Thermodynamics Lecture Notes: Chapter 9

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9 Thermal Machines

9.1 Thermal/Heat Engines

Note of caution: signs of Q can be a bit confusing in this section 9.1 of the original lecture script, better follow the approach on the lecture slides.

A heat engine takes heat, $Q_1 > 0$, from a reservoir with temperature T_1, and coverts it to work. The fact that the work, W, done by change the state of the system, depends on the path it takes, it is used to extract the work. In order to extract work continuously, the path has to come back to the original state making a cycle. Since the state of the heat engine comes back to the original one, the entropy of the heat engine remains unchanged after the cycle (if we consider reversible processes). On the other hand, the Entropy change of the heat reservoir after one cycle is given by

$$\Delta S_1 = -\frac{Q_1}{T} < 0 \tag{1}$$

and the total entropy change is given by

$$\Delta S_{total} = \Delta S_1 = -\frac{Q_1}{T} < 0 \tag{2}$$

which does not agree with the second law of thermodynamic, stating that $\Delta S_{total} \geq 0$ for an isolated system. In order to fulfil the second law, we need to introduce another heat reservoir with a temperature T_2, where $T_2 < T_1$ and the engine ejects heat, $Q_2 < 0$, to the second reservoir. The entropy change of the second reservoir is then

$$\Delta S_2 = -\frac{Q_2}{T} > 0 \tag{3}$$

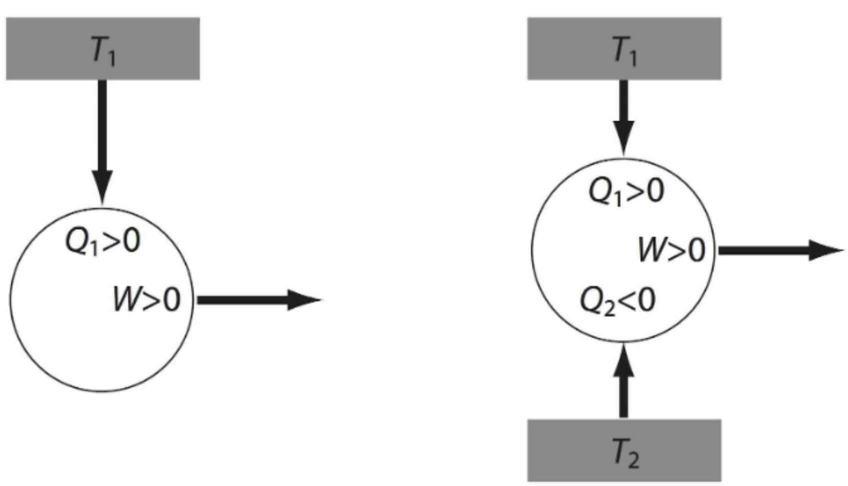

Figure 1: Schematic sketch of a heat engine.

In this case, the first law gives, $\Delta E_{int} = Q_1 + Q_2 - W = 0$, i.e.

$$Q_2 = -Q_1 + W \tag{4}$$

and the total entropy change is given by

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \tag{5}$$

From the second law, we have

$$\Delta S_{total} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \geq 0 \tag{6}$$

leads to

$$\frac{Q_2}{T_2} \leq -\frac{Q_1}{T_1}, \text{ i.e. } \frac{Q_2}{Q_1} \leq -\frac{T_2}{T_1} \tag{7}$$

The efficiency of the heat engine is given by

$$\epsilon = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1} \tag{8}$$

While a perfect engine has $\epsilon = 1$, a real engine has an efficiency less than 1, i.e.

$$\epsilon \leq 1 - \frac{T_2}{T_1} < 1 \tag{9}$$

9.2 Carnot Cycle

To demonstrate the result on the efficiency above, the Carnot cycle, a combination of isothermal and adiabatic processes, was invented, see Fig. 2. There is no real engine using the Carnot cycle, but it can be used to demonstrate the second law of thermodynamic, with four states, A, B, C, and D:

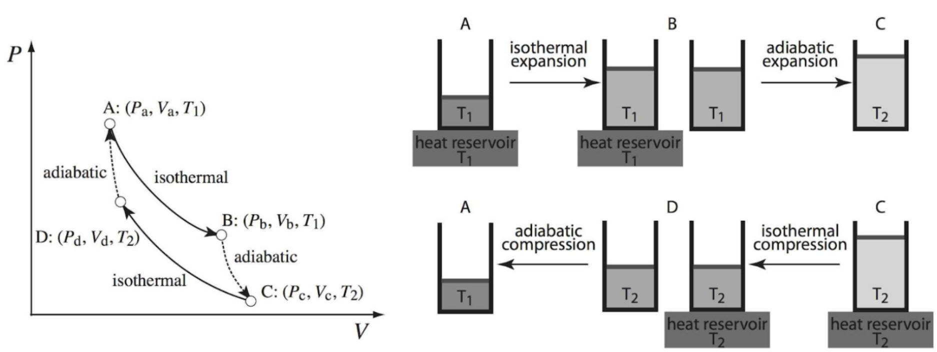

Figure 2: Carnot cycle in PV diagram

- $A(V_a, P_a, T_1)$: A cylinder with an ideal gas is attached to a heat reservoir with a temperature T_1.

- $A \to B$: Isothermal expansion with a constant temperature T_1, heat $Q_1 > 0$ into the cylinder from the reservoir, and work $W_{ab} > 0$ being done.
- $B(V_b, P_b, T_1)$: The cylinder is removed from the heat reservoir and thermally isolated.
- $B \to C$: Adiabatic expansion (Q = 0) till the temperature drops to T_2 and work done, W_{bc}
- $C(V_c, P_c, T_2)$: The cylinder is attached to another heat reservoir with a temperature T_2.
- $C \to D$: Isothermal compression with a constant temperature T_2, heat $Q_2 < 0$ out of the cylinder to the reservoir, and work $W_{cd} < 0$ being done.
- $D(V_d, P_d, T_2)$: The cylinder is removed from the heat reservoir and thermally isolated.
- DA: Adiabatic compression (Q = 0) till the temperature raise to T_1 and work, $W_{da} < 0$, done from the outside.

As done previously for the isothermal process, we have

$$W_{ab} = \int_{V_a}^{V_b} PdV = nRT_1 \int_{V_a}^{V_b} \frac{dV}{V} = nRT_1 \ln \frac{V_b}{V_a} \tag{10}$$

and for ideal gas $\Delta E_{int} = 0$, leading to $\Delta E_{int} = Q - W = 0$, and thus, to

$$Q_1 = W_{ab} = nRT_1 \ln \frac{V_b}{V_a} > 0 \tag{11}$$

Equally,

$$Q_2 = W_{cd} = nRT_2 \ln \frac{V_d}{V_c} < 0 \tag{12}$$

In the adiabatic expansion, we have $PV^\gamma = P_b V_b^\gamma$, thus the work between $B \to C$ is given by

$$\begin{aligned} W_{bc} = \int_{V_b}^{V_c} PdV = P_b V_b^\gamma \int_{V_b}^{V_c} V^{-\gamma} dV = \frac{P_b V_b^\gamma}{1-\gamma} V^{1-\gamma}\Big|_{V_b}^{V_c} &= \frac{P_b V_b^\gamma}{1-\gamma}(V_c^{1-\gamma} - V_b^{1-\gamma}) \\ &= \frac{P_b V_b}{1-\gamma}\left[\left(\frac{V_c}{V_b}\right)^{1-\gamma} - 1\right] \end{aligned} \tag{13}$$

Equally for the adiabatic compression, the work for $D \to A$ is given by

$$\begin{aligned} W_{da} = \int_{V_d}^{V_a} PdV = P_a V_a^\gamma \int_{V_d}^{V_a} V^{-\gamma} dV = \frac{P_a V_a^\gamma}{1-\gamma} V^{1-\gamma}\Big|_{V_d}^{V_a} &= \frac{P_a V_a^\gamma}{1-\gamma}(V_a^{1-\gamma} - V_d^{1-\gamma}) \\ &= \frac{P_a V_a}{1-\gamma}\left[\left(1 - \frac{V_d}{V_a}\right)^{1-\gamma}\right] \end{aligned} \tag{14}$$

For the isothermal processes, we have $P_a V_a = P_b V_b$ and $P_c V_c = P_d V_d$. And for the adiabatic processes it follows that $P_b V_b^\gamma = P_c V_c^\gamma$ and $P_a V_a^\gamma = P_d V_d^\gamma$.

