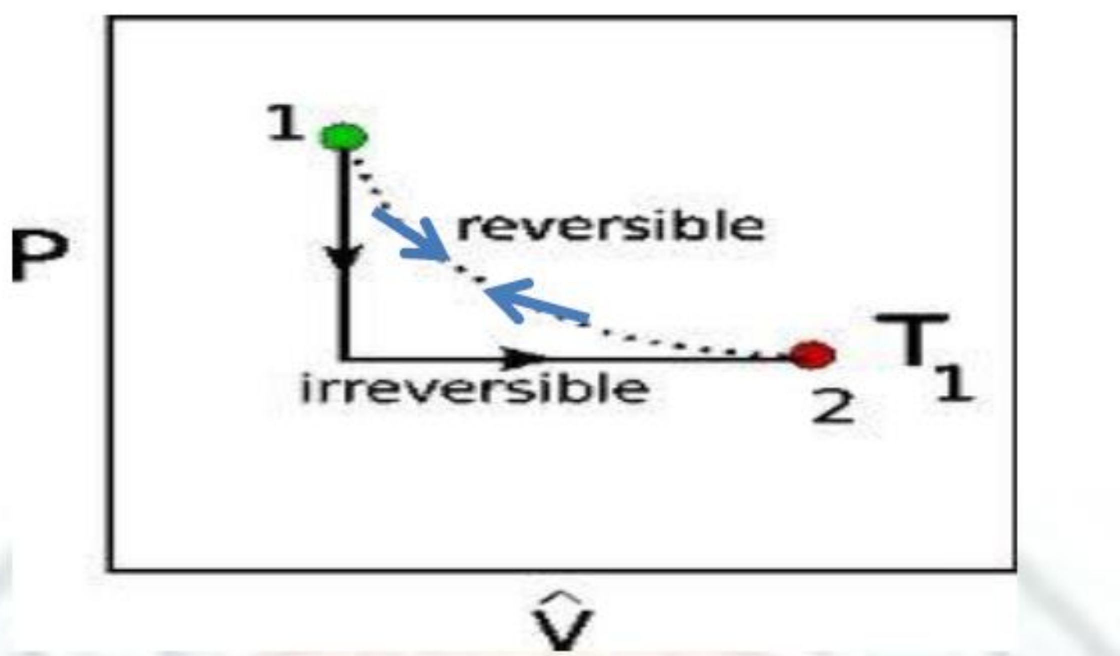


Figure 1.5: Graphical representation of irreversible and reversible process

Here from state 1 to state 2, along the thick line the two arrows in the same direction represent unidirectionality of the process showing irreversibility.
Whereas from state 1 to state 2, the two arrows in opposite directions on the dotted curve represent bidirectionality of the process, showing reversibility.

The second law is a generalisation of certain experiences and observations and is concerned with the direction in which energy transfer takes place. There are two basic statements which governs the working of a heat engine (Kelvin Plank) and a refrigerator (Clausius).

1.3 Conversion of work into heat and heat into work

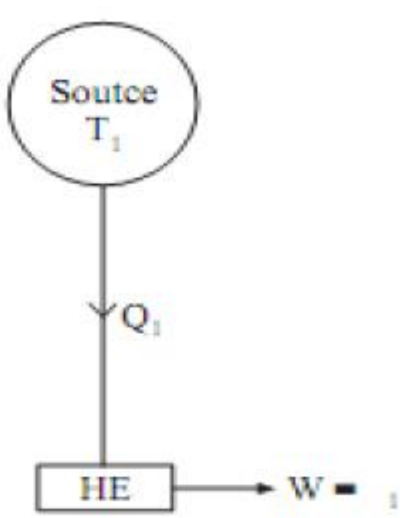
Thermodynamics is the study of conversion of heat into work and work into heat. The work done is directly proportional to the amount of heat transferred i.e. $W \propto Q$

$$or,\ W = JQ$$

Here, is the work done in Joules (J)
is the amount of heat transferred in calories (C)
is proportionality constant, called as the "mechanical equivalent of heat" .Its value is 4.18 J/C.
The first and the second law of thermodynamics explain the connection between heat and work. First law is the law of conservation of energy, and it says "energy cannot be created nor destroyed but can only be converted from one form into another".
When a cold body is placed in contact with a hot body then at equilibrium, the heat gained by the colder body is equal to the heat lost by the hotter body. The first law does not rule out this possibility but gives no information about the direction of heat flow which is given by the second law, according to which, heat always flows from a body at higher temperature to a body at lower temperature.
Second law also says that there is some heat which is wasted in the process of conversion of heat into work. According to this law whole of the heat cannot be transformed but only a part of it, into work.
A heat engine is a device which converts heat into mechanical work and according to second law 100% efficient engine is not possible. A refrigerator is a device, which converts work into heat and cannot produce cooling without any external aid. According to second law a self-acting refrigerator is not possible.
So one cannot achieve complete conversion of work into heat and heat into work. There is always loss of energy due to **dissipative effects**.

