3 SECOND LAW OF THERMODYNAMICS

3.0 INTRODUCTION

The Second Law of Thermodynamics together with the First Law constitutes the fundamental laws governing thermodynamics processes. The First Law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to quality. The First Law provides us with guidelines for energy conversion processes; it places no restriction on the direction of a process but in practice satisfying the first law does not ensure that a process will actually take place. They inadequacy of the first law to identify whether a process can take place is remedied by introducing the second law of thermodynamics. All that the First Law states is that work cannot be produced during a cycle without some supply of heat, i.e. t*hat a perpetual- motion machine of the first kind is impossible*. The second law is an expression of the fact that some heat must always be rejected during a cycle, and therefore that the cycle efficiency is always less than unity.

The objective of this chapter is to motivate the need for the usefulness of the second law, which asserts that processes occur in a certain direction and that energy has quality as well as quantity. In the presentation of the contents of this chapter, the thermal energy reservoirs, reversible and irreversible process, heat engines, refrigerators and heat pumps are introduced first. A number of deductions called corollaries of the second law are also considered and are followed by a discussion of perpetual-motion machines and the concept of quality of energy.

3.1 DEFINITIONS

Before stating the Second Law it is important to clarify the concept of the thermal energy reservoir and bring into perspective the meaning and working principles of heat engines, refrigerators and heat pumps.

3.1.1 Thermal Energy Reservoirs (Heat Rservoirs)

A *heat reservoir (thermal energy reservoir* is a closed system whose temperature is not affected by the flow of heat across as boundaries. The heat reservoir is hypothetical body with a relatively large thermal energy (heat) capacity that can supply or absorb finite amounts of heat without undergoing any change in temperature. The only significant property of a heat reservoir is that its temperature must remain constant so that any processes that take place in the reservoir must be reversible.

Examples of heat reservoirs are atmosphere, industrial furnace, air in a room in the analysis of heat dissipation from a TV set in the room, oceans, lakes, and rivers. A two-phase system (a mixture of solid and its liquid or a liquid and its vapour) can be modelled as a reservoir since it cannot absorb and release large quantities of heat while remaining at a constant 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*. Thermal energy reservoirs are often referred to as heat reservoirs since they supply or absorb energy in the form of heat.

3.1.2 A heat engine <u>is a closed system which operates in a cycle and produces a net quantity of work from a supply of heat</u>. The schematic representation of a heat engine operating between two heat reservoirs, a heat source and a heat sink, is shown in Fig. 3.1a

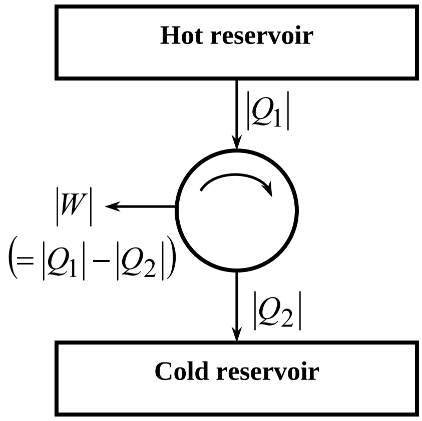


Fig.3.1a Schematic representation of heat engine

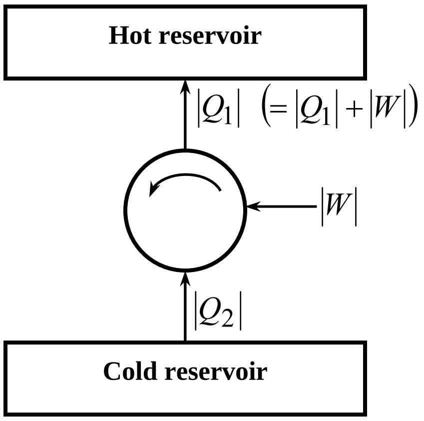


Fig.3.1b Heat Pump or refrigerator

Heat engines differ considerably from one another, but all can be characterised by the following: (Fig.3.2)

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 rotating shaft)
3. They reject the remaining waste heat into a low-temperature sink (atmosphere, rivers, etc.) thus causing thermal pollution.
4. They operate in a cycle.

