4 - 2nd Law of Thermodynamics

Directions of Thermodynamic Processes

Thermodynamic processes that occur in nature are irreversible processes (e.g. flow of heat from a hot body to a cooler boy, free expansion of gas).

The second law of thermodynamics determines the preferred direction of such processes.

However, there are some idealized processes that would be reversible, where these reversible processes are very close (i.e. infinitesimally) to being in thermodynamic equilibrium with itself and its surroundings.

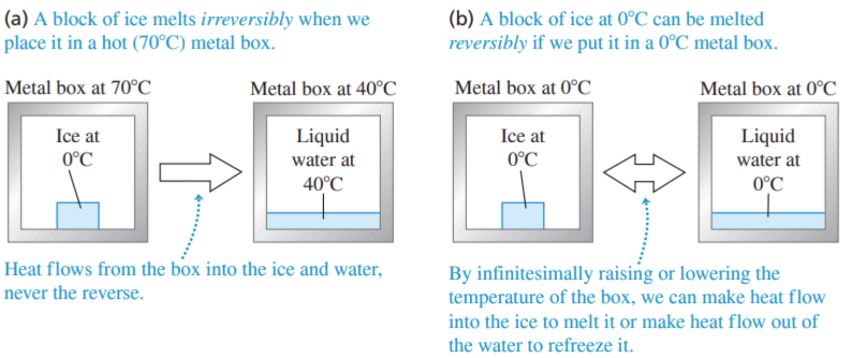


Figure 20.1 Reversible and irreversible processes.

Heat Engines

These include gasoline engines, jet engines, steam turbines, etc. This refers to a device that converts heat into work or mechanical energy.

Working Substance
A quantity of matter inside the engine that undergoes inflow and outflow of heat, expansion and compression, and sometimes change of phase (e.g. water in a steam turbine, or mixture of air and fuel in an internal-combustion engine).

Now consider a cyclic process (a sequence of processes that leaves the working substance in the same state it started)

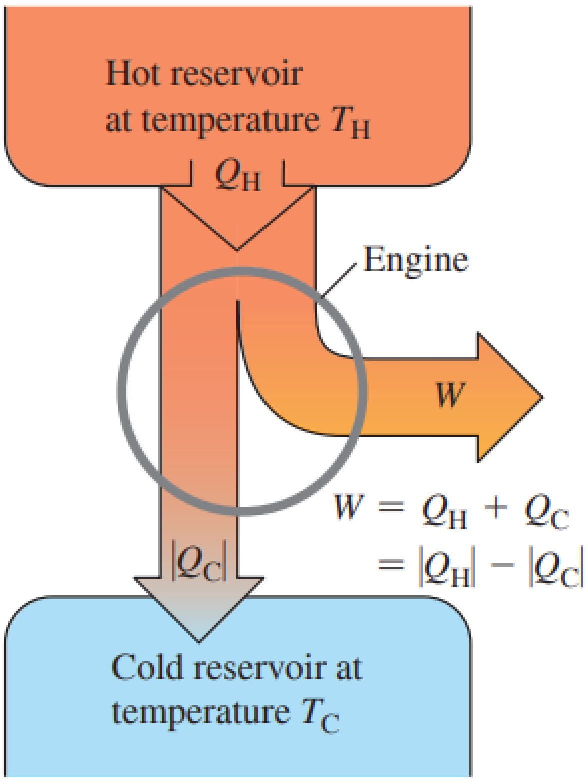
$$\Delta = U_2 - U_1 = 0 = Q - W$$

therefore

$$Q = W$$

Hot and Cold Reservoirs

Figure 20.3 Schematic energy-flow diagram for a heat engine.



We would have $Q_h > 0$ as heat is transferred to the working substance and $Q_c < 0$ as heat leaves the working substance. Then the net heat absorbed per cycle is

$$Q = Q_h + Q_c = |Q_h| - |Q_c$$

Then through the first law:

$$W = Q = Q_h + Q_c = |Q_h| - |Q_c|$$

We define the thermal efficiency of an engine to be

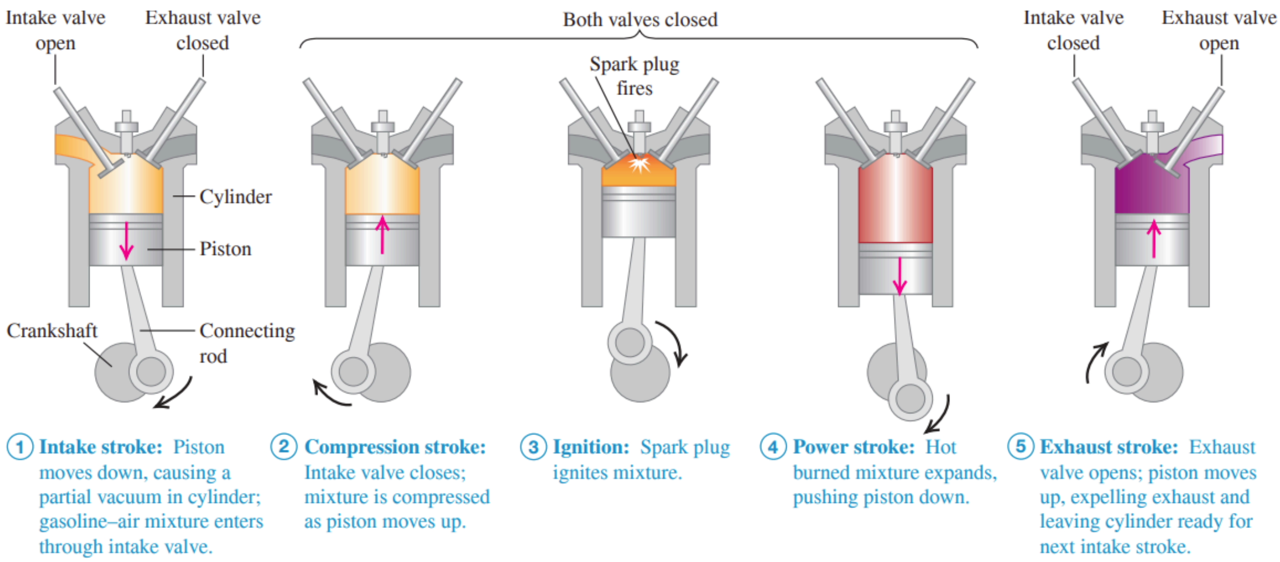
$$e = \frac{W}{Q_h}$$

so we can get

$$e = 1 + \frac{Q_c}{Q_h} = 1 - \left|\frac{Q_c}{Q_h}\right|$$

Internal Combustion Engines

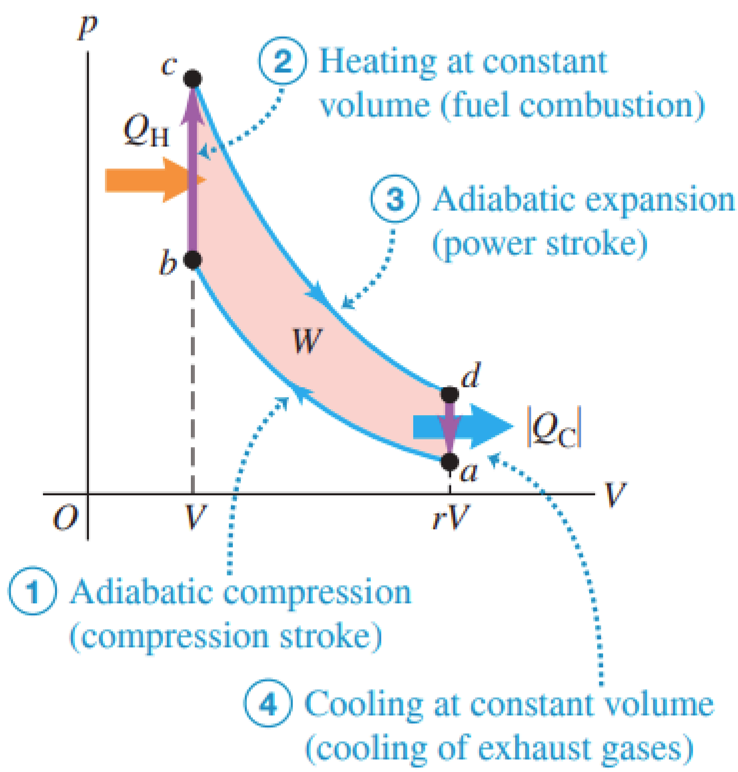
Figure 20.5 Cycle of a four-stroke internal-combustion engine.



Otto Cycle

The following is a pV diagram for the Otto cycle an idealized model of the thermodynamic processes in a gasoline engine.