1.4 Kelvin Plank statement

Kelvin Planck Statement: - "It is impossible to construct a type of engine which works in cyclic process and produces no effect other than work output and exchange of heat with a single **reservoir**."
Alternatively, no process is possible whose sole result is the complete conversion of heat into work.



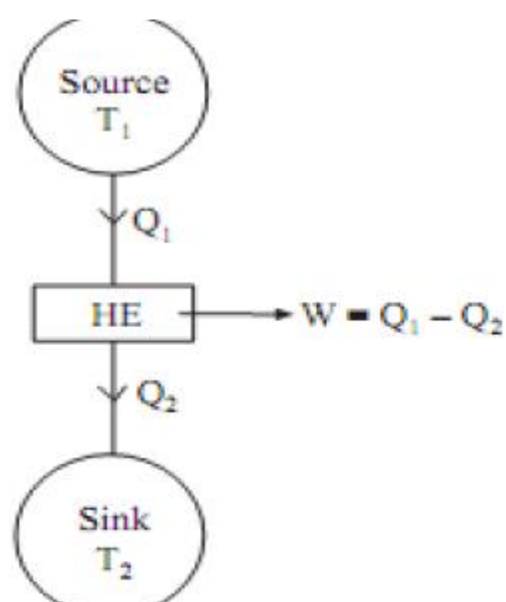
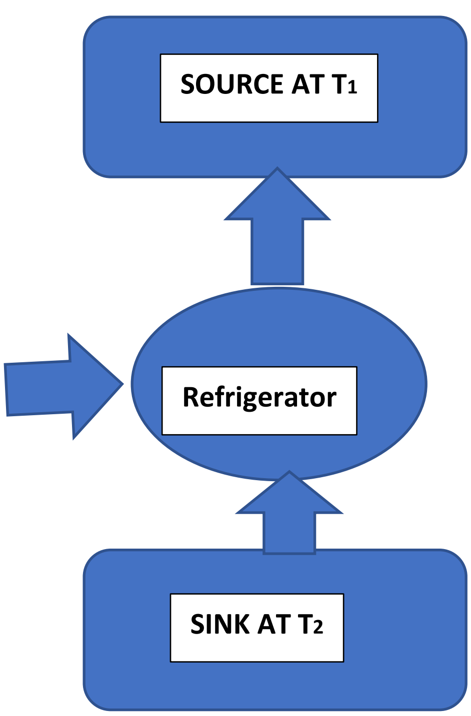


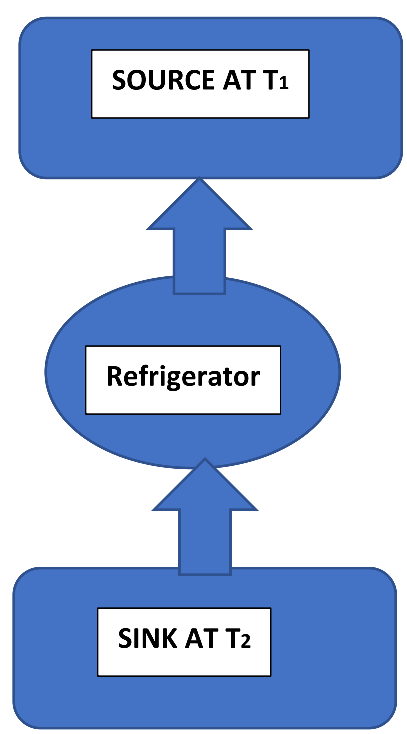
Figure 1.6(a): Impossible arrangement **Figure 1.6(b):** Kelvin Plank statement
Conclusions drawn from the statement:

1. No cyclic heat engine (HE) can convert whole heat into equivalent work. Fig 1.6a not possible.
2. There is degradation of energy in a cyclic heat engine as some of the heat has to be rejected. Fig 1.6b is possible.
Second law of thermodynamics is also called as law of degradation of energy. For satisfactory operation of heat engine there should be at least 2 heat reservoirs, source (at higher temperature) and sink (at lower temperature).
As per the statement the network will be produced in the cycle as long as there is difference in temperature between the source and sink. In due course of time if source loses too much heat and sink gains too much heat and their temperatures become equal, the network produced in the cycle will be zero.
The Kelvin-Planck statement tells the condition for producing work within the cycle. All heat engines work according to Kelvin Plank statement.

1.5 Clausius statement

Clausius statement :"It is impossible to construct a device which operates in a cyclic process and produces no effect other than transfer heat from one reservoir at low temperature to another reservoir at high temperature." Clausius statement points out the essence of work input required in refrigeration and heat pumps.
Alternatively, it is impossible for a self-acting machine working in a cyclic process unaided by external agency to transfer heat from a body at higher temperature to a body at lower temperature.
Or we can say that heat cannot flow from a colder body to a hotter body.





