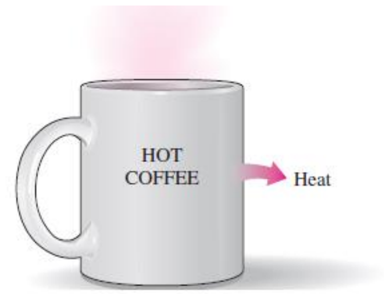
SECOND LAW OF THERMODYNAMICS

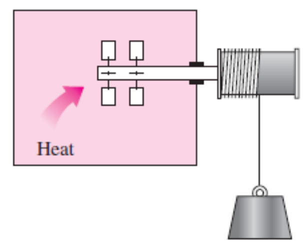
COMMON EXPERIENCE

1.It is common experience that a cup of hot coffee left in a cooler room eventually cools off . This process satisfies the first law of thermodynamics since the amount of energy lost by the coffee is equal to the amount gained by the surrounding air. Now let us consider the reverse process—the hot coffee getting even hotter in a cooler room as a result of heat transfer from the room air. We all know that this process never takes place. Yet, doing so would not violate the first law as long as the amount of energy lost by the air is equal to the amount gained by the coffee.



A cup of hot coffee does not get hotter in a cooler room.

2. Finally, consider a paddle-wheel mechanism that is operated by the fall of a mass. The paddle wheel rotates as the mass falls and stirs a fluid within an insulated container. As a result, the potential energy of the mass decreases, and the internal energy of the fluid increases in accordance with the conservation of energy principle. However, the reverse process, raising the mass by transferring heat from the fluid to the paddle wheel, does not occur in nature, although doing so would not violate the first law of thermodynamics.



Transferring heat to a paddle wheel will not cause it to rotate.

It is clear from these arguments that processes proceed in a certain direction and not in the reverse direction. The first law places no restriction on the direction of a process, but satisfying the first law does not ensure that the process can actually occur. This inadequacy of the first law to identify whether a process can take place is remedied by introducing another general principle, the second law of thermodynamics.

USES OF 2ND LAW OF THERMODYNAMICS

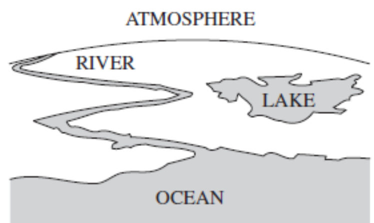
1. Predicting the direction of processes.
2. Establishing conditions for equilibrium.
3. Determining the best *theoretical* performance of engineering devices like heat engines, refrigerators and other devices as well as predicting the degree of completion of chemical reactions.
4. It provides the necessary means to determine the quality as well as degree of degradation during a process.

   Additional uses of the second law include its roles in
5. Defining a temperature scale independent of the properties of any thermometric substance.
6. developing means for evaluating properties such as u and h in terms of properties that are more readily obtained experimentally

THERMAL ENERGY RESERVOIRS

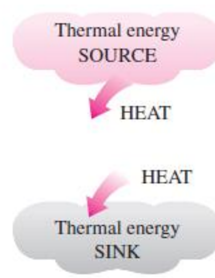
It is defined as large hypothetical body of infinite thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. Such a body is called a **thermal energy reservoir.**

eg: In practice, large bodies of water such as oceans, lakes, and rivers as well as the atmospheric air can be modeled accurately as thermal energy reservoirs because of their large thermal energy storage capabilities or thermal masses.



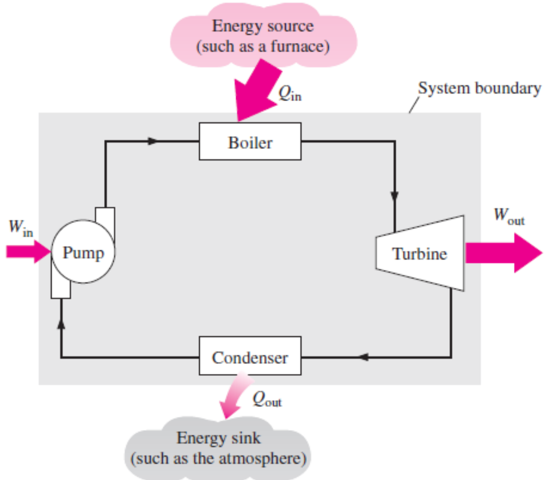
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

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.**



A source supplies energy in the form of heat, and a sink absorbs it.

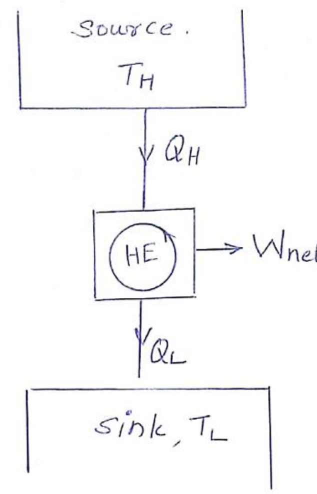
HEAT ENGINES



It is a cyclically operating energy conversion device that receives heat from high temperature source (combustor,nuclear reactor,boiler) and converts a part of this heat in to mechanical work and rejects the remaining heat to the low temperature sink (atmosphere,river,lakes etc).