Furthermore, the ideal gas law gives

$$\frac{P_aV_a}{T_1} = \frac{P_bV_b}{T_1} = \frac{P_cV_c}{T_2} = \frac{P_dV_d}{T_2} \tag{15}$$

It follows that

$$\begin{aligned} &P_bV_b^\gamma = P_cV_c^\gamma \\ &P_bV_b^\gamma \frac{T_1}{P_bV_b} = P_cV_c^\gamma \frac{T_2}{P_cV_c} \\ &V_b^{\gamma-1}T_1 = V_c^{\gamma-1}T_2 \\ &\frac{T_1}{T_2} = \left(\frac{V_c}{V_b}\right)^{\gamma-1} \end{aligned} \tag{16}$$

and

$$\begin{aligned} &P_aV_a^\gamma = P_dV_d^\gamma \\ &P_aV_a^\gamma \frac{T_1}{P_aV_a} = P_dV_d^\gamma \frac{T_2}{P_dV_d} \\ &V_a^{\gamma-1}T_1 = V_d^{\gamma-1}T_2 \\ &\frac{T_1}{T_2} = \left(\frac{V_d}{V_a}\right)^{\gamma-1} \end{aligned} \tag{17}$$

giving

$$\begin{aligned} W_{bc} + W_{da} = &\frac{P_bV_b}{1-\gamma}\left[\left(\frac{V_c}{V_b}\right)^{1-\gamma} - 1\right] + \frac{P_aV_a}{1-\gamma}\left[\left(1 - \frac{V_d}{V_a}\right)^{1-\gamma}\right] \\ &\frac{P_aV_a}{1-\gamma}\left[\frac{T_1}{T_2} - 1 + 1 - \frac{T_1}{T_2}\right] \\ &= 0 \end{aligned} \tag{18}$$

i.e. the adiabatic parts of works cancel each other.

This conclusion can be reached in a much simpler way. As indicated before, $\Delta E_{int} = nC_V\Delta T$ and for an adiabatic process, $Q = 0$ leads to $\Delta E_{int} = -W$. It follows that

$$W_{bc} = -\Delta E_{int}^{bc} = -nC_V(T_2 - T_1) \quad \text{and} \quad W_{da} = -\Delta E_{int}^{da} = -nC_V(T_1 - T_2) \tag{19}$$

which leads to

$$W_{bc} + W_{da} = 0 \tag{20}$$

The total work is now given by

$$W = W_{ab} + W_{cd} = nRT_1 \ln\frac{V_b}{V_a} + nRT_2 \ln\frac{V_d}{V_c} = nRT_1 \ln\frac{V_b}{V_a} - nRT_2 \ln\frac{V_c}{V_d} \tag{21}$$

Note that the first law of thermodynamic is valid and $W = Q_1 + Q_2$. Using

$$\frac{T_1}{T_2} = \left(\frac{V_c}{V_b}\right)^{\gamma-1} = \left(\frac{V_d}{V_a}\right)^{\gamma-1} \tag{22}$$

we obtain

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}, \text{ i.e. } \frac{V_b}{V_a} = \frac{V_c}{V_d} \tag{23}$$

thus,

$$W = W_{ab} + W_{cd} = nR(T_1 - T_2) \ln \frac{V_b}{V_a} \tag{24}$$

and the efficiency is given by

$$\epsilon = \frac{W}{Q_1} = \frac{nR(T_1 - T_2) \ln \frac{V_b}{V_a}}{nRT_1 \ln \frac{V_b}{V_a}} = 1 - \frac{T_2}{T_1} \tag{25}$$

i.e the Carnot cycle gives the maximum efficiency allowed by the second law of thermodynamic.

Carnot cycle and T-S plot

In the previous section, the Carnot cycle was drawn on the pressure (P) versus volume (V) plane. From the relation, $\delta W = PdV$, valid for a reversible process, the area surrounded by the Carnot cycle, $A \to B \to C \to D$, on the P-V plane gives the total work of the Carnot engine. By recalling the expression, $\delta Q = TdS$, for a reversible process, let us draw the Carnot cycle on the temperature (T) versus entropy (S) plane. On this plane, an isothermal process, T constant, is a horizontal line and an adiabatic process, $Q = 0$, thus S constant, is a vertical line. Therefore, a Carnot cycle is a rectangular box on the T-S plane as shown in Fig. 3. Similar for the work, the area surrounded by $A \to B \to C \to D$ on the T-S plane give the total heat of the Carnot engine.