POSSIBLE **IMPOSSIBLE**

To transfer heat from a body at lower temperature to a body at higher temperature external work is required. Thus in the above figure left part is possible while on the right is not possible.

The Kelvin Planck Statement is regarding heat engines and the Clausius statement is regarding Refrigerators and Heat pumps. Both the statements have no proof. These Laws are based on experimental observations. There is no other statement which contradicts these laws.

1.6 Carnot's theorem

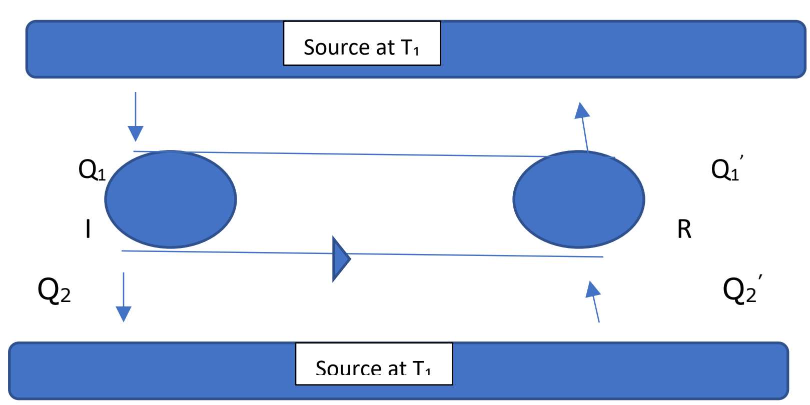
Carnot's theorem is stated conveniently in two parts:

(i) No engine working between two given temperatures can be more efficient than a reversible engine working between the same two temperatures.

(ii) All reversible engines working between the same temperatures have the same efficiency.

Here efficiency is defined as the ratio of useful output and total input energy.

Proof:



Let ***I*** represents an irreversible engine and ***R*** represents a reversible engine. Both work between the same source and the sink with temperatures *T1* and *T2* respectively. Further, both of them perform the same work, *W*, per cycle.

Let ***I*** absorb Q_1 , heat from the source, does external work *W*, and rejects $Q_2 (= Q_1 - w)$ heat to the sink. Its efficiency will be,

$$\eta_1 = \frac{w}{Q_1}$$

Let R absorb Q'_1 heat from the source, does external work W, and rejects $Q'_2 (= Q'_1 - W)$ heat to the sink. Its efficiency will be,

$$n_R = \frac{W}{Q'_1}$$

If I is supposed to be more efficient than R, then

$$n_I > n_R$$

Or,

$$\frac{W}{Q_1} > \frac{W}{Q'_1}$$

Or,

$$Q'_1 > Q_1$$

Therefore,

$$Q'_1 - Q_1 = +ve$$

The two engines are now coupled together in such a way that **I** is working in forward direction, drives **R** backwards, as shown in the figure. In this arrangement, **I** works as a heat engine and **R** works as a refrigerator. Then **R** will extract $Q'_1 - W$ heat from the sink, has W work done upon it, and will reject Q'_1 heat to the source, and after doing external work W will reject $(Q_1 - W)$ heat to the sink. Thus during each cycle, the source will lose Q_1 heat and will gain Q'_1 heat. So heat gained by the source $= Q'_1 - Q_1$.

In the same cycle, the sink gains (Q_1 – W) heat and loses $(Q'_1 - W)$ heat. So, heat lost by the sink = $(Q'_1 - W)$ – $(Q_1 - W)$ = Q'_1 – Q_1.

Since $(Q'_1 - Q_1)$ is positive, so during each cycle of operation, an amount of heat equal to $(Q'_1 - Q_1)$ is transferred from the sink which is at lower temperature T_1, without any external aid. But this type of heat transfer is in violation of the second law of thermodynamics, hence is not possible. So, our supposition that **I** is more efficient than **R** is wrong. Hence **I** cannot be more efficient than **R**. Thus first part of the theorem is proved.

(ii) To prove the second part of the theorem, let us replace the irreversible engine **I** by a reversible engine **R'**.

Supposing **R'** to be more efficient than **R**, and following the same argument as in (i) with **I** replacing **R'**, we come to the conclusion that **R'** cannot be more efficient than **R**. Similarly, **R** cannot be more efficient than **R'**. It means that all reversible engines working between the same temperature limits must have the same efficiency. Thus the second part of the theorem is also proved.

Moreover Carnot's engine is the most efficient engine working between the same source and sink is the most efficient engine because this is an ideal engine.

Thus Carnot's theorem is completely proved.