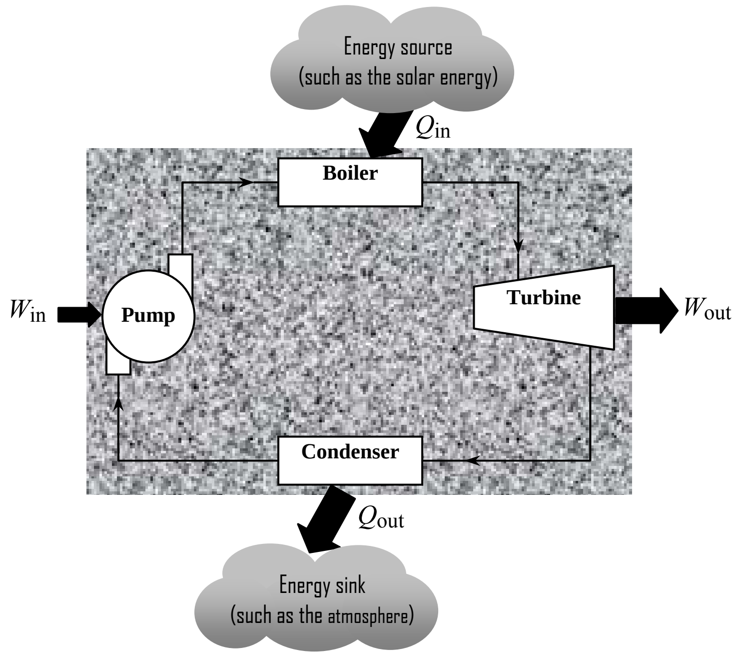


Fig.3.2 Schematic of a steam power plant

From the first law of thermodynamics, $\boxed{Q_{net} + W_{net} = 0 \Rightarrow Q_{in} + Q_{out} + W_{in} + W_{out} = 0}$

3.1.3 Thermal Efficiency of a heat engine

The fraction of the heat input that is covered to net work is a measure of the performance of a heat engine and is called the thermal efficiency η_{th}.

Performance or efficiency, in general, can be expressed in terms of the desired output and the required input as:

$$\text{Performance} = \frac{\text{Desired output}}{\text{Required input}}$$

For a hat engine the desired output is the net work output, and the required input is the amount of heat supplied to the working fluid. Steam power plant is a net work producing plant, and from the sign convention adopted it is a negative quantity and therefore the thermal efficiency of a heat engine can be expressed as

$$\eta_{th} = \frac{\left|W_{net,out}\right|}{Q_{in}} = \frac{\left|Q_{in}\right| - \left|Q_{out}\right|}{\left|Q_{in}\right|} = 1 - \frac{\left|Q_{out}\right|}{\left|Q_{in}\right|} \qquad (3.1)$$

The quantities $\left|Q_{in}\right|$ and $\left|Q_{out}\right|$ may be regarded as the heat supplied and rejected, respectively. The First Law of thermodynamics says that the net work can never be greater than the heat supplied, while the Second Law goes further and states that it must always be less. If $\left|W_{net,out}\right| < \left|Q_{in}\right|$, then it follows from equation (3.1) that $\left|Q_{out}\right|$ must have some definite value.

3.1.4 Refrigerator and heat pump

A refrigerator is a reversed heat engine. Thus, it is a closed system which operates in a cycle such that it extracts heat from a low-temperature reservoir and rejects heat to a high-temperature reservoir, while a net work is done one the system by the surroundings.

The refrigerator, therefore, receives a net quantity of work from the surroundings and rejects a net quantity of heat to the surroundings. Again, in accordance with the First Law, the magnitudes quantities of net heat and net work are equal. It is known that a refrigerator extracts heat from a cold space and, therefore, some heat is absorbed by the refrigerating system. A schematic representation of a refrigerator operating between two heat reservoirs, a heat source and heat sink, is shown in fig. 3.1b.

