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Semester-II
Paper No: Thermal Physics : Physics-IIA
Lesson: Second law of thermodynamics
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Learning Objectives:

After studying this lesson, you will be able to;

- ✓ define reversible and irreversible processes.
- ✓ state the second law of thermodynamics in different ways.
- ✓ establish equivalence between different statements of the second law.
- ✓ state and explain Carnot's theorem.

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.

Few reversible processes are discussed below:

1. In absence of air the movement of a pendulum is a reversible process. When a simple pendulum oscillates freely, its total enegry remains constant at every position. During oscillation, the pendulum moves from its mean position towards right end, comes back to mean position and then goes to the left end. In the reverse process, it moves from left end to the mean position, goes to the right end and then comes back to mean position. Thus, the pedulum reaches its original position without loss of energy and hence the process is reversible.

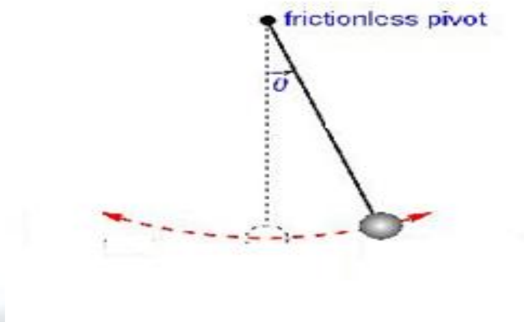
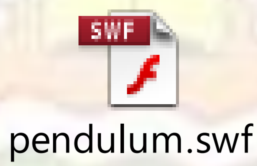


Figure1.3: Motion of a pendulum.

Double click the following icon to see the motion of the pendulum.



2. By changing the weight on the piston slowly by small value, the state of a gas can be reversed back. Consider a gas enclosed in a cylinder fitted with a piston. Now if pressure on the gas is increased slowly by putting weights on the piston in small steps,the gas gets compressed and its volume decreases. In the reverse process, if the pressure is decreased slowly by lifting weights in the same way as earlier, the volume of the gas increases slowly by the same amount and the system regains its original position ,hence this process is reversible.

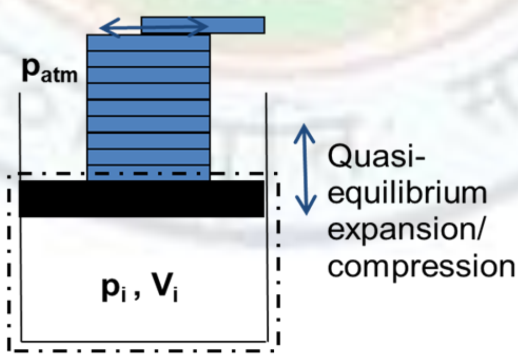


Figure1.4: Compression and expansion of a gas.

Double click the following icon to see the animation for **Figure 1.4.**

reversible process.swf

The basic concept is that most of the thermodynamic processes have a preferred direction just as the direction of heat which is from a body at higher temperature to a body at lower temperature.

But in some systems, the reverse occurs. Normally, it happens when that system is close to **thermal equilibrium**. This equilibrium has to be inside the system itself and also within the system and its surroundings. When this stage is reached, even a small change can change the direction of the process and therefore such a reversible process is also known as an equilibrium 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 regaind.

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 100^0c in contact with a similar body at 0^0c, after some time both acquire an equilibrium temperature of 50^0c.

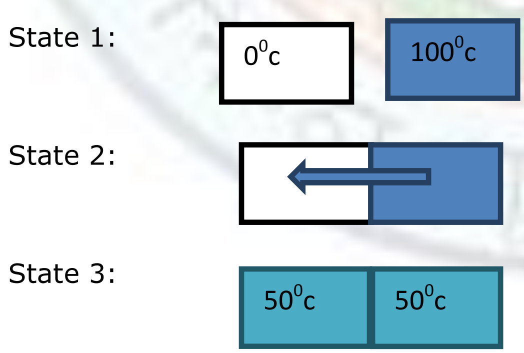


Figure 1.1: Heat transfer is an irreversible process

Is it possible that if we put two similar bodies at 50^0c in contact and after sometime one becomes 100^0c and the other becomes 0^0c? The answer is NO, because this process of heat transfer from a hotter to a colder body is irreversible.