Heat engine: steam power plant

Here no mass goes out of the system (closed system)



According to 1 st law of thermodynamics, $\oint dQ = \oint dW$

$Q_H - Q_L = W_T - W_P = W_{net}$

Where Q_L →energy wasted to complete the cycle.

The thermal efficiency of this power cycle or heat engine , $\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H}$ $= 1 - \frac{Q_L}{Q_H} < 1$

It indicates that thermal efficiency of heat engine can never be 100%.

Every heat engine must waste some energy by transferring it to a low temperature reservoir in order to complete the cycle, even under idealised conditions.ie no heat engine can convert all the heat it receives from source in to an equivalent work.

Other examples of Heat engine

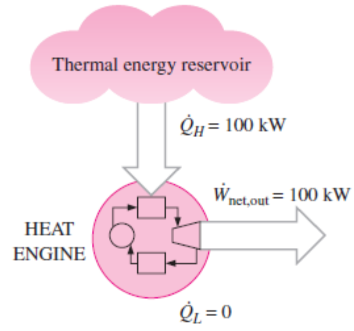
1. internal combustion engine
2. gas turbine engines
3. wankel engine(rotary engine)

KELVIN–PLANCK STATEMENT OF THE SECOND LAW

It is impossible for any device (heat engine; system operate in thermodynamic cycle) to produce net work in a complete cycle if it exchanges heat only with single reservoir (bodies at a single fixed temperature)

The Kelvin–Planck statement can also be expressed as no heat engine can have a thermal efficiency of 100 percent or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.

If $Q_L=0 \rightarrow W_{net}=Q_H \rightarrow \eta=1(100\%)$.ie heat engine will produce net work in a complete cycle by exchanging heat with only one reservoir thus violating Kelvin plancks statement ,such a hypothetical heat engine is called perpetual motion machine of the second kind (PMM2).A PMM2 is impossible.



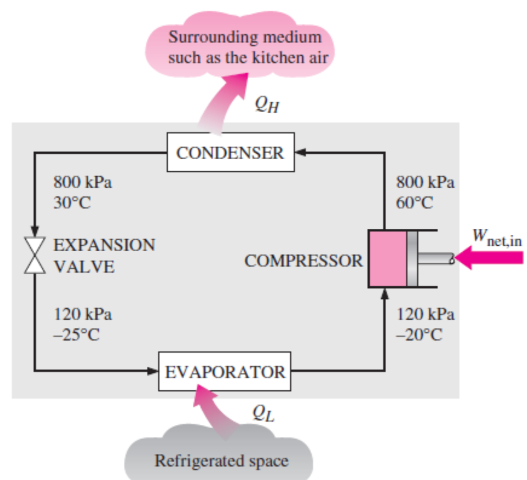
A heat engine that violates the Kelvin–Planck statement of the second law.

REFRIGERATOR AND HEAT PUMP

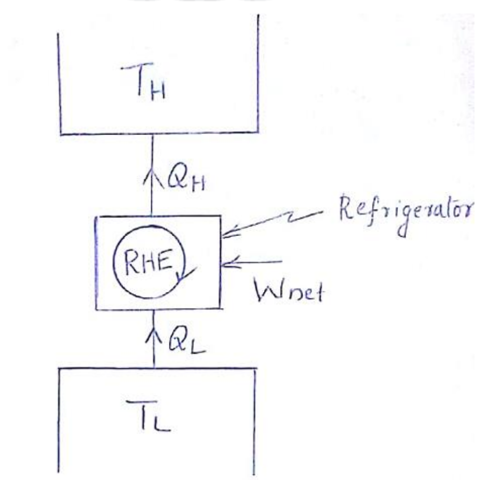
The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called **refrigerators.** Refrigerators, like heat engines, are cyclic devices. The working fluid used in the refrigeration cycle is called a **refrigerant.**

CLAUSIUS STATEMENT

It is impossible for any system (cyclic device) to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.



The most frequently used refrigeration cycle is the vapor-compression refrigeration cycle, which involves four main components: a compressor, a condenser, an expansion valve, and an evaporator, as shown in Fig.on the right hand side.



In a household refrigerator, the freezer compartment where heat is absorbed by the refrigerant serves as the evaporator, and the coils usually behind the refrigerator where heat is dissipated to the kitchen air serve as the condenser.

COEFFICIENT OF PERFORMANCE

The *efficiency* of a refrigerator is expressed in terms of the **coefficient of performance** (COP), denoted by COP_R. The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space.

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

The conservation of energy principle for a cyclic device requires that

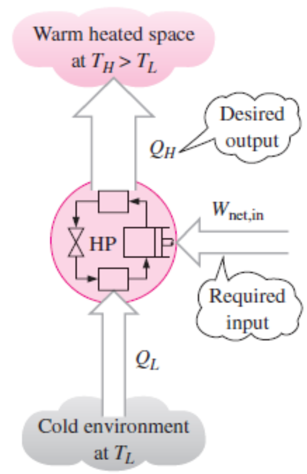
$$W_{net,in} = Q_H - Q_L \qquad (kJ)$$

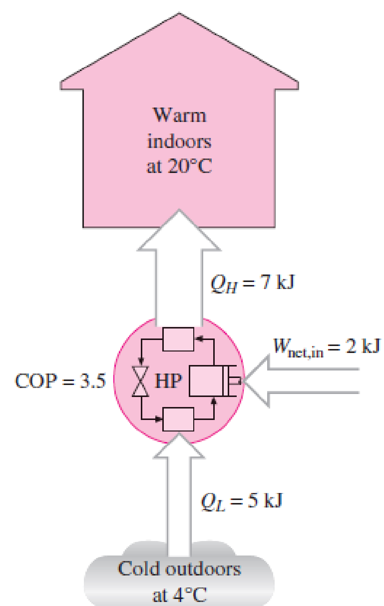
$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

Notice that the value of COP_R can be greater than unity.

HEAT PUMP

It is a cyclically operating device that transfers heat from a low-temperature medium to a high-temperature one. The objective of a heat pump is to supply heat QH in to the warmer space.thw work supplied to the heat pump is used to extract energy from the cold outdoors and carry it in to the warm indoors.





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

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

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

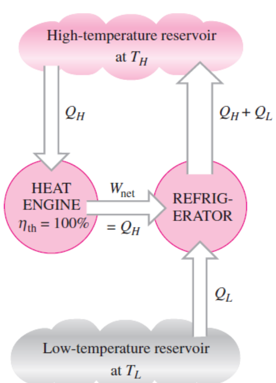
EQUIVALENCE OF KELVIN PLANCKS AND CLAUSIUS STATEMENT OF 2 ND LAW OF THERMODYNAMICS

Kelvin Planck and Clausius statements are equivalent in their consequences and either statement can be used as the expression of 2nd law of thermodynamics.

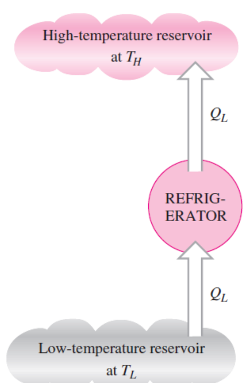
The equivalence of the two statements can be proved if it can be shown that the violation of one statement implies the violation of the second and viceversa.Any device that violates Kelvin Plancks statement also violates the Clausius statement and vice versa.

Consider Heat Engine+Refrigerator combination operating between two thermal reservoirs. The heat engine is assumed to have in violation of the Kelvin Plancks statement,a thermal efficiency of 100% and therefore it converts all the heat Q_H it receives to work,$W(Q_H)$this work is now supplied to a refrigerator that removes heat in the amount of $Q_H + Q_L$ to the high temperature reservoir. During this process, the high temperature reservoir receives a net amount of heat $Q_L(Q_H+Q_L-Q_H=Q_L)$

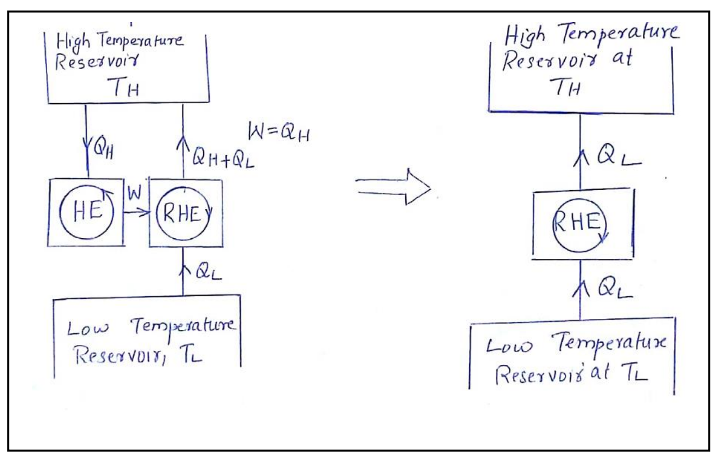
Thus the combination of these two devices can be viewed as a refrigerator that transfers heat by an amount of Q_L from a cooler body to a warmer one without requiring any input from outside. This is clearly a violation of Clausius statement. Therefore a violation of the Kelvin Planck statement results in the violation of the Clausius statement.



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



(b) The equivalent refrigerator



CARNOT CYCLE

Note: reversible cycle → It is an ideal hypothetical cycle in which all the processes constituting the cycle are reversible.