<u>For refrigeration cycles and heat pump</u>, Q_{in} is transferred by heat into the system undergoing the cycle from a cold body, and Q_{out} is the energy discharged by heat transfer from the system to the hot body. To accomplish these energy transfers requires a net work input, W_{cycle}. The performance of a refrigeration cycle is described as the ratio of the amount of *energy received by the system* undergoing the cycle from the cold body, Q_{in}, to the net work transfer of energy into the system to

accomplish this effect, W_{cycle}. This parameter is called the coefficient of performance and is given by

$$\boxed{COP_R = \frac{Q_{in}}{W_{cycle}}} \text{(Refrigeration cycle)} \qquad (3.2)$$

For household refrigerator, Q_{out} is discharged to space in which the refrigerator is located. W_{cycle} is usually provided in the form of electricity to run the motor that drives the refrigerator.
For a heat pump the coefficient of performance is

$$\boxed{COP_{HP} = \frac{Q_{out}}{W_{cycle}}} \text{(heat pump)} \qquad (3.3)$$

From the First Law for a closed cycle, Q_{in} + Q_{out} + W_{cycle} = 0. Dividing through expression and rearranging the term we obtain:

$$\boxed{COP_{HP} = COP_R + 0} \qquad (3.4)$$

3.2 The Second Law of Thermodynamics

The law be stated as follows: It is impossible to construct a system, which will operate in a thermodynamic cycle, extract heat from a single reservoir, and do an equivalent amount of work on the surroundings.

This is often referred to as the Kelvin-Planck's statement of the Second Law, which is related to heat engines.

If energy is to be supplied to a system in the form of heat, the system must be in contact with a reservoir at a temperature higher than that of the system at some point in the cycle. Similarly, if heat is to be rejected, the system must at some time be in contact with a reservoir of lower temperature than the system. Thus the Second Law implies that if a system is to undergo a cycle and produce work, it must operate between at least two reservoirs of different temperature, however small this temperature may be. A machine which will produce work continuously, while exchanging heat with only a single reservoir, is known as a *perpetual motion machine of the second kind*; and such a machine contradicts the Second Law.

The Kelvin-Planck statement can also be expressed as *no heat engine can have a thermal efficiency of 100%* (**See Fig. 3.3**) or as *for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.*

It is now possible to see why an engine using the ocean as the source of heat cannot drive a ship, or why a power station could not be run using the atmosphere as the source of heat. There is nothing in the First law to say that these desirable projects are not feasible. Neither project will contradict the principle of conservation of energy; their impossibility is a consequence of the Second Law. They are impossible because there is no natural infinite sink of heat at a lower temperature than the atmosphere or ocean, and they would therefore be perpetual motion machines of the second kind. Another example of perpetual-motion machine of the second kind is a car engine without neither an exhaust nor a cooling system.

It should be noted that the Second Law does not imply that work cannot be continuously and completely converted into heat. Indeed, any process involving friction achieves this without the need for the system to operate in a cycle. An important consequence of the Second Law is, therefore, that *work is a more valuable energy transfer than heat*; heat can never be transformed continuously and completely into work, whereas work can always be transformed continuously and completely into heat and, if properly used, can even result in a supply of heat which is greater than the work expended.

The following statement summarise the more obvious consequences of the Second Law:

a. If a system is taken through a cycle and does a net amount of work on the surroundings, it must be exchanging heat with at least two reservoirs at different temperatures.
b. If a system is taken through a cycle while, exchanging heat with only one reservoir, the work transfer must either be zero or positive.
c. Since heat can never be converted continuously and completely into work, whereas work can always be converted continuously and completely into heat, work is more valuable form energy transfer than heat.

3.3 The Clausius Statement of the Second Law

This statement of the Second Law, which is related to refrigerators and heat pumps

> *Corollary 1: it is impossible to construct a system, which will operate in a cycle and transfer heat from a cooler to a hotter body without work being done on the system by the surroundings.*

Proof: We assume the converse is true. The system could be represented by a heat pump for which $|W|$=0, as in Fig. 3.4. If it takes $|Q|$ units of heat from the cold reservoir, it must deliver $|Q|$ units to the hot reservoir to satisfy the First Law. A heat engine cold also be operated between the two reservoirs, let it be such as size that it delivers $|Q|$ units of heat to a cold reservoir while performing $|W|$ units of work. Then the First Law states that the engine must be supplied with $|W|+|Q|$ units of heat from the hot reservoir. The combined plant represents a heat engine extracting $\left(|W|+|Q|-|Q|=|W|\right)$units of heat from a reservoir, and delivering an equivalent amount of work. This is impossible according to the Second law.