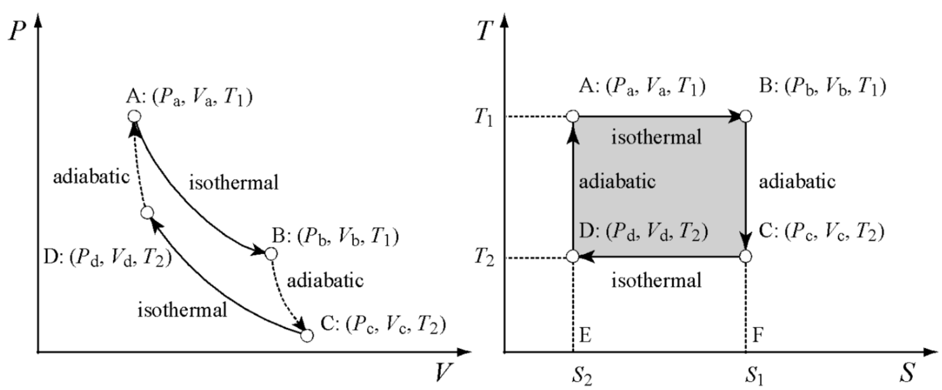

Figure 3: Carnot cycle in the PV and TS diagrams.

As introduced in Chapter 6, the infinitesimal change in the internal energy can be given from the first law of thermodynamics as

$$dE_{int} = TdS - PdV \tag{26}$$

By recalling that the internal energy depends only on the temperature, i.e.

$$dE_{int} = \left(\frac{\partial E_{int}}{\partial T} \right) dT = nC_V dT \tag{27}$$

it follows that

$$dS = \frac{dE_{int}}{T} + \frac{P}{T}dV = nC_V\frac{dT}{T} + nR\frac{dV}{V} \tag{28}$$

For a change of state from (P_1, V_1, T_1) to (P_2, V_2, T_2), the change of the entropy, ΔS, is given by the integration as

$$\Delta S = nC_V\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V} = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} \tag{29}$$

The entropy change for the isothermal expansion $A \to B$, ΔS, is given by

$$\Delta S = nR\ln\frac{V_b}{V_a} \tag{30}$$

thus the area of the rectangular box is given by

$$Q_{total} = \Delta S(T_1 - T_2) = nR(T_1 - T_2)\ln\frac{V_b}{V_a} \tag{31}$$

in agreement with the analysis before without using the entropy.

9.3 Refrigerators and air conditioning

The operation principle of refrigerators and air conditioners are the reverse of a heat engine, transferring heat from a cool environment to a warm environment by work (shown in Fig. 4). In order to demonstrate how a refrigerator works, we operate the Carnot cycle in the reversed order: $A \to D \to C \to B \to A$. In this case, the upper and lower limits for the integration in the heat and work calculations must be exchanged. Thus, the sign of the heat and work need to be flipped (again, considering reversible processes). The efficiency or coefficient of performance (COP) of a refrigerator is defined as

$$\epsilon_{refrigerator} = \frac{|\text{Thermal energy extracted from the heat reservoir with } T = T_2|}{|\text{Total work given to the refrigerator}|} \tag{32}$$

From the Carnot engine calculations, heats for $A \to D$ and $B \to A$, Q_{dc} and Q_{ba}, respectively are given by

$$Q_{dc} = nRT_2\ln\frac{V_c}{V_d} > 0 \quad \text{and} \quad Q_{ba} = nRT_1\ln\frac{V_a}{V_b} < 0 \tag{33}$$

and similarly for the work, $A \to D$, $D \to C$, $C \to B$, and $B \to A$

$$\begin{aligned} W_{ad} &= \frac{P_bV_b}{1-\gamma}\left[\left(\frac{V_c}{V_b}\right)^{1-\gamma} - 1\right] \\ W_{dc} &= nRT_2\ln\frac{V_c}{V_d} \\ W_{cb} &= \frac{P_bV_b}{1-\gamma}\left[\left(1 - \frac{V_c}{V_b}\right)^{1-\gamma}\right] \\ W_{ba} &= nRT_1\ln\frac{V_d}{V_c} \end{aligned} \tag{34}$$

