Heat Engines, The Second Law, Entropy

$\Delta U = Q - W$ (the First Law) does not distinguish between heat and work but there is a difference.

- It is possible to convert work completely to heat but it is impossible to convert heat completely to work.

The Second Law establishes:

- which thermodynamic processes are possible
- in which direction those processes proceed

Heat Engines

A *heat engine* is a device that converts thermal energy into other forms of energy such as mechanical, electrical, etc.

Heat engines are cyclic devices.

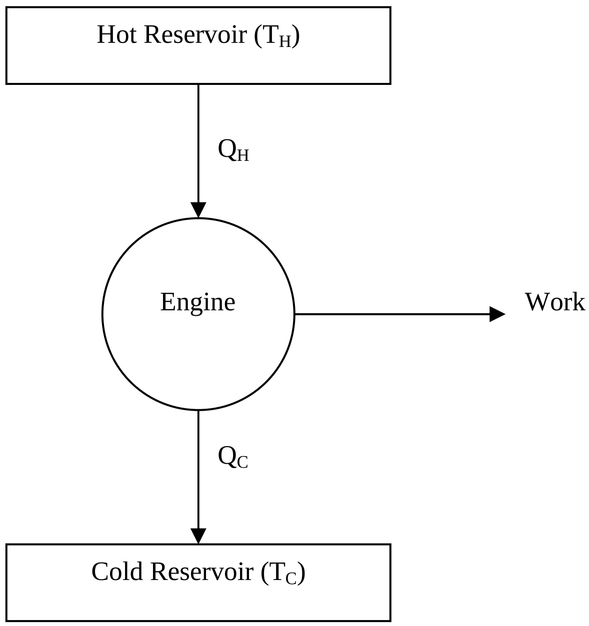
1. Heat is absorbed from a high temperature reservoir
2. Work is done by the engine
3. Heat is expelled by the engine to a lower temperature reservoir
4. The engine returns to its initial state

Heat engines employ some working substance that is carried through a cyclic thermodynamic process in which the working substance is eventually returned to its initial state. The working substance is most often a fluid or a gas.

Consider a standard heat engine utilizing combustion:

- A fuel/air mixture is burned to create a high temperature gas (hot reservoir).
- The volume of the gas expands doing work on a piston/crankshaft
- The heat is expelled through a manifold to the atmosphere (cold reservoir).

Schematically:



Since this process is cyclic, $\Delta U = 0$ & $Q = W$ $\therefore$ according to the first law, the <u>net work</u> W done by a heat engine equals the heat flowing into the engine where:

$$Q_{net} = Q_H - Q_C$$

- Q_H & Q_C are intrinsically positive quantities.
- The *thermal efficiency* of a heat engine, *e*, is defined as the ratio of the net work done to the heat absorbed in 1 cycle of the engine.

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- *e* = 100% only if $Q_C = 0$, i.e., only of the 2nd law is violated and no heat is expelled to the cold reservoir.
- In practice, *e* is on the order of 20 – 40%.

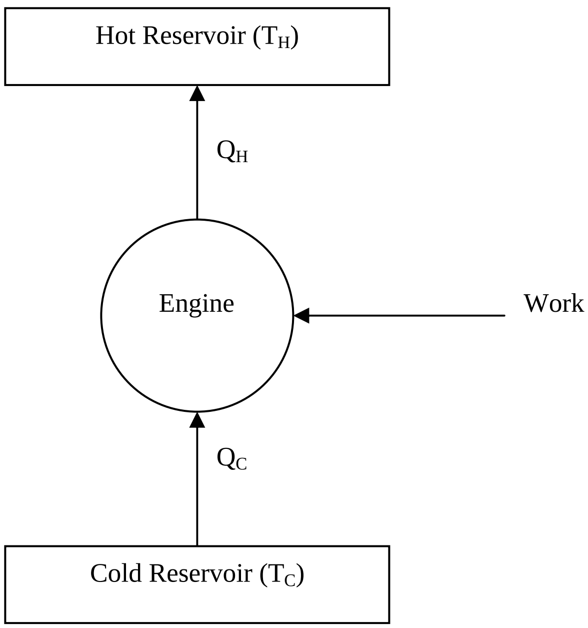
Example: The burning of a fuel-air mixture in a piston driven heat engine produces 10,000J of heat of which 7000J exits the engine at the exhaust manifold. What is the efficiency of this engine?

$$e = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{7000J}{10000J} = 30\%$$

The 1st and 2nd Laws preclude the invention of perpetual motion machines.