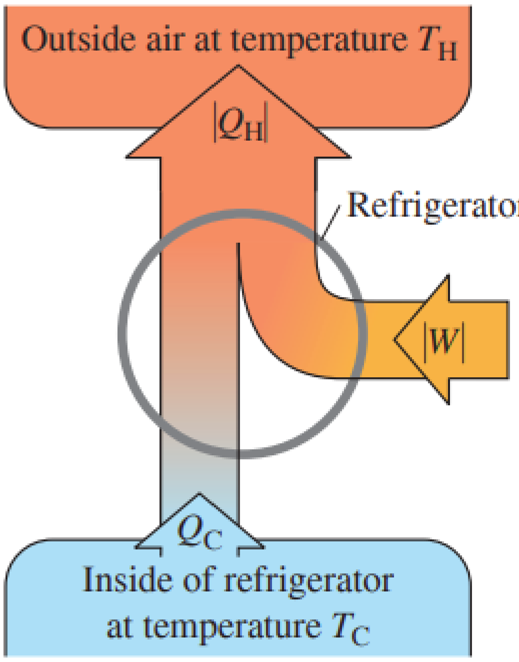
Figure 20.6 The *pV*-diagram for the Otto cycle, an idealized model of the thermodynamic processes in a gasoline engine.



Refrigerators

These are essentially heat engines operating in reverse, where heat is taken from a cold place and is given to a warmer place. This requires a net input of mechanical work, as it is a non-natural process.

Figure 20.8 Schematic energy-flow diagram of a refrigerator.



Q_c would be positive and Q_h, W would be negative, where $Q_h > Q_c$ such that

$$Q_h + Q_c - W = 0$$

Because Q_h and W are negative, then

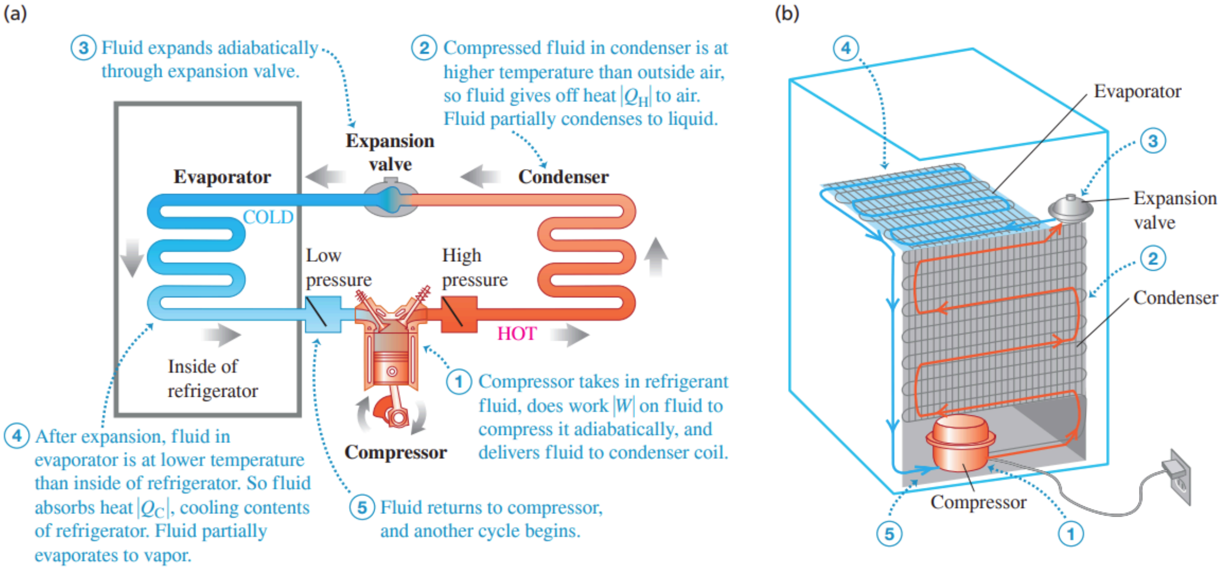
$$|Q_h| = Q_c + |W|$$

We can get a refrigerator's coefficient of performance K:

$$K = |Q_c|$$

Practical Refrigerators

Figure 20.9 (a) Principle of the mechanical refrigeration cycle. (b) How the key elements are arranged in a practical refrigerator.



Clausius Statement

"Heat never flows spontaneously from lower temperature to higher temperature without work."

