Second Law of Thermodynamics

9.1

Second Law of Thermodynamics
Carnot cycle efficiency
- Heat engines
- Refrigerators

Heat Engines

A heat engine takes in heat at a high temperature and exhausts heat at a low temperature.
In the process of heat flow some of the input heat is converted to work

First Law (for a cycle)
\[ Q = Q_h + Q_c = W \]

Second Law (puts limits on \( Q_h \) and \( Q_c \))

Efficiency of a heat engine

The efficiency is the fraction of the heat input at high temperature converted to work.
\[ e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} \]

In calculating efficiencies \( Q_h \) and \( Q_c \) are taken as positive quantities (i.e. the magnitude of the heat)

The second law says that a heat engine cannot be 100% efficient.

Kelvin-Planck Statement of the second law of thermodynamics

It is impossible to construct a heat engine operating in a cycle that extracts heat from a reservoir and delivers an equal amount of work.

No perfect heat engine

Carnot Cycle

Sadi Carnot, a French engineer (1796-1832) proposed a cycle set the limits to the efficiency of a heat engine operating between two temperatures.

The cycle consists of 4 reversible steps.
1. Isothermal expansion at \( T_h \)
2. Adiabatic expansion from \( T_h \) to \( T_c \)
3. Isothermal compression at \( T_c \)
4. Adiabatic compression from \( T_c \) to \( T_h \)
Heat engine.

Heat engine undergoing the Carnot cycle.

Work is done by the gas in expansion
Work must be done on the gas to compress it to the initial state

Heat transfer in the Carnot cycle

In the Carnot cycle the magnitude of the heat transferred at T is proportional to the absolute temperature T.

\[ \frac{Q_H}{Q_C} = \frac{T_H}{T_C} \]

(here Q is always positive)

From the relations

Isothermal expansion and compression

\[ Q_H = RT_H \ln \frac{V_B}{V_A} \]

Adiabatic expansion and compression

\[ T_H V_A^{\gamma - 1} = T_C V_C^{\gamma - 1} \]

\[ T_H V_A^{\gamma - 1} = T_C V_C^{\gamma - 1} \]

\[ \frac{V_B}{V_A} \]

\[ \frac{V_C}{V_D} \]

\[ \frac{Q_H}{T_H} = \frac{Q_C}{T_C} \]

Efficiency of the Carnot cycle

\[ e = 1 - \frac{Q_C}{Q_H} \]

becomes

\[ e = 1 - \frac{T_C}{T_H} \]

The efficiency only depends on the ratio of the absolute temperatures.

The efficiency would be 100% if \( Q_C = 0 \).
This is only possible if \( T_C = 0 \) K (i.e. absolute Zero)
A temperature of absolute zero cannot be attained.
(Third law of thermodynamics)

Carnot’s Theorem

All Carnot engines operating between temperatures \( T_H \) and \( T_C \) have the same efficiency.

\[ e = 1 - \frac{T_C}{T_H} \]

No other heat engine operating between these temperatures can have a greater efficiency

Stirling Engine

Maximum efficiency is less than the Carnot efficiency.

\[ w_2 = w_4 = 0 \]

then

\[ e = \frac{Q_H - Q_C}{Q_H + Q_C} \]

For isothermal processes same volume change

\[ \frac{Q_H}{T_H} = \frac{Q_C}{T_C} \]

then

\[ e = e_{carnot} \left( \frac{1}{1 + \frac{Q_C}{Q_H}} \right) \]

Efficiency lower due to extra heat added.
Refrigerator and heat pump

A heat engine run in reverse is a refrigerator and heat pump. Work is done to move heat from a cold temperature source to a hot sink. This device can be used for cooling or heating.

Clausius Statement of the Second Law of Thermodynamics.

It is impossible to construct a refrigerator operating in a cycle whose sole effect is to transfer heat from a cooler object to a hotter one. Heat always flows from high temperature to low temperature.

Equivalence of the Kelvin-Planck and Clausius statements.

If a perfect refrigerator were possible (Clausius) then a perfect heat engine could be constructed (Kelvin-Planck). Thus, the impossibility one implies the impossibility of the other.

Proof of the Carnot Principle

If a heat engine with a higher efficiency than a Carnot engine could exist. Then it could convert heat to work with 100% efficiency. The Carnot engine has the highest efficiency for any heat engine acting between two temperatures.

Real Heat Engines

Example

In a wood burning power plant the steam in the turbine operates between the high temperature of 810 K and a low temperature of 366 K. What is the Carnot efficiency for this plant?

The actual efficiency is less than the Carnot efficiency.

\[ e = 1 - \frac{T_2}{T_1} = 1 - \frac{366}{810} = 0.55 \]

Compare this to the efficiency calculated from the electrical power output of 59 MW and heat power input of 165 MW (see prob. 60)

\[ e = \frac{W}{Q_H} = \frac{59MW}{165MW} = 0.35 \]
How to improve the efficiency of a heat engine.

Increase $T_h$ This requires high temperature materials
Decrease $T_c$ This requires efficient heat transfer.

Cogeneration
Use of waste heat

This power plant in Denmark uses the waste heat to heat green houses nearby.

Refrigerators

Coefficient of performance
COP - the heat removed from the cold source divided by the work done.

\[
\text{COP} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}
\]

The maximum Carnot COP

\[
\text{COP} = \frac{T_h}{T_c}
\]

since

\[
\frac{Q_c}{T_c} = \frac{Q_h}{T_h}
\]

Refrigerator

The refrigerator uses a liquid with a low boiling point. The evaporation takes up heat from the refrigerator and the condensation of the gas releases the heat outside the refrigerator.

1 Compressor – gas is compresses and heated
2 Heat exchange coils - the heat is released from the gas and exhausted outside of the refrigerator.
3 Expansion valve – The pressure is decreased after going through the valve. The gas is cooled
4 Cooling coils- Heat is absorbed from within the refrigerator. The gas is heated.

Refrigerator

A freezer is kept at a temperature of 0°F. What is the maximum COP for a Carnot refrigerator with output temperature of 85°F. If the electrical energy use is 500kWh/year how much heat is removed in one year, assume 90% conversion of electrical energy to work.

\[
\text{COP} = \frac{T_h}{T_c} = \frac{255}{305 - 255} = 5.4
\]

\[
T_h = (0 - 32)(5/9) + 273 = 255 \text{ K}
\]

\[
T_c = (85 - 32)(5/9) + 273 = 302 \text{ K}
\]

\[
\text{Work} = 0.9(500 \times 10^3 \text{W} \text{ hr}) \left( \frac{60 \text{ min}}{1 \text{ hr}} \right) \left( \frac{60 \text{ sec}}{1 \text{ min}} \right) = 1.62 \times 10^9 \text{ J}
\]

Heat

\[
\text{COP} = \frac{Q_c}{W} = \frac{5.4 \times 1.62 \times 10^9}{8.7 \times 10^9} = 0.8 \times 10^9
\]

Summary

- The second law of thermodynamics limits the efficiency of heat engines to less than 100%
- The Carnot cycle is a reversible cycle taking in heat at high T and exhausting heat at low T.
- The maximum efficiency of a heat engine working between two temperatures is the Carnot efficiency that depends only on the ratio of the absolute temperatures.
- Refrigerators and heat pumps are heat engines run in reverse.
- The maximum coefficient of performance is determined by a Carnot cycle.