Lecture 9

Corollaries of Second Law of Thermodynamics

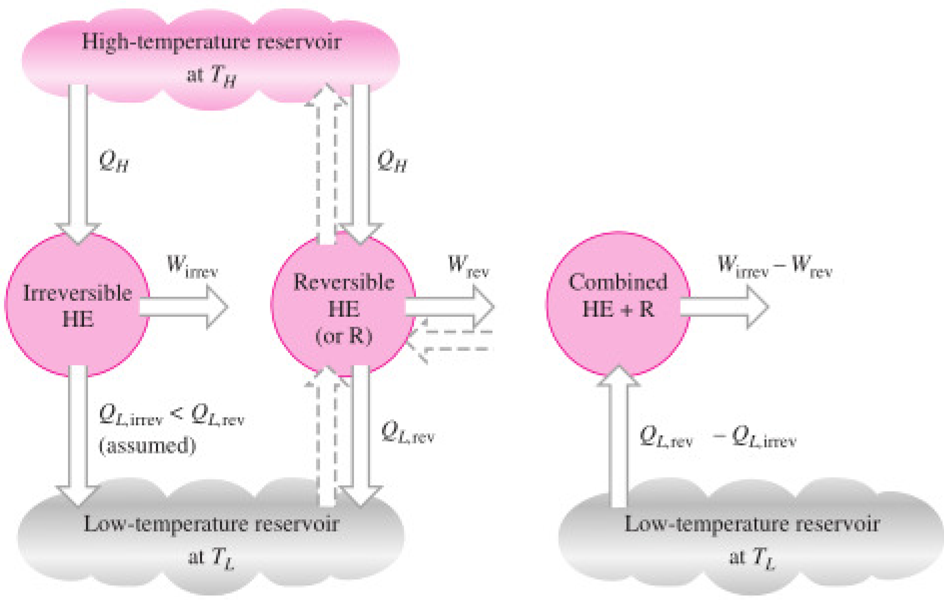
Some of the corollaries or deductions from the second law of thermodynamics are listed below.

- It is impossible to create a cyclic heat engine with 100% efficiency.
- The thermal efficiency of an irreversible power cycle is always less than the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs.
- All reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency

The last two statements are known as Carnot corollaries or Carnot principles or Carnot theorem.

Proof of Carnot corollaries

The Carnot corollaries can be proved by showing that the violation of these statements results in the violation of second law of thermodynamics.



(*a*) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(*b*) The equivalent combined system

For proving the first Carnot principle we consider an irreversible heat engine and a reversible heat engine operating between a high temperature source and a low temperature sink. Both engines receive same quantity of heat input Q_H. For proving the statement we assume that the irreversible heat engine is more efficient than the reversible heat engine. Therefore $W_{irr} > W_{rev}$. And $Q_{L,irr} < Q_{L,rev}$. We now reverse the reversible engine to work as a reversible refrigerator. The refrigerator receives work W_{rev} from the irreversible engine and transfers Q_H to the source. Now we combine the irreversible heat engine HE and the reversible refrigerator R. The combined HE +R has no net heat transfer to the high temperature reservoir. The net heat transfer to the low temperature reservoir is $Q_{L,irr} - Q_{L,rev}$ and the net work output is $W_{irr} - W_{rev}$. The combined system operates in a cycle and exchanges heat with a single reservoir producing a net work output, which is a violation of the Kelvin-Plank statement. Therefore our original assumption of irreversible engine being more efficient than the reversible engine is wrong. So we can conclude that no heat engine can be more efficient than a reversible heat engine operating between the same reservoirs.

The second Carnot principle can be proved in a similar way by replacing the irreversible engine with a reversible engine.

Thermodynamic Temperature Scale

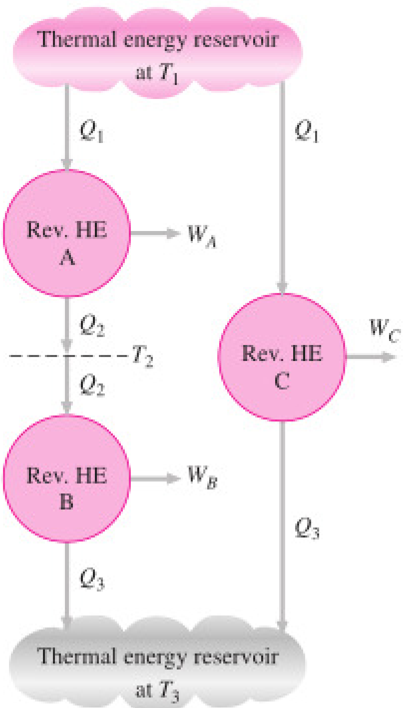
A temperature scale that is independent of the properties of the substances is called a thermodynamic temperature scale.

From the second Carnot corollary we know that all reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency. The efficiency value can be related only to the nature of the reservoirs, i.e. the temperatures of the two reservoirs, which is the common factor for all the reversible engines.

$$\eta = 1 - \frac{Q_L}{Q_H} = g(T_H, T_L)$$

$$\frac{Q_H}{Q_L} = f(T_H, T_L) \text{...eq (1)}$$

The function $f(T_H, T_L)$ can be found out by considering three reversible engines A, B and C as shown in the figure.



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.

