7. The Second Law of Thermodynamics

It can be started that, according to the first law of thermodynamics, **when a system undergoes a complete cycle then the net heat supplied is equal to the net work done**. This is based on the conservation of energy principle, which follows from observation of natural events. The second law came up as embodiment of real happenings while retaining the basic nature of the first law of thermodynamics. Feasibility of process, direction of process and grades of energy such as low and high are the potential answers provided by the 2nd law. The second law of thermodynamics is capable of indicating the maximum possible efficiencies of heat engines, coefficient of performance of heat pumps and refrigerators, defining a temperature scale independent of physical properties etc. The Second Law of thermodynamics, which is also a natural law, indicates that, although the net heat supplied in a cycle is equal to the net work done, **the gross heat supplied must be greater than the net work done**; some heat must always be rejected by the system. This law can be understood by considering the heat pump and heat engine.

Thermal Reservoir

A thermal reservoir is defined as a sufficiently large system in stable equilibrium to which and from which a finite amount of heat can be transferred without any change in its temperature.

Heat source: is a high temperature reservoir such as: boiler, furnace, combustion chamber, nuclear reactor, the sun, etc.

Heat sink: is a low temperature reservoir such as: condenser, atmospheric air, river water, ocean, etc.

Heat Engine

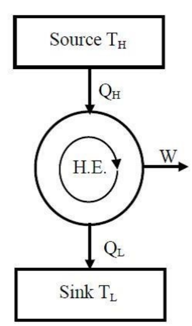
It is defined as the system operating in a complete cycle and developing a net work from a supply of heat. The second law implies a source of heat and sink of heat are both necessary. Let the heat supplied from the source be Q_H, let the heat rejected to the sink be Q_L and let the net work done by the engine be W. apply the first law of thermodynamics:

$$\sum dQ = \sum dW \qquad \dots\dots\dots\dots\dots\dots\dots (7.1)$$

$$Q_H - Q_L = W \qquad \dots\dots\dots\dots\dots\dots\dots (7.2)$$

According to the second law the gross heat supplied must be greater than the net work.

$$Q_H > W \qquad \dots\dots\dots\dots\dots\dots\dots (7.3)$$



$T_H > T_L$

Heat Engine

The thermal efficiency is defined as the ratio of the net work done during the cycle to gross heat supplied during the cycle.

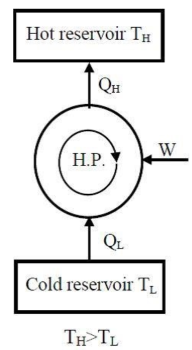
$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \qquad \dots\dots\dots\dots\dots\dots\dots (7.4)$$

The thermal efficiency of a heat engine is always less than 100%.

It can be seen that a temperature difference is always required for heat to flow; therefore the source must be at higher temperature than the sink.

Heat Pump and Refrigerator

It is the inverse of heat engine. Work is done on the system. The net work done on the system equals the net heat rejected by the system. In the heat pump an amount of heat Q_L is supplied from cold reservoir and amount of heat Q_H is rejected to the hot reservoir. According to the first law of thermodynamics:



Heat Pump

$$\sum dQ = \sum dW \qquad \dots\dots\dots\dots\dots\dots\dots (7.5)$$

$$Q_H - Q_L = W$$

$$Q_H = Q_L + W \qquad \dots\dots\dots\dots\dots\dots\dots (7.6)$$

Therefore, in order to transfer heat from a cold reservoir to a hot reservoir a work must be done.

$$W > 0 \qquad \dots\dots\dots\dots\dots\dots\dots (7.7)$$

As heat a pump is not a work producing machine and also its objective is to maintain a body at higher temperature, so its performance can't be defined using efficiency as in the case of heat engines. Performance of a heat pump is quantified through a parameter called coefficient of performance $(C.O.P)$. Coefficient of performance is defined by the ratio of desired effect and net work done for getting the desired effect.