- energy must be conserved
- $e < 100\%$

A refrigerator (or heat pump) is a heat engine running in reverse.



Work is done <u>on</u> the refrigerator.

A refrigerator transfers heat from a cold reservoir to a hot reservoir. Work must be done <u>on</u> the system to accomplish this because heat will not spontaneously flow from cold to hot.

Reversible/Irreversible Processes

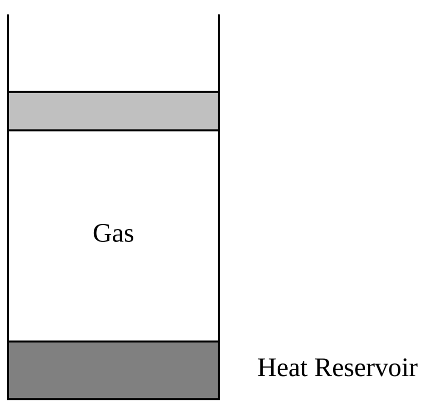
Irreversible processes go only in one direction without the influence of some external agent.

Examples

- Heat always flows from hot to cold
- A bouncing rubber ball always bounces with less amplitude on successive bounces.
- A pile of sand will always eventually spread out.

A process may be reversible if it passes from its initial state to its final state through a series of equilibrium states that are both quasi-static and close together.

Consider a piston containing gas in contact with some source of heat:



- If grains of sand are dropped one by one onto the piston and heat is allowed to move from the gas to the reservoir in the process the gas is compressed isothermally.
- P and V change slowly as each grain of sand is added defining a series of thermodynamic states in which P, V, & T are discrete.
- Each grain of sand decreases the volume of the gas and increases the pressure in the system.
- The states change slowly and are close together.
- The process may be reversed by slowly removing grains and allowing heat to flow back from the reservoir to the gas.

This is an example of a quasi-static, reversible process

- A reversible process is defined by a succession of equilibrium states.
- Irreversible processes cannot be represented on a PV diagram.
- Anything that creates non-equilibrium states renders a process non-reversible.

Equilibrium stopping effects:

- Friction
- Conduction
- Convection
- Radiation
- Anything that dissipates heat

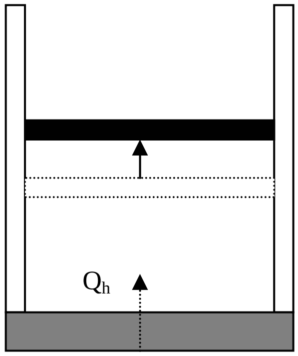
Since these factors are always found in nature, truly reversible processes are not found in nature.

- Approximately reversible processes may be created but require careful process management.
- These principles are very important in establishing an upper limit on the efficiency of heat engines.

Carnot Cycle Heat Engines

- Governed by a reversible cycle between heat reservoirs.
- The epitome of efficiency in heat engines, but an idealized process.
- No real engine may exceed the efficiency of a Carnot cycle engine.
- The working substance in a Carnot engine is an ideal gas.
- The walls of a Carnot engine are non-conducting.

The Carnot Cycle

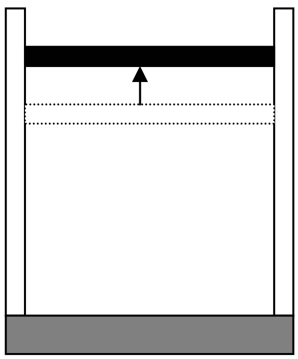


Heat Reservoir @ T_h

$A \rightarrow B$

Isothermal expansion

The process $A \rightarrow B$ is an isothermal expansion at temperature T_h, in which the gas is placed in thermal contact with a heat reservoir through the base of the cylinder and does work W_{AB} in raising the piston.

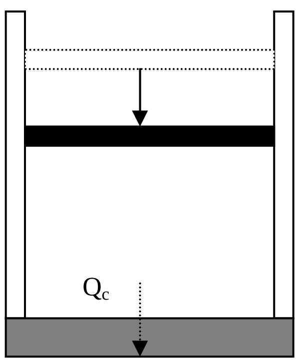


$B \rightarrow C$

Adiabatic expansion

$Q = 0$

In the process $B \rightarrow C$, the base of the cylinder is replaced by a thermally nonconducting wall that the gas expands adiabatically. During this process the temperature falls from T_h to T_c and the gas does work W_{BC} in raising the piston.