Engine C and combined engine A + B have same thermal efficiency since both these engines operate between the same thermal reservoirs. Therefore heat input to engine C is the same as the heat input to the combined engines A and B. Also the heat rejected by engine C is the same as the heat rejected by engine B.

Applying eq (1) to all three engines separately

For engine A $\quad \frac{Q_1}{Q_2} = f(T_1, T_2)$

For engine B $\quad \frac{Q_2}{Q_3} = f(T_2, T_3)$

For engine C $\quad \frac{Q_1}{Q_3} = f(T_1, T_3)$

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

So $f(T_1, T_3) = f(T_1, T_2).f(T_2, T_3)$

The left-hand side of the equation 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. i.e., 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

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

$$f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_2)} \cdot \frac{\phi(T_2)}{\phi(T_3)} = \frac{\phi(T_1)}{\phi(T_3)}$$

$$\text{Or } \frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)} \text{ .... eq (2)}$$

For a heat engine operating between QH and QL eq (2) can be written as

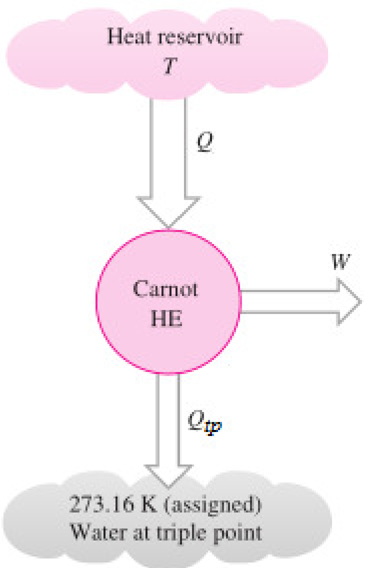
$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

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 *φ(T)* satisfy this equation, and the choice is completely arbitrary. Lord Kelvin first proposed taking *φ(T)* = T to define a thermodynamic temperature scale as

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

This temperature scale is called the **Kelvin scale**, and the temperatures on this scale are called **absolute temperatures**.

The above equation gives only a ratio of temperatures. To complete the definition of the Kelvin scale, it is necessary to provide a reference point. A value 273.16 K is assigned to the temperature at the triple point of water as a reference.



Then, if a reversible cycle is operated between a reservoir at 273.16 K and another reservoir at temperature T, the two temperatures are related according to

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

or

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

The above equation provides the complete definition of the Kelvin scale. This scale is independent of any properties of substances (thermometric property) since the efficiency of a reversible engine depend only on source and sink temperatures.

If we want to measure a temperature T using Kelvin scale make it a thermal reservoir and the reference is another reservoir. A reversible heat engine is operated between these reservoirs and the heat supplied Q and heat rejected Q_{tp} are measured. The unknown temperature T can now be calculated from the above equation.

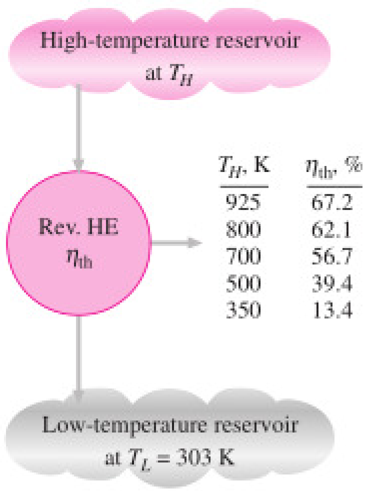
In the above equation as Q approaches zero the temperature T approaches zero. As Q cannot be negative it can be concluded that a temperature of zero on the Kelvin scale is the lowest conceivable temperature. This temperature is called the absolute zero, and the Kelvin scale is called an **absolute temperature scale.**

International Temperature Scale (ITS-90)

In order to define a practical temperature scale or to assign numerical values to temperatures it is not possible to use reversible engines since they exist only in our imagination. To provide a standard for temperature measurement taking into account both theoretical and practical considerations, the International Temperature Scale (ITS) was adopted in 1927. This scale has been refined and extended in several revisions, most recently in 1990. The International Temperature Scale of 1990 (ITS-90) is defined in such a way that the temperature measured on it conforms with the thermodynamic temperature, the unit of which is kelvin.

In the range from 0.65 to 5.0 K, ITS-90 is defined by equations giving the temperature as functions of the vapor pressures of particular helium isotopes. The range from 3.0 to 24.5561 K is based on measurements using a helium constant-volume gas thermometer. In the range from 13.8033 to 1234.93 K, ITS-90 is defined by means of certain platinum resistance thermometers. Above 1234.9 K the temperature is defined using Planck's equation for blackbody radiation and measurements of the intensity of visible-spectrum radiation.

The Quality of Energy



The thermal efficiency of a Carnot heat engine that rejects heat to a sink at 303 K is evaluated at various source temperatures. Clearly the thermal efficiency decreases as the source temperature is lowered.

These efficiency values show that energy has quality as well as quantity. It is clear 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.**

Work is a more valuable form of energy than heat since 100 percent of work can be converted to heat, but only a fraction of heat can be converted to work.

When heat is transferred from a high-temperature body to a lower temperature one, it is degraded since less of it now can be converted to work. For example, if 100 kJ of heat is transferred from a body at 1000 K to a body at 300 K, at the end we will have 100 kJ of thermal energy stored at 300 K, which has no practical value. Work potential is wasted as a result of this heat transfer, and energy is degraded.