Maximal Efficiency of Heat Engine. Carnot Cycle

The Second Law of Thermodynamics. The Gibbs distribution realizes the maximum of entropy at fixed energy, total number of particles, and volume. This means that the entropy of a closed system is either constant (if the system is in equilibrium), or increasing (if the system is not in the equilibrium). The same is true for a non-closed—say, kept at constant pressure,— but an isolated from heat sources system. Indeed, if there is no heat transfer and we change the system volume (or any other external parameter) adiabatically, then the entropy remains constant. If we change external parameters non-adiabatically, then we render the system non-equilibrium, and get the increase of entropy due to the relaxation processes towards an equilibrium. Hence, no matter what we are doing with a heat-insulated system, its entropy cannot decrease. This statement is known as The Second Law of Thermodynamics. If the system is not thermally isolated, but is in equilibrium, then we have the following thermodynamic relation between a small entropy change, $\mathrm{d}S$, and corresponding heat, $\mathrm{d}Q$, transferred to the system:

$$\mathrm{d}S \; = \; \mathrm{d}Q/T \; . \tag{1}$$

If the heat $\mathrm{d}Q$ has been transferred to the system in a non-equilibrium fashion, then, in accordance with The Second Law, we have

$$\mathrm{d}S \; \geq \; \mathrm{d}Q/T \; . \tag{2}$$

For our purposes, it is also useful to specially consider Eq. (2) under the conditions when we remove some small amount of heat from the system and want to know how large is the corresponding *decrease* in entropy. In this case, Eq. (2) yields

$$|\mathrm{d}Q| \; \geq \; T\,|\mathrm{d}S| \qquad\qquad (\mathrm{d}Q,\, \mathrm{d}S \, < \, 0) \; . \tag{3}$$

That is to remove some amount of entropy from the system we need to also remove some sufficiently large amount of heat. And it is precisely this circumstance that leads to an *upper bound on the efficiency of the heat engines.*

Heat Engine. By heat engine we mean some device that takes heat from some infinitely large heat reservoir and transforms it into mechanical work. The efficiency of the engine, η, is defined as the ratio of the amount of work, ΔW, to the corresponding amount of heat, ΔQ:

$$\eta \; = \; \frac{\Delta W}{\Delta Q} \; . \tag{4}$$

Eq. (3) states that together with the heat ΔQ our engine inevitably gets the entropy

$$\Delta S \; \geq \; \Delta Q/T \; , \tag{5}$$

where T is the temperature of the heat reservoir. Now we need to clarify the statement of our problem. We assume that the engine uses *only* the energy of the heat bath and does it for an arbitrarily long time. This is equivalent to a requirement that the engine works in a cyclic fashion always returning to some “initial” state. Then, at some stage of the cycle the engine should get rid of the entropy price paid for getting the heat ΔQ. But, in accordance with (3), getting rid of entropy will cost a heat price:

$$\Delta Q_1 \; \geq \; T_1 \Delta S \; , \tag{6}$$

where T_1 is the temperature of *another* reservoir, absorbing the heat. By energy conservation,

$$\Delta W \; \leq \; \Delta Q - \Delta Q_1 \; . \tag{7}$$

[The inequality corresponds to possible energy losses.] Hence,

$$\eta \;\le\; \frac{\Delta Q - \Delta Q_1}{\Delta Q} \;=\; 1 - \frac{\Delta Q_1}{\Delta Q} \;, \tag{8}$$

and taking into account Eqs. (5) and (6) we finally get

$$\eta \;\le\; 1 - \frac{T_1}{T} \;. \tag{9}$$

So, for the efficiency to be at least non zero we need $T_1 < T$, that is we always need a heat bath with lower energy than our energy reservoir. We also see that if $T - T_1 \ll T$, then the efficiency is very low, while at $T_1 \ll T$ the efficiency is close to 100%.

Carnot Cycle. Given the constraint (9), we wonder what particular scheme, if any, can realize the maximal efficiency

$$\eta_{\rm max} \;=\; 1 - \frac{T_1}{T} \;. \tag{10}$$

The simplest scheme is the *Carnot cycle.* The "engine" is nothing else than any macroscopic equilibrium system with a possibility of adiabatically varying its volume. The cycle consists of the following four steps.

(i) *Isothermal expansion.* At this stage the system is in a contact with the heat reservoir at the temperature T. The system expands in a quasi-equilibrium fashion. It simultaneously performs some work and absorbs some heat. The quasi-equilibrium means that during the process the state of the system is arbitrarily close to the equilibrium at the temperature T and the given instant volume. The change of the entropy of the system, ΔS, is thus exactly equal to $\Delta Q/T$.
(ii) *Adiabatic expansion.* At some point, the system is detached from the heat reservoir, and the isothermal expansion is replaced by the adiabatic expansion. This stage is necessary to lower the temperature of the system down to T_1, to prepare the system for passing heat to the colder reservoir, which is important to get rid of the entropy. At the stage of adiabatic expansion the system continues to perform a work.
(iii) *Isothermal compression.* At this stage the system is in a contact with the heat reservoir at the temperature T_1, and is being compressed in a quasi-equilibrium fashion. The stage of the isothermal compression ends when the heat $\Delta Q_1 = T_1 \Delta S$ is transferred to the reservoir. The work performed at this stage is negative.
(iv) *Adiabatic compression.* The system is detached from the reservoir T_1 and is adiabatically compressed till its temperature becomes equal to T. This is necessary to end up the cycle by returning the system to its starting position in terms of the original volume and temperature equal to T. The work performed at this stage is also negative.

All the stages of the Carnot cycle are quasi-equilibrium. This means that the entropy changes are related by the amounts of heat by exact equalities rather than inequalities. We thus have

$$\Delta Q_1 \;=\; T_1\,\Delta S \;=\; (T_1/T)\,\Delta Q \;. \tag{11}$$

We also assume absence of any energy losses:

$$\Delta W \;=\; \Delta Q - \Delta Q_1 \;. \tag{12}$$

From (11)-(12) we see that $\eta = \eta_{\rm max}$.