Limitations of First Law

First law is a statement of conservation of energy principle. Satisfaction of first law alone does not ensure that the process will actually take place.

Examples:

1. A cup of hot coffee left in a cooler room eventually cools off. The reverse of this process- coffee getting hotter as a result of heat transfer from a cooler room does not take place.
2. Consider heating of a room 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.

Conclusion:

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.

Second law not only identifies the direction of process, it also asserts that energy has quality as well as quantity.

Thermal Reservoir

A thermal reservoir is a large system (very high mass x specific heat value) from which a quantity of energy can be absorbed or added as heat without changing its temperature. The atmosphere and sea are examples of thermal reservoirs.

Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as a thermal reservoir.

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.

Heat Engine

It is a cyclically operating device which absorbs energy as heat from a high temperature reservoir, converts part of the energy into work and rejects the rest of the energy as heat to a thermal reservoir at low temperature.

The working fluid is a substance, which absorbs energy as heat from a source, and rejects energy as heat to a sink.

Thermal Power Plant
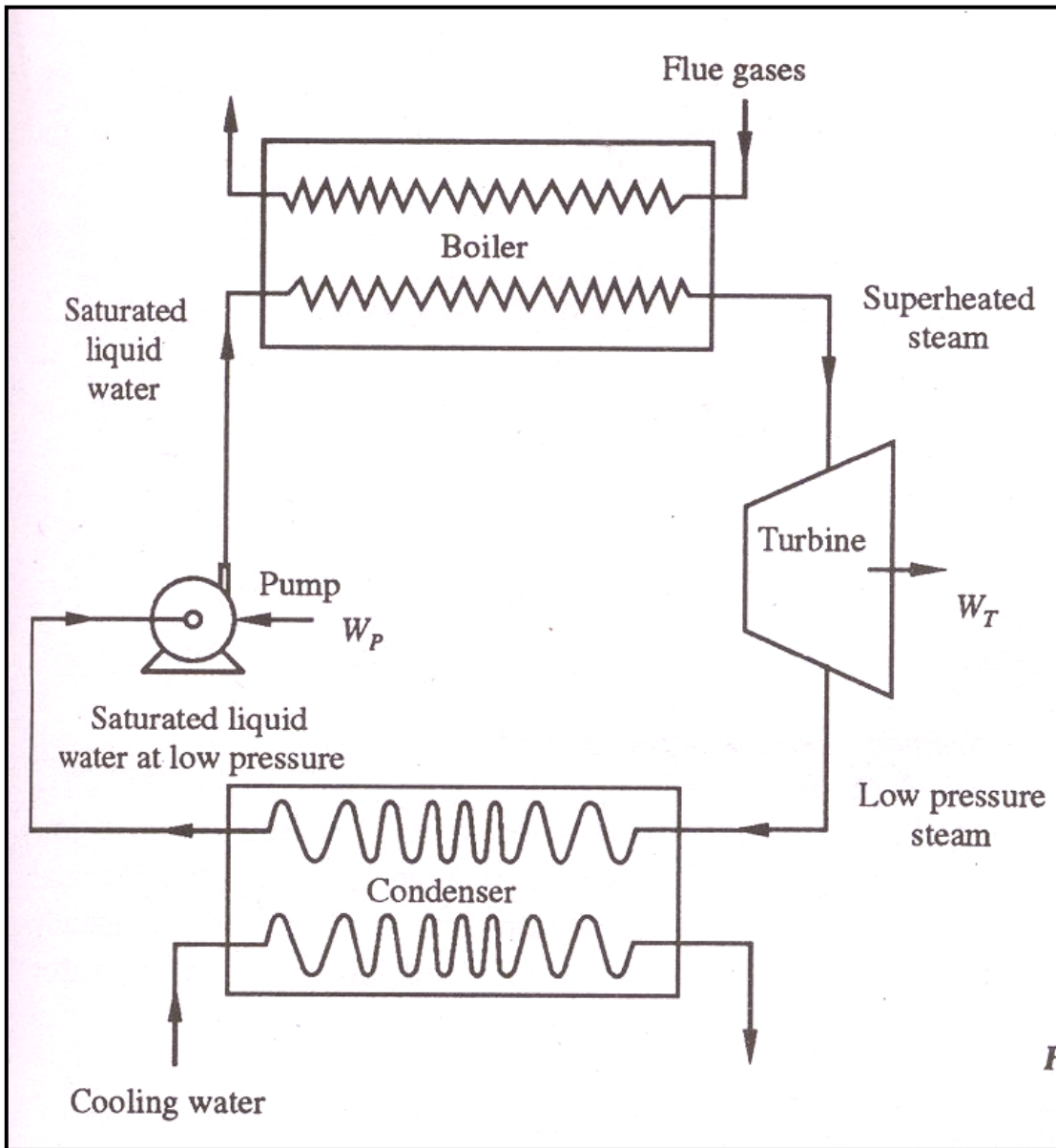
Working Fluid ------- Water

Q_1 – Heat received from hot gases

W_T – Shaft work by turbine

Q_2 – Heat rejected to cooling water in condenser
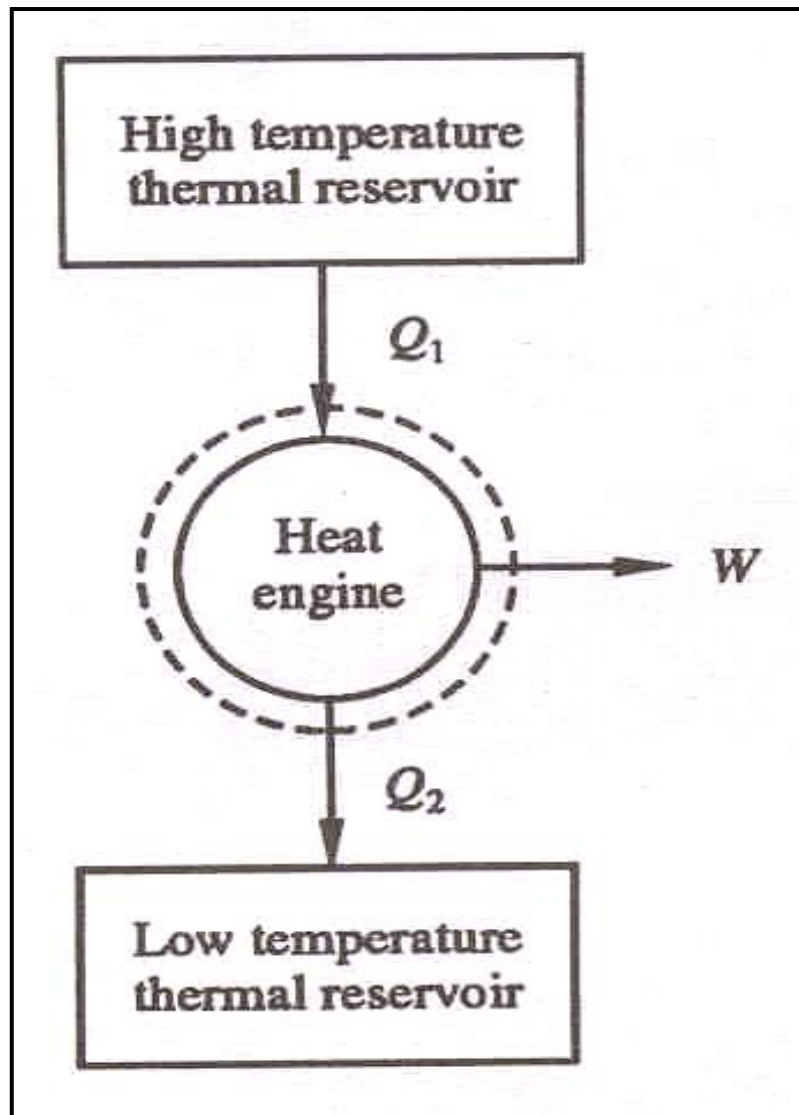
W_P – Work done on the pump
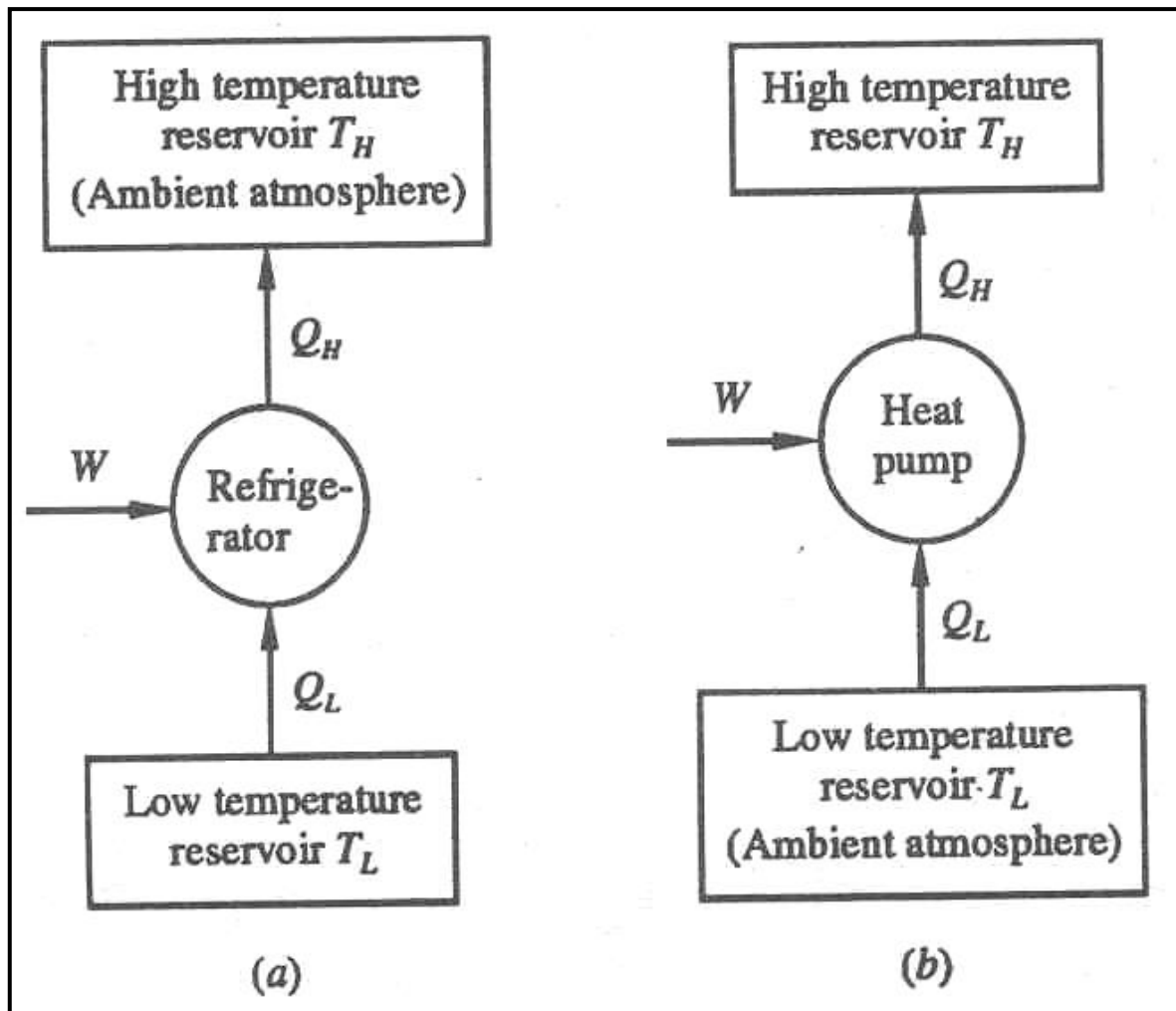
$W_{net} = W_T - W_P$
$W = Q_1 - Q_2$

Thermal Efficiency,

$$\eta = \frac{W_{net}}{Q_1} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Schematic representation of Heat Engine

Schematic representation of Refrigerator and Heat pump.

(a)

(b)

Q$_L$ – Heat absorbed from low temperature thermal reservoir

Q$_H$ – Heat rejected to a high temperature thermal reservoir when work (W) is done on it.

$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

In a reversible, isothermal expansion of an ideal gas, all the energy absorbed as heat by the system is converted completely into work. However this cannot produce work continuously (not a cycle).

Single reservoir heat engine (1 T engine) is not possible.

Second Law of Thermodynamics

Kelvin-Planck Statement: - It is impossible to devise a cyclically operating device, which produces no other effect than the extraction of heat from a single thermal reservoir and delivers an equivalent amount of work.

Heat engine with single thermal reservoir is not possible.

For a 1-T engine the thermal efficiency $\eta=W/Q=1$. No heat engine can have efficiency equal to unity.
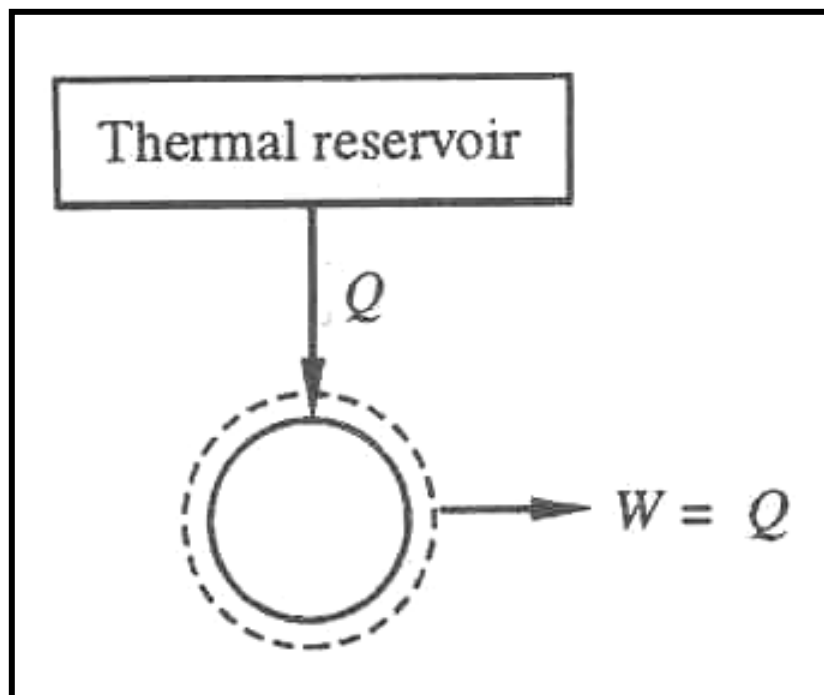
Clausius Statement: - It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body.

Equivalence of the two statements

(a)   (b)

(a)   (b)
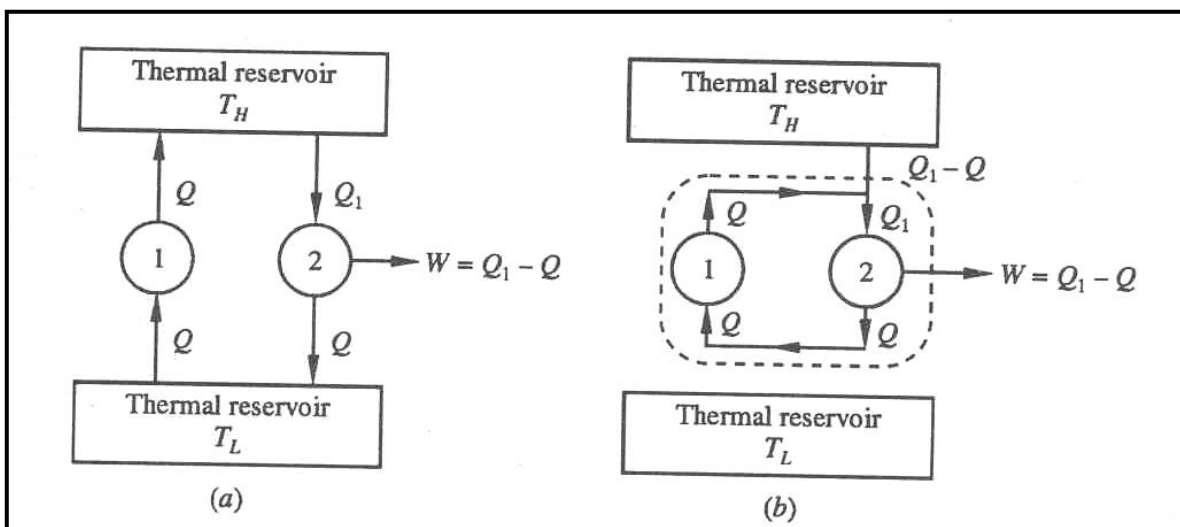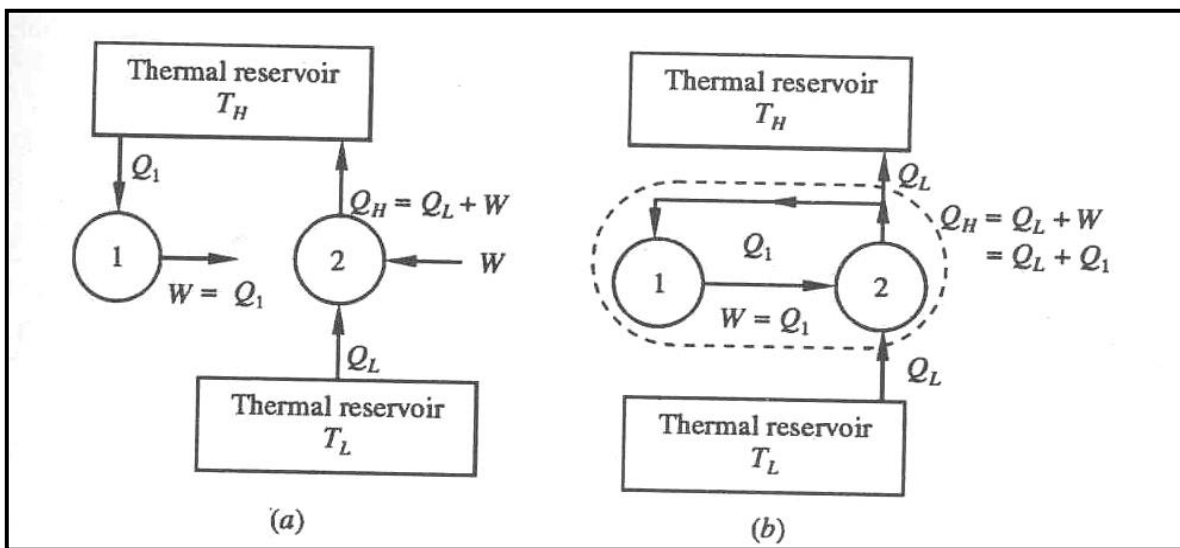
To prove that violation of the Kelvin-Planck Statement leads to a violation of the Clausius Statement, let us assume that Kelvin-Planck statement is incorrect.

Consider a cyclically working device 1, which absorbs energy Q_1 as heat from a thermal reservoir at T_H. Equivalent amount of work $W(W=Q_1)$ is performed.

Consider another device 2 operating as a cycle, which absorbs energy Q_L as heat from a low temperature thermal reservoir at T_L and rejects energy Q_H $(Q_H=Q_L+W)$. Such a device does not violate Clausius statement.

If the two devices are now combined, the combined device (enclosed by the dotted boundary) transfers heat Q_L from the low temperature reservoir at T_L to a high temperature reservoir at T_H with out receiving any aid from an external agent, which is the violation of the Clausius statement.

Likewise let us assume that the Clausius statement is incorrect. So we have a device 1, cyclically working transferring heat Q from a low temperature reservoir at T_L to a high temperature thermal reservoir at T_H . Consider another device 2, which absorbs heat Q_1 from a high temperature reservoir at T_H does work W and rejects energy Q as heat tot the low temperature reservoir at T_L as shown in figure.

If the two devices are combined (shown in figure by a dotted enclosure), then the combined device receives energy (Q_1-Q) as heat from a thermal reservoir and delivers equivalent work $(W=Q_1-Q)$ in violation of the Kelvin-Planck statement.

Therefore violation of Clausius statement leads to the violation of the Kelvin-Planck statement. Hence, these two statements are equivalent.

Perpetual Motion Machines

A device that violates the First law of thermodynamics (by creating energy) is called a Perpetual Motion Machine of the first kind.

A device that violates the Second law of thermodynamics is called a Perpetual Motion Machine of the Second kind.
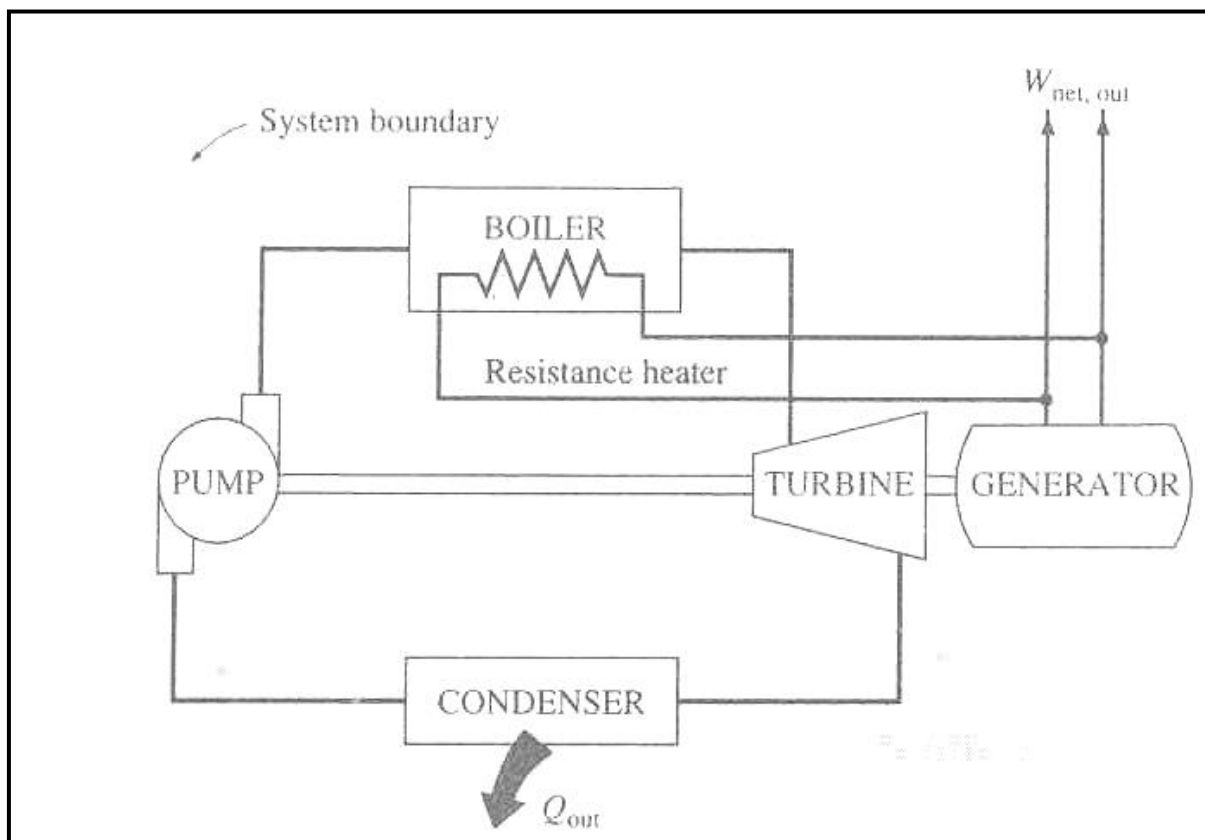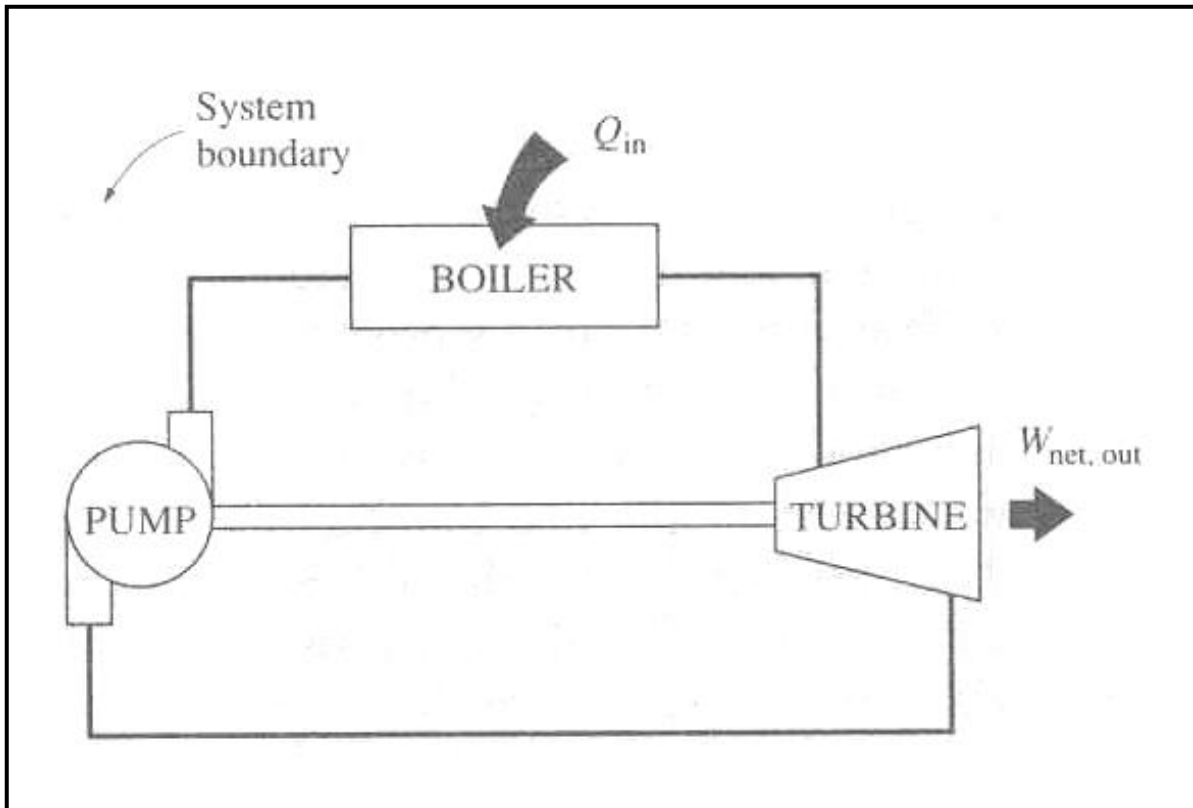
The first device supplies continuously energy with out receiving it. So this is a system creating energy and therefore violating the first law.

The second device exchanges heat with a single reservoir and thus a net amount of work. This need not violate the first law, but violates the second law and therefore will not work.

Reversible and Irreversible Processes

A process is said to be reversible if both the system and the surroundings can be restored to their respective initial states, by reversing the direction of the process. A reversible process is a process that can be reversed without leaving a trace on the surroundings. Processes that are not reversible are called Irreversible processes.

Irreversibilities

The factors that cause a process to be irreversible are called irreversibilities. Examples:

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions
6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

Carnot Cycle