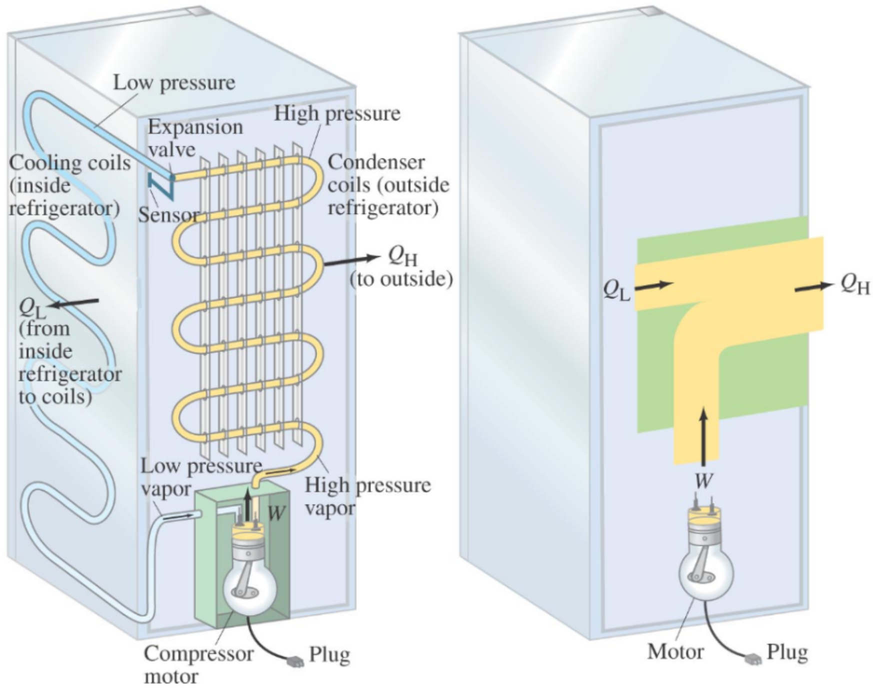

Figure 4: Schematic sketch of a refrigerator.

The total work is given by

$$W_{total} = W_{ad} + W_{dc} + W_{cb} + W_{ba} = nR(T_2 - T_1) \ln \frac{V_c}{V_d} \tag{35}$$

The thermal energy extracted from the heat reservoir with $T = T_2$ is given by Q_{dc}, and the work given to the refrigerator is $-W_{total}$. Thus the efficiency is then given by

$$\epsilon_{refrigerator} = \frac{|Q_{dc}|}{|W_{total}|} = \frac{nRT_2 \ln \frac{V_c}{V_d}}{nR(T_1 - T_2) \ln \frac{V_c}{V_d}} = \frac{T_2}{T_1 - T_2} \tag{36}$$

Note: ϵ of refrigerators, air conditioners, also heat pumps is typically called "Coefficient of Performance", and can be larger than 1 (the term efficiency might be misleading).

9.4 Heat Pumps

Also heat pumps work as reversed heat/Carnot engines; as shown in Fig. 5, in contrast to refrigerators, we consider here the heat Q_1 put into the hotter reservoir T_1 when computing the efficiency of a heat pump:

$$\epsilon_{\text{heat pump}} = \frac{|\text{Thermal heat put into hot heat reservoir } T = T_1|}{|\text{Total work given to the heat pump}|} = \frac{T_1}{T_1 - T_2} \tag{37}$$

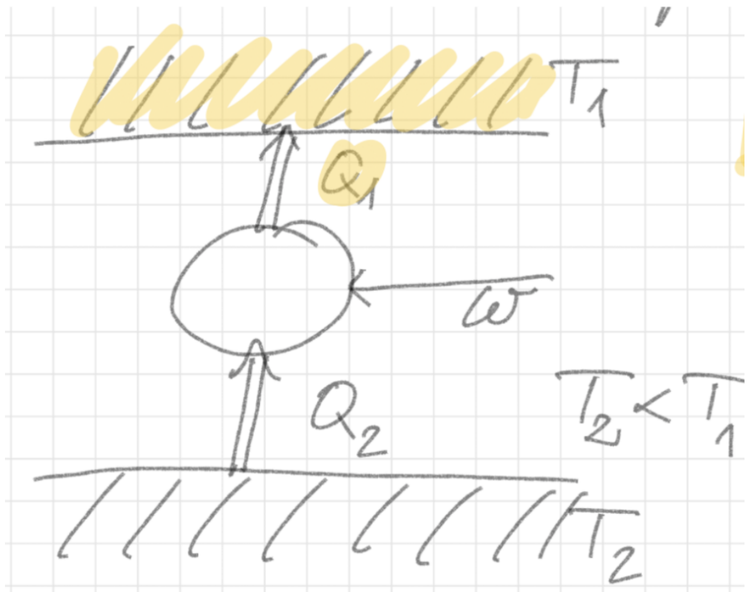

Figure 5: Schematic sketch of a heat Pump.