Reversible cycles cannot be achieved in practice because the irreversibilities associated with each process cannot be eliminated. However, reversible cycles provide upper limits on the performance of real cycles. Heat engines and refrigerators that work on reversible cycles serve as models to which actual heat engines and refrigerators can be compared. Reversible cycles also serve as starting points in the development of actual cycles and are modified as needed to meet certain requirements.

Carnot cycle is a reversible cycle consisting of four reversible processes.

1. 2 isothermal processes
2. 2 adiabatic processes

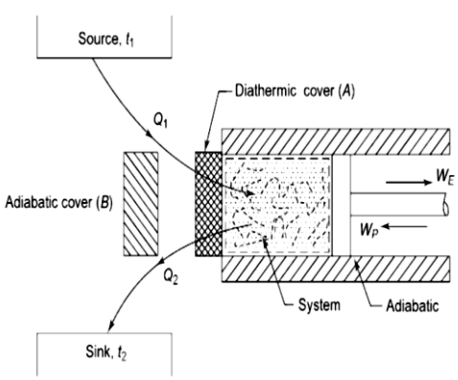
Process 1–2: The assembly is placed in contact with the reservoir at T_H. The gas expands *isothermally* while receiving energy Q_H from the hot reservoir by heat transfer.

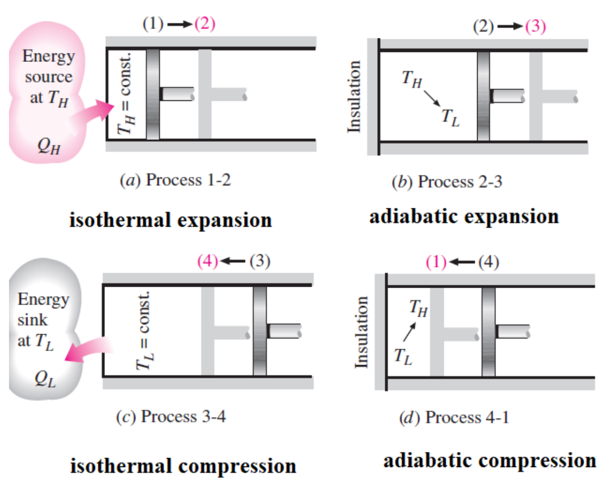
Process 2–3: The assembly is again placed on the insulating stand and the gas is allowed to continue to expand *adiabatically* until the temperature drops to T_C.

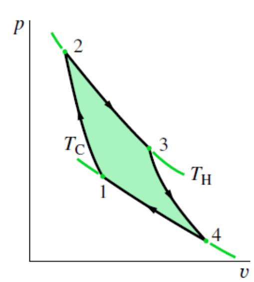
Process 3–4: The assembly is placed in contact with the reservoir at T_C. The gas is compressed *isothermally* to its initial state while it discharges energy Q_C to the cold reservoir by heat transfer.

Process 4–1: The gas is compressed *adiabatically* to state **4**, where the temperature is T_H.

Note → Process 1-2: the gas is allowed to expand slowly, doing work on its surroundings. As gas expands, the temperature of gas tends to decrease .But as soon as the temperature drops by an infinitesimal amount dT, some heat flows from the reservoir in to system, raising gas temperature by to T_H. It continues until piston reaches position 2







p–v diagram for a Carnot gas power cycle.

Thermal efficiency of carnot engine

$\boldsymbol{\eta}=\frac{W_{net}}{Q_H}=\frac{Q_H-Q_L}{Q_H}$

According to 1 st law of thermodynamics for a cycle ,$\oint dW=\oint dQ$

For isothermal expansion 1-2

Applying 1st law to cyclic process ;dU=dQ – dW

dQ=dW ;since dU=0

$Q_{12}=Q_H=W_{12}=\int_1^2 Pdv=RT_1 \ln\left(\frac{v_2}{v_1}\right)=RT_H \ln\left(\frac{v_2}{v_1}\right)$

Similarly for isothermal compression 3-4

$Q_{34}=W_{34}=RT_L \ln\left(\frac{v_4}{v_3}\right)$

For isentropic process (2-3 &4-1);dQ =0→ $Q_{23}=Q_{41}=0$

According to 1 st law of thermodynamics for a cycle ,$\oint dW=\oint dQ$

Wnet $=Q_{12}+Q_{23}+Q_{34}+Q_{41}=Q_{12}+Q_{34}=RT_H \ln\left(\frac{v_2}{v_1}\right)+RT_L \ln\left(\frac{v_4}{v_3}\right)$

$$\boldsymbol{\eta}=\frac{W_{net}}{Q_H}=\frac{RT_H \ln\left(\frac{v_2}{v_1}\right)+RT_L \ln\left(\frac{v_4}{v_3}\right)}{RT_H \ln\left(\frac{v_2}{v_1}\right)}=\frac{RT_H \ln\left(\frac{v_2}{v_1}\right)+(-1)(-1)RT_L \ln\left(\frac{v_4}{v_3}\right)}{RT_H \ln\left(\frac{v_2}{v_1}\right)}=\frac{RT_H \ln\left(\frac{v_2}{v_1}\right)-RT_L \ln\left(\frac{v_3}{v_4}\right)}{RT_H \ln\left(\frac{v_2}{v_1}\right)}$$

$$\boldsymbol{\eta}=1-\frac{T_L}{T_H}\left(\frac{\ln(v_3/v_4)}{\ln(v_2/v_1)}\right)\rightarrow 1$$

for isentropic process (2-3 &4-1)

