Lecture 7

Limitations of First Law of Thermodynamics

First law of thermodynamics is the conservation of energy principle. First law is not sufficient to tell whether a process will actually take place. It does not tell in what *direction* a process will happen.

For example

1 If a cup of hot coffee is left in a room it eventually cools off. The reverse of this process does not happen i.e. coffee doesn't get hot as a result of heat transfer from the room.

2. A room can be heated by passage of electric current through an electric resistor. Transferring of heat from room will not cause electrical energy to be generated through the wire.

3. Consider a paddle-wheel mechanism operated by fall of mass. Potential energy of mass decreases and internal energy of the fluid increases. Reverse process does not happen, although this would not violate first law.

4. Water flows down hill where by potential energy is converted into K.E. Reverse of this process does not occur in nature.

Processes proceed in a certain *direction* and not in the reverse direction. The first law places no restriction on direction.

A process will not occur unless it satisfies both the first and second laws of thermodynamics.

First law does not differentiate between different forms of energy. Second law states that energy has *quality* as well as quantity.

Therefore for a thermodynamic analysis both the first and second laws are required.

Second Law of Thermodynamics

Second law is useful in

- predicting the direction of processes, using the property entropy.
- determining the best theoretical performance of cycles, engines, and other devices.
- evaluating the factors that affect the performance level of devices.
- defining a temperature scale independent of the properties of any thermometric substance.
- developing means for evaluating properties such as u and h in terms of properties that are more readily obtained experimentally.
- establishing conditions for equilibrium

Heat Engines

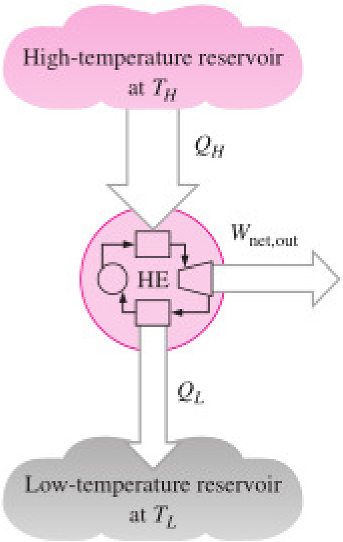
Work can easily be converted to other forms of energy, but converting other forms of energy to work is not that easy. Heat is a form of energy which is easily available. Converting heat to work requires the use of some special devices. These devices are called heat engines.

Characteristics of a heat engine

1. They receive heat from a high-temperature **source** (solar energy, oil furnace, nuclear reactor, etc.).
2. They convert part of this heat to work (usually in the form of a rotating shaft).

3. They reject the remaining waste heat to a low-temperature **sink** (the atmosphere, rivers, etc.).
4. They operate on a cycle.

Heat engines usually involve a fluid to and from which heat is transferred while undergoing a cycle called the **working fluid**.



Q_H = amount of heat supplied to the engine from the high temperature source

Q_L = amount of heat rejected from the engine to a low-temperature sink (the atmosphere, a river, etc.)

Wout = amount of work delivered by the engine

Win = amount of work given to the engine

Wnet = Wout – Win

A **thermal energy reservoir** is a hypothetical body with a relatively large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. A reservoir that supplies energy in the form of heat is called a **source**, and one that absorbs energy in the form of heat is called a **sink.**

Source and sink remain at constant temperatures no matter how much heat is taken from or supplied into it. A furnace where fuel is burned in a controlled manner is an example of a source. Atmosphere or river is an example of a sink.

Thermal Efficiency

The fraction of the heat input that is converted to net work output is a measure of the performance of a heat engine and is called the thermal efficiency, η

$$\eta = \frac{Output}{Input} = \frac{W_{net}}{Q_H}$$

Applying first law on a heat engine cycle

$$W_{net} = Q_{net} = Q_H - Q_L$$

$$\eta = \frac{Q_H - Q_L}{Q_H}$$

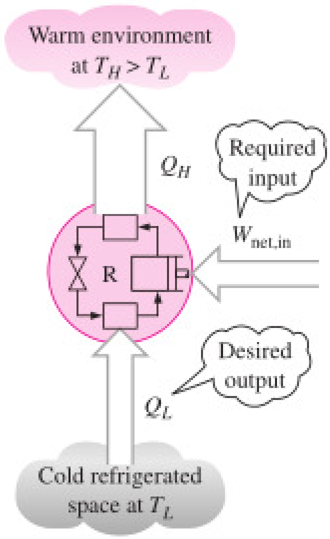
$$\eta = 1 - \frac{Q_L}{Q_H}$$

Thermal efficiency is a measure of how efficiently a heat engine converts the heat that it receives to work. Increase in efficiency means less fuel consumption and less pollution. The efficiency of a petrol engine is approximately 25% and that of a diesel engine is 40%. Therefore for even the most efficient engines large amount of energy is wasted into atmosphere.