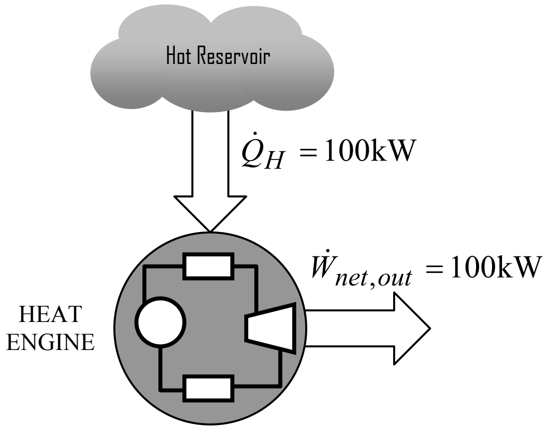


Fig.3.3 A heat engine that violates Kelvin-Planck statement

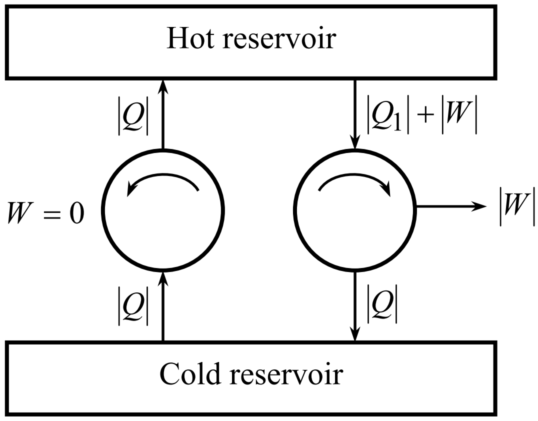


Fig.3.4 Can a heat pump operate without a work input

3.4 Other Corollaries

Reversible engines operating between only two temperature reservoirs

> *Corollary 2: it is impossible to construct an engine operating between only two reservoirs, which will have a higher efficiency than a reversible engine operating between the same two reservoirs.*

Proof: Assume the converse is true. Let X be such an engine, having efficiency η_X. Let it receive heat Q_1 from the source, do work W_X, and reject () to the sink. Then it is assumed that $\eta_X > \eta_R$ where η_R is the efficiency of a reversible engine R operating between the same two reservoirs (See Fig. 3.5). If the reversible engine also receives heat Q_1 from the source, it will do work W_R such that $W_R < W_X$ and the heat rejected will be $(Q_1 - W_R)$ which is greater $(Q_1 - W_X)$.

Let the reversible engine be reversed and act as a heat pump (See Fig. 3.5b). It now receives heat $(Q_1 - W_X)$ from the low-temperature reservoir, receives work W_R from the surroundings, and rejects heat Q_1 to the high-temperature reservoir. If the engine X is coupled to the heat pumps, and the latter feeds heat Q_1 directly into the former, the combined plant represents a heat engine receiving heat $(Q_1 - W_R) - (Q_1 - W_X) = (W_X < W_R)$ from the surroundings, and delivering an equivalent amount of work. According to the Second law this is impossible, and the assumption that $\eta_X > \eta_R$ cannot be true. Consequently, the original proposition must be true.