$Tv^{\gamma-1}$ =constant

$$T_2{v_2}^{\gamma-1}=T_3{v_3}^{\gamma-1}\rightarrow T_H{v_2}^{\gamma-1}=T_L{v_3}^{\gamma-1}\rightarrow \frac{T_L}{T_H}=\left(\frac{v_2}{v_3}\right)^{\gamma-1}\rightarrow 2$$

Similarly for process 4-1; $\frac{T_L}{T_H}=\left(\frac{v_1}{v_4}\right)^{\gamma-1}\rightarrow 3$

From 2 and 3 , we have $\frac{v_2}{v_3}=\frac{v_1}{v_4}\rightarrow\frac{v_3}{v_4}=\frac{v_2}{v_1}$

$$\eta=1-\frac{T_L}{T_H}\left(\frac{\ln(v_3/v_4)}{\ln(v_2/v_1)}\right)=1-\frac{T_L}{T_H}$$

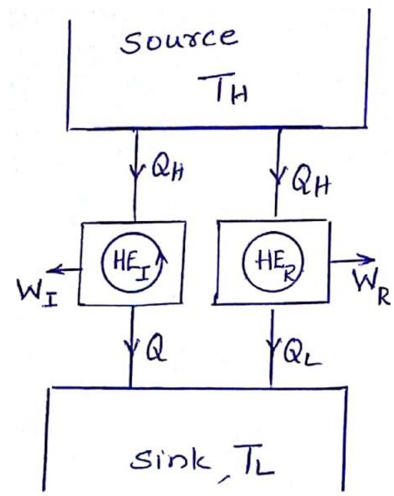
Carnots Theorem 1: It states that of all heat engines operating between a given constant temperature source and a given constant temperature sink, none has higher efficiency than a reversible engine.

ie The thermal efficiency of an irreversible heat engine (irreversible power cycle) is always less than the thermal efficiency of a reversible one operating between the same two thermal reservoirs.

Carnots Theorem 2: All reversible heat engines (power cycles) operating between the same two thermal reservoirs have the same thermal efficiency.

These two statements can be proved by demonstrating that the violation of either statement results in the violation of the second law of thermodynamics.

Carnot theorem 1 proof :

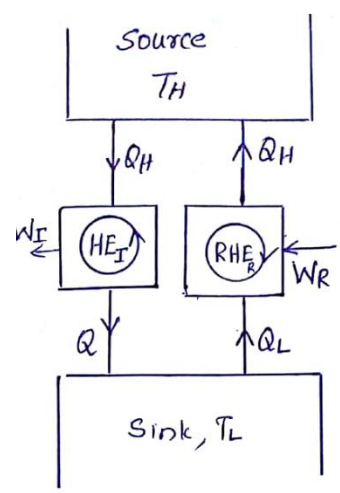


A reversible power cycle (engine) HE_R and irreversible power cycle HE_I operate between the same two thermal reservoirs and each receive the same amount of energy Q_H from hot reservoir. The reversible engine produces work W_R while irreversible cycle produces work W_I .In accordance with conservation of energy principle ,each cycle discharges energy to the cold reservoir equal to the difference between Q_H and work produced.

In violation of 1st carnot principle,we assume that irreversible heat engine is more efficient than reversible one. $\eta_{HEI} > \eta_{HER} \rightarrow \frac{W_I}{Q_H} > \frac{W_R}{Q_H} \rightarrow W_I > W_R$.

HE→Heat engine reversible;

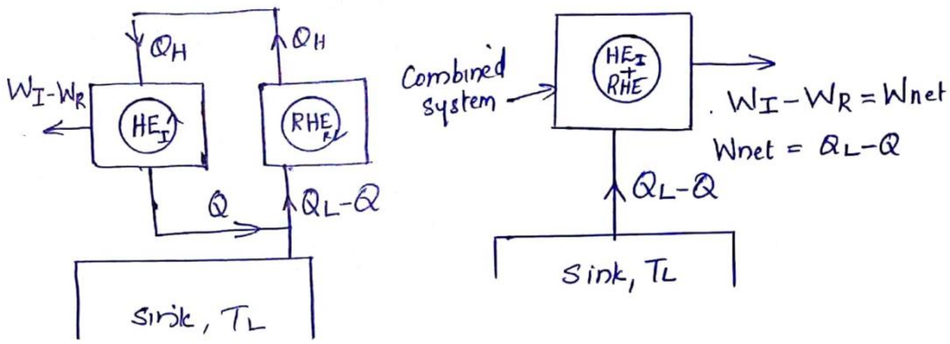
RHE→Reversed heat engine(refrigerator or heat pump)