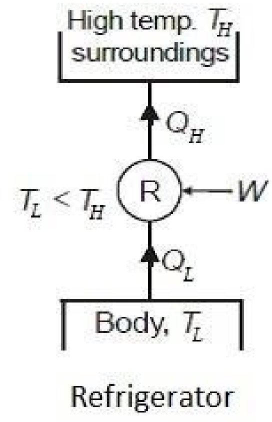
$$C.O.P. = \frac{\text{Desired effect}}{\text{Net work done}} \qquad \dots\dots\dots\dots\dots\dots\dots (7.8)$$

$$C.O.P. = \frac{Q_H}{W} \qquad \dots\dots\dots\dots\dots\dots\dots (7.9)$$

$$W = Q_H - Q_L \qquad \dots\dots\dots\dots\dots\dots\dots (7.10)$$

$$C.O.P. = \frac{Q_H}{Q_H - Q_L} \qquad \dots\dots\dots\dots\dots\dots\dots (7.11)$$

A **Refrigerator** is a device similar to a heat pump but with reverse objective. It maintains a body at a temperature lower than that of the surroundings while operating in a cycle.



Refrigerator also performs a non-spontaneous process of extracting heat from low temperature body for maintaining it cool, therefore external work W is to be done for realizing it. The block diagram shows how refrigerator extracts heat Q_L for maintaining body at low temperature T_L at the expense of work W and rejects heat to high temperature surroundings.

Performance of refrigerator is also quantified by coefficient of performance, which could be defined as:

$$(C.O.P.)_{ref.} = \frac{\text{Desired effect}}{\text{Net work}} = \frac{Q_L}{W} \qquad \dots\dots\dots\dots\dots\dots\dots (7.12)$$

$$W = Q_H - Q_L \qquad \dots\dots\dots\dots\dots\dots\dots (7.13)$$

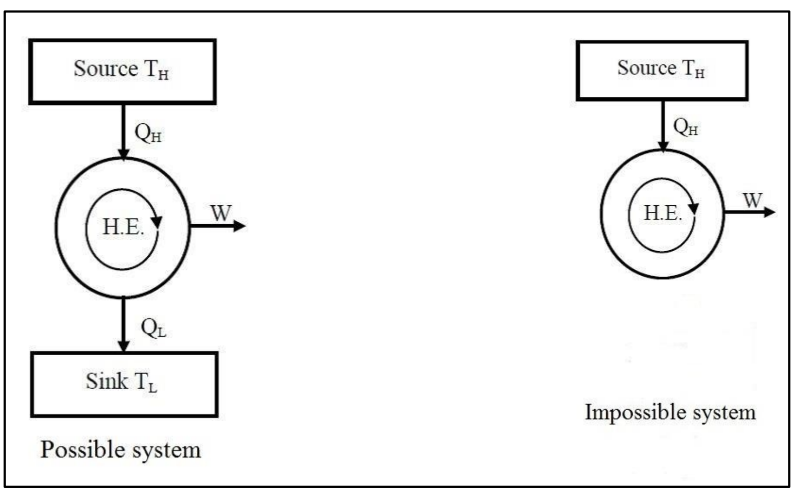
$$(C.O.P.)_{ref.} = \frac{Q_L}{Q_H - Q_L} \qquad \dots\dots\dots\dots\dots\dots\dots (7.14)$$

$(C.O.P.)$ values of a heat pump and a refrigerator can be interrelated as:

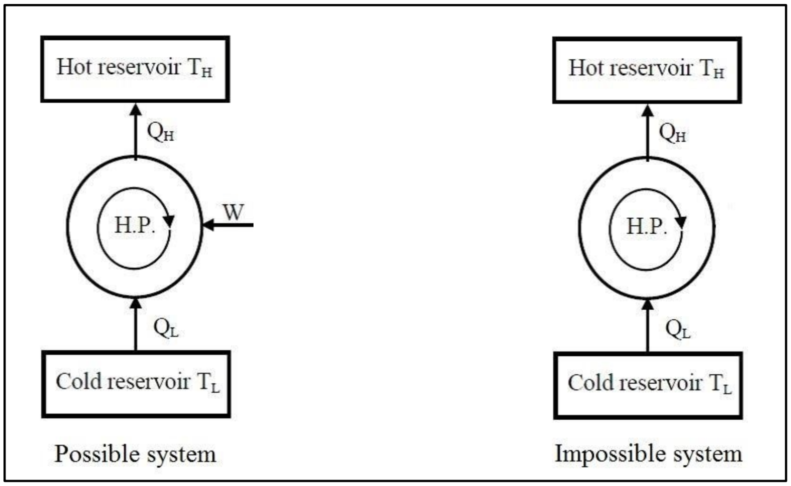
$$(C.O.P.)_{HP} = (C.O.P.)_{ref.} + 1 \qquad \dots\dots\dots\dots\dots\dots\dots (7.15)$$

Statements of the Second Law of Thermodynamics

1. Kelvin-Planck statement: no process is possible whose sole effect is the removal of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work.