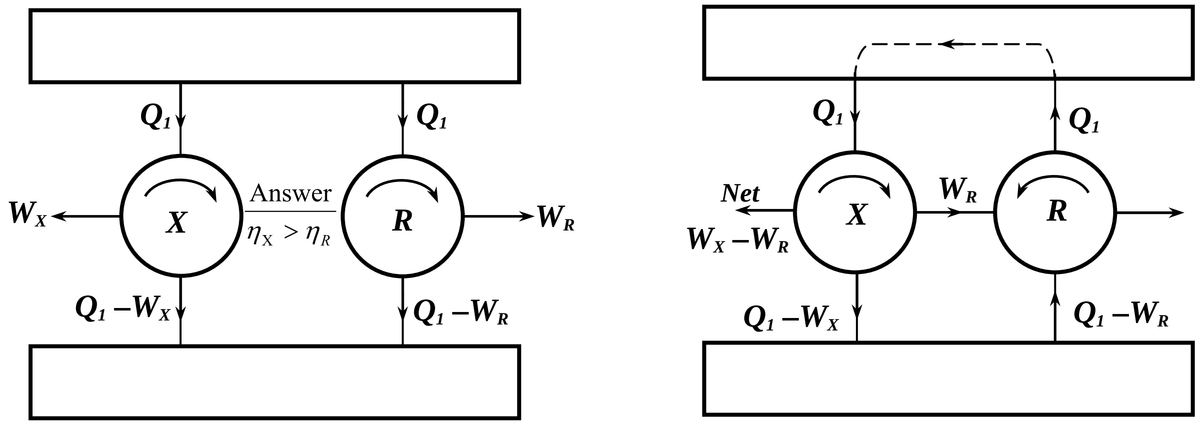


Fig.3.5 Can an engine have a higher efficiency than its reversible equivalent?

Corollary 3: All reversible engines operating between the same two reservoirs have the same efficiency

Once the second corollary is proved there is no need for the proof of the third. The Corollaries 2 and 3 are referred to as the Carnot Principles.

Thermodynamic temperature scale

Corollary 4: A scale of temperature can be defined which is independent of any particular thermometric substance, and which provides an absolute zero of temperature

The scale is based on the fact that <u>the efficiency of the reversible engine depends solely on the temperatures of the reservoirs with which the engine exchanges heat</u>. By definition the only significant property of a heat reservoir is temperature, not its substance. Therefore, for any reversible engine operating between two reservoirs the thermal efficiency of the engine must be a function of the temperature of the reservoirs.

With the aid of Fig.6 and equ.(3.1), the efficiency of a heat engine is given as

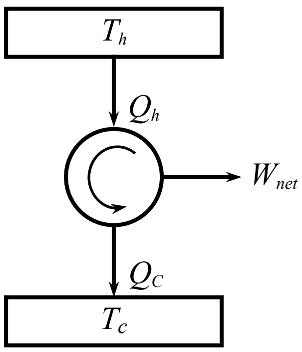


Fig. 3.6

$$\eta_{th} = \frac{|Q_h| - |Q_C|}{|Q_h|} = 1 - \frac{|Q_C|}{|Q_h|} \qquad (3.5)$$

It follows that $|Q_C|/|Q_h|$ must be a function of only the temperatures of the hot and cold reservoirs, T_h and T_C, i.e.

$$\frac{|Q_C|}{|Q_h|} = f(T_h, T_C) \tag{3.6}$$

The simplest relationship chosen for the definition of the absolute temperature scale is

$$\frac{|Q_C|}{|Q_h|} = \frac{T_C}{T_h} \qquad T_h = T_C \bullet \frac{|Q_h|}{|Q_C|} \tag{3.7}$$

This is called the Kelvin scale and the temperatures on this scale are called absolute temperatures. On this scale temperatures vary between zero and infinity. The triple point of water is assigned the temperature of 273.16 K. The absolute temperature of any reservoir is given by

$$T = 273.16\frac{Q}{Q_{tp}} \tag{3.8}$$

where Q and Q_{tp} are the heat transfers from a reversible engine operating between the reservoir and another reservoir at the triple point of water. Note when $T = 0$ then $Q = 0$. A reversible engine operating between any reservoir and another at absolute zero must convert all heat supplied into work since zero heat would be rejected to the reservoir at absolute zero. The Second Law says such a system is impossible. Therefore, the temperature absolute is unattainable, it can be approached but never realised.

Hence, for reversible engine $\dfrac{Q_{C,rev}}{Q_{h,rev}} = \dfrac{T_C}{T_h}$

The efficiency of a reversible heat engine (Carnot Cycle) is given by

$$\boxed{\eta_{th,rev} = 1 - \frac{T_C}{T_h}} \tag{3.9}$$

Note that for a given sink temperature, as the source temperature increases the efficiency of the engine increases. This shows that energy has quality and the higher the temperature the more heat can be converted to work.

Note that

$$\eta_{th} \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine} \end{cases} \tag{3.10}$$

It can be inferred from equation (3.9) that the efficiency of actual cycles can be maximised by supplying heat to the engine at the highest possible temperature, and rejecting heat from the engine at the lowest possible temperature.

Engines operating between more than two reservoirs

In many practical cycles, the heat is received and rejected during processes which involve a continuous change in the temperature of the fluid. These cycles can still be considered reversible if the source and sink are each assumed to consist of an infinite number of reservoirs differing infinitesimally from one another in temperature. At any instant during a heating and cooling process, heat must be exchanged between the system and a source or sink which differs infinitesimally in temperature from the fluid in the system.