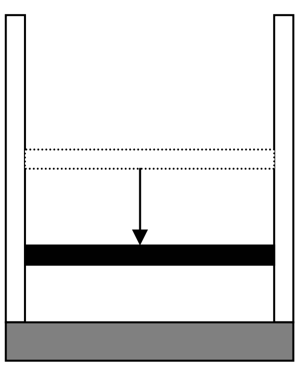


Heat Reservoir @ T_c

$C \rightarrow D$

Isothermal compression

In the process $C \rightarrow D$, the gas is placed in thermal contact with a heat reservoir at temperature Tc and is compressed isothermally at temperature T_c. During this time the gas expels heat to Q_c to the reservoir and the work done on the gas by the external agent is W_{CD}.



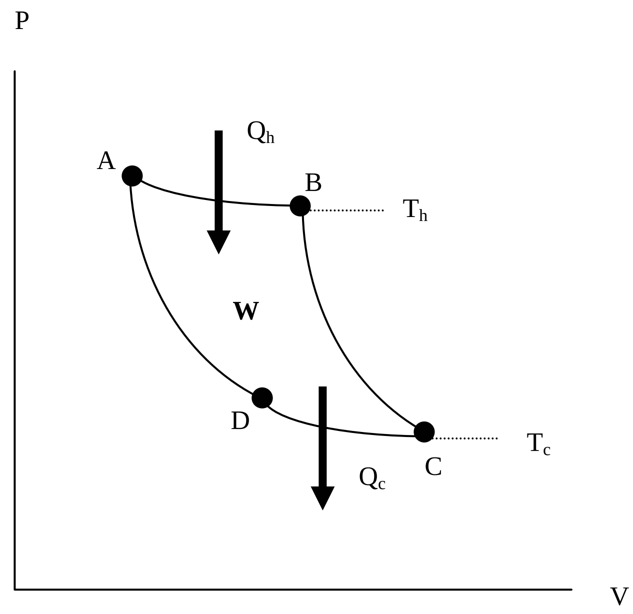
$D \rightarrow A$

Adiabatic compression

$Q = 0$

In the final stage $D \rightarrow A$, the base of the cylinder is replaced by a non-conducting wall and the gas is compressed adiabatically. The temperature of the gas increases to T_h and the work done on the gas by an external agent is W_{DA}.

PV Diagram for a Carnot cycle.



- The net work done, *W*, equals the net heat received in one cycle, $Q_b - Q_c$.
- $\Delta U = 0$ for the cycle.

Recall: $e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$ for a heat engine.

For a Carnot engine: $\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \therefore e = 1 - \frac{T_C}{T_H}$.

- All Carnot engines operating between the same two reservoirs have the same efficiency.

- The greater the difference between T_H and T_C, the greater the efficiency of a Carnot engine.

- As $T_C \rightarrow T_H$, $e \rightarrow 0$.

- As a practical matter, it is usually easier to raise the temperature of the hot reservoir than to lower the temperature of the cold reservoir.

It is possible to define a temperature scale that is completely independent of material properties using the Carnot cycle.

Recall: $\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$ for the Carnot cycle. The ratio of the temperatures may be obtained by operating an engine in a Carnot cycle between reservoirs at these two temperatures and measuring Q_C and Q_H. A temperature scale may then be determined with reference to some fixed-point temperatures.

The *absolute* or Kelvin scale is defined by choosing 273.16 as the absolute temperature of the triple point of water.

$$T = (273.16K)\frac{Q}{Q_3}$$

The absolute temperature scale is identical to the ideal gas temperature scale. It is also independent of the working substance and may be used at very low temperatures.

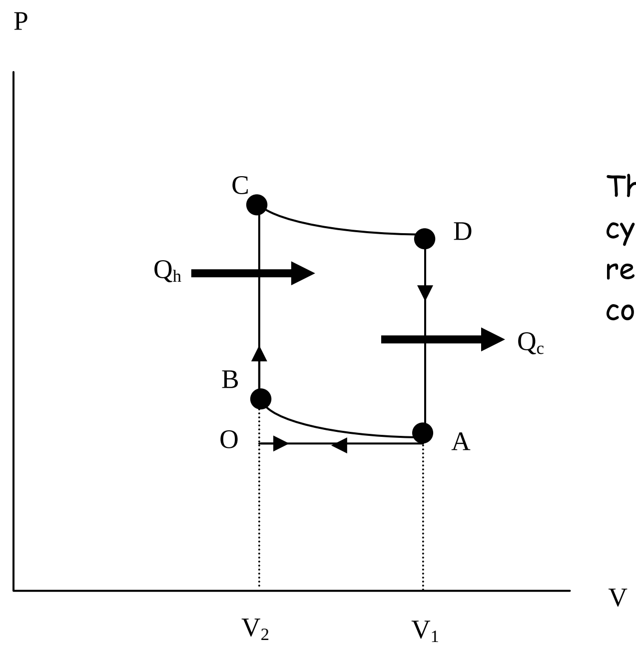
Recall: $e = 1 - \frac{T_C}{T_H}$ for a Carnot engine. If T_C is maintained at absolute zero, a 100% Carnot cycle is possible.