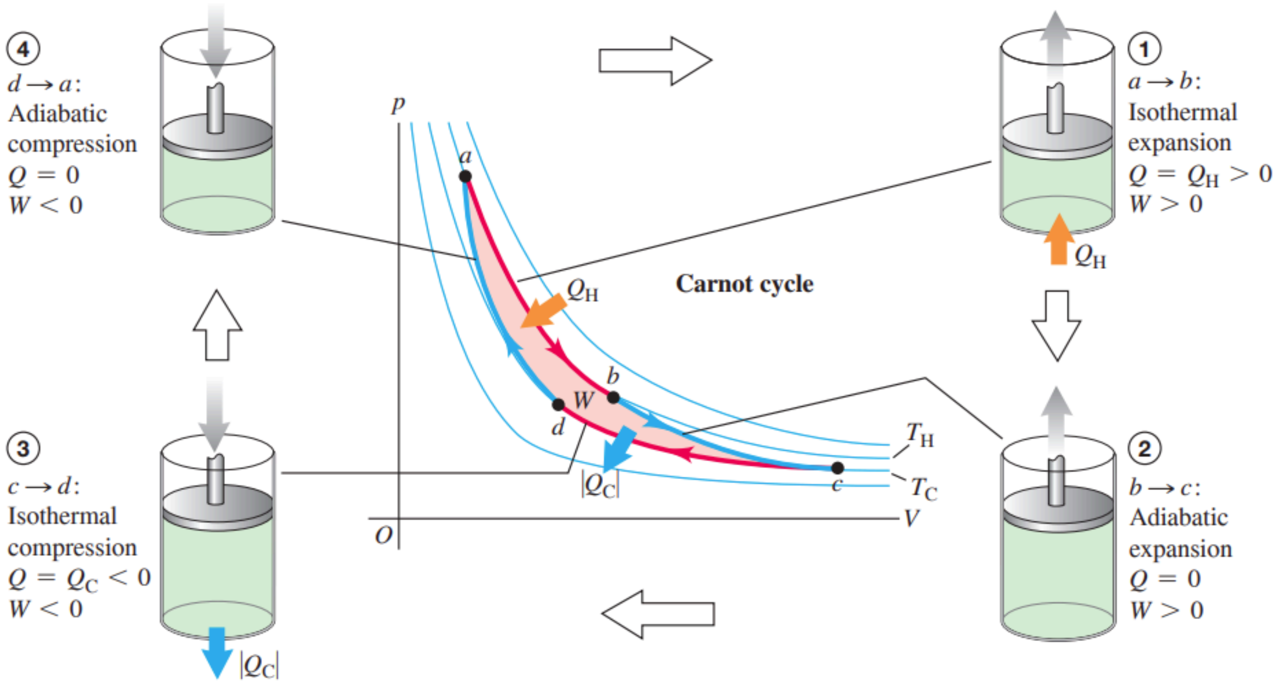
Carnot Cycle

No heat engine can have 100% efficiency.
Sadi Carnot then asks: "What is the maximum possible efficiency can an engine have, given two heat reservoirs at temperatures T_h and T_c?" He then answers this in 1824, where he develops an idealized heat engine that has the maximum possible efficiency consistent with the second law.

To get maximum heat-engine efficiency, we avoid all irreversible process. During heat transfer in a Carnot cycle, there must be no finite temperature drop. In addition, when temperature of working substance is between T_h and T_c, there must be no heat transfer between the engine and reservoir.

We would then have two reversible isothermal and two reversible adiabatic processes:

Figure 20.13 The Carnot cycle for an ideal gas. The light blue lines in the pV-diagram are isotherms (curves of constant temperature) and the dark blue lines are adiabats (curves of zero heat flow).



The heat transfer in a Carnot engine would be equivalent to

$$\frac{Q_c}{Q_h} = -\frac{T_c}{T_h} \text{ or } \frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$$

and our efficiency would be

$$e_{\text{carnot}} = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h}$$

These can be derived by looking through the processes one by one.
In the isothermal expansion from point a to b:

$$Q_h = W_{ab} = \int p\,dV = \int_a^b \frac{nRT_h}{V}\,dV = nRT_h \ln(\frac{V_b}{V_a})$$

Similarly, in the isothermal compression from c to d:

$$Q_C = W_{cd} = \int p\,dV = \int_c^d \frac{nRT_c}{V}\,dV = nRT_c \ln\left(\frac{V_d}{V_c}\right) = -nRT_c \ln\left(\frac{V_c}{V_d}\right)$$

Such that we can get the ratio

$$\frac{Q_c}{Q_H} = -\frac{T_c \ln\left(\frac{V_c}{V_d}\right)}{T_h \ln\left(\frac{V_b}{V_a}\right)}$$

Now we can take a look at the adiabatic processes at b to c and d to a:

$$\frac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \frac{V_c^{\gamma-1}}{V_d^{\gamma-1}}$$

which is equivalent to

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

So then we have

$$\frac{Q_c}{Q_H} = -\frac{T_c \ln\left(\frac{V_c}{V_d}\right)}{T_h \ln\left(\frac{V_b}{V_a}\right)} = -\frac{T_c}{T_h}$$