We note that the efficiency with which a given quantity of heat can be converted into work in a reversible engine operating reservoirs at T_1 and T_2 is given by $(T_1 - T_2)/T_1$ or $(1 - T_2/T_1)$. Let T_1' and T_2' be maximum and minimum temperatures of the working fluid in a reversible engine operating between more than two reservoirs. Only a fraction of the heat can be supplied at T_1' and only a fraction of the heat can be rejected at T_2'. The remaining part of the heat supplied must be converted into work with an efficiency less than $(1 - T_2'/T_1')$, because the temperatures of the remaining sources are less than T_1' and the temperatures of the remaining sinks are greater than T_2'. Thus the efficiency with which the total heat received is converted into work must be less than $(T_1' - T_2')/T_1'$. This result is summarised as the following corollary:

Corollary 5: The efficiency of any reversible engine operating between more than two reservoirs must be less than that of a reversible engine operating between two reservoirs which have temperatures equal to the highest and lowest temperatures of the fluid in the original engine.

The Clausius Inequality

Corollary 6: Whenever a system undergoes a cycle. $\oint(\delta Q/T)$ *is zero if the cycle is reversible and negative if irreversible, i.e. in general* $\oint(\delta Q/T) \leq 0$

Consequences of the Second Law for non-flow processes

Corollary 7: There exists is property of a closed system such that a change in its value is equal to $\int_1^2 dQ/T$ *for any reversible process undergone by the system between states 1 and 2.*

This property is called entropy and therefore $\int_1^2 \left(\frac{dQ}{T}\right)_{rev} = S_2 - S_1$. Entropy is an exclusive property.

Corollary 8: The entropy of any closed system, which is thermally isolated from the surroundings, either increases or, if the process undergone by the system is reversible, remains constant.

Entropy of isolated closed system never decreases. In the absence of heat transfer, the entropy change is due to irreversible only, and these effect is always to increase entropy. (pump, turbine work)

NOTES

1. None that any process that does not produce a net entropy is reversible. During a heat transfer process, the net disorder (entropy) increases. That is the increase in the disorder of the cold body will be more than the decrease in the disorder of the hot body.

2. The quantity of energy is always preserved during an actual process (the first law) but the quality is bound to decrease (the second law). This decrease in quality is always accompanied by an increase in entropy. As an example, consider the transfer of 10 *kJ* of energy as heat from a hot medium to a cold one. At the end of the process, we still have the 10 *kJ* of energy, but at lower temperature and thus at a lower quality.

3. It is possible to increase entropy but is not possible to destroy it.

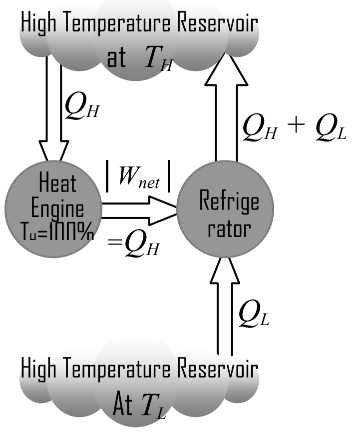
4. Heat transfer, irreversibilities and entropy transport with mass cause entropy of a control volume to change.

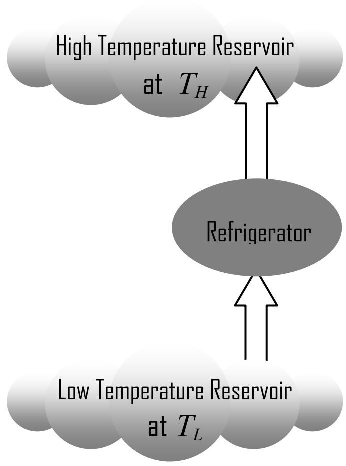
5. There is no entropy transfer associated with energy transfer as work.

