Chapter 5
The Second Law of Thermodynamics

The differences between the two forms of energy, heat and work, provide some insight into the second law.

Work is readily transformed into other forms of energy: for example, into potential energy by elevation of a weight, into kinetic energy by acceleration of a mass, into electrical energy by operation of a generator. These processes can be made to approach a conversion efficiency of 100% by elimination of friction, a dissipative process that transforms work into heat. **Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments.**

On the other hand, all efforts to devise a process for the continuous conversion of heat completely into work or into mechanical or electrical energy have failed.

Drawing further on our experience, we know that the flow of heat between two bodies always takes place from the hotter to the cooler body, and never in the reverse direction. This fact is of such significance that its restatement serves as an acceptable expression of the second law.

5.1 STATEMENTS OF THE SECOND LAW

Statement 1: No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system**.**

Statement 2: No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

5.2 HEAT ENGINES

Heat engines, devices or machines that produce work from heat in a **cyclic process**. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state. In such a power plant the cycle (in its simplest form) consists of the following steps:

The word **cyclic** requires that the system be restored periodically to its original state.

- Liquid water at ambient temperature is pumped into a boiler at high pressure.
- Heat from a fuel (heat of combustion of a fossil fuel or heat from a nuclear reaction) is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.
- Energy is transferred as shaft work from the steam to the surroundings by a device such as a **turbine**, in which the steam expands to reduced pressure and temperature.

- Exhaust steam from the turbine is condensed by transfer of heat to the surroundings, producing liquid water for return to the boiler, thus completing the cycle.

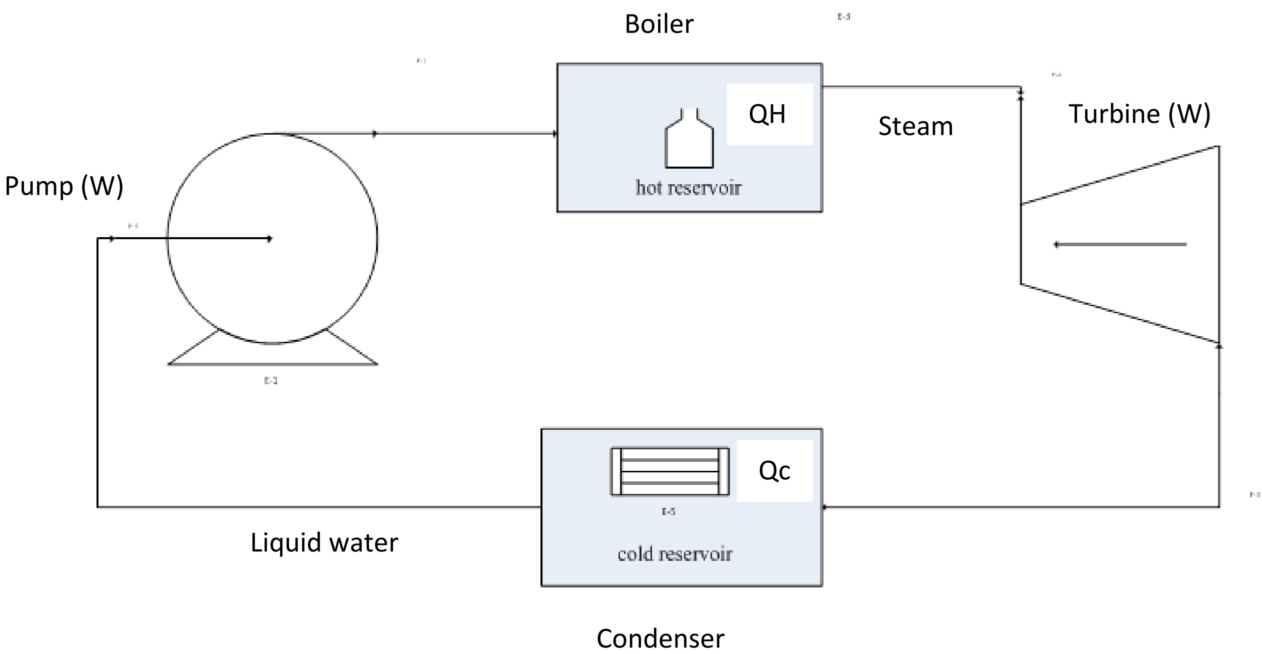


Figure (1) Steps of heat engine

Essential to all heat-engine cycles are absorption of heat into the system at a high temperature, rejection of heat to the surroundings at a lower temperature, and production of work. In the theoretical treatment of heat engines, the two temperature levels which characterize their operation are maintained by heat reservoirs, bodies imagined capable of absorbing or rejecting an infinite quantity of heat without temperature change.

