Chapter 5
Thermodynamic Processes and Engines

The postulates of thermodynamics are valid for equilibrium states. Relations derived from the postulates are applicable for changes of states where, following the change (or release) of internal constraints, a new equilibrium is achieved. Quantities characterizing equilibrium states can be given as functions of state variables. According to Postulate 1, variables U, V, and $\boldsymbol{n}$ completely determine the equilibrium state. Postulate 2 assigns the entropy function $S\,(U, V, \boldsymbol{n})$ to the equilibrium states. On the basis of this, we can refer to the coordinate space spanned by the variables U, V, and $\boldsymbol{n}$ as a *thermodynamic configuration space* where the possible configurations (the equilibrium states of the composite systems) are determined by the values of the entropy function lying on a continuous surface we can call *state surface*. The graph of this function is a tridimensional surface that conforms Postulates 2 and 3 and their consequences; its constant-energy section is concave, while its constant-entropy section is convex (cf. Fig. 3.1).

It is important to know that nonequilibrium states cannot be represented in this space. Nonequilibrium states could only be represented in a space having much greater dimension. As mentioned in Chap. 2, macroscopic properties in equilibrium are time-independent average values of the system consisting of a very large number of particles. If there is no equilibrium, these averages (expectation values) do not exist, or are strongly time-dependent. This is the reason that only equilibrium systems can be represented in the thermodynamic configuration space and they always lie on the state surface determined by the fundamental equation $S = S\,(U, V, \boldsymbol{n})$. The first part of this chapter explores the consequences of this property.

5.1 Quasistatic, Reversible and Irreversible Processes

The equilibrium state is also called *static* state, using a Latin word of Greek origin. To move a system from an actual static state – let us denote the corresponding point on the $S(U, V, \boldsymbol{n})$ state surface by A – to another state C, some internal constraints should be changed. For example, we can initiate a state change by changing an

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internal rigid wall to become flexible. If pressure was different in the two subsystems, the suddenly flexible wall begins to move, and there is no equilibrium within the parts of the system that are influenced by sudden changes during pressure equilibration.

However, we can also proceed so that the system does not directly go to state C from A, but successively to some intermediate points denoted by B$_i$. Accordingly, we can change the internal constraint (e.g., in this case, let the piston move only slightly) so that, after the first change of state, the next equilibrium state will be B$_1$, then B$_2$, etc., until it gradually reaches state C. It is obvious that placing the successive points B$_i$ closer and closer to each other, we disturb the equilibrium states during the changes less and less. With arbitrarily dense division of the path from A to C, we allow only for arbitrarily small deviation from equilibrium. At the limiting case with infinitely dense division, the system is always on the state surface. (Of course, this cannot be realized in practice as no difference in pressure results in no change. But arbitrarily small finite changes – at least in principle – could be realized.) This approximation of a real change is called a *quasistatic*[1] *process*.

A quasistatic process can be realized in practice to a good approximation, provided that changes in the state of a large number of molecules are slow enough that the expectation value corresponding to a macroscopic quantity would exist and it would change more slowly than the recovery of an equilibrium distribution. In case of the example mentioned – the equilibration of pressure – the pressure suddenly drops near the moving wall, as molecules cannot follow this move instantaneously. Molecules are able to follow the displacement of the wall not faster than the speed of sound. During this procedure, shock waves can be formed which reflect from opposite walls and get damped within the system. Shock waves can also induce hydrodynamic flow, which also gets damped within the medium. The spread of shock waves is related to the velocity of sound in the medium, while hydrodynamic flow is related to viscosity. These two quantities determine the *relaxation time* of the system necessary to calm. The velocity of sound is several hundred m/s in a gas or liquid. This means that in liquids or near-atmospheric pressure gases the "void space" of the size of a few micrometers is replenished within about 10^{-5} s, and in a system of the extension of about 1 m, shock waves are reflected at least once from opposite walls within 10^{-3}–10^{-2} s. Consequently, if a piston is moved not faster than 1 μm within 0.001 s, the system can relax and equilibrium states can be sustained during changes. 1 μm/0.001 s is equivalent to 10^{-3} m/s, which practically ensures conditions for a quasistatic change. In practical devices, the speed of change is usually greater than this. Let us examine the consequences of deviations from the quasistatic change.

