# Chapter 5
# Energy Conversion and the Second Law

## 5.1 Energy Conversion

In the preceding sections we have evaluated the second law with respect to its ability for the description of basic equilibration processes, e.g., the equilibration of temperature, the direction of heat transfer, the dissipation of kinetic energy, and friction losses in gears. Now we shall apply thermodynamic analysis to conversion processes between work and heat.

The science of thermodynamics emerged from an engineering question: How much work can be obtained from a given amount of heat? This question arose when the first steam engines were built, which had efficiencies of only a few percent. The question is still of outmost importance, as a sustainable way of living requires the optimal use of resources. Having a good understanding of the possibilities and limitations in energy conversion processes is the first step in building better—more efficient—engines.

Before we discuss more complex energy conversion processes, we consider a relatively simple problem: Energy conversion processes between two thermal reservoirs at different temperatures $T_H$ and $T_L$, with $T_H > T_L$.

The natural environment, usually assumed to be at $T_0 = 25\,^\circ\mathrm{C}$, is the prototype of a thermal reservoir. Due to its size, the environment has almost infinite thermal mass $mc_v$, and hence it can provide or accept a large amount of heat without changing its temperature. Ultimately, all systems are in thermal contact with the natural environment, and it serves as heat sink or source for most energy conversion processes.

Many of today's heat engines rely on the combustion of a fuel (coal, oil, gas). Combustion processes do not create a reservoir of constant high temperature, but rather a flow of hot combustion gases that provides heat at varying temperature. Therefore, the following considerations are not always directly applicable to combustion systems. Nevertheless, the subsequent sections give important and relevant insights, to which we shall come back again and again.

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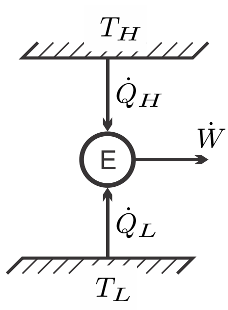


**Fig. 5.1** Two heat reservoirs at $T_H$ and $T_L$ connected by a thermal engine $E$

Pure heat transfer between the two reservoirs was discussed already in Sec. 4.8, with the statement that by itself heat goes from warm to cold, but cannot go from cold to warm. We now consider processes that involve heat and work. The systems considered are engines that operate at steady state, that is they do not accumulate or loose energy or entropy over time, $\frac{dE}{dt} = \frac{dS}{dt} = 0$. The detailed processes inside the engines will be discussed extensively later. For the present overall evaluation, however, they are of no concern, and thus the set-up considered is as simple as shown in Fig. 5.1: The thermal engine E exchanges heat with both reservoirs, and produces or consumes power. The direction of the arrows in Fig. 5.1 simply indicates the convention for heat and work: heat in and work out are positive. In the following figures, however, we will use absolute values of heat and work, and the direction of the flows will be indicated by the directions of the arrows.

For steady state processes, the first and second law for this set-up read

$$0 = \dot{Q}_H + \dot{Q}_L - \dot{W} \quad , \quad -\frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_L}{T_L} = \dot{S}_{gen} \geq 0 \,. \tag{5.1}$$

## 5.2 Heat Engines

First we consider power generation, that is the conversion of heat into work in a *heat engine*, so that $\dot{W} = \left|\dot{W}\right| > 0$. Elimination of $\dot{Q}_L$ between the first and second law (5.1) gives the work

$$\dot{W} = \left(1 - \frac{T_L}{T_H}\right) \dot{Q}_H - T_L \dot{S}_{gen} \,. \tag{5.2}$$

Since we require $\dot{W} > 0$, the right hand side of this equation must be positive as well. The last term, $-T_L \dot{S}_{gen}$, is zero or negative, since thermodynamic temperature and entropy generation rate are both non-negative; therefore, the first term, $\left(1 - \frac{T_L}{T_H}\right) \dot{Q}_H$, must be positive. Since the bracket is always positive, this implies positive heat input from the hot reservoir, $\dot{Q}_H = \left|\dot{Q}_H\right| > 0$. The heat rejected to the colder reservoir is $\dot{Q}_L = -\frac{T_L}{T_H}\dot{Q}_H - T_L\dot{S}_{gen} < 0$. Figure 5.2 shows the direction of heat and work flow for a heat engine between the reservoirs.

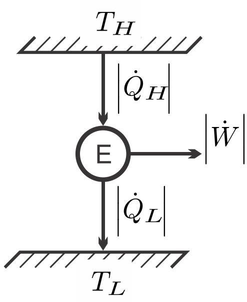


**Fig. 5.2** Heat and work directions in a heat engine

According to (5.2), for given $T_H$, $T_L$, the work output is larger for smaller entropy generation rate $\dot{S}_{gen} \geq 0$. Entropy generation is due to heat transfer and friction processes within the engine, and between engine and reservoirs, and cannot be totally avoided in real engines. Instead, the engineering task is to minimize entropy generation within the system as much as possible, in order to achieve the best possible performance of the engine. The work loss to irreversibilities is proportional to the entropy generation,

$$\dot{W}_{\text{loss}} = T_L\dot{S}_{gen} \geq 0 \, . \tag{5.3}$$

The theoretical limit for the power generated from two reservoirs with constant temperatures is obtained for $\dot{S}_{gen} = 0$, that is for a fully reversible engine, as

$$\dot{W}_C = \left(1 - \frac{T_L}{T_H}\right)\dot{Q}_H \, . \tag{5.4}$$

This is the work output of a Carnot engine, named after Sadi Carnot (1796-1832), who established this theoretical limit. Any entropy generation $\dot{S}_{gen}$ in the engine reduces the work output by $T_L\dot{S}_{gen}$.

To quantify the performance of engines, it is useful to define dimensionless efficiency measures that compare the output ("what you get") to the input ("what you pay for"). For heat engines, accordingly, one defines the thermal efficiency $\eta_{th}$ as the ratio between work output and heat input. For heat engines operating between two reservoirs, we obtain

$$\eta_{th} = \frac{\dot{W}}{\dot{Q}_H} = 1 - \frac{T_L}{T_H} - \frac{T_L\dot{S}_{gen}}{\dot{Q}_H} < 1 \tag{5.5}$$

for irreversible engines, and

$$\eta_C = \frac{\dot{W}_C}{\dot{Q}_H} = 1 - \frac{T_L}{T_H} < 1 \tag{5.6}$$

for the Carnot engine.

The Carnot efficiency $\eta_C$ is the efficiency of a fully reversible engine operating between two reservoirs at constant temperatures. Since it was computed from general considerations, its value is completely independent of the details of the engine, i.e., it does not depend on the working fluid used, nor on the realization of the engine. The Carnot efficiency is a universal limit for the thermal efficiency *any* engine operating between two reservoirs at $T_H$, $T_L$ can have. We summarize the above in two statements:

(a) *The thermal efficiency of a fully reversible engine operating between two reservoirs is independent of the realization of the engine; it is given by the Carnot efficiency* $\eta_C$.

(b) *Any engine operating between two reservoirs in which irreversible processes occur has a thermal efficiency below that of a fully reversible engine.*

The amount of work produced grows with the temperature ratio $T_H/T_L$ between the reservoirs. In technical energy conversion processes one will aim for high upper temperature $T_H$ to ensure high energy conversion efficiency. At high temperatures material strength is limited, so that the upper temperatures are limited through the materials used for building the engines. Typically, the lower temperature $T_L$ is the temperature of the environment, $T_0$.

For temperature ratios $T_H/T_L$ close to unity, i.e., small temperature differences, the thermal efficiency is small, and only little power can be produced. Hence, low temperature waste heat (low $T_H$) is relatively useless for power production, and, if possible, should rather be used for space heating. High temperature waste heat (high $T_H$), however, has considerable work potential that should be used. In other words:

*Energy at high temperature is more valuable than energy at low temperature, since more work can be extracted from it.*

## 5.3 The Kelvin-Planck Statement

Even the—fully reversible—Carnot engine has a thermal efficiency $\eta_C$ below unity: Not all heat received from the hot reservoir can be converted into work, some heat must be rejected to a colder reservoir. The Kelvin-Planck formulation of the second law states this as follows:

*No steady state thermodynamic process is possible in which heat is completely converted into work.*

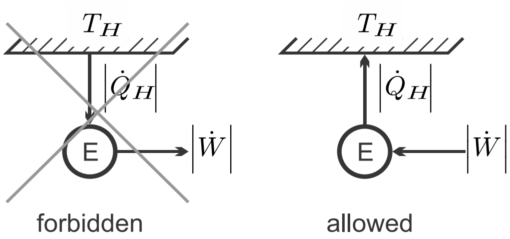


**Fig. 5.3** Heat cannot be completely converted into work, but work can be completely converted to heat

This statement is a direct consequence of the first and second law. For a steady state process with just one heat exchange the laws require

$$-\frac{\dot{Q}_H}{T_H} = -\frac{\dot{W}}{T_H} \geq 0 \, , \tag{5.7}$$

hence heat and work must both be negative. Figure 5.3 shows the forbidden process, and also the—allowed—inverse process, the complete conversion of work into heat through friction. A typical example for the latter are resistance heaters in which electrical work is converted to heat through electric resistance.

## 5.4 Refrigerators and Heat Pumps

While heat cannot go from cold to warm by itself, one can use work consuming devices to perform this task, a refrigerator or heat pump as depicted in Fig. 5.4.

A refrigerator removes heat from a cold reservoir, e.g., the interior of a freezer, at $T_L$, and rejects heat to the environment at $T_H$—the goal is to cool the cold reservoir. A heat pump is used for space heating, it takes heat from the environment at $T_L$, and rejects heat into the room that is being heated at $T_H$. While the values of the temperatures $T_L$, $T_H$ differ for refrigerator and heat pump, both operate according to the same principles.

With heat being removed from the colder reservoir, and heat rejected into the warm reservoir, we have $\dot{Q}_H = -\left|\dot{Q}_H\right| < 0$, and $\dot{Q}_L = \left|\dot{Q}_L\right| > 0$. From combining first and second law by eliminating $\dot{Q}_H$, we find the condition

$$-\dot{W} - \left(\frac{T_H}{T_L} - 1\right)\left|\dot{Q}_L\right| = T_H \dot{S}_{gen} \geq 0 \, . \tag{5.8}$$

Since $\left(\frac{T_H}{T_L} - 1\right) > 0$, the sign requirement can only be fulfilled if work is done on the system, $\dot{W} = -\left|\dot{W}\right| < 0$, where

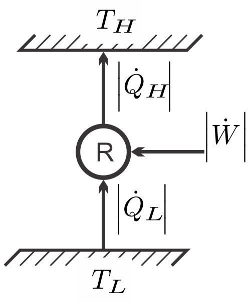


**Fig. 5.4** Heat and work directions in a refrigerator/heat pump

$$\left|\dot{W}\right| = \left(\frac{T_H}{T_L} - 1\right)\left|\dot{Q}_L\right| + T_H \dot{S}_{gen} \,. \tag{5.9}$$

This equation relates the work requirement, $\dot{W}$, to the heat removed from the colder reservoir, $\dot{Q}_L$; it is well suited for evaluating refrigerators.

For heat pump systems one is interested in the work required in relation to the heat supply $\dot{Q}_H$ to the warmer reservoir. Eliminating $\left|\dot{Q}_L\right|$ one finds

$$\left|\dot{W}\right| = \left(1 - \frac{T_L}{T_H}\right)\left|\dot{Q}_H\right| + T_L \dot{S}_{gen} \,. \tag{5.10}$$

Since $T\dot{S}_{gen} \geq 0$, any generation of entropy within a refrigeration or heat pump system increases the work requirement $\left|\dot{W}\right|$, and thus the operating cost. The extra work to overcome irreversibilities is $T_H\dot{S}_{gen}$ for a refrigerator and $T_L\dot{S}_{gen}$ for a heat pump. One will aim at reducing all causes for entropy generation, i.e., friction, heat transfer over finite temperature difference, etc., as much as possible.

The theoretical limit for the work of the refrigeration and heat pump systems are obtained for fully reversible engines, for which $\dot{S}_{gen} = 0$. This results in the expressions for a Carnot refrigerator and a Carnot heat pump, respectively, which read

$$\left|\dot{W}\right|_{R,C} = \left(\frac{T_H}{T_L} - 1\right)\left|\dot{Q}_L\right| \quad , \quad \left|\dot{W}\right|_{HP,C} = \left(1 - \frac{T_L}{T_H}\right)\left|\dot{Q}_H\right| \,. \tag{5.11}$$

Also the performance of refrigerators and heat pumps is measured by dimensionless efficiency measures that compare the output ("what you get") to the input ("what you pay for"), which here are the ratios of heat removed/supplied to the work required to run the device, known as the *coefficients of performance* (COP). We obtain, for refrigerator and heat pump operating between two reservoirs,

$$\mathrm{COP_R} = \frac{\left|\dot{Q}_L\right|}{\left|\dot{W}\right|} = \frac{1}{\frac{T_H}{T_L} - 1 + \frac{T_H \dot{S}_{gen}}{\left|\dot{Q}_L\right|}} \lessgtr 1 \,, \tag{5.12}$$

$$\mathrm{COP_{HP}} = \frac{\left|\dot{Q}_H\right|}{\left|\dot{W}\right|} = \frac{1}{1 - \frac{T_L}{T_H} + \frac{T_L \dot{S}_{gen}}{\left|\dot{Q}_H\right|}} \geq 1 \,. \tag{5.13}$$

The COP of a refrigerator can be above or below unity, but the COP of a heat pump is never below unity. A resistance heater (RH), which converts electrical power $\dot{W}_{RH}$ fully into heat $\dot{Q}_{RH} = \dot{W}_{RH}$ has a COP of unity, $\mathrm{COP_{RH}} = 1$, which is the lower bound for heat pumps. A typical heat pump has a COP above unity and gives more efficient heating.

Irreversible processes in engines lead to entropy generation and reduce the COP. For fully reversible engines we find the COP of Carnot engines,

$$\mathrm{COP}_{\mathrm{R},C} = \frac{1}{\frac{T_H}{T_L} - 1} \gtrless 1 \quad , \quad \mathrm{COP}_{\mathrm{HP},C} = \frac{1}{1 - \frac{T_L}{T_H}} > 1 \,. \tag{5.14}$$

The COPs for the Carnot refrigerator and Carnot heat pump are the maximum possible COP for refrigeration or heat pump processes between two heat reservoirs at $T_H$, $T_L$.

## 5.5 Kelvin-Planck and Clausius Statements

Clausius' statement of the second law says that *heat will not go from cold to warm by itself.* Note that the two words "by itself" are important here: a heat pump system can transfer heat from cold to warm, but work must be supplied, so the heat transfer is not "by itself."

The Kelvin-Planck statement of the second law says that it is *impossible to construct a device operating at steady state that receives heat from a single reservoir and produces work.* In other words, no heat engine can be build that has a thermal efficiency of $\eta_{th} = 1$. In our treatment, this statement followed from the evaluation of the second law, while the Clausius statement was used explicitly in its development.

The Clausius statement is a daily experience—when we touch a hot plate, we do not expect to get colder hands—but the Kelvin-Planck statement might be more difficult to grasp. It is instructive to show that both statements are equivalent. To this end, we consider the setting shown in Fig. 5.5, consisting of an engine I that completely converts the heat $\left|\dot{Q}_H\right|$ to power $\left|\dot{W}\right| = \left|\dot{Q}_H\right|$, and an engine II, a heat pump that consumes the work produced by engine I. Engine I is forbidden by the Kelvin-Planck statement while engine II is allowed by the Clausius statement. As the figure shows, the net effect of the

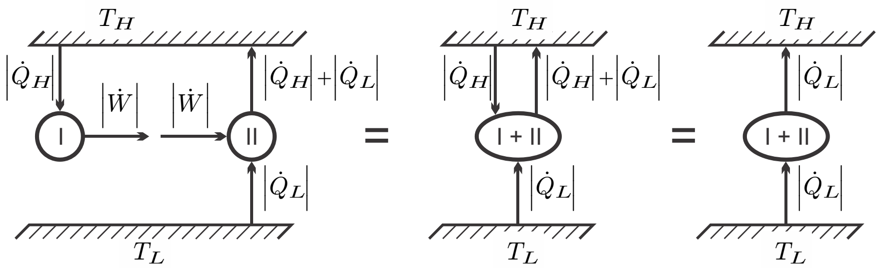


**Fig. 5.5** The equivalency of the Kelvin-Planck (K/P) and Clausius (C) statements of the second law

combined system [I + II] is heat transfer from cold to warm "by itself", which is forbidden by the Clausius statement. Both statements are equivalent.

## 5.6 Thermodynamic Temperature

In the derivation of the second law we have introduced thermodynamic temperature $T$ as the factor of proportionality between the heat transfer rate $\dot{Q}$ and the entropy flux $\dot{\Psi}$.

In previous sections we have seen that this definition of thermodynamic temperature stands in agreement with the direction of heat transfer: heat flows from hot (high $T$) to cold (low $T$) by itself. The heat flow aims at equilibrating the temperature within any isolated system that is left to itself, so that two systems in thermal equilibrium have the same thermodynamic temperature. Moreover, the discussion of internal friction showed that thermodynamic temperature must be positive.

The discussion of energy conversion processes between two reservoirs adds another requirement for thermodynamic temperature: For any reversible engine operating between two reservoirs, it must fulfill the relation

$$\frac{T_H}{T_L} = -\frac{\dot{Q}_H}{\dot{Q}_L} \,. \tag{5.15}$$

This relation follows from $(5.1)_2$ for the case of a fully reversible engine, $\dot{S}_{gen} = 0$, independent of the realization of the reversible engine, or the working substance employed.

It is therefore possible, at least in principle, to measure temperature ratios through measurement of the heat exchange in fully reversible engines. Accordingly, to define the thermodynamic temperature scale, only a single reference temperature is required.

The Kelvin temperature scale, named after William Thomson, Lord Kelvin (1824 - 1907), uses the triple point of water (611 kPa, 0.01 °C) as reference. The triple point is the state at which a substance can coexist in all three phases, solid, liquid and vapor, see Sec. 6.3. The Kelvin scales assigns the value of $T_{Tr} = 273.16\,\mathrm{K}$ to this unique point, which can be reproduced easily in laboratories.

Since thermodynamic temperature cannot be negative, the smallest possible thermodynamic temperature is $0\,\mathrm{K}$, known as *absolute zero.*

The ideal gas temperature scale, introduced in Sec. 2.13, coincides with the Kelvin scale. This will be seen later, in Sec. 8.2, when we explicitly compute the thermal efficiency of a Carnot cycle operating with an ideal gas.

## 5.7 Perpetual Motion Engines

Perpetual motion engines are engines that violate the first or the second law of thermodynamics, or both. Naturally, one will never meet these engines since they are impossible to build—the thermodynamic laws are not to be violated! One might meet inventors, however, who claim to have invented engines that do miraculous things. Inevitably, the inventors will never be able to show their engines in working condition, and their claims remain eternally unproven.

A *perpetual motion engine of the first kind* is an engine that violates the first law of thermodynamics, e.g., an engine that produces more work than the net heat exchange, $\left|\dot{W}\right| > \left|\dot{Q}_H\right| - \left|\dot{Q}_L\right|$.

A *perpetual motion engine of the second kind* is an engine that violates the second law of thermodynamics, e.g., a heat engine operating between two reservoirs at $T_L, T_H$ with an efficiency above the Carnot efficiency, $\eta > 1-\frac{T_L}{T_H}$. Violations of the second law are sometimes difficult to understand, and thus perpetual motion engines of the second kind are more difficult to identify for not so clever inventors, and their gullible investors.

## 5.8 Reversible and Irreversible Processes

Irreversible processes are associated with entropy generation which reduces the performance of engines. So far the terms *reversible* and *irreversible* were rather loosely defined in Sec. 2.10. A more exact definition of these terms will make it easier to identify irreversible processes, and the related losses. We define:

> *A thermodynamic process from state 1 to state 2 is* reversible*, if the process can be inverted so that the system returns to its initial state (state 1), and no changes remain in its surroundings.*
>
> *A thermodynamic process from state 1 to state 2 is* irreversible*, if, when the system is brought back into its initial state (state 1), changes remain in its surroundings.*

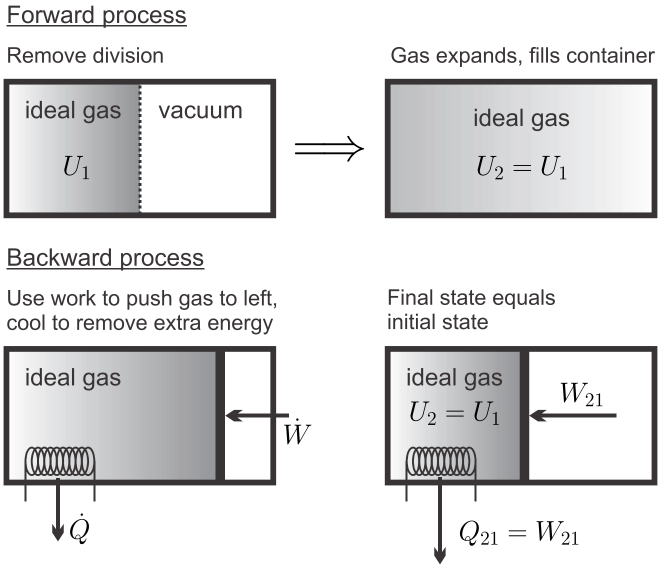


**Fig. 5.6** Upper row: Irreversible expansion of a gas into vacuum. Lower row: The intial state is recovered by pushing the piston and removing heat. Since the heat added to the surroundings, $Q_{21}$, cannot be fully converted into the work needed to push, $W_{21}$, changes remain in the surroundings.

For an example, we return to the uncontrolled expansion of an ideal gas, which is shown again in Fig. 5.6. We found, in Sec. 3.13, that the internal energies of initial and final states are the same, $U_2 = U_1$, while the gas fills a bigger volume in the final state, $V_2 > V_1$. To return the gas to the initial state, its volume must be reduced by compression, which requires the (reversible) work $W_{21} = \int_{V_2}^{V_1} pdV < 0$. The first law for any process from state 2 back to the initial state 1 reads

$$U_1 - U_2 = Q_{21} - W_{21} = 0 \; ,$$

so that the heat $Q_{21} = W_{21} < 0$ must be removed from the system, as shown in the figure. Thus, the process 2-1 draws the work $W_{21}$ from the surroundings and transfers the heat $Q_{21}$ to the surroundings. The process would be reversible, if the heat $Q_{21}$ could be completely converted to the work $W_{21}$ by an engine residing in the surroundings. This, however, is forbidden by the Kelvin-Planck statement of the second law, which states that only some of the heat can be converted to work, but not all. Thus, some extra work has to be provided to return the system to its original state, the system's surroundings have changed: the original process is irreversible.

Heat transfer serves as another example: The heat $|Q_{AB}|$ has flown from a hot body $A$ to a cold body $B$ by itself. To return both bodies to their original state one can use a heat pump, which consumes the work $W_{HP}$, removes the heat $Q_{AB}$ from the colder body $B$, and delivers the heat $|Q'_{AB}| = |Q_{AB}|+|W_{HP}|$ to the warmer body $A$. After this, body $B$ is in its initial state. Body $A$ received too much heat, however. To return $A$ into its initial state, the heat $|Q''_{AB}| = |W_{HP}|$ must be moved from $A$ to the surroundings. Due to the Kelvin-Planck statement, the heat added to the surroundings $|Q''_{AB}|$ can only provide part of the work $|W_{HP}|$ required to drive the heat pump: the process is irreversible.

## 5.9 Internally and Externally Reversible Processes

For a sound thermodynamic evaluation of processes it is important to identify and understand *all* causes for work loss to irreversible processes. Even if a process is reversible within the boundaries of the system considered, there might be associated irreversible processes outside the system boundaries. For the thorough evaluation of the performance of a system, in particular for accounting for the associated work losses inside and outside the system, the following definitions are useful:

*Internally reversible process:* No irreversible processes occur inside the system boundaries.

*Externally reversible process:* No irreversibilities occur outside the system boundaries.

*Fully reversible process*: A process which is both, externally and internally reversible.

## 5.10 Irreversibility and Work Loss

The thermodynamic laws for closed systems that exchange heat with an arbitrary number of reservoirs read

$$\frac{d\left(U+E_{kin}\right)}{dt}=\dot{Q}_0+\sum\dot{Q}_k-\dot{W}\quad,\quad\frac{dS}{dt}-\frac{\dot{Q}_0}{T_0}-\sum\frac{\dot{Q}_k}{T_k}=\dot{S}_{gen}\geq 0\ ,\quad(5.16)$$

where the heat exchange $\dot{Q}_0$ with a reservoir at $T_0$ is highlighted. Most thermodynamic engines utilize the environment as heat source or sink, and in this case $\dot{Q}_0$ should be considered as the heat exchanged with the environment. Note that the environment is freely available, and no cost is associated with removing heat from, or rejecting heat into, the environment. For the heat engines of Sec. 5.2 and the heat pumps of Sec. 5.4 the environmental temperature is $T_0 = T_L$, while for the refrigerators of Sec. 5.4 we have $T_0 = T_H$.

Elimination of $\dot{Q}_0$ between the two laws and solving for work gives

$$\dot{W} = \sum \left(1 - \frac{T_0}{T_k}\right) \dot{Q}_k - \frac{d\left(U + E_{kin} - T_0 S\right)}{dt} - T_0 \dot{S}_{gen} \ . \tag{5.17}$$

This equation generalizes the findings of the previous sections to arbitrary processes in closed systems: The generation of entropy in irreversible processes reduces the work output of work producing devices (where $\dot{W} > 0$, e.g., heat engines) and increases the work requirement of work consuming devices (where $\dot{W} < 0$, e.g., heat pumps and refrigerators). We note the appearance of the Carnot factor $\left(1 - \frac{T_0}{T_k}\right)$ multiplying the heating rates $\dot{Q}_k$.

The amount of work lost to irreversible processes is

$$\dot{W}_{\text{loss}} = T_0 \dot{S}_{gen} \geq 0 \ , \tag{5.18}$$

sometimes it is denoted as the *irreversibility*. It is an important engineering task to identify and quantify the irreversible work losses, and to reduce them by redesigning the system, or use of alternative processes.

## 5.11 Examples

### *5.11.1 Entropy Generation in Cooling*

A 2 kg block of copper at $T_1 = 250\,°\mathrm{C}$ equilibrates with the environment at $T_0 = 20\,°\mathrm{C}$ through heat transfer. The left part of Fig. 5.7 shows a sketch of the process, where the system boundary is chosen such that heat is transferred at the environmental temperature $T_0$. Copper can be considered as an incompressible solid with constant specific heat $c = 0.4 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$, specific internal energy $u = c\,(T - T_0)$, and specific entropy $s = c \ln \frac{T}{T_0}$. We compute the amount of heat transferred into the environment, and the total entropy generated.

The first and second law for this process read

$$\frac{dU}{dt} = \dot{Q} \quad , \quad \frac{dS}{dt} = \frac{\dot{Q}}{T_0} + \dot{S}_{gen} \ .$$

Integrating over time between initial state ($T_1$) and final state ($T_2 = T_0$) gives

$$U_2 - U_1 = Q_{12} \quad , \quad S_2 - S_1 = \frac{Q_{12}}{T_0} + S_{gen} \ ,$$

where $S_{gen} = \int_1^2 \dot{S}_{gen} dt$ is the total entropy generation. With the given property relations we find

$$mc\,(T_0 - T_1) = Q_{12} \quad , \quad mc \ln \frac{T_0}{T_1} = \frac{Q_{12}}{T_0} + S_{gen}$$

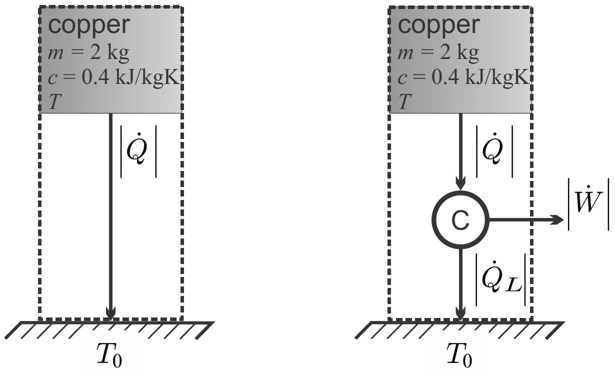


**Fig. 5.7** A block of copper initially at $T_1$ cools to environmental temperature $T_0$ by heat transfer (left), or by driving a reversible engine (Carnot engine, right); $T$ is the actual temperature at time $t$.

and thus, with $T_0 = 293\,\text{K}$, $T_1 = 523\,\text{K}$ (thermodynamic temperature must be used for entropy and the second law!),

$$Q_{12} = -184\,\text{kJ} \quad , \quad S_{gen} = \frac{mc}{T_0}\left[(T_1 - T_0) - T_0 \ln \frac{T_1}{T_0}\right] = 0.163\frac{\text{kJ}}{\text{K}} \ .$$

Since entropy is generated, an irreversible loss is associated with the process. The entropy generating process is heat transfer over the finite temperature difference between copper block and environment.

## 5.11.2 Work Generation in Cooling

In the this example we determine the amount of work that could have been obtained if the heat was not just transferred, but used to drive a heat engine. We consider the same block of copper as before, but now the heat is used to drive a Carnot engine in contact with the environment, as shown in the right part of Fig. 5.7. In this case, there is no entropy generation, since the Carnot engine is fully reversible. Thus, the first and second laws read (system boundaries include the Carnot engine)

$$\frac{dU}{dt} = \dot{Q}_L - \dot{W} \quad , \quad \frac{dS}{dt} = \frac{\dot{Q}_L}{T_0} \ .$$

Integration gives

$$U_2 - U_1 = Q_L - W \quad , \quad S_2 - S_1 = \frac{Q_L}{T_0} \ ,$$

so that

$$Q_L = mcT_0 \ln \frac{T_0}{T_1} = -135.8\,\text{kJ} \,,$$

$$W = Q_L - mc\,(T_0 - T_1) = mc\left[T_1 - T_0 - T_0 \ln \frac{T_1}{T_0}\right] = 48.2\,\text{kJ} \,.$$

A temperature difference can be used to drive a heat engine. If heat is just transferred over a finite temperature difference, entropy is created, and the opportunity to provide work is lost. In this example about 26% of the heat leaving the copper ($Q_H = 184\,\text{kJ}$) could be converted to work in the best case. Note that $W = T_0 S_{gen}$, where $S_{gen}$ is the entropy generation in case that no work is produced as computed in the previous section.

### *5.11.3 Perpetual Motion Engines*

We consider some perpetual motion engines.

(a) A company claims to produce a power generation device that produces 7 kW of power, takes in 11 kW of heat at a temperature of 840 K and rejects 8 kW of heat at 280 K.

We evaluate this claim: The work and heat flows are as in Fig. 5.2. Evaluation of the first law shows that $\left|\dot{Q}_H\right| = \left|\dot{Q}_L\right| + \left|\dot{W}\right|$ should hold. With $\left|\dot{Q}_H\right| = 11\,\text{kW}$, $\left|\dot{W}\right| = 7\,\text{kW}$ and $\left|\dot{Q}_L\right| = 8\,\text{kW}$ the first law is *not* fulfilled—the device is a perpetual motion engine of the first kind.

(b) Another company claims to produce a power generation device that produces 7 kW of power, takes in 10 kW of heat at a temperature of 840 K and rejects 3 kW of heat at 280 K.

We evaluate this claim: The first law is balanced now, we need to check the second law. The thermal efficiency of the device would be $\eta = \dot{W}/\dot{Q}_H = 0.7$. The work of a Carnot engine operating between the same temperatures is $\eta_C = 1 - T_L/T_H = 2/3$. Thus the efficiency claimed is bigger than the Carnot efficiency, which violates the second law—this engine is a perpetual motion engine of the second kind.

(c) Yet another company markets a refrigeration device that removes 1 kW of heat from a cold space that is kept at $-10\,^\circ\text{C}$, and rejects heat into an environment at $22\,^\circ\text{C}$. The company claims a power consumption of 122 W.

We evaluate this claim: The coefficient of performance for a Carnot refrigeration device operating between the same temperatures is $\text{COP}_{\text{R},C} = \frac{|\dot{Q}|}{|\dot{W}|} = \frac{1}{T_H/T_L - 1} = 8.219$ which would give a power consumption of $\dot{W}_C = 122\,\text{W}$. Thus, the company claims to have a Carnot refrigeration device. While this claim does not violate the first or the second law, it stands in contrast to the fact that *any real process is irreversible.* Thus, for an actual device one must expect efficiencies and COP's below the Carnot values, which are the maxima obtained for fully reversible processes. The company's claim must be wrong.

### *5.11.4 A Heat Engine*

An engine that operates at steady state between two reservoirs at $T_H = 750\,°\mathrm{C}$ and $T_L = 15\,°\mathrm{C}$, has a heat intake of 0.1 MW, and rejects 50 kW of heat to the low temperature environment. We compute the power produced, the thermal efficiency, the entropy generation rate, and the work loss to irreversibilities.

We identify $\dot{Q}_H = 100\,\mathrm{kW}$ and $\dot{Q}_L = -50\,\mathrm{kW}$. The first law applied to the engine gives $\dot{W} = \dot{Q}_H + \dot{Q}_L = 50\,\mathrm{kW}$. Accordingly, the engine's thermal efficiency is $\eta = \frac{\dot{W}}{\dot{Q}_H} = 0.5$.

The second law gives $\frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_L}{T_L} + \dot{S}_{gen} = 0$ and thus the entropy generation rate is $\dot{S}_{gen} = \frac{|\dot{Q}_L|}{T_L} - \frac{\dot{Q}_H}{T_H} = 0.076\frac{\mathrm{kW}}{\mathrm{K}}$. Since $\dot{S}_{gen} > 0$, the second law is fulfilled.

The thermal efficiency for a Carnot engine operating between the same temperatures is $\eta_C = 1 - \frac{T_L}{T_H} = 0.718$ (Kelvin temperatures!) which is above the efficiency of the engine, as it must be. A Carnot engine would produce the power $\dot{W}_C = \eta_C \dot{Q}_H = 71.8\,\mathrm{kW}$. The work loss to irreversibilities is $\dot{W}_{loss} = \dot{W}_C - \dot{W} = 21.8\,\mathrm{kW}$.

A more instructive way to compute the work loss is as follows: Eliminating the heat exchange with the environment, $\dot{Q}_L$, between first and second law gives

$$\dot{W} = \left(1 - \frac{T_L}{T_H}\right)\dot{Q}_H - T_L \dot{S}_{gen} \,.$$

The work loss to irreversibilities is $\dot{W}_{\mathrm{loss}} = T_L \dot{S}_{gen} = 21.8\,\mathrm{kW}$.

### *5.11.5 Refrigerator*

A restaurant refrigerator located in a kitchen at $21\,°\mathrm{C}$ maintains its interior at $4\,°\mathrm{C}$. The refrigerator consumes 300 W of power with a coefficient of performance $\mathrm{COP_R} = 3$. We compute entropy generation and work loss.

The heat withdrawn from the interior is $\dot{Q}_L = \mathrm{COP_R}\left|\dot{W}\right| = 900\,\mathrm{W}$. According to the first law, the heat rejected into the kitchen is $\left|\dot{Q}_H\right| = \left|\dot{W}\right| + \dot{Q}_L = 1200\,\mathrm{W}$. The entropy generation rate follows from the second law as

$$\dot{S}_{gen} = -\frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_L}{T_L} = \frac{\left|\dot{Q}_H\right|}{T_H} - \frac{\dot{Q}_L}{T_L} = 0.083\frac{\mathrm{W}}{\mathrm{K}} \,,$$

where $T_L = 277\,\mathrm{K}$ and $T_H = 294\,\mathrm{K}$. Eliminating the heat rejected into the kitchen between first and second law yields

$$\left|\dot{W}\right| = -\dot{W} = \left(\frac{T_H}{T_L} - 1\right)\dot{Q}_L + T_H \dot{S}_{gen} \,.$$

The work loss to irreversibilities is $\dot{W}_{\text{loss}} = T_H \dot{S}_{gen} = 247.7\,\text{W}$; this work is required as input to overcome irreversibilities. A fully reversible refrigerator, i.e., a Carnot refrigerator, which removes the same amount of heat $\dot{Q}_L$ has a $\text{COP}_{\text{R},C} = 1/\left(\frac{T_H}{T_L} - 1\right) = 16.3$, and would consume 55 W of electrical power.

Note that efficient operation of a refrigerator is not only achieved by increasing its COP, but also by improving the thermal insulation. Indeed, the heat $\dot{Q}_L$ that is removed from the interior has crept in through the insulated walls of the refrigerator. Better insulation reduces the amount of heat that must be removed, and thus the work consumption of the refrigerator.

### *5.11.6 Heat Pump with Internal and External Irreversibilities*

A heat pump is used to keep a home at 20 °C. The heat pump draws heat from the outside environment at 0 °C; its heating power is $\left|\dot{Q}_H\right| = 2\,\text{kW}$ for a power consumption of $\left|\dot{W}\right| = 0.5\,\text{kW}$. In order to facilitate sufficient heat transfer, a temperature difference of 10 K is required between the working substance of the heat pump and the respective environments. Figure 5.8 gives a sketch of the heat and work flows, and the relevant temperature levels.

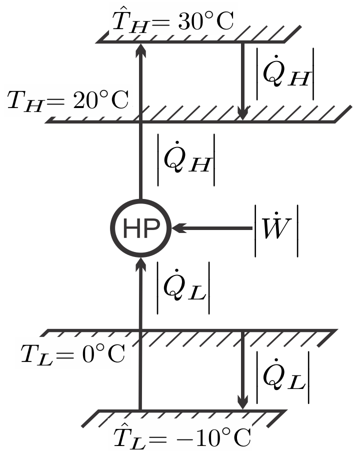


**Fig. 5.8** A heat pump that requires a finite temperature difference of 10K for heat exchange

We evaluate the process step by step. Let us first consider a perfectly reversible Carnot heat pump, that is a device that can operate at the actual temperatures of the two environments, $T_H = 293\,\text{K}$ and $T_L = 273\,\text{K}$. The coefficient of performance of such an ideal engine is

$$\text{COP}_{\text{HP},C} = \frac{\left|\dot{Q}_H\right|}{\left|\dot{W}_C\right|} = \frac{1}{1 - \frac{T_L}{T_H}} = 14.65 \,.$$

For the given heating power the fully reversible heat pump would consume $\left|\dot{W}_C\right| = 0.137\,\text{kW}$ of power.

A internally reversible heat pump with external irreversibilities due to heat transfer over finite temperatures is a Carnot heat pump operating between the temperatures $\hat{T}_H = 303\,\text{K}$ and $\hat{T}_L = 263\,\text{K}$. This engine would have a coefficient of performance

$$\text{COP}_{\text{HP},C-int} = \frac{1}{1 - \frac{\hat{T}_L}{\hat{T}_H}} = 7.58$$

and would consume $\dot{W}_{C-int} = 0.264\,\text{kW}$ of power. The internally reversible engine requires more work than the fully reversible engine, since a bigger temperature interval is bridged. Entropy is generated in the heat transfer over finite temperature differences, with the generation rate

$$\dot{S}_{gen} = \left|\dot{Q}_H\right| \left(\frac{1}{T_H} - \frac{1}{\hat{T}_H}\right) + \left|\dot{Q}_L\right| \left(\frac{1}{\hat{T}_L} - \frac{1}{T_L}\right) \,.$$

Since the engine is internally reversible, the relation $\frac{|\dot{Q}_L|}{\hat{T}_L} = \frac{|\dot{Q}_H|}{\hat{T}_H}$ holds, so that

$$\dot{S}_{gen} = \frac{\left|\dot{Q}_H\right|}{\hat{T}_H} \left[\frac{\hat{T}_H}{T_H} - \frac{\hat{T}_L}{T_L}\right] = 0.467\frac{\text{W}}{\text{K}} \,.$$

As always, the work loss is more interesting than the entropy generation rate. We find the work loss to *external irreversibilities* as

$$\dot{W}_{\text{loss}-ext} = \dot{W}_{C-int} - \dot{W}_C = T_L \dot{S}_{gen} = 0.127\,\text{kW} \,.$$

The actual engine consumes $\left|\dot{W}\right| = 0.5\,\text{kW}$ of power, that is it loses an additional 0.236 kW to *internal irreversibilities*. Its coefficient of performance, $\text{COP}_{\text{HP}} = \dot{Q}_H \big/ \left|\dot{W}\right| = 4$, is typical for a commercial heat pump system.

The realistic heat pump system is 4 times more efficient than a resistance heater ($\text{COP}_{\text{RH}} = 1$), but the perfect—i.e., fully reversible—Carnot heat pump is 3.7 times more efficient than the real engine.

We note that the heat required to keep the home at a comfortable temperature needs to be provided since the home loses the same amount of heat through its walls. Better insulation significantly reduces the heat requirement, and thus the heating costs.

## Problems

**5.1. Heat Engines**

An engine that operates between two reservoirs at $T_H = 500\,°\mathrm{C}$ and $T_L = 25\,°\mathrm{C}$ produces 1 MW of power from a heat intake of 2.5 MW. Compute the heat rejected, the thermal efficiency, the entropy generation rate, and the work loss to irreversibilities.

Another engine operates between two reservoirs at $T_H = 1000\,°\mathrm{C}$ and $T_L = 10\,°\mathrm{C}$, and has a thermal efficiency of 45% and its heat rejection rate is 1.76 MW. Compute the power produced, the heat intake rate, the entropy generation rate, and the work loss to irreversibilities.

**5.2. Investment Advice**

A friend asks whether he should invest in a new start-up company. The company claims to sell a power generation device that produces 12.5 kW of power, takes in 21 kW of heat at a temperature of 800 K and rejects 13 kW of heat at 300 K. What advice do you give? Why?

**5.3. More Investment Advice**

Another friend asks whether she should invest in a company which claims to make a power generation device that produces 12 kW of power, takes in heat at a temperature of 800 K and rejects 8 kW of heat at 350 K. What advice do you give? Why?

**5.4. Your Friends Keep Asking You for Advice**

A neighbor would like to have an air conditioning system. He finds a product with the following specifications: For keeping a room at 20 °C when the outside temperature is 30 °C the product consumes 0.5 kW to remove 9 kW of heat. What's your advice here, and why?

**5.5. The Perfect Heater?**

A relative needs a new heating system. She shows you a flyer from a company marketing baseboard heaters. The flyer claims a 100% heating efficiency. Is that a valid claim? Can your relative find a more efficient alternative? If so, what would it be?

**5.6. A Refrigerator**

Yet another friend asks whether he should invest in a company which claims to produce a refrigeration device with a COP of 7, that consumes 0.9 kW of power to keep the inside at 4 °C, and rejects of heat to the warm environment at 32 °C. What advice do you give? Why?

**5.7. A Heat Pump**

An off-the shelf heat pump system has a COP of 3.5 for operation between 30 °C and −10 °C. Determine the entropy generation per kW of heating, and the percentage of consumed power required to overcome irreversibilities.

**5.8. Another Heat Pump**
A heat pump providing 2 kW of heat operates between the temperatures of 23 °C and −2 °C ; its entropy generation rate is $\dot{S}_{gen} = 1.3\frac{\text{W}}{\text{K}}$. Determine the power needed to drive the heat pump, and its COP.

**5.9. Heat Engine with External Irreversibilities**
A internally reversible heat engine operates between two reservoirs at 300 K and 400 K; the engine produces 40 kW of power. The heat exchangers between the engine and the reservoirs require a temperature difference of 20 K. Determine the heat exchanged with the two environments, the entropy generated in heat transfer, and the work loss.

**5.10. Refrigerator with Internal and External Irreversibilities**
In a frozen pizza factory, the freezing compartment is kept at a temperature of −30 °C, while the outside temperature is 25 °C. The cooling system removes 2.25 MW of heat, and consumes 1.5 MW of power. Measurements show that both heat exchangers operate at a temperature difference of 12 °C to their respective environments.

1. Determine the COP of the refrigeration system, and the COP and power requirement of a fully reversible system used for the same cooling purpose.
2. Determine the work losses to internal and external irreversibilities.

**5.11. Heat for Cooling**
A chemical plant rejects 1 MW of waste heat at 400 °C. Elsewhere in the plant, 5 MW of heat have to be removed from a warehouse at −10 °C. Can the waste heat be used to cool the warehouse when the environment is at 17 °C? If so, how? Give arguments based on 1st and 2nd law, discuss your assumptions.

**5.12. Entropy Generation**
In an industrial process, a device conducts heat between two hot reservoirs, which are at 200 °C and 400 °C, and the environment at 23 °C. Specifically, the conductor exchanges 4 kW of heat with the hottest reservoir, and 6 kW of heat with the environment. Determine the entropy generation, and the respective work loss.

**5.13. Heat in the T-S-Diagram**
In a reversible process in a closed system the heat is given as the area below the process curve in the T-S-diagram, $Q_{12} = \int_1^2 TdS$ , or, when we divide by mass, $q_{12} = \frac{Q_{12}}{m} = \int_1^2 Tds$. To make use of this formula, one therefore needs temperature as a function of entropy, $T(s)$, for the process.

Consider a reversible process in air, as ideal gas with constant specific heats, for which pressure and temperature are related as $p = p_1\left(\frac{T}{T_1}\right)^n$ with a constant $n$. A process of this kind is called a polytropic process.

1. Find the function $T\,(s,p)$ by inverting the property relation for entropy, $s\,(T,p)$.
2. Simplify for the polytropic process to obtain $T\,(s)$.
3. Make a sketch of the curve for polytropic processes with various values of $n$. How does it change when $n$ gets bigger?
4. Find heat by integration: $q_{12} = \int_1^2 T ds$. Also compute the work per unit mass, $w_{12} = \frac{W_{12}}{m}$.
5. Specify for a polytropic process with $n = 2$ that starts at $20\,°\mathrm{C}$, $7\,\mathrm{bar}$ (state 1) and proceeds until pressure has doubled.