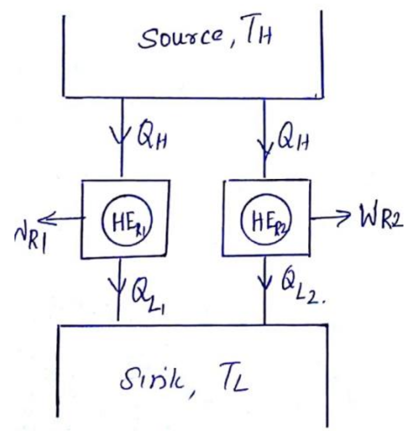
Let HE_R now operate in opposite direction as a refrigeration (heat pump)cycle .since HE_R is reversible ,the magnitude of energy transfers W_R,Q_H and Q_L remains the same ,but the energy transfer are oppositely directed as shown in fig. on the right side .

The refrigerator receives a work input of W_R and rejects heat Q_H to the high temperature reservoir .Since the refrigerator rejects Q_H amount to high temperature reservoir and the same is received by the irreversible heat engine. Thus net heat exchange for this reservoir is zero. Thus high temperature reservoir could be eliminated by having refrigerator discharge Q_H directly in to irreversible heat engine.

The demonstration of the first Carnot corollary is completed by considering the combined system(irreversible engine + refrigerator together) ,thus we have a heat engine that produces a net work of an amount of $W_I - W_R$,while exchanging heat with a single reservoir ,violation of Kelvin plancks statement of 2nd law of thermodynamics .

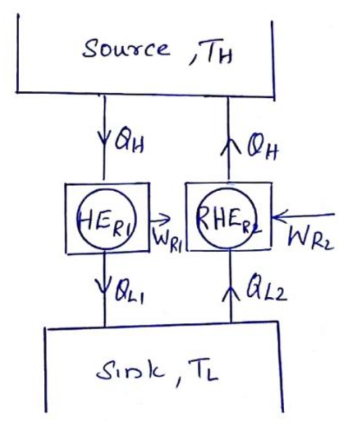


Proof of Carnot Theorem 2



2 Reversible power cycle (engine) HE_{R1} and HE_{R2} operate between the same two thermal reservoirs and each receive the same amount of energy Q_H from hot reservoir. The 2 reversible engines produces work W_{R1} and W_{R2} respectively .In accordance with conservation of energy principle ,each cycle discharges energy to the cold reservoir equal to the difference between Q_H and work produced.

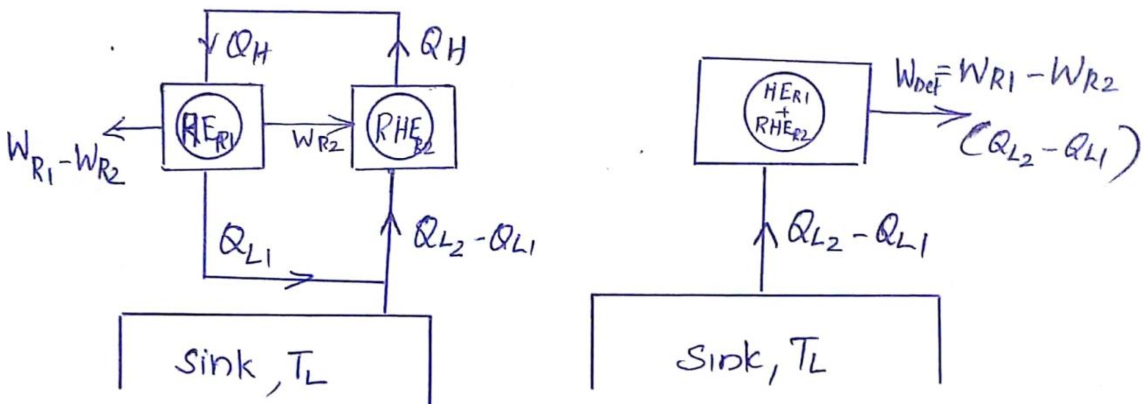
In violation of 2nd carnot principle,we assume that carnot theorem 2 is not correct. $\eta_{HER1} > \eta_{HER2} \rightarrow \frac{W_{R1}}{Q_H} > \frac{W_{R2}}{Q_H} \rightarrow W_{R1} > W_{R2}$.



Let HE_{R2} now operate in opposite direction as a refrigeration (heat pump)cycle .since HE_{R2} is reversible ,the magnitude of energy transfers W_{R2},Q_H and Q_L remains the same ,but the energy transfer are oppositely directed as shown in fig on the right side .