9.5 On the impossibility of perpetual motion machines

Is it possible to build a perpetual motion with two Carnot engines?

The first low of thermodynamics does not allow drawing work from nothing. The second law of thermodynamics does not allow to covert 100% of heat to work. Now we consider two Carnot engines where the first one works in a normal way producing a positive work, W, to the outside. Those work is then fed to the second Carnot engine operates in the reverse direction (see visualisation in Fig. 6). The thermal energy transferred from the high temperature heat reservoir to the low temperature by the first engine is restored by the second one. Thus, the two engines seem to work forever. This third kind of perpetual motion is not allowed by the energy losses such as the frictions and heat losses of a real machine (as thermal processes are never fully reversible in reality).

9.6 Examples for heat engines

9.6.1 Stirling Engine

The thermal cycle of a Stirling consists of the following four steps: 1) isothermal expansion, 2) isovolumetric heat exhaustion, 3) isothermal compression, 4) isovolumetric heat absorption as shown in Fig. 7.

Questions: What is the heat and work of each subprocess? What is the efficiency? How does this process look like in the TS diagram?
⇒ see lecture slides.

Fig. 8 further visualises how a real Stirling engine works.

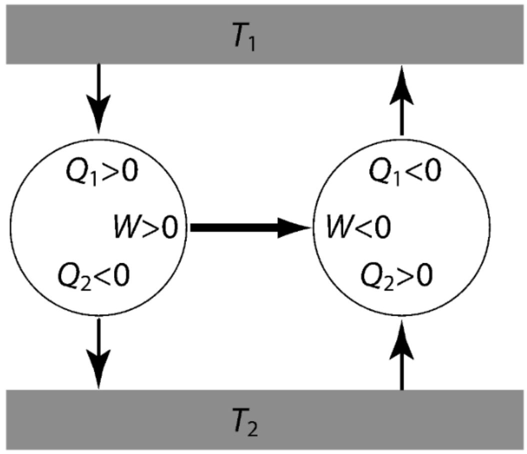

Figure 6: Schematic sketch of a hypothetic perpetual motion machine.

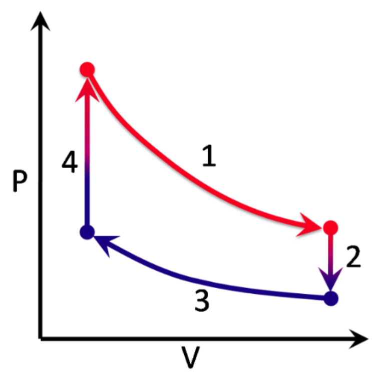

Figure 7: Thermal cycle of a Sterling Engine.

9.6.2 Otto Cycle

Many cars are built around an Otto engine, whose cycle is composed of two adiabatic and two isochoric processes (shown in Fig. 9):

- $1 \to 2$: adiabatic compression of air-gasoline mix
- $2 \to 3$: isochoric heating
- $3 \to 4$: adiabatic expansion
- $4 \to 1$: isochoric cooling (gas exhaust)

9.6.3 Diesel Engine Cycle

Lastly, also a Diesel engine is still used in some cars/trucks. A Diesel cycle is composed of adiabatic compression ($1 \to 2$), isobaric decompression ($2 \to 3$), adiabatic decompression

(3→4), and isochoric compression (4→1) as shown in Fig. 10.
Note that isentropic means a reversible adiabatic process (with $dS = 0$).

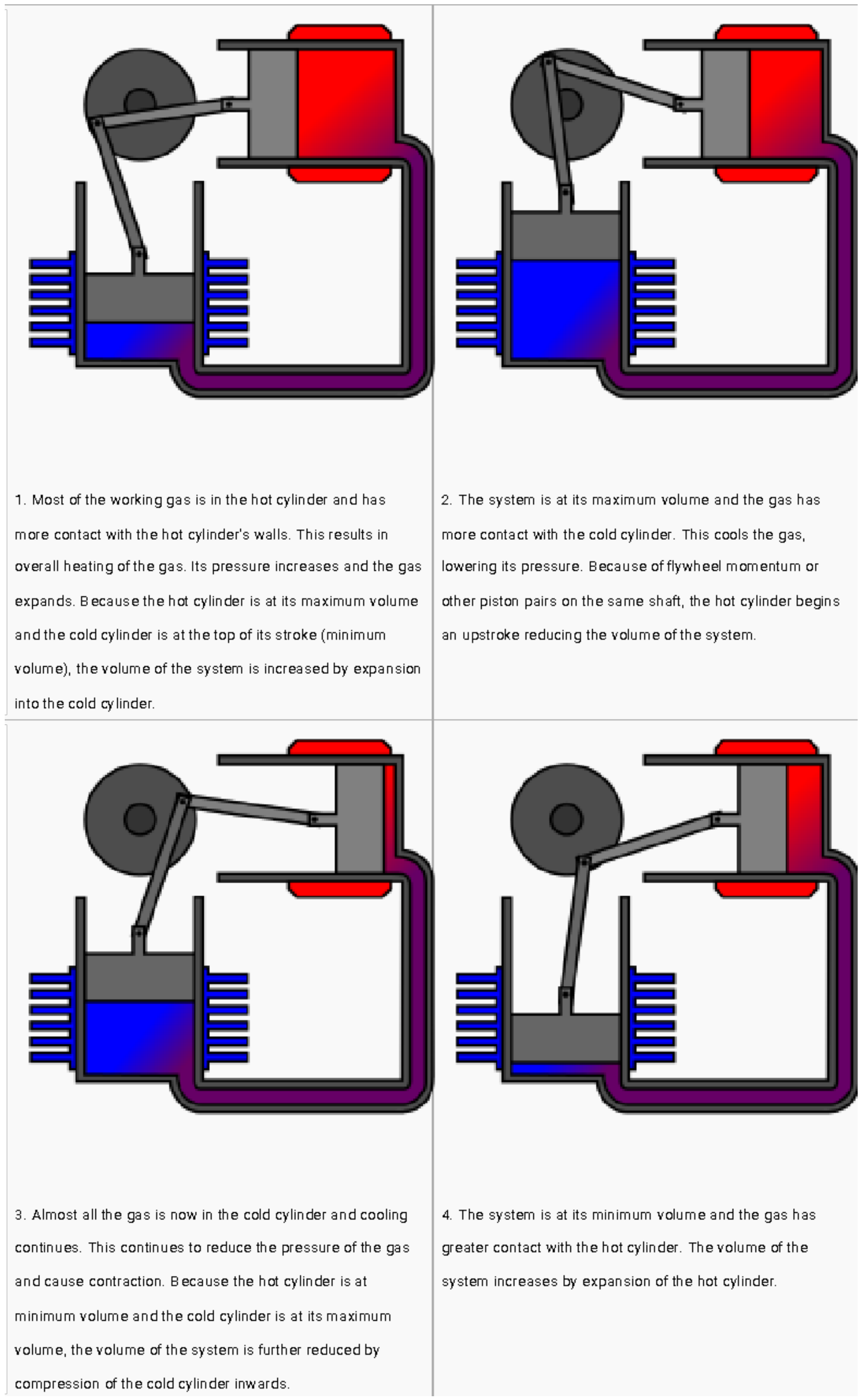

Figure 8: Visualisation of the Sterling engine cycle processes.

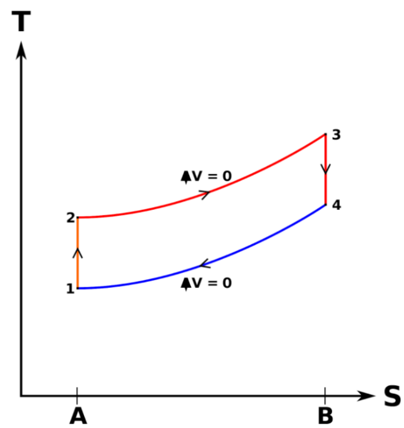

Figure 9: Otto cycle in the PV diagram.

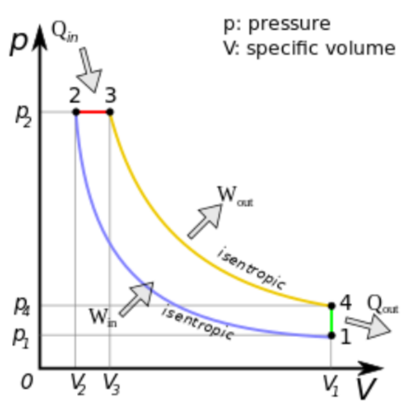

Figure 10: Diesel engine cycle.