3.5 Equivalence of the Kelvin-Planck and the Clausius Statements of the Second Law

Any device that violates the Kelvin-Planck statement violates the Clausius statement, and vice versa. This can be demonstrated as follows:

Consider the heat-engine-refrigerator combination shown in Fig. 3.7a operating between the same two reservoirs. The heat engine is assumed to have, in violation to the Kelvin-Planck statement an efficiency of 10%, and therefore it converts all the heat Q_H it receives to work W. This work is then supplied to a refrigerator that removes heat in the amount of Q_L from the low-temperature reservoir and rejects heat in the amount of $Q_H + Q_L$ to the high-temperature reservoir. During this process, the high-temperature reservoir receives and net amount of heat Q_L (the difference of $Q_H + Q_L$ and Q_H). Thus, the combination of these two devices can be viewed as a refrigerator, as shown in Fig. 3.7b, that transfers heat in an amount of Q_L from a cooler body to a warmer one without requiring any input from outside. This clearly violates the Clausius statement. Therefore, a violation of the Kelvin-Planck statement results in the violation of the Clausius statement.





3.6 Perpetual-motion machines

Any device that violates either the First Law or the Second Law of Thermodynamics is called a perpetual-motion machine (PMM).

A device that violates the First Law of Thermodynamics (by *creating* energy) is called a ***Perpetual-motion machine of the first kind (PMM1)*** and a device that violates the Second Law of Thermodynamics is called a ***Perpetual-motion machine of the second kind (PMM2)***.

Examples of PMM1 and PMM2 are shown in Fig.3.8a and Fig.3.8b, respectively.

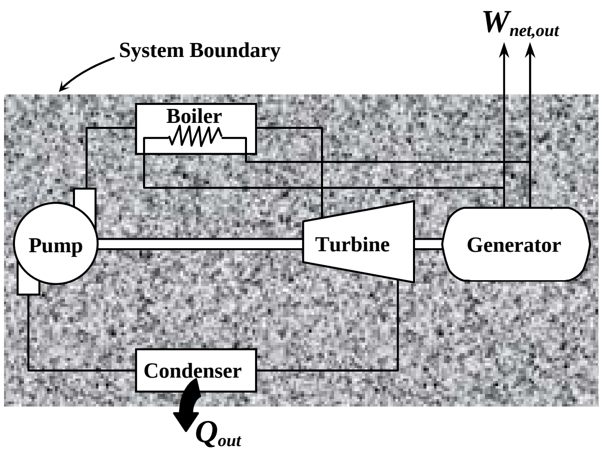


Fig. 3.8a PMM1

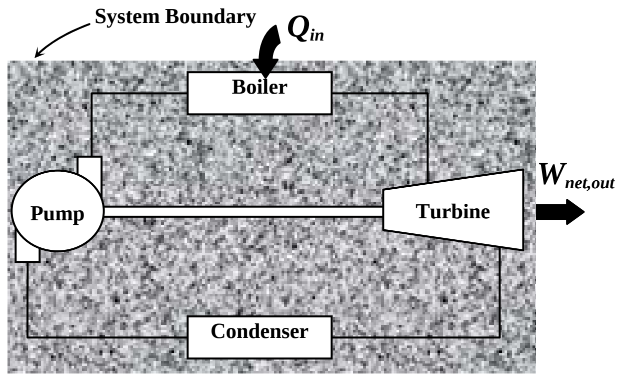


Fig. 3.8b PMM2

3.7 The quality of Energy

Let us consider a heat engine that receives heat from a source at 1000 *K* and rejects heat to a sink at 300 *K*. This heat engines is able to convert 70% of the heat supplied to work and rejects 30% to a sink. Let us now examine how the thermal efficiency varies with the source temperatures of 800 *K*, 700 *K*, 600 *K*, 500 *K*, and 400 *K* when the sink temperature is held constant.

The thermal efficiency of a Carnot heat engine that rejects heat to a sink at 300 *K* is evaluated at various source temperatures using Eq. 3.9. if can be shown that he thermal efficiency decreases with as the source temperature decreases. When the source temperature is 400 *K* the efficiency drop to 25%.

These efficiency values show that energy has quality as well as quantity. It can be shown from the thermal efficiency values that *more of the high-temperature thermal energy can be converted to work.* Therefore, *the higher the temperature, the higher the quality of the energy.*

TUTORIAL SET 3

1 An inventor claims to have developed a car that runs on water instead of gasoline. What is your response to this claim?