Refrigerators and Heat Pumps

Heat transfers from high-temperature mediums to low temperature ones. The reverse process i.e. the transfer of heat from a low temperature body to a high temperature body requires a special device known as **refrigerator**.

Refrigerators are also cyclic devices. The working fluid is known as **refrigerant**.



Coefficient of Performance

The efficiency of a refrigerator is termed as Coefficient of Performance (COP). The desired output of a refrigerator is to remove heat (Q_L)from the refrigerated space. For that a work input (Wnet)is required

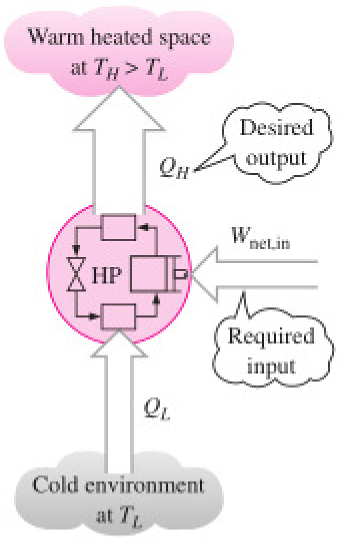
$$COP_R = \frac{Desired\ output}{Required\ input} = \frac{Q_L}{W_{net}}$$

COP can be *greater than unity*. Whereas efficiency of a heat engine cannot be greater than unity. So one of the reasons for expressing the performance of a refrigerator by another term i.e. COP, is to avoid the oddity of having efficiencies greater than unity.

Heat Pumps

Heat pumps also transfers heat from a lower temperature body to a higher temperature body. The difference between a refrigerator is that it is used to **maintain** a heated **space at a higher temperature.**

This is accomplished by absorbing heat from a low-temperature source, and supplying this heat to the high-temperature medium.



Coefficient of performance of a heat pump

$$COP_{HP} = \frac{Desired\ output}{Required\ input} = \frac{Q_H}{W_{net}}$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L}$$

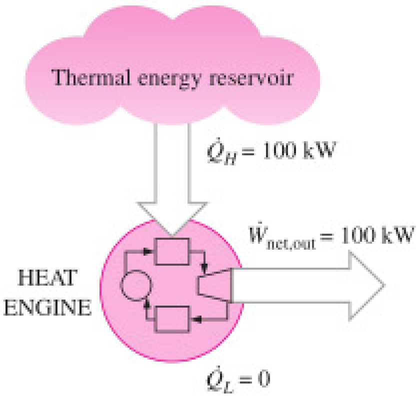
Comparing COP of the refrigerator and heat pump we get

$$COP_{HP} = COP_R + 1$$

Question: In order to heat a room in a winter which is efficient, electric heater or a heat pump?

The Second Law of Thermodynamics: Kelvin–Planck Statement

It is impossible for any device that operates on a cycle to deliver work to its surroundings while receiving heat from a single reservoir.



A heat engine that violates Kelvin-Plank statement

Kelvin-Plank statement states that inorder to produce net positive work output the heat engine should exchange heat with a lower temperature reservoir (sink) as well as a higher temperature source.

No heat engine can produce net work output in a cycle

if $Q_L = 0$

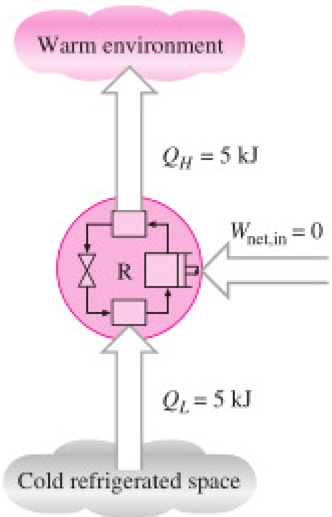
$$\eta = 1 - \frac{Q_L}{Q_H}$$

Or, no heat engine can have 100% efficiency according to Kelvin-Plank statement

Note that Kelvin–Planck statement does not rule out the possibility of the net work output being zero.or negative

The Second Law of Thermodynamics: Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.



It simply states that a refrigerator cannot operate unless it is driven by an external power source.

Both the Kelvin–Planck and the Clausius statements of the second law are negative statements, and a negative statement cannot be proved.

Like any other physical law, the second law of thermodynamics is based on experimental observations.