In the previous discussion, the example was the displacement of a piston in a cylinder. To get the maximum work from an expansion, we should gain the entire

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[1] The Greek word στατικος [statikos] means steady or standstill. The Latin comparative and conjunctive *quasi* is a compound word coined from *quam* and *si*, meaning "as if", "approximately", or "nearly". In this context, quasistatic means "nearly equilibrium".

energy change in the form of volume work. According to (2.22), it can be achieved in a closed system if the heat $T\mathrm{d}S$ is zero, i.e., in the case of an adiabatic expansion. However, if the expansion is not quasistatic, then turbulence and friction resulting from shock waves increase the thermal energy of molecules in the system, leading to a warming up of the system. Thus, the heat $T\mathrm{d}S$ were greater than zero, suggesting an increase in entropy. As spontaneous changes toward equilibrium increase the entropy, the energy due to the change $T\mathrm{d}S$ would "remain in the system". This dissipation would manifest as a loss in the useful work. As a general conclusion, we can state that processes deviating from quasistatic changes always result in a *loss of the work* gained, and they *increase the entropy* of the system. In the above example, the heat exchanged with the surroundings was zero, but the change $T\mathrm{d}S$ was greater than zero. In case of a nonzero heat exchange with the surroundings, this would have meant that the change $T\mathrm{d}S$ was greater than the heat exchanged. Therefore, it can be formulated the following way:

$$T\mathrm{d}S \geq \delta Q \quad \text{or} \quad \mathrm{d}S \geq \frac{\delta Q}{T}. \tag{5.1}$$

The symbol δ (lower case Greek delta) is used to express that, though δQ is an infinitesimal quantity, it cannot be determined by any change in state variables, as it is a change during a nonquasistatic process. (Infinitesimal quasistatic work or heat is sometimes denoted by the symbol $đ$ instead of a simple d, but we will not use this notation in the book. We know anyway from heat and work that they are not state functions.) Equality in (5.1) is only valid for quasistatic changes; in all other cases, inequality holds.

Having made a change in the state of the system from state A to state B, we can reverse the change depending on the accompanying change of entropy. If the entropy increased while passing from A to B, the process was spontaneous, but the reverse process can only be realized by the investment of energy. Namely, by changing internal constraints in an isolated composite system, the entropy will become maximal over the manifold of all unconstrained systems; thus, it can only increase during spontaneous changes. Would entropy have decreased while passing from state A to B (which would have been possible only by investment of energy), the reverse process could occur spontaneously. There are limiting cases when the value of entropy is the same in states A and B and also in every state in between during a quasistatic process. In this case, the forward process from A to B and the reverse process from B to A is possible to realize without investing energy. Due to this property, this latter process is referred to as a *reversible process*.[2] It should be noted that a nonquasistatic process is obviously not reversible (i.e., it is *irreversible*), as it implies an increase in entropy – as seen from (5.1).

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[2] The word *reversible* is a derivative of the Latin noun *reversio* meaning return to a former state. Thus, reversible means "able to return".

Let us summarize the above discussion in more formal terms. In the relations below, ΔS means a finite change, while $\mathrm{d}S$ means an infinitesimal change of entropy.

$$\Delta \mathrm{S} > 0: \text{natural (irreversible) process,}$$

$$\Delta S = 0: \text{reversible process,}$$

$$\Delta S < 0: \text{unnatural(not spontaneous) process,}$$

$$\mathrm{d}S > \frac{\delta Q}{T}: \text{non-quasistatic (irreversible) process,}$$

$$\mathrm{d}S = \frac{\delta Q}{T}: \text{quasistatic (reversible) process,}$$

$$\mathrm{d}S < \frac{\delta Q}{T}: \text{impossible process.}$$

It is important to note that thermodynamics strictly speaking describes only quasistatic processes. In case of real processes, thermodynamic calculations can only be used as an approximation as they cannot take into account any losses. This limitation also applies if we describe the operation of heat engines, refrigerators, and other thermodynamic devices using thermodynamic formalism.

5.2 Heat Engines: The Carnot Cycle and the Carnot Engine

Heat engines perform the conversion of thermal energy (heat) to mechanical work. Their schematic operational diagram is illustrated in Fig. 5.1. The conceptually most simple and most efficient heat engine is the *Carnot engine*, which operates on the *reversible Carnot cycle*. (The working fluid of a continuously operating engine should return over and over again into the same states; this is called a cyclic process or more simply a cycle.) The name is given after the author of the first theoretical treatment on devices converting heat into work.[3] We know from the previous section that a quasistatic process is needed to avoid losses. It was Carnot who first suggested building engines in which change of temperature can only occur in processes delivering work in such a way that it is without any losses. The particular cycle realized in a Carnot engine is illustrated in Fig. 5.2.