2. Mixing of two different substances is an irreversible process.

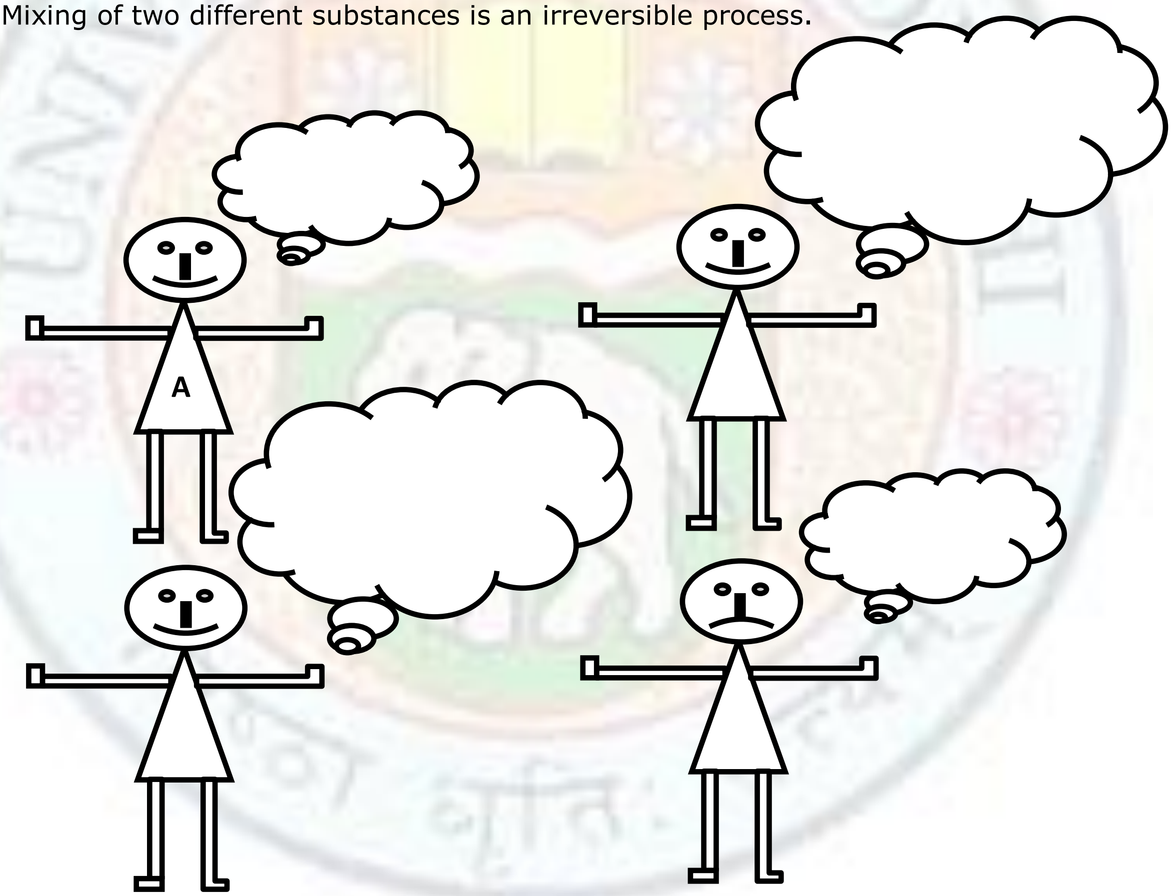


Figure 1.2: Mixing of substances is an irreversible process

All the natural processes are irreversible. e.g. Ageing, reproduction, digestion, ripening of fruits etc.

Graphically, we can represent both the processes in Figure (1.5):

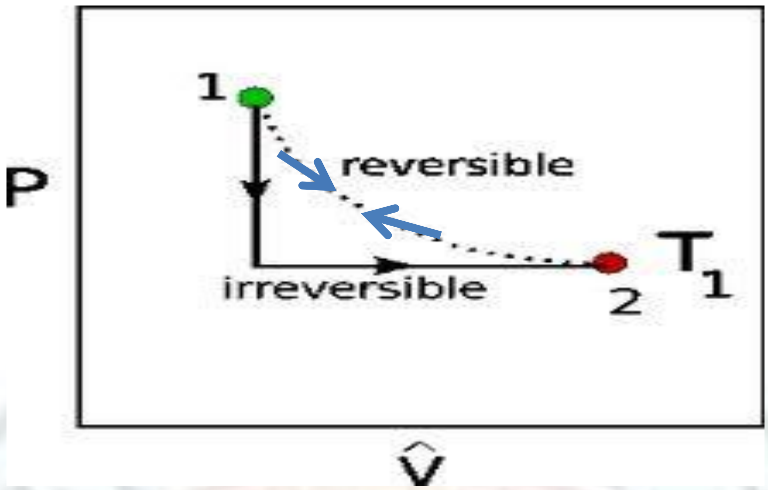


Figure 1.5: Graphical representation of irreversible and reversible process

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, W is the work done in Joules (J)

Q is the amount of heat transferred in calories (C)

J 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.

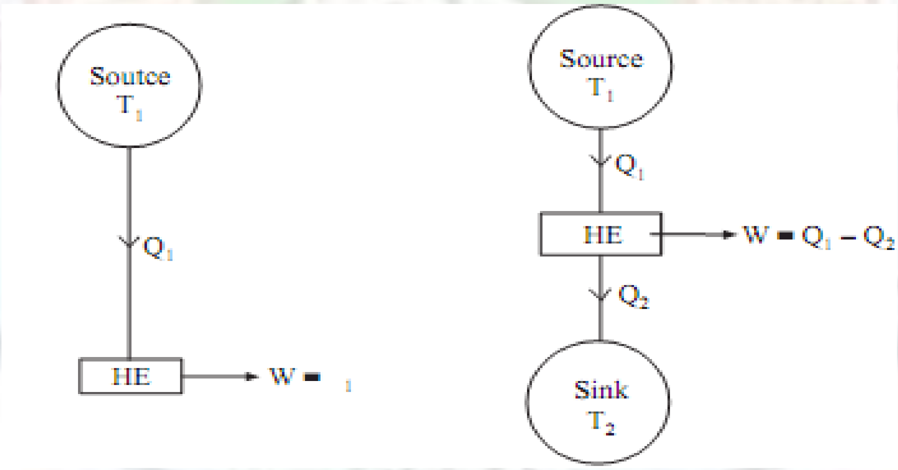


Figure 1.6(a): Impossible arrangement **Figure 1.6(b):** Kelvin Plank statement

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.