If this were possible (which it is not) any Carnot engine operating between T_C = 0K and any T_H would convert all of the heat absorbed to work.

An alternative definition of absolute zero.

- *Absolute zero is the temperature of a reservoir at which a Carnot engine will expel no heat.*

Otto Cycle Gasoline Engines



The PV diagram for the Otto cycle. This process approximately represents the internal combustion engine.

1. During the *intake stroke* (O → A), air at atmospheric pressure is drawn into the cylinder and the volume increases @ atmospheric pressure from V_2 to V_1 (<u>isobaric</u>).

2. During the *compression stroke* (A → B), the fuel-air mixture is compressed <u>adiabatically</u> from volume V_1 to volume V_2, and the temperature increases from T_A to T_B. The work done on the gas is the area under the AB curve.

3. Combustion occurs in the process B → C and heat Q_H is added to the gas. This heat is not from the outside of the system. It is heat released during the combustion process. During this process the pressure and temperature increase rapidly but the volume remains essentially constant (<u>isovolumetric</u>). No work is done on the gas.

4. During the *power stroke* (C → D), the gas expands <u>adiabatically</u> from V_2 to V_1, causing the temperature to drop from T_C to T_D. The work done by the gas is the area under the CD curve.
5. In the process D → A, heat QC is extracted from the gas as its pressure decreases at <u>constant volume</u> (hot gas is replaced by cool gas). No work is done during this process.

6. During the *exhaust stroke* (A → O), the residual gases are exhausted at atmospheric pressure and the volume decreases from V_1 to V_2 (<u>isobaric</u>).

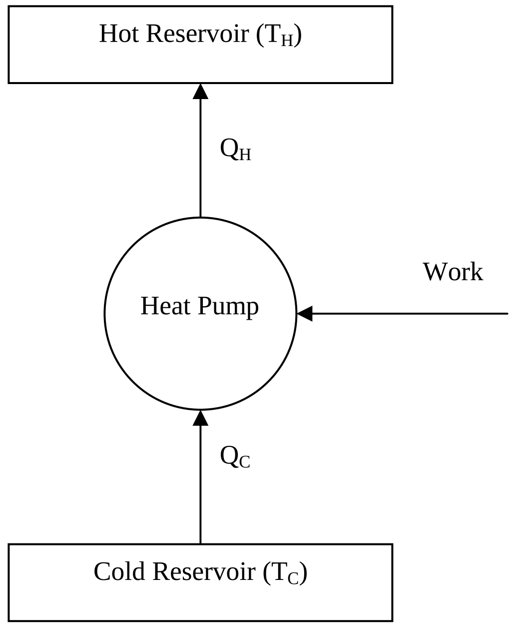
If the fuel-air mixture is assumed to be approximately an ideal gas, the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma - 1}}$$

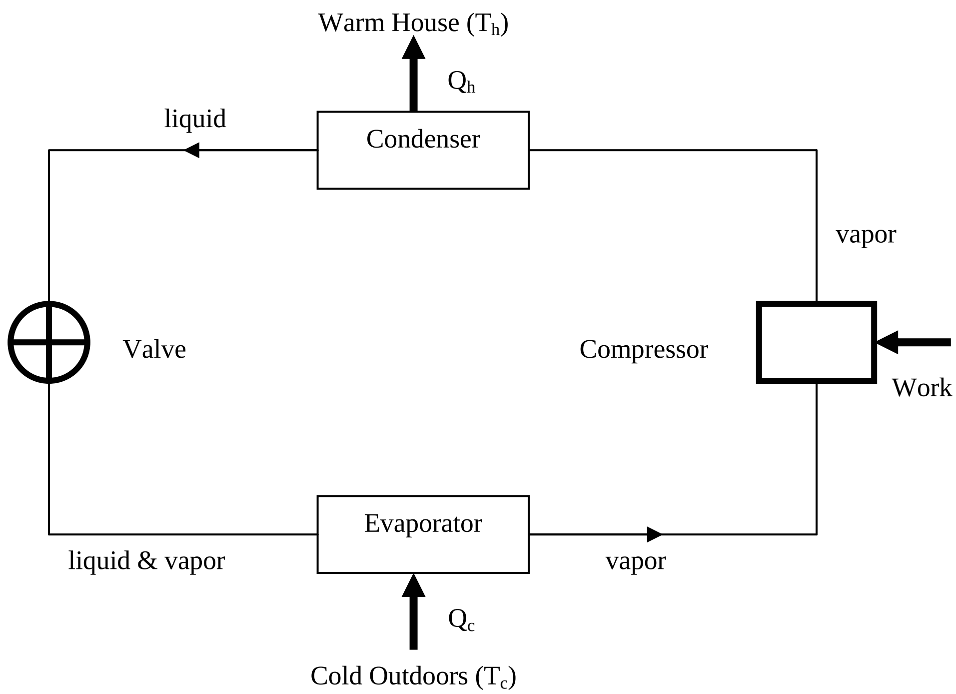
where γ is a constant related to molar heat capacities and V_1/V_2 is called the *compression ratio*. This expression yields a higher efficiency for higher compression ratios.

For typical values of γ = 1.4 and compression ratios of about 8:1, a theoretical efficiency of 56% is predicted by this expression. Real world efficiencies are on the order of 15 – 20%.

Heat Pumps and Refrigerators



A heat pump is a mechanical device that is used to both heat and cool the interiors of homes and buildings. Heat pumps use a circulatory fluid to absorb heat from the outside of the structure and release it in the interior. When operated as an air conditioner, the cycle is reversed.



- The *evaporator* contains a mixture of the working fluid (Freon or a more uv friendly substitute) in both liquid and vapor states. Evaporation is a process that absorbs heat. As the working fluid evaporates, heat is absorbed from the outside.

- The *compressor* does work on the vapor, compressing it adiabatically. The energy used by the compressor is the energy paid for in a heating pump.

- The *condenser* contains a mixture of the vapor and liquid. As the working fluid condenses, heat is liberated into the interior of the structure.

- A *valve* regulates the circulation of the working fluid back to the evaporator.

The coefficient of performance for a heat pump is defined as the ratio of the heat transferred to the work done by the pump:

$$COP_{HeatPump} = \frac{Q_h}{W}$$

If the outside temperature is 25^0F or higher, the COP for a heat pump is about 4, i.e., about four times more heat is transferred into the structure than the work done by the pump. COP's for heat pumps diminish when the outside temperature drops below zero degrees F. In many cold areas, heat pumps are *ground coupled*.

A heat pump may be operated in reverse to function as an air conditioner during the summer.

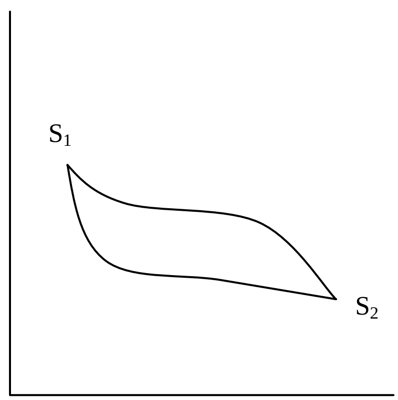
Entropy

Temperature and Internal energy are linked with the zero^th and first laws, respectively.

Temperature and Internal Energy are state functions, i.e., they may be used to specify a thermodynamic state.

Entropy, S, is another state function.

Consider a quasi-static, reversible process between two equilibrium states:



If $\Delta Q_{reversible}$ is the heat absorbed or expelled by the system in some infinitesimal of the path:

- The change in entropy, dS, between two equilibrium states is given by the heat transferred, ΔQ_r, divided by the absolute temperature, T, of the system in this interval, i.e., $\Delta S = \frac{\Delta Q_r}{T}$

Convention: Change of Entropy

- heat absorbed → ΔQ_r (+) → S increases
- heat expelled → ΔQ_r (-) → S decreases

Entropy

- Isolated systems tend towards disorder and entropy is a measure of this disorder

An alternative statement of the Second Law in entropic terms:

- The entropy of the Universe increases in all natural processes