It can be seen from the T–S diagram that both heat absorption and heat rejection occur at constant temperature. The expansion and cooling from the higher temperature T_h to the lower temperature T_c and the reverse direction heating occur

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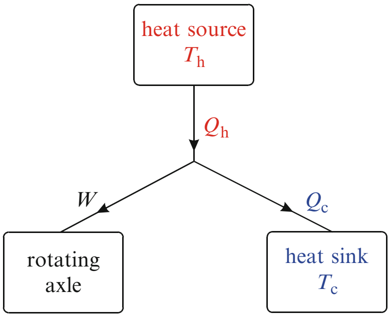
[3] Nicolas Léonard Sadi Carnot (1796–1832), a French engineer and military officer, published his 118-page book "*Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*" 1824 in Paris. The long title means: reflections on the motive power of fire (i.e., heat) and on machines fitted to develop that power.

Fig. 5.1 Schematic diagram of a heat engine. During the operation of the engine, part of the energy Q_h absorbed from the hot heat reservoir (heat source) is used to drive a rotating axle (this is the useful work, W). Another part (Q_c) is rejected to the cold heat reservoir (heat sink) and delivered to the surroundings



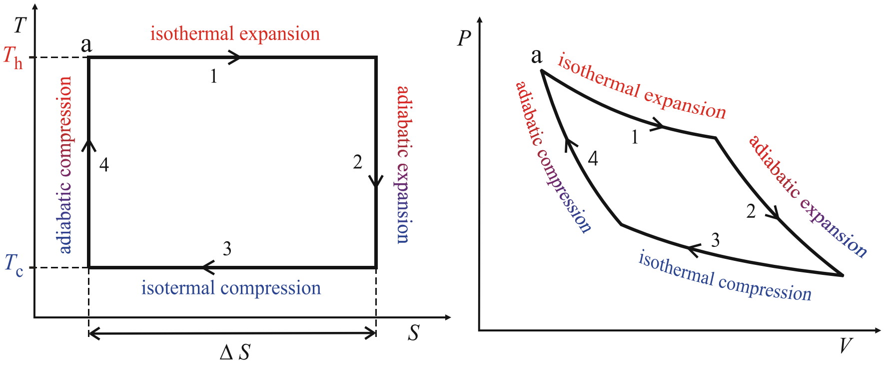


Fig. 5.2 The T–S and P–V diagram for the working fluid in a Carnot heat engine cycle. The four steps of the cycle are denoted by subsequent numbers starting from state a. A Carnot refrigerator or heat pump operates on the same cycle but in the reverse direction; its steps follow each other as 4 – 3 – 2 – 1

adiabatically, enabling to convert the complete change in internal energy as volume work.

The *thermodynamic efficiency* of a heat engine is defined by the ratio:

$$\eta = \frac{\text{work gained}}{\text{energy consumed as heat}}. \tag{5.2}$$

It is easy to calculate heat based on the T–S diagram, while the P–V diagram is practical for calculating work. In the P–V diagram of the Carnot cycle, we can see that work is done in all four steps of the cycle. During expansions, it is the working fluid that delivers work to the surroundings. Steps 1 and 3 occur at constant temperature and result in an exchange of heat between the working fluid and the surroundings. As temperature is constant, the exchanged heat (integral of $T\mathrm{d}S$) can easily be calculated resulting in $T\Delta S$. Steps 2 and 4 are adiabatic changes avoiding heat exchange with the surroundings so that entropy would not change. After a complete cycle, the working fluid returns to the initial state (denoted by a) which requires that the entropy is the same at the end of the cycle as it was in the initial state; thus, its increase in step 1 is the same as its decrease in step 3. (See also the previous figure.) In the complete cycle, the change of the internal energy should also be zero. Let us make use of these two relations to calculate the efficiency of the engine.

The internal energy changes due to the heat exchange in steps 1 and 3, and to the work done in each of the four steps. Let us denote the work done by the working fluid in steps 1 and 2 by W_{out}, and the work done by the surroundings in steps 2 and 4 by W_{in}. The difference $|W_{\text{out}}| - |W_{\text{in}}|$ is exactly the work gained in the numerator on the right-hand side of (5.2). In a similar manner, Q_{in} be the absorbed heat in step 1 and Q_{out} be the rejected heat in step 3. As mentioned above, the sum of all the work and heat during the complete cycle – the change in internal energy – is zero:

$$\Delta_1^4 U = |W_{\text{in}}| - |W_{\text{out}}| + |Q_{\text{in}}| - |Q_{\text{out}}| = 0. \tag{5.3}$$

Let us express the work gained $|W_{\text{out}}| - |W_{\text{in}}|$ from the above equation:

$$|W_{\text{out}}| - |W_{\text{in}}| = |Q_{\text{out}}| - |Q_{\text{in}}|. \tag{5.4}$$

By substituting this into (5.2), we get the efficiency of the Carnot engine:

$$\eta = \frac{\text{work gained}}{\text{energy consumed as heat}} = \frac{|W_{\text{out}}| - |W_{\text{in}}|}{|Q_{\text{in}}|} = \frac{|Q_{\text{in}}| - |Q_{\text{out}}|}{|Q_{\text{in}}|}. \tag{5.5}$$

As stated before, the heat exchange Q_{in} and Q_{out} can easily be calculated as $T_{\text{h}}\Delta S$ and $T_{\text{c}}\Delta S$. By substituting, we get:

$$\eta = \frac{T_{\text{h}}\Delta S - T_{\text{c}}\Delta S}{T_{\text{h}}\Delta S} = \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}}. \tag{5.6}$$

By summing up the results, we can give the efficiency of the Carnot engine as

$$\eta = 1 - \frac{T_{\text{c}}}{T_{\text{h}}}. \tag{5.7}$$

We can see from the above result that the efficiency increases with decreasing heat sink temperature T_{c}. Unit efficiency can only be achieved if the temperature of the heat sink becomes $T_{\text{c}} = 0$ K. If the temperature of the heat sink is greater than 0 K – which is the case in practical heat engines – the efficiency is always smaller than 1. Thus, thermal energy cannot be completely converted into work. As we shall see later, to achieve the temperature 0 K, infinite energy was needed. Thus, we can state that, in general, the efficiency of heat engines is always inferior to one.

Heat engines used in power plants at the beginning of the twenty-first century operate with heat sources around 500°C and heat sinks around 80°C, equivalent to about 773 K and 353 K. The maximum efficiency calculated is 54.3%; thus, existing power plants have somewhat smaller efficiency. Recently, the construction of smaller power plants that are built at riversides, using river water of about 20°C as a heat sink, is spreading. Their efficiency can be as high as 60%. The rejected heat ("waste heat") can be used to domestic or industrial heating. Plants operating this way are called *cogeneration* or *combined heat and power* (CHP) plants. This is one of the most common forms of energy recycling.

5.3 Refrigerators and Heat Pumps: The Carnot Refrigerating and Heat-Pump Cycle

Refrigerators extract thermal energy (heat) from a cold room by consuming energy (mechanical work) and reject heat to a higher temperature room. (There are refrigerators consuming directly heat or electric energy to cool a cold room, but they are not discussed here.) Heat pumps operate the same way, but the goal using them is not to cool the cold room but to heat the hot room. The schematic operational diagrams of both devices are illustrated in Fig. 5.3.

On comparing Figs. 5.1 and 5.3, it can be seen that the operating cycle of a refrigerator or heat pump is basically the same as that of a heat engine, but they run in the opposite direction. The efficiency of these devices is thus calculated based on the same principles and quantities as for a heat engine.

The *coefficient of performance* (COP) *of a refrigerator* is the ratio of the heat withdrawn to the consumed work needed to withdraw this heat:

$$\varepsilon = \frac{\text{heat withdrawn from the cold room}}{\text{work consumed}}. \tag{5.8}$$

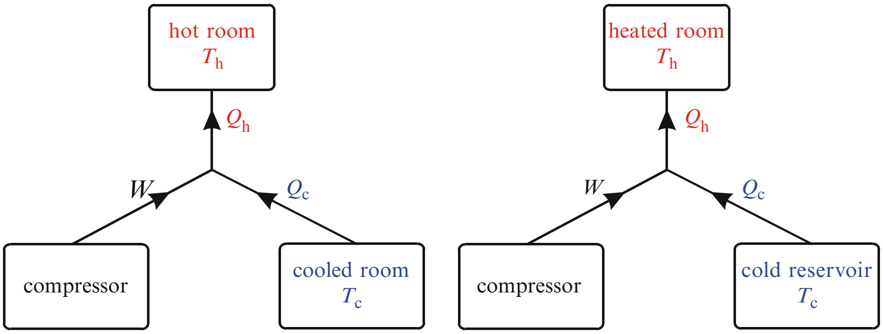


Fig. 5.3 Schematic diagram of a refrigerator (*left*) and a heat pump (right). The refrigerator consumes work W to withdraw heat Q_c from the refrigerated room at temperature T_c and to reject heat to the hot room at ambient temperature T_h. The heat pump consumes work W to withdraw heat Q_c from the cold reservoir at temperature T_c and to reject heat to the heated room at ambient temperature T_h

For a Carnot refrigerator, we can readily enter Q_c in the numerator, $|W_\mathrm{in}| - |W_\mathrm{out}|$ in the denominator. From the energy conservation principle, this latter can be replaced by $|Q_\mathrm{out}| - |Q_\mathrm{in}|$, or, using the notation of Fig. 5.3, by $|Q_\mathrm{h}| - |Q_\mathrm{c}|$:

$$\varepsilon = \frac{|Q_\mathrm{c}|}{|Q_\mathrm{h}| - |Q_\mathrm{c}|} = \frac{T_\mathrm{c}\Delta S}{T_\mathrm{h}\Delta S - T_\mathrm{c}\Delta S} = \frac{T_\mathrm{c}}{T_\mathrm{h} - T_\mathrm{c}}. \tag{5.9}$$

It can be seen form the resulting expression in terms of temperatures that the coefficient of performance decreases with decreasing temperature of the cooled room and with increasing temperature of the hot room. Unlike the efficiency η of a heat engine, the coefficient of performance ε of a refrigerator can be larger than 1. Domestic refrigerators usually reject heat to ambient air at temperatures somewhat higher than 20°C. The normal refrigerated room of temperature about 5°C can be cooled with an ideal coefficient of performance close to 14, while the freezer of temperature about – 20°C only with that of less than 6. The waste heat of industrial refrigerators is also recycled; shopping centers are typically heated by the heat withdrawn from cooled storage rooms.

The *coefficient of performance of a heat pump* can be formulated in accordance with the task of the device: the ratio of the heat delivered to the heated room and the consumed work:

$$\varepsilon' = \frac{\text{heat delivered to the heated room}}{\text{work consumed}}. \tag{5.10}$$

Thus, we can enter Q_h in the numerator, and again, $|W_\mathrm{in}| - |W_\mathrm{out}|$ in the denominator. According to the energy conservation principle, this latter can be replaced by $|Q_\mathrm{out}| - |Q_\mathrm{in}|$, or equivalently $|Q_\mathrm{h}| - |Q_\mathrm{c}|$:

$$\varepsilon' = \frac{|Q_\mathrm{h}|}{|Q_\mathrm{h}| - |Q_\mathrm{c}|} = \frac{T_\mathrm{h}\Delta S}{T_\mathrm{h}\Delta S - T_\mathrm{c}\Delta S} = \frac{T_\mathrm{h}}{T_\mathrm{h} - T_\mathrm{c}}. \tag{5.11}$$

We can see that the coefficient of performance of the heat pumps also diminishes with increasing difference between the temperatures of the hot and cold rooms.

It is interesting to compare the coefficient of performance of a refrigerator and a heat pump which operate between heat reservoirs of the same temperatures:

$$\varepsilon' - \varepsilon = \frac{T_\mathrm{h}}{T_\mathrm{h} - T_\mathrm{c}} - \frac{T_\mathrm{c}}{T_\mathrm{m} - T_\mathrm{c}} = 1. \tag{5.12}$$

Accordingly, the coefficient of performance of basically the same device is always greater by 1 if it is working as a heat pump.

The coefficient of performance of an ideal Carnot heat pump is 10.9 if an inner room of 22°C is heated from an outer temperature reservoir of –5°C. Though actual devices do not have this large a coefficient due to losses, it is still worth of using a heat pump even if the actual coefficient of performance is only around 2. This means that twice the amount of heat can be gained from the work consumed in the heat pump than with direct electric heating using resistors. Where air conditioning is common practice, heating in winter can be done by slight modifications in the refrigerator of the air conditioner. The most frequent use of heat pumps for domestic heating is therefore seen in the Southern parts of the USA.