The refrigerator receives a work input of W_{R2} and rejects heat Q_H to the high temperature reservoir .Since the refrigerator rejects Q_H amount to high temperature reservoir and the same is received by the reversible heat engine 1. Thus net heat exchange for this reservoir is zero. Thus high temperature reservoir could be eliminated by having refrigerator discharge Q_H directly in to reversible heat engine 1.

The demonstration of the second Carnot corollary is completed by considering the combined system(R_1+R_2) ,thus we have a heat engine that produces a net work of an amount of W_{R1} –W_{R2},while exchanging heat with a single reservoir ,violation of Kelvin Plancks statement of 2nd law of thermodynamics .



Thus $\eta_{HER1} > \eta_{HER2}$ is not correct.

ie $\eta_{HER2} \geq \eta_{HER1}$ is the possibility .

By similar argument, we can prove $\eta_{HER2} > \eta_{HER1}$ is not correct. Then only possibility is $\eta_{HER1} = \eta_{HER2}$.

Therefore, we conclude that no reversible heat engine can be more efficient than a reversible one operating between the same two thermal reservoirs, regardless of how the cycle is completed or the kind of working fluid used.

The thermal efficiency doesnot depend on the type of working fluid used in heat engines, rather it depends only on the temperature of the reservoirs between which it operates.

Absolute Thermodynamic temperature scale

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale.

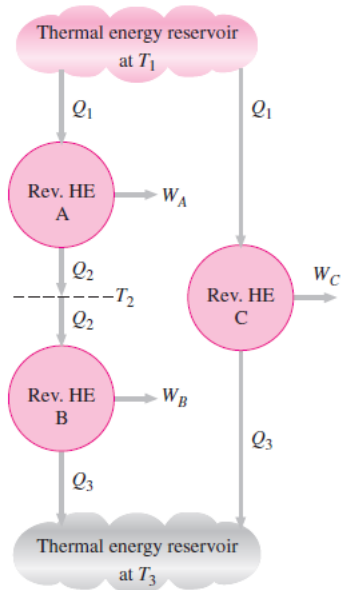
Why is it required?

A Hg glass and alcohol glass thermometer may indicate same T at both ice point and boiling point respectively. But two thermometers show different temperature at other temperature points.

Eg: Hg in glass thermometer→ 50.12^0C, where as alcohol in glass thermometer→50.45^0C

Why readings are different?

Since Hg and alcohol have different T-v relationship. Hence it is very much required to devise a temperature scale which is independent of thermometric fluid.



The second Carnot principle states that all reversible heat engines have the same thermal efficiency when operating between the same two reservoirs. That is, the efficiency of a reversible engine is independent of the working fluid employed and its properties, the way the cycle is executed, or the type of reversible engine used. Since energy reservoirs are characterized by their temperatures, the thermal efficiency of reversible heat engines is a function of the reservoir temperatures only.

That is, $\eta_R = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} = f(T_H, T_L)$ or $\frac{Q_H}{Q_L} = f(T_H, T_L)$ →(1)

The functional form of f (T_H, T_L) can be developed with the help of the three reversible heat engines shown in Fig. above . Engines A and C are supplied with the same amount of heat Q_1 from the high-temperature reservoir at T_1. Engine C rejects Q_3 to the low-temperature reservoir at T_3. Engine B receives the heat Q_2 rejected by engine A at temperature T_2 and rejects heat in the amount of Q_3 to a reservoir at T_3.

The amounts of heat rejected by engines B and C must be the same since engines A and B can be combined into one reversible engine operating between the same reservoirs as engine C and thus the combined engine will have the same efficiency as engine C. Since the heat input to engine C is the same as the heat input to the combined engines A and B, both systems must reject the same amount of heat.

Applying Eq. 1 to all three engines separately, we obtain

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \quad \frac{Q_2}{Q_3} = f(T_2, T_3), \quad \text{and} \quad \frac{Q_1}{Q_3} = f(T_1, T_3)$$

Now consider the identity ,

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3}$$

which corresponds to

$$f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3)$$

The above equation reveals that the left-hand side is a function of T_1 and T_3, and therefore the right-hand side must also be a function of T_1 and T_3 only, and not T_2. That is, the value of the product on the right-hand side of this equation is independent of the value of T_2. This condition will be satisfied only if the function *f has* the following form:

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \text{and} \quad f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

so that $\emptyset(T_2)$ will cancel from the product of f (T_1, T2) and f (T_2, T_3), yielding

$$\frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$

For a reversible heat engine operating between two reservoirs at temperatures T_H and T_L, can be written as