2 Describe an imaginary process satisfies the first law but violates the second law of thermodynamics.

3 Describe an imaginary process that satisfies the second law but violates the first law.

4 Describe an imaginary process that violates both the first and the second laws of thermodynamics.

5 Does a heat engine that has a thermal efficiency of 100% necessarily violate (a) the first law and (b) the second law of thermodynamics.

6 In absence of any friction and other irreversibilities, can a heat engine have an efficiency of 100%? Explain.

7 Are the efficiencies of all the work producing devices, including hydroelectric power plants, limited by Kelvin-Planck statement of the second law?

8 A cold canned drink is left in a warmer room where its temperature rises as result of heat transfer. Is this a reversible process? Explain.

9 A hot baked potato is left on a table where it cools to the room temperature. Is this a reversible or irreversible process?

10 Why are engineers interested in reversible process even though they can never be achieved?

11 A refrigerator has a COP of. 1.5. That is, the refrigerator receives 1.6 *KWh* of energy from the refrigerated space for each 1.5 *kWh* of electricity it consumes. Is this a violation of the first law of thermodynamics? Explain.

12 A household refrigerator with a COP of 1.8 removes heat from the refrigerated space at a rate of 90 *kJ*/min. Determine

a) the electric power consumed by the refrigerator and
b) the rate of heat transfer to the kitchen air [a.0.83 *kW,* b.140 *kJ*/min]

13 An air conditioner removes heat steadily from a house at a rate of 750 *kJ*/min while drawing electric power at a rate of 5 *kW*. Determine

a) the COP of this air conditioner and
b) the rate of heat transfer to the outside air [a.2.08 , b.1110 *kJ*/min]

14 Determine the COP of a heat pump that supplies energy to a house at a rate of 8000 *kJ*/*h* for each *kW* of electric it draws. Also determine the rate of energy absorption from the outside air. [2.22, 4400 *kJ*/*h*]

15 A Carnot heat engine receives 500 *kJ* of heat from a source of unknown temperature and rejects 200 *kJ* of it to a sink at 17°*C*. Determine

a) the temperature of the source and
b) the thermal efficiency of the heat engine

16 An air-conditioning system is used to maintain a house at a constant temperature of 20°*C*. The house is gaining heat from outdoors at rate of 20,000 *kJ/h*, and the heat generated in the house from the people, lights, and appliances amounts to 8000 *kJ/h*. For a COP of 2.5, determine the required power input to this air-conditioning system.

17 A power cycle operating between two reservoirs receives energy Q_H by heat transfer from a hot reservoir at T_H = 2000*K* and rejects energy Q_C by heat transfer to a cold reservoir at T_C = 400*K*. For each of the following cases, determine whether the cycle operates reversibly, irreversibly, or is impossible.

a) $Q_H = 1000\ kJ$, $\left|W_{cycle}\right| = 850\ kJ$
b) $Q_H = 2000\ kJ$, $\left|Q_C\right| = 400\ kJ$
c) $\left|W_{cycle}\right| = 1600\ kJ$, $\left|Q_C\right| = 500\ kJ$
d) $Q_H = 1000\ kJ$, $\eta = 30\%$

18 The data listed below are claimed for a power cycle operating between reservoirs at 727 and 127°*C*. For each case, determine if any principles of thermodynamics would be violated.

19 A refrigeration cycle operating between two reservoirs receives energy Q_C from a cold reservoir at T_C = 250 *K* and rejects energy Q_H to a hot reservoir at T_H = 300 *K* for each of the following cases, determine whether the cycle operates reversibly, irreversibly, or is impossible.

a) $\left|Q_C\right| = 1000kJ,\ \left|W_{cycle}\right| = 400kJ$
b) $\left|Q_C\right| = 2000kJ,\ \left|W_{cycle}\right| = 2200kJ$
c) $\left|Q_H\right| = 3000kJ,\ \left|W_{cycle}\right| = 500kJ$
d) $\left|W_{cycle}\right| = 400kJ,\ \mathrm{COP_R} = 6$

20 A reversible engine employs a cycle consisting of three different processes which constitute a triangle such that

$$T_1 = T_3 = 323\ K; \qquad T_2 = 573\ K; \qquad s_2 = s_3$$

Determine the efficiency of an engine operating on this cycle and compare its efficiency with that for a Carnot engine operating between the highest and the lowest temperatures.