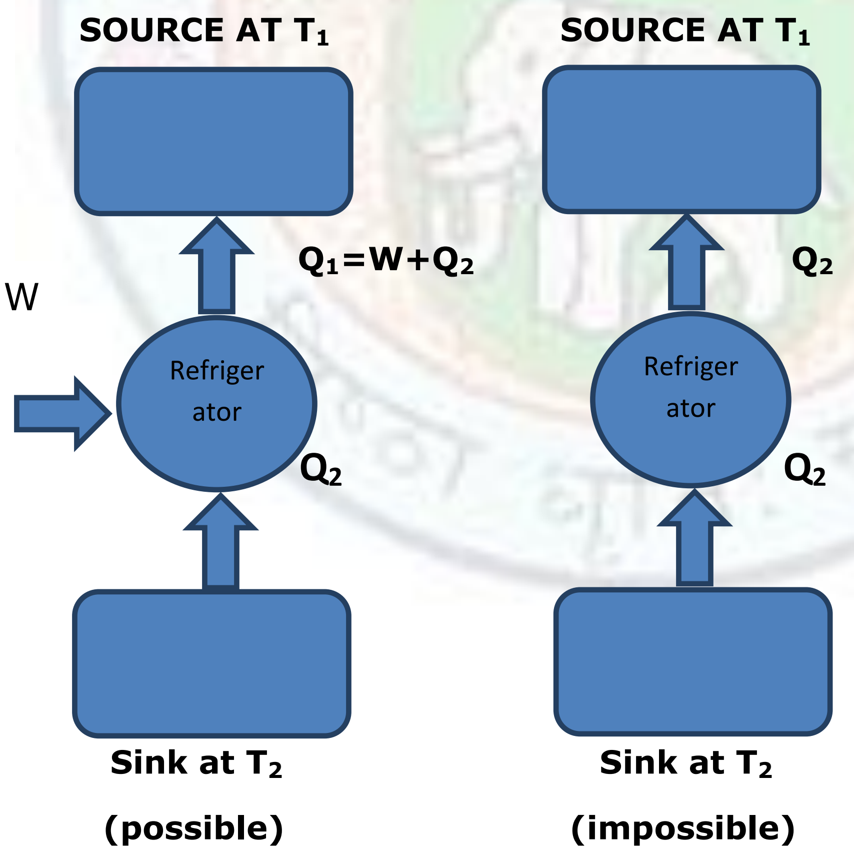


Figure 1.7: Clausius statement

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.

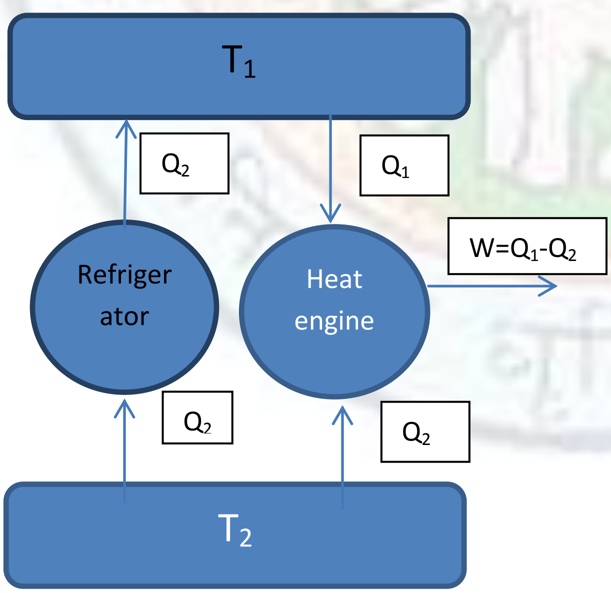
1.6 Equivalence of Kelvin Plank and Clausius statements.

It is remarkable that above two statements of the second Law are in fact equivalent and their consequences are identical. In fact each statement implies the other. This means:

- Violation of Clausius statement➔Violation of Kelvin-Planck statement
- Violation of Kelvin-Planck statement➔Violation of Clausius statement

In order to demonstrate their equivalence consider the following diagram.

Let us suppose there is a refrigerator and a heat engine, both working between the same source at T_1 and sink at T_2. Let Q_2 heat is drawn from the sink by the refrigerator and is transferred to the source without any external agency. This is violation of the Clausius statement of the second law. Let us now assume that the heat engine draws heat Q_1 from the source and rejects heat Q_2 to the sink and performs a work $W(=Q_1-Q_2)$ in one cycle. This is the case of Kelvin Plank statement, Figure (1.8 a).



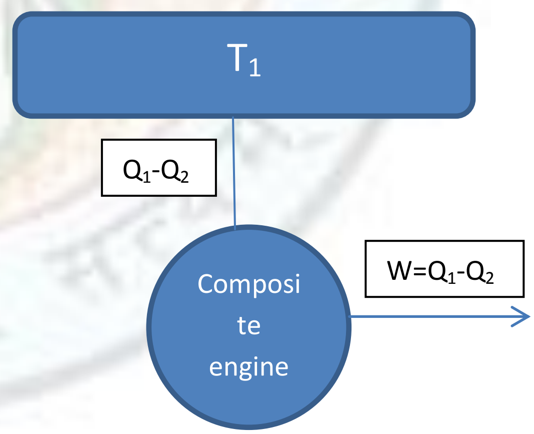


Figure 1.8(a): Violation of Clausius

Figure 1.8(b) Violation of Kelvin Plank

Further suppose, they are coupled together in such a way that the coupled system draws heat Q_1-Q_2 from the source and converts it completely into work, $W=Q_1-Q_2$. Such an arrangement violates Kelvin Plank statement, Figure (1.8 b).

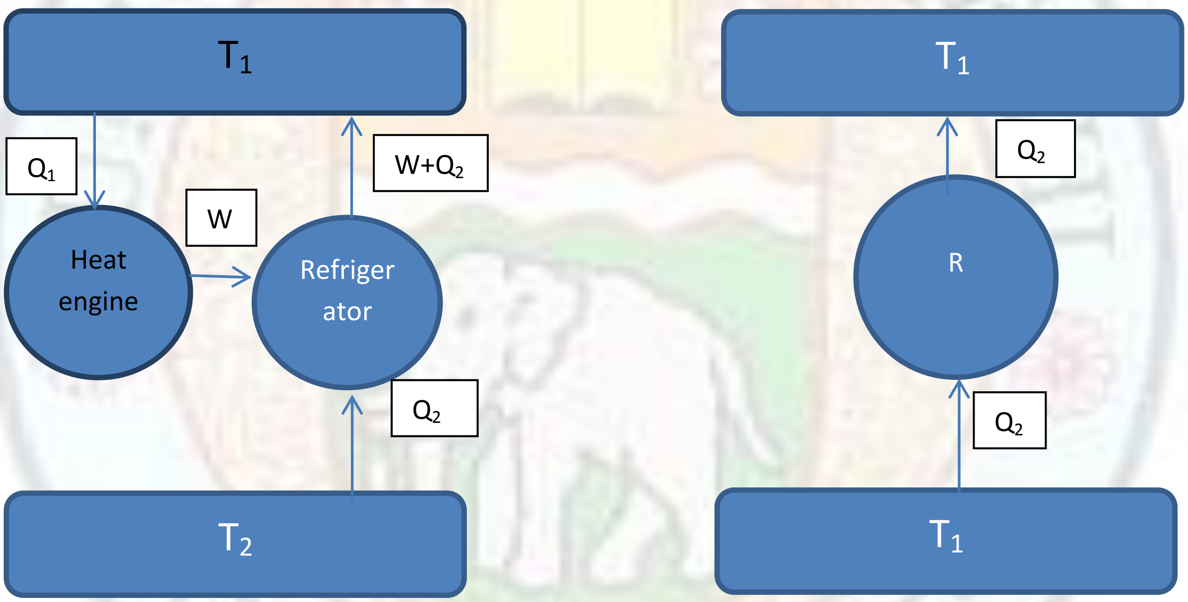


Figure1.9(a): Violation of Kelvin Plank **Figure 1.9(b):** Violation of Clausius

To prove that when Kelvin Plank statement is violated, the Clausius statement is also violated. Let us suppose that heat engine working between same source and sink as heat engine draws heat Q_1 from the source and converts it completely into work, $W=Q_1$ and no heat is rejected to the sink.

This is the violation of the Kelvin Plank statement. Suppose that the work performed by the heat engine is used to drive a refrigerator between same source and sink. Further suppose that the refrigerator absorbs heat Q_2 from the sink and rejects heat W+ Q_2 to the source per cycle. As before if we couple the two we note that the net result of operation of the coupled system working as a refrigerator transfers heat Q_2 from the sink to the source without any external work. This arrangement violates Clausius statement of the second law.

Here it was assumed that the refrigerator completes one cycle in the same period as does the heat engine

Now we conclude that the violation of Kelvin Plank leads to the violation of Clausius statement and vice-versa. This leads to the conclusion that both the statements of the second law are equivalent.

1.7 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:

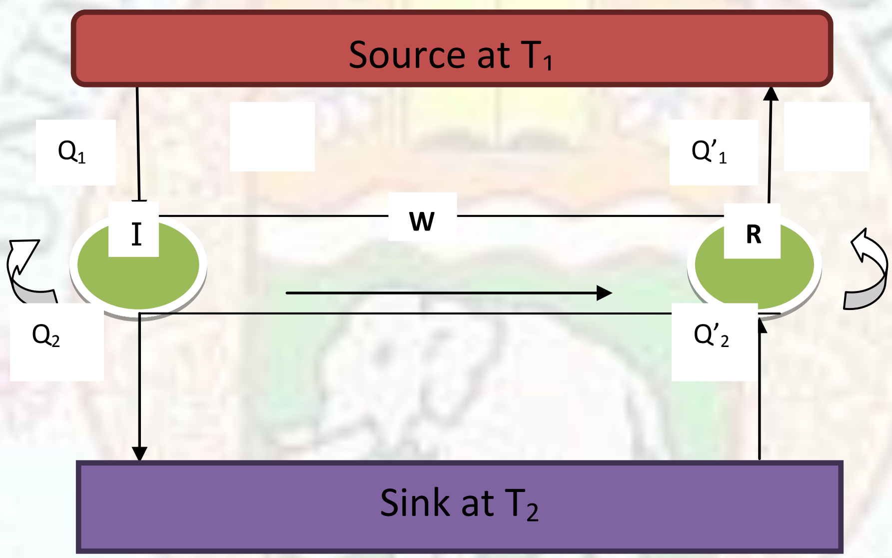


Figure 1.10: Carnot's Theorem

(i) Let ***I*** represents an irreversible engine and ***R*** represents a reversible engine. Both work between the same source and the sink with temperatures T_1 and T_2 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,

$$n_I = \frac{W}{Q_1}$$

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,

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

$$Q'_1 > Q_1$$

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 temperatureT_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.

Did you know?

If all the dissipative effects such as friction, viscosity or electrical resistance are removed, the motion once started in a device would continue forever.

Problem: A scientist claims to have developed an engine working between 800K and 400K capable of having an efficiency of 55 %. Comment on his claim.

The efficiency of a Carnot's engine, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{400}{800} = 0.5 = 50\%$

Solution: The efficiency claimed is 55% which is more than the efficiency of a Carnot's engine working between the same two temperature limits. Thus his claim contradicts Carnot's theorem.

1.8 Summary

- ✓ Since all practical processes in the universe are irreversible hence we can say that rigorous reversibility is an ideal conception while irreversibility is the rule.
- ✓ There are a number of ways to state second law.
- ✓ Kelvin Plank and Clausius statements are two different ways of stating the same law.
- ✓ Carnot's engine is an ideal heat engine which does not exist in the real world.
- ✓ Carnot's theorem is a result of the second law of thermodynamics.
- ✓ No engine can be more efficient than the Carnot's engine.
- ✓ All the reversible heat engines working between same two temperature limits have same efficiency.

1.9 Exercise

I. Fill in the blanks:

1. If the change in internal energy is zero the process in called as___________.

2. If two or more engines are working between the same source and different sink then the engine working over the largest temperature difference has the ___________efficiency.

3. The presence of colder body is a must for the ____________of heat into work.

4. The perfectly reversible heat engine is the _____________engine.

5. Kelvin Plank statement is for ________________and Clausius statement is for _____________________.

II. State true /false for each of the following sentences:

1. Reversible process is an ideal concept.

2. Irreversible process takes place only when there is some dissipative force.

3. In an irreversible process removal of constraints cannot restore the system in its initial state.

4. Carnot engine is a reversible engine.

5. All reversible engines working between same temperature limits are of equal efficiency and independent of the nature of the working substance.

6. Reversible engine is the most efficient engine.

III. Answer the following:

1. Explain the concept of reversible and irreversible processes with examples.

2. Show that for the same pair of working temperature the efficiency of all reversible engines is the same.

3. State and prove Carnot's theorem.

4. State the second law of thermodynamics.

5. Show the equivalence between Kelvin Plank and Clausius statement and justify your answer.

1.10 Glossary

Reservoir: A device having **infinite thermal capacity**.

Infinite thermal capacity: The body with infinite thermal capacity can absorb, retain and reject unlimited quantity of heat without the change in temperature.

Perpetual motion: Motion that continues indefinitely without any external source of energy.

Thermal equilibrium: For a system to be in thermal equilibrium there should be no temperature difference between the parts of the system or between the system and its surroundings.

Dissipative effects: A dissipative effect is loss of energy due to friction, radiation, conduction, external resistances etc.

Non conducting: Thermally insulated from the surroundings.

1.11 References

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Further readings
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2. Thermodynamics by Enrico Fermi (Courier Dover Publications, 1956).