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

This is the only requirement that the second law places on the ratio of heat transfers to and from the reversible heat engines. Several functions $\emptyset(T)$ satisfy this equation, and the choice is completely arbitrary. Lord Kelvin first proposed taking $\emptyset(T) = T$ to define a thermodynamic temperature scale as

$$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$$

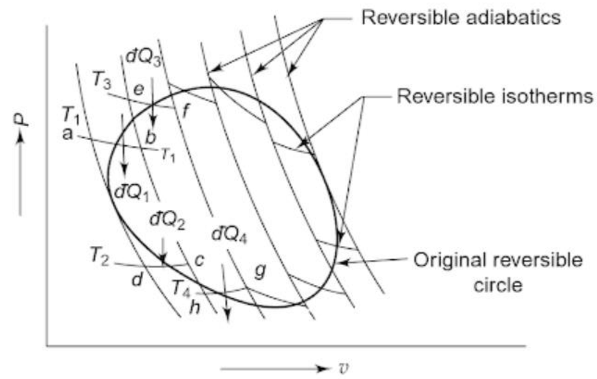
This temperature scale is called the **Kelvin scale,** and the temperatures on this scale are called **absolute temperatures.** On the Kelvin scale, the temperature ratios depend on the ratios of heat transfer between a reversible heat engine and the reservoirs and are independent of the physical properties of any substance. On this scale, temperatures vary between zero and infinity.

The thermodynamic temperature scale is not completely defined by the expression $\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$; since it gives us only a ratio of absolute temperatures. In 1954, International conference on weights and measures assign a value 273.16 K to the triple point of water (T_L). The magnitude of a kelvin is defined as 1/273.16 of the temperature interval between absolute zero and the triple-point temperature of water.

How can we apply 2nd law for the analysis of engineering problem?

Clausius theorem

Let a smooth closed curve representing a reversible cycle be considered. Let the closed cycle be divided into a large number of strips by means of reversible adiabatics. Each strip may be closed at the top and bottom by reversible isotherms. The original closed cycle is thus replaced by a zigzag closed path consisting of alternate adiabatic and isothermal processes, such that the heat transferred during all the isothermal processes is equal to the heat transferred in the original cycle.



A reversible cycle split into a large number of Carnot cycles

Thus the original cycle is replaced by a large number of Carnot cycles. If the adiabatics are close to one another and the number of Carnot cycles is large, the saw-toothed zigzag line will coincide with the original cycle.

For the elemental cycle *abcd* $đQ_1$ heat is absorbed reversibly at T_1, and $đQ_2$ heat is rejected reversibly at T_2

$$\frac{đQ_1}{T_1} = \frac{đQ_2}{T_2}$$

If heat supplied is taken as positive and heat rejected as negative

$$\frac{đQ_1}{T_1} + \frac{đQ_2}{T_2} = 0$$

Similarly, for the elemental cycle *efgh*

$$\frac{đQ_3}{T_3} + \frac{đQ_4}{T_4} = 0$$

If similar equations are written for all the elemental Carnot cycles, then for the whole original cycle

$$\frac{đQ_1}{T_1} + \frac{đQ_2}{T_2} + \frac{đQ_3}{T_3} + \frac{đQ_4}{T_4} + \ldots = 0$$

or

$$\oint_R \frac{đQ}{T} = 0$$

The cyclic integral of $đQ/T$ for a reversible cycle is equal to zero. This is known as *Clausius' theorem*.

Clausius Inequality

Whenever a system undergoes a cyclic change ,however complex the cycle may be ,the algebraic sum of all the heat interactions divided by the respective absolute temperature at which heat interactions take place, considered for the entire cycle is less than or equal to zero.

$\oint \frac{Q_i}{T_i} \leq 0.$

This inequality is valid for all cycles (heat engines and refrigeration cycles), reversible or irreversible.

Let us consider a Carnot cycle

For a Carnot cycle, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$ (for reversible engine)

Using the proper sign convention,

$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \rightarrow \sum_{i=1}^{n} \frac{Q_i}{T_i} = 0 \rightarrow (1)$

For an irreversible engine ,

$\eta_I < \eta_R \rightarrow 1 - \frac{{Q_2}^1}{Q_1} < 1 - \frac{Q_2}{Q_1}$

$1 - \frac{{Q_2}^1}{Q_1} < 1 - \frac{T_2}{T_1} \rightarrow \frac{{Q_2}^1}{Q_1} > \frac{T_2}{T_1}$

$\frac{{Q_2}^1}{T_2} > \frac{Q_1}{T_1}$

$\frac{Q_1}{T_1} - \frac{{Q_2}^1}{T_2} < 0$ →Using sign convention for Q

$\frac{Q_1}{T_1} + \frac{{Q_2}^1}{T_2} < 0$

$\sum_{i=1}^{n} \frac{Q_i}{T_i} < 0$ (Irreversible engine)→ (2)

Combining equations 1 and 2, we get $\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0$ or $\oint \frac{Q}{T} \leq 0$ (Clausius inequality)

$\oint \frac{dQ}{T} \leq 0$(Clausius inequality)