2. Clausius statement: no process is possible whose sole effect is the removal of heat from a reservoir at a lower temperature and the absorption of equal amount of heat by a reservoir at a higher temperature.



Carnot Cycle

Carnot cycle is a reversible thermodynamic cycle comprising of four reversible processes. The concept of this cycle provided basics upon which the second law of thermodynamics was stated by Clausius and others. Thermodynamic processes constituting Carnot cycle are:

1. Reversible isothermal expansion process in which heat is added (Q_{add}).
2. Reversible adiabatic (isentropic) expansion process (W_{exp}).
3. Reversible isothermal compression process in which heat is rejected (Q_{rej}).
4. Reversible adiabatic (isentropic) compression process (W_{comp}).

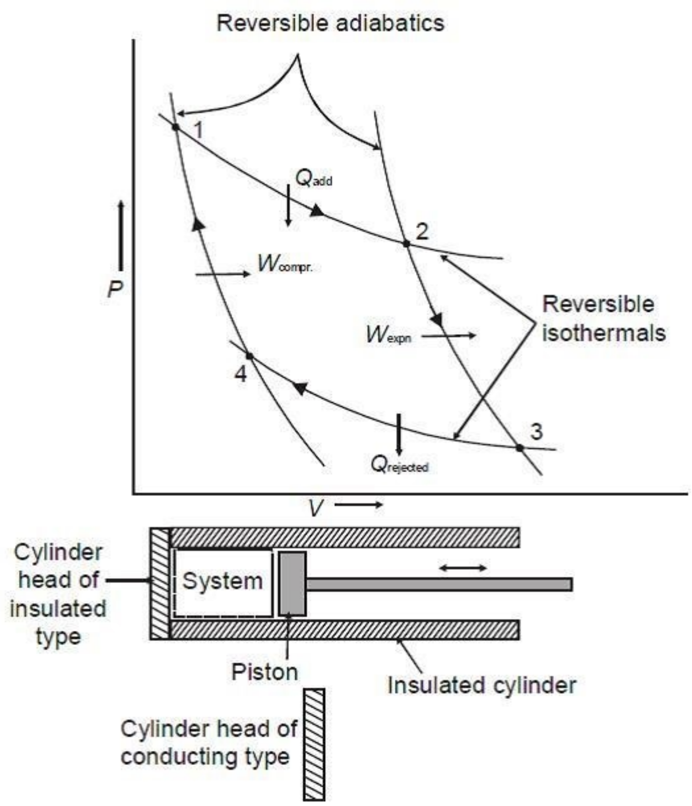
Carnot cycle is shown on the (*P-V*) diagram between states 1, 2, 3, 4 and 1. A reciprocating piston-cylinder assembly is also shown below.

Process (1–2) is a reversible isothermal expansion process in which heat is transferred to the system isothermally. In the piston cylinder arrangement heat Q_{add} can be transferred to the gas from a constant temperature source T_1 through a cylinder head of conductor type.

Process (2–3) is a reversible adiabatic expansion process which may be held inside the cylinder with cylinder head being replaced by insulating type so that the complete arrangement is insulated and adiabatic expansion is carried out. During adiabatic expansion the work W_{exp} is available and $Q_{2-3} = 0$.

Process (3–4) is a reversible isothermal compression process in which heat is rejected from the system. The cylinder head of insulating type may be replaced by a conducting type as in process (1–2) and heat Q_{rej} is extracted out isothermally.

Process (4–1) is a reversible adiabatic compression process with work requirement for compression. In the piston-cylinder arrangement the cylinder head of conducting type as used in process (3–4) is replaced by an insulating type, so that the whole arrangement becomes insulated and adiabatic compression may be realized.



The efficiency of the Carnot cycle can be given as:

$$\eta_{Carnot} = \frac{\text{Net work}}{\text{Heat supplied}}$$

$$\text{Net work} = W_{exp} - W_{comp}$$

$$\text{Heat supllied} = Q_{add}$$

Substituting gives:

$$\eta_{Carnot} = \frac{W_{exp} - W_{comp}}{Q_{add}} \qquad \dots\dots\dots\dots\dots\dots\dots (7.16)$$

For a cycle: $\sum_{cycle} W = \sum_{cycle} Q$

So we can say that: $W_{net} = Q_{add} - Q_{rej}$

Hence: