# Equilibrium Thermodynamics II:
# Engines <sub>[tsc2]</sub>

Engines as understood here involve a thermodynamic system undergoing a cyclic process while exchanging heat $\Delta Q$ with and performing work $\Delta W$ on the environment. Extensive $X$ and intensive $Y$ are conjugate variables.

We adopt the convention that $\Delta Q > 0$ means positive heat flowing into the system and $\Delta W > 0$ means positive work done on the system, thus both increasing its internal energy $U$.
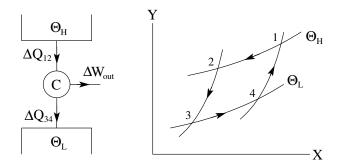
## Carnot engine:

Zeroth law: Any state of thermal equilibrium can be characterized by a measurable empirical temperatures $\Theta$.

Second law: Heat flows spontaneously from high to low temperature.

Thermal contact: Temperature differences $\Delta\Theta$ disappear without producing work. They are, in a sense, wasteful.

Heat engine: Part of the heat flowing from high to low temperature is converted into work via a cyclic process.

Carnot engine: Wasteful heat flows are eliminated, which requires that the cyclic process is fully reversible. The Carnot cycle has four steps.



$1 \to 2$  Engine in contact with reservoir at high temperature $\Theta_H$.
Isothermal absorption of heat: $\Delta Q_{12} > 0$ at $\Theta_H$.

$2 \to 3$  Engine thermally isolated from environment.
Adiabatic cooling: $\Theta_H \to \Theta_L$ with $\Delta Q_{23} = 0$.

$3 \to 4$  Engine in contact with reservoir at low temperature $\Theta_L$.
Isothermal expulsion of heat: $\Delta Q_{34} < 0$ at $\Theta_L$.

$4 \to 1$  Engine thermally isolated from environment.
Adiabatic heating: $\Theta_L \to \Theta_H$ with $\Delta Q_{41} = 0$.

**Efficiency of Carnot engine:**

The internal energy $U$ is a state variable. During each step it changes due to heat exchange and/or work performance. At the end of the cycle, its original value is restored.

$$\Rightarrow \ \Delta U = \Delta Q_{12} + \Delta W_{12} + \Delta W_{23} + \Delta Q_{34} + \Delta W_{34} + \Delta W_{41} = 0.$$

Total heat input: $\Delta Q_{\text{in}} = \Delta Q_{12}$.

Net work output: $\Delta W_{\text{out}} = -\Delta W_{12} - \Delta W_{23} - \Delta W_{34} - \Delta W_{41}$.

$$\Delta U = 0 \Rightarrow \ \Delta W_{\text{out}} = \Delta Q_{12} + \Delta Q_{34} = \Delta Q_{12} - |\Delta Q_{34}|.$$

Efficiency: $\eta \doteq \dfrac{\Delta W_{\text{out}}}{\Delta Q_{\text{in}}} = 1 - \dfrac{|\Delta Q_{34}|}{\Delta Q_{12}}.$
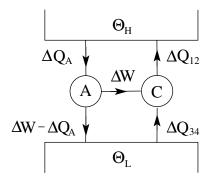
**Maximum efficiency of heat engines:**

Efficiencies of different engines can be compared if they operate between heat reservoirs at the same (empirical) temperatures.

Is it possible to construct a heat engine $A$ which is more efficient than the Carnot engine $C$?

The Carnot engine involves only reversible processes. Therefore, it can be run in reverse with same heat transfers and work performances.

Use engine $A$ to drive engine $C$ in the reverse i.e. as a refrigerator.



Heat transfers: $\Delta Q_A > 0, \ \Delta Q_{12} < 0, \ \Delta Q_{34} > 0.$

Work performance: $\Delta W = \Delta W_{out}^{(A)} = \Delta W_{in}^{(C)} > 0.$

Efficiencies: $\eta_A = \dfrac{\Delta W}{\Delta Q_A}, \quad \eta_C = \dfrac{\Delta W}{|\Delta Q_{12}|}$

Since engine $C$ operates reversibly, $\eta_C$ is the same in the forward and reverse directions. Note: $\eta_C$ is not an efficiency in the reverse mode.

Implications if engine $A$ were more efficient than engine $C$:

$$\eta_A > \eta_C \quad \Rightarrow \quad \Delta Q_A < |\Delta Q_{12}|.$$
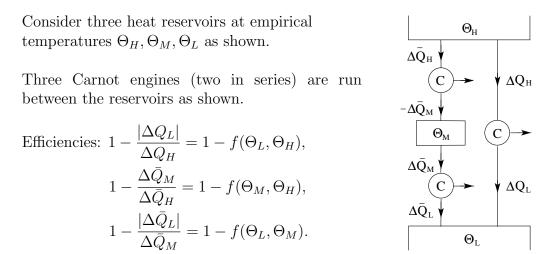
The two engines running in tandem would then cause a net heat flow from low to high temperature with no work input, which represents a violation of the second law.

Conclusions:

- Engine $A$ cannot be more efficient than engine $C$.
- All Carnot engines operating between empirical temperatures $\Theta_H$ and $\Theta_L$ must have the same efficiency.

### Absolute temperature:

The universal efficiency of Carnot engines operating between reservoirs of given empirical temperatures makes it possible to define an absolute temperature, a monotonic function, $T = g(\Theta)$, of empirical temperature $\Theta$.

Consider three heat reservoirs at empirical temperatures $\Theta_H, \Theta_M, \Theta_L$ as shown.

Three Carnot engines (two in series) are run between the reservoirs as shown.

Efficiencies: $1 - \dfrac{|\Delta Q_L|}{\Delta Q_H} = 1 - f(\Theta_L, \Theta_H)$,

$\qquad\qquad 1 - \dfrac{\Delta \bar{Q}_M}{\Delta \bar{Q}_H} = 1 - f(\Theta_M, \Theta_H)$,

$\qquad\qquad 1 - \dfrac{|\Delta \bar{Q}_L|}{\Delta \bar{Q}_M} = 1 - f(\Theta_L, \Theta_M)$.

Note that $\Delta \bar{Q}_H$, $\Delta \bar{Q}_M$, and $\Delta Q_H$ are positive, whereas $\Delta \bar{Q}_L$ and $\Delta Q_L$ are negative, according to the convention adopted.

Implication of the second law: if $\Delta \bar{Q}_L = \Delta Q_L$ then $\Delta \bar{Q}_H = \Delta Q_H$.

If $\Delta \bar{Q}_H \neq \Delta Q_H$, we could run the engines on the left or right in reverse mode and create a net heat flow from low to high temperature.

Consequence of equalities:

$$\frac{|\Delta\bar{Q}_L|}{\Delta\bar{Q}_H} = \frac{|\Delta\bar{Q}_L|}{\Delta\bar{Q}_M}\frac{\Delta\bar{Q}_M}{\Delta\bar{Q}_H} = \frac{|\Delta Q_L|}{\Delta Q_H}.$$

Implication for universal Carnot efficiency:

$$\Rightarrow\ f(\Theta_L,\Theta_M)f(\Theta_M,\Theta_H) = f(\Theta_L,\Theta_H).$$

Functional form which satisfies functional equation:

$$f(\Theta_L,\Theta_H) = \frac{g(\Theta_L)}{g(\Theta_H)}.$$

Running Carnot engines makes it possible to determine the function $g(\Theta)$ for any choice of empirical temperature.

Definition of absolute temperature ratios:

$$\frac{T_L}{T_H} \doteq \frac{g(\Theta_L)}{g(\Theta_H)}.$$

Kelvin scale of absolute temperature is fixed by triple point of water (unique temperature and pressure for which $H_2O$ coexists as gas, liquid, and solid):

$$T_{\text{trp}} = 273.16\text{K}.$$

**Entropy:**

Heat is not a state variable.
In the Carnot cycle the net heat transfer is nonzero: $\Delta Q_H + \Delta Q_L \neq 0$.

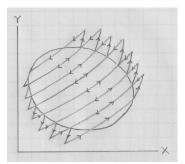A state variable associated with heat transfer can be constructed from the efficiency expression of the Carnot cycle:

$$\eta = 1 - \frac{|\Delta Q_L|}{\Delta Q_H} = 1 - \frac{T_L}{T_H} \quad \Rightarrow \quad \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_H}{T_H} = 0.$$

Any reversible cyclic process is equivalent to an array of Carnot cycles running in parallel.



For any reversible cyclic process we have:

$$\oint \frac{dQ}{T} \doteq \oint dS = 0.$$

The state variable thus constructed is the entropy $S$. The equality, $dS = dQ/T$, only holds for reversible processes.

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Implications for the zero-temperature limit:

- Maximum efficiency $\eta = 1$ can only be realized if $T_L = 0$.
- The third law states that $dQ = TdS = 0$ in the limit $T \to 0$.
- Hence all reversible processes become adiabatic as $T \to 0$.
- Cooling a thermodynamic system requires extraction of heat.
- A Carnot engine run in reverse extracts heat most efficiently.
- Heat extraction loses traction in the limit $T \to 0$.
- Cooling a macroscopic system to $T = 0$ is an elusive goal.

Irreversible generalization of the Carnot cycle:

$$\eta = 1 - \frac{|\Delta Q_L|}{\Delta Q_H} < 1 - \frac{T_L}{T_H} \;\Rightarrow\; \frac{|\Delta Q_L|}{\Delta Q_H} > \frac{T_L}{T_H} \;\Rightarrow\; \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_H}{T_H} < 0.$$

In a more general quasistatic cyclic process we have:

$$\oint \frac{dQ}{T} \le 0, \;\; \oint dS = 0 \;\Rightarrow\; dS \ge \frac{dQ}{T}.$$

For all irreversible process in isolated system we have:

$$\Delta Q = 0 \;\Rightarrow\; \Delta S > 0.$$

**Internal energy:**

The first law states that $U$ is a state variable. In the expression,

$$dU = dQ + dW + dZ,$$

the differential $dU$ is exact, but the differentials $dQ$ for heat transfer, $dW$ for work performance, and $dZ$ for matter transfer are not.

Expressing the inexact differentials in terms of state variables,[1]

$$dQ = TdS, \qquad dW = -pdV + HdM + \dots, \qquad dZ = \mu dN,$$

enables us to combine the first and second laws into an exact differential for the internal energy:

$$dU = TdS - pdV + HdM + \mu dN + \dots$$

This exact differential will be used in practical application and in the further development of equilibrium thermodynamics.

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[1]Among the many different ways of work performance we cite just the two most prominent ones: mechanical work of a piston and work by an external magnetic field.

**Reversible processes in fluid system:**

Most heat engines employ a fluid as the working medium. Here we summarize some relevant facts that will be used in the description of various heat-engine designs.

We focus on reversible processes with heat transfer, $dQ = TdS$, work performance, $dW = -pdV$, and no transfer of matter, $dN = 0$.

- Isothermal process: $T = $ const.   $dQ \neq 0$ in general.
- Isochoric process: $V = $ const.   $dQ = C_V dT$, $dU = C_V dT$.
- Isobaric process: $p = $ const.   $dQ = C_p dT$.
- Isentropic (adiabatic) process: $S = $ const.   $dQ = 0$.

The heat capacities $C_V$ and $C_p$ will be properly introduced later.
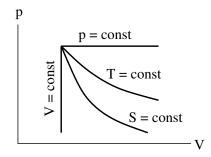
Internal energy: $dU = dQ + dW = TdS - pdV$.

$$V = \text{const.} \; \Rightarrow \; dW = 0 \; \Rightarrow \; dU = dQ \quad \text{(no work performed)}.$$
$$S = \text{const.} \; \Rightarrow \; dQ = 0 \; \Rightarrow \; dU = dW \quad \text{(no heat transferred)}.$$

Classical ideal gas as an approximate realization of a very dilute fluid:

- Equation of state: $pV = nRT$.
- Internal energy: $U = C_V T$, $C_V = \alpha n R = $ const [tex1].
    - monatomic gas: $\alpha = \frac{3}{2}$, $\gamma = \frac{5}{3}$.
    - diatomic gas: $\alpha = \frac{5}{2}$, $\gamma = \frac{7}{5}$.
    - polyatomic gas: $\alpha = 3$, $\gamma = \frac{4}{3}$.

- Isotherm: $T = $ const. $\Rightarrow pV = $ const.
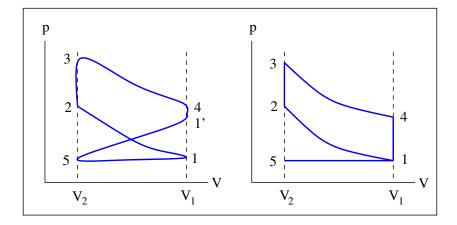- Adiabate: $S = $ const. $\Rightarrow pV^\gamma = $ const., $\gamma = 1 + 1/\alpha$

**Gasoline engine (Otto cycle):**

Four-stroke Otto cycle (left)

1-2: compression stroke

2-3-4: power stroke (spark plug ignites at 2)

4-1'-5: exhaust stroke (exhaust valve opens at 4)

5-1: intake stroke (intake valve opens at 5)



Idealized Otto cycle (right)

1-2: adiabatic compression of air-fuel mixture ($S = $ const)

2-3: explosion of air-fuel mixture ($V = $ const)

3-4: adiabatic expansion of exhaust gas ($S = $ const)

4-1: isochoric release of exhaust gas ($V = $ const).

1-5-1: intake stroke (thermodynamically ignored)

Parameter: $K \doteq V_1/V_2$ (compression ratio).

The compression ratio $K$ must not be chosen too large to prevent the air-fuel mixture from igniting spontaneously, i.e. prematurely.
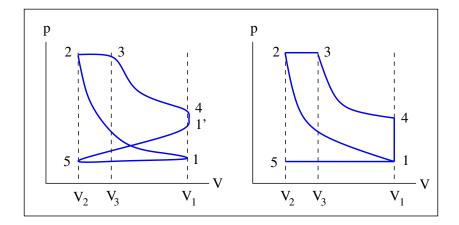
**Diesel engine:**

Four-stroke Diesel cycle (left)

1-2: compression stroke (fuel injected and spontaneously ignited at 2)

2-3-4: power stroke (Diesel fuel burns more slowly than gasoline)

4-1'-5: exhaust stroke (exhaust valve opens at 4)

5-1: intake stroke (intake valve opens at 5)



Idealized Diesel cycle (right)

1-2: adiabatic compression of air ($S = $ const)

2-3: isobaric expansion as fuel explodes ($p = $ const)

3-4: adiabatic expansion of exhaust gas ($S = $ const)

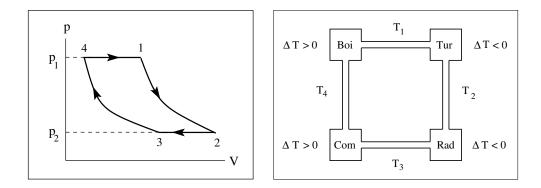4-1: isochoric release of exhaust gas ($V = $ const).

1-5-1: intake stroke (thermodynamically ignored)

Parameters: $K \doteq V_1/V_2$ (compression ratio), $\quad L \doteq V_3/V_2$

**Escher-Wyss gas turbine:**

A gas flows in a closed system from the boiler via the turbine to the radiator and then via the compressor back into the boiler.

As the beam of hot gas hits the blades of the turbine during the power stroke it expands with little heat transfer. The compression of the cooled gas is also roughly adiabatic. The gas is heated up inside the boiler and cooled down inside the radiator at different but roughly constant pressures.
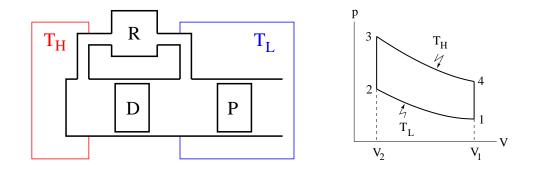


Idealized process (Joule cycle)

1-2: Adiabatic expansion of the hot gas after ejection from the boiler as it drives the turbine ($S = $ const).

2-3: Isobaric contraction as the gas flows through the radiator and cools down further in the process ($p = $ const).

3-4: Adiabatic compression of the cooled gas for injection into the boiler ($S = $ const).

4-1: Isobaric expansion of the gas as it heats up inside the boiler ($p = $ const).

The pressure inside the boiler is regulated by the rates of gas injection and ejection and the rate of heat transfer from the energy source to the gas.

The injection and ejection rates are the same in mass units but the ejection rate is larger than the injection rate in volume units. This accounts for the expansion of the gas inside the boiler as described in step 4-1.

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**Stirling engine:**

The Stirling engine is an external combustion engine. It isolates the working fluid from the heat source. Combustion is better controlled than in internal combustion engines.



Piston P expands gas at high temperature $T_H$ and compresses gas at low temperature $T_L$.

Displacer D moves gas between regions of high temperature $T_H$ and low temperature $T_L$ through the regenerator.

Regenerator R acts as a heat exchanger. It stores heat when hot gas flows from left to right and releases heat when colder gas flows from right to left.

Idealized Stirling cycle:

1-2: Isothermal compression at temperature $T_L$.
   Displacer stationary at left. Piston moving left.

2-3: Isochoric heating up at volume $V_2$.
   Piston stationary at left. Displacer moving right.

3-4: Isothermal expansion at temperature $T_H$.
   Displacer and piston moving right.

4-1: Isochoric cooling down at volume $V_1$.
   Piston stationary at right. Displacer moving left.

Some of the heat is recycled in the regenerator. This amount should not be counted in the expression $\eta = \Delta W_{out}/\Delta Q_{in}$ of the efficiency.

**Exercises:**

▷ Entropy change by expanding ideal gas [tex1]

▷ Heating the air in a room [tex2]

▷ Carnot engine of a classical ideal gas [tex3]

▷ Carnot engine of an ideal paramagnet [tex4]

▷ Idealized Otto cycle [tex8]

▷ Adiabates of the classical ideal gas [tex7]

▷ Work extracted from finite heat reservoir in infinite environment [tex9]

▷ Work extracted from finite heat reservoir in finite environment [tex10]

▷ Mayer's relation for heat capacities of the classical ideal gas [tex12]

▷ Room heater: electric radiator versus heat pump [tex13]

▷ Idealized Diesel cycle [tex16]

▷ Roads from 1 to 2: isothermal, isentropic, isochoric, isobaric [tex25]

▷ Positive and negative heat capacities [tex26]

▷ Ideal-gas engine with two-step cycle I [tex106]

▷ Ideal-gas engine with two-step cycle II [tex107]

▷ Joule cycle [tex108]

▷ Idealized Stirling cycle [tex131]

▷ Circular heat engine I [tex147]

▷ Circular heat engine II [tex148]

▷ Square heat engine [tex149]

▷ Work performance and heat transfer [tex155]