No experiment has been conducted till date that contradicts the second law.

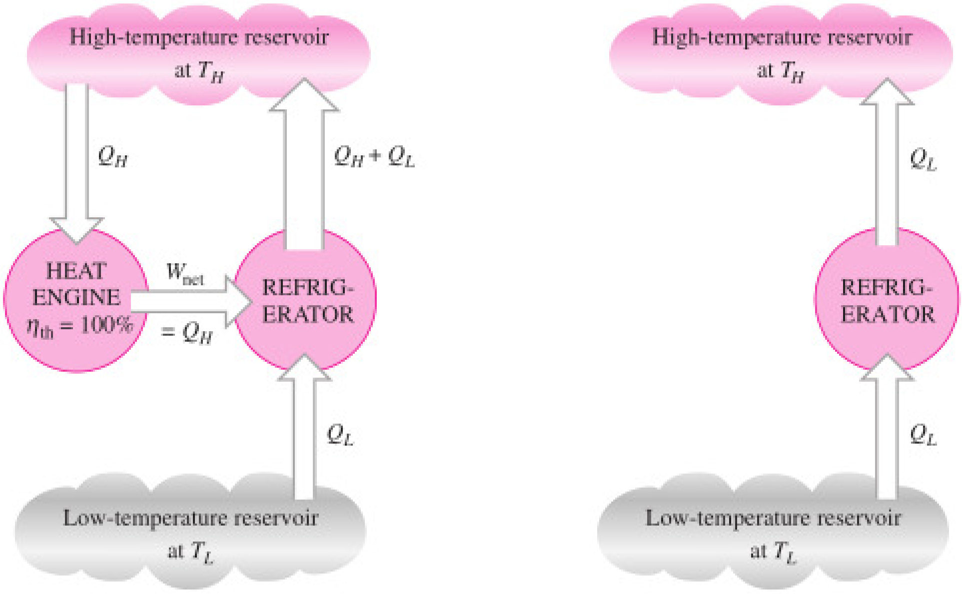
This should be taken as a proof of its validity.

Equivalence of the Two Statements

Though it may look different both Kelvin–Planck and the Clausius statements are equivalent in their consequences.

Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa.

This can be shown as follows. Here a 100% efficient heat engine that violates the Kelvin-Plank statement, powers a refrigerator. The equivalent refrigerator i.e. the refrigerator + the heat engine has a net heat transfer of Q_L to the high temperature reservoir. Therefore it becomes a device that transfers heat (Q_L) from a lower temperature reservoir to a higher temperature reservoir. This is the violation of the Clausius statement. Hence the violation of Kelvin-Plank statement implies the violation of Clausius statement



(*a*) A refrigerator that is powered by a 100 percent efficient heat engine

(*b*) The equivalent refrigerator

Question:

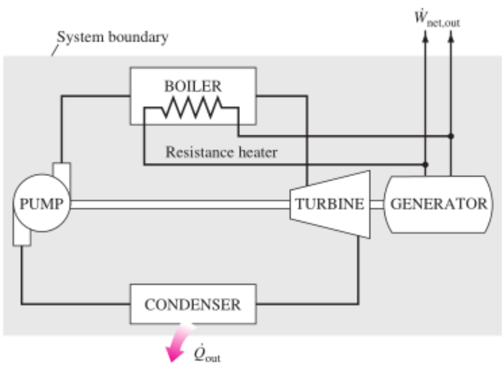
Show that the violation of Clausius statement implies the violation of the Kelvin-Plank statement.

Perpetual-Motion Machines

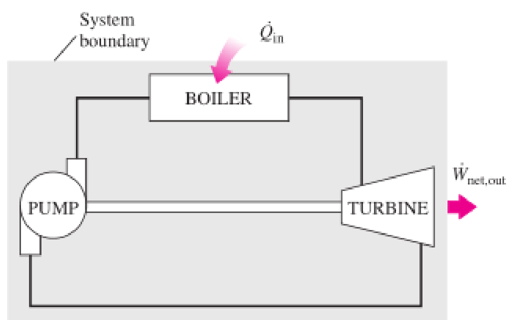
Any device that violates either the first or the second law of thermodynamics is called a perpetual-motion machine.

A device that violates the first law of thermodynamics (by creating energy) is called a perpetual-motion machine of the first kind (PMM1).

A device that violates the second law of thermodynamics is called a perpetual-motion machine of the second kind (PMM2).



PMM1



PMM2

PMM1 creates energy without any energy input and PMM2 operates in a cycle and produces positive net work output without transferring energy to a low temperature reservoir.