In operation, the working fluid of a heat engine absorbs heat $|QH|$ from a hot reservoir, produces a net amount of work $|W|$, discards heat $|Qc|$ to a cold reservoir, and returns to its initial state. The first law therefore reduces to:

$$|W| = |Q_H| - |Q_C| \qquad (5.1)$$

The thermal efficiency of the engine is defined as: **η= net work output/heat absorbed**
With Eq. (5.1) this becomes:

$$\eta \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \qquad (5.2)$$

Absolute-value signs are used to make the equations independent of the sign conventions for Q and W. For q to be unity (100% thermal efficiency), $|Qc|$ must be zero. No engine has ever been built for which this is true; some heat is always rejected to the cold reservoir

The Carnot Cycle (Carnot engine)

If a thermal efficiency of 100% is not possible for heat engines, what then determines the upper limit? One would certainly expect the thermal efficiency of a heat engine to depend on the degree of reversibility of its operation. Indeed, a heat engine operating in a completely reversible manner is very special, and is called a Carnot engine. The characteristics of such an ideal engine were first described by N. L. S. Carnot in 1824. The four steps that make up a Carnot cycle are performed in the following order:

Step 1: A system at the temperature of a cold reservoir Tc undergoes a reversible adiabatic process that causes its temperature to rise to that of a hot reservoir at TH.

Step 2: The system maintains contact with the hot reservoir at TH, and undergoes a reversible isothermal process during which heat $|QH|$ is absorbed from the hot reservoir.

Step 3: The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings its temperature back to that of the cold reservoir at Tc.

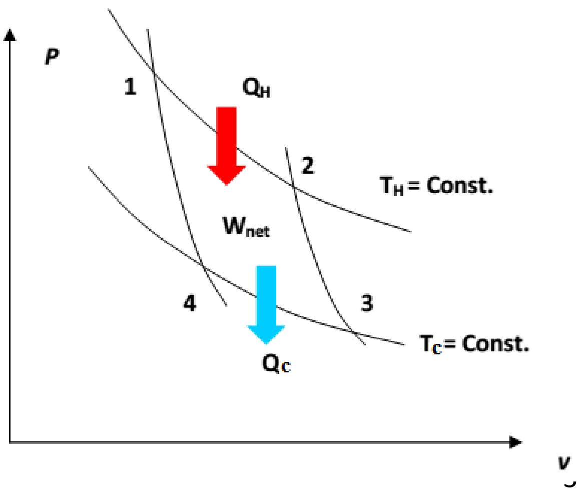
Step 4: The system maintains contact with the reservoir at Tc, and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Qc|$ to the cold reservoir.

That means two adiabatic reversible processes and two isothermal processes

Ideal-Gas Temperature Scale; Carnot's Equations

The cycle traversed by an ideal gas serving as the working fluid in a Carnot engine is shown by a PV diagram in Fig. 5.3. It consists of four reversible steps:

Figure 5.3 PV diagram showing Carnot cycle for an ideal gas



a $\longrightarrow$ b Adiabatic compression until the temperature rises from Tc to TH.
b $\longrightarrow$ c Isothermal expansion to arbitrary point c with absorption of heat $|QH|$.
c $\longrightarrow$ d Adiabatic expansion until the temperature decreases to Tc .
d $\longrightarrow$ a Isothermal compression to the initial state with rejection of heat $|Qc|$.

For the isothermal steps b $\longrightarrow$ c and d $\longrightarrow$ a, Eq. (3.27) yields:

$$|Q_H| = RT_H \ln \frac{V_c}{V_b} \qquad \text{and} \qquad |Q_C| = RT_C \ln \frac{V_d}{V_a}$$

Therefore,

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \frac{\ln(V_c/V_b)}{\ln(V_d/V_a)} \tag{5.6}$$

For an adiabatic process Eq. (3.22) with dQ=0 becomes, P=RT/v

$$-\frac{C_V}{R}\frac{dT}{T} = \frac{dV}{V}$$

For step $a \rightarrow$ b and c $\rightarrow$ d, integration gives:

$$\int_{T_C}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln \frac{V_a}{V_b} \qquad \text{and} \qquad \int_{T_C}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln \frac{V_d}{V_c}$$

Because of the left sides of these two equations are the same,

$$\ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c} \qquad \text{or} \qquad \ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$$

Equation (5.6) now becomes:

$$\boxed{\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}} \tag{5.7}$$

Substitution of Eq. (5.7) into Eq. (5.2) gives:

$$\boxed{\eta \equiv \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}} \tag{5.8}$$

Equations (5.7) and (5.8) are known as Carnot's equations. **Theses equations can use only for Carnot engine, but Eq. 5.2 can be used for the entire engine if it is ideal or not.** Equation (5.8) shows that the thermal efficiency of a Carnot engine can approach unity only when TH approaches infinity or Tc approaches zero. Neither of these conditions is attainable; all heat engines therefore operate with thermal efficiencies less than unity.

There are some terms when you see or hear it directly remember the Carnot engine like:

1. Ideal
2. Theoretical
3. Reversible
4. Maximum work
5. Maximum temperature.

The cold reservoirs naturally available on earth are the atmosphere, lakes and rivers, and the oceans, for which Tc = 300 K. Hot reservoirs are objects such as furnaces where the temperature is maintained by combustion of fossil fuels and nuclear reactors where the temperature is maintained by fission of radioactive elements. For these practical heat sources, TH = 600 K. With these values,

$$\eta = 1 - \frac{300}{600} = 0.5$$

This is a rough practical limit for the thermal efficiency of a Carnot engine; actual heat engines are irreversible, and their thermal efficiencies rarely exceed 0.35.

Example 5.1

A central power plant, rated at 800,000 kW, generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

Solution 5.1

The maximum possible thermal efficiency is given by Eq. (5.8). With T_H as the steam-generation temperature and T_C as the river temperature:

$$\eta_{max} = 1 - \frac{295}{585} = 0.4957 \qquad \text{and} \qquad \eta = (0.7)(0.4957) = 0.3470$$

where η is the actual thermal efficiency. Equations (5.1) and (5.2) may be combined to eliminate $|Q_H|$; solution for $|Q_C|$ then yields:

$$|Q_C| = \left(\frac{1-\eta}{\eta}\right)|W| = \left(\frac{1-0.347}{0.347}\right)(800{,}000) = 1{,}505{,}500 \text{ kW}$$

This heat rate of 1,505,500 kJ s^{-1} would cause a temperature rise of several °C in a modest river.

5.4 ENTROPY

Equation (5.7) for a Carnot engine may be written:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

If the heat quantities refer to working fluid in the engine (rather than to the heat reservoirs), the numerical value of QH is positive and that of Qc is negative. The equivalent equation written without absolute-value signs is therefore

$$\frac{Q_H}{T_H} = \frac{-Q_C}{T_C}$$

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \qquad (5.9)$$

Our purpose now is to show that Eq. (5.9), applicable to the reversible Carnot cycle, also applies to other reversible cycles.

Each Carnot cycle has its own pair of isotherms TH and Tc and associated heat quantities QH and QC. When the adiabatic curves are so closely spaced that the isothermal steps are infinitesimal, the heat quantities become dQH and dQc, and Eq. (5.9) for each Carnot cycle is written:

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

In this equation TH and Tc, absolute temperatures of the working fluid of the Carnot engines, are also the temperatures traversed by the working fluid of the arbitrary cycle. Summation of all quantities dQ/ T for the Carnot engines leads to the integral:

$$\oint \frac{dQ_{\text{rev}}}{T} = 0 \qquad (5.10)$$

where the circle in the integral sign signifies integration over the arbitrary cycle, and the subscript "rev" indicates that the cycle is reversible.

Thus the quantities Qrev/ T sum to zero for the arbitrary cycle, exhibiting the characteristic of a property. The property is called entropy (en'-tro-py), and its differential changes are:

$$dS^t = \frac{d_{Qrev}}{T} \qquad (5.11)$$

where S^t is the total (rather than molar) entropy of the system. Alternatively,

$$\boxed{dQ_{rev} = T\, dS^t} \qquad (5.12)$$

If a process is reversible and adiabatic, $dQ_{rev} = 0$; then by Eq. (5.11), $dS^t = 0$. Thus the entropy of a system is constant during a reversible adiabatic process, and the process is said to be isentropic.

This discussion of entropy can be summarized as follows:

- There exists a property called entropy S, which is an intrinsic property of a system, functionally related to the measurable coordinates which characterize the system. For a reversible process, changes in this property are given by Eq. (5.11).
- The change in entropy of any system undergoing a finite reversible process is:

$$\Delta S^t = \int \frac{dQ_{rev}}{T} \qquad (5.13)$$

When a system undergoes an irreversible process between two equilibrium states, the entropy change of the system ΔS^t is evaluated by application of Eq. (5.13).

Integration is not carried out for the irreversible path. Since entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.