5.4 Heat Engines and Refrigerators Used in Practice

Though Carnot engines have the highest possible efficiency, their practical construction would be rather complicated. In the isothermal expansion step, the working fluid should absorb heat from the hot reservoir at the same temperature as that of the reservoir. This is of course impossible as if the temperatures are identical, there is equilibrium and no heat transfer. In principle, if the temperature of the working fluid is just slightly smaller than that of the reservoir, heat transfer could occur. This can be achieved if the working fluid is a liquid in equilibrium with its vapor at constant pressure. In this case, heat transfer can occur at constant temperature vaporizing the liquid, resulting in an expansion. Similarly, in contact with the cold reservoir, the fluid can condense (vapor transformed into liquid), thus rejecting heat to the reservoir. However, in the adiabatic expansion step of the Carnot cycle there would be liquid droplets besides the vapor, which would mechanically destroy the piston of a cylinder or the blades of a turbine. The compression of a liquid–vapor mixture would also raise serious mechanical problems. To compress a vapor, large compressors were needed which would lead to important energy losses, and the parts of the compressor would also be destroyed by liquid droplets. To avoid these problems, practical devices – heat engines, refrigerators, and heat pumps – operate on cycles different from the Carnot cycle. We only deal here with the *Rankine cycle* widely used in power plants, compressor refrigerators and heat pumps. It should be mentioned, however, that besides the closed Rankine vapor power cycle, there are different operational principles used, e.g., in internal combustion engines. Most important of them are the Otto cycle in petrol fuel engines and the Diesel cycle for diesel fuel engines.

5.4.1 Heat Engines Based on the Rankine Cycle

The Scottish engineer and physicist Rankine[4] constructed a heat engine that is pretty close to the conditions formulated by Carnot. In his engine, the compression

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[4] William John Macquorn Rankine (1820–1872), a Scottish engineer and physicist, played an important role during the early development of thermodynamics both in theory and construction of devices of practical use. He elaborated the modern theory of steam engines in 1850s and 1860s.

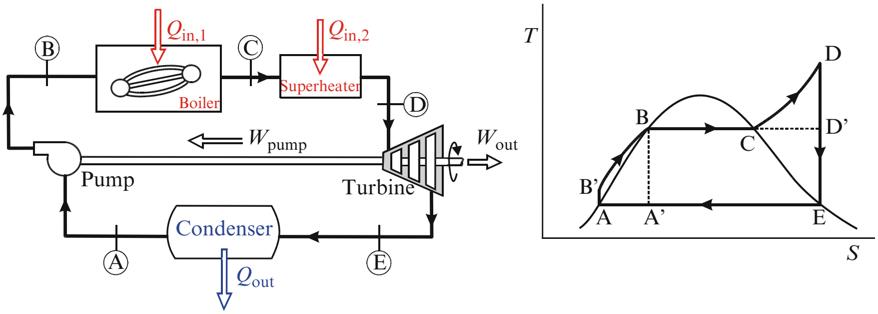

Fig. 5.4 Schematic diagram of a heat engine working on a Rankine vapor power cycle, and the *T*–*S* diagram of the cycle. Part of the heat absorbed in the boiler and the superheater by the working fluid is transformed into work in the turbine by expansion, making its axle turn. The exhaust steam becomes liquid water in the condenser, which is pumped into the boiler again. *Letters* in the schematic diagram indicate states in the *T*–*S* diagram. The flow direction of the working fluid is indicated by *arrows*. Large power plants are operating on this cycle with some modifications increasing efficiency

step (Fig. 5.2, step 4) is done with the smallest possible volume change, as the compressor only operates on the liquid, while the work production (adiabatic expansion) is done with the greatest possible volume change, using mostly vapor as expanding medium, with only an ignorable quantity of liquid. This cycle can be realized with minimal losses, while its efficiency is not much inferior to that of the Carnot engine. A schematic diagram of the device operating on the basis of the Rankine cycle along with a *T*–*S* diagram of the cycle is shown in Fig. 5.4.

The working fluid is pumped from state A into the boiler of higher pressure and temperature, where it evaporates between points B and C at constant temperature forming saturated vapor. During this process, its entropy (i.e., its heat content) increases. (The bell-shaped curve in the *T*–*S* diagram is the liquid–vapor equilibrium curve. To its left side, there is liquid; to its right side, there is vapor. Below the curve, there exist no phases; if the state of the system coincides with such a point, the system exists at the intersection points of a horizontal line with the curve as the corresponding liquid and vapor. The ratio of vapor to liquid depends on the distance of the point from the two intersections along the horizontal line. A detailed discussion of liquid–vapor equilibrium can be found in Sect. 7.2.) Following evaporation, the steam is superheated at constant pressure between states C and D. The next step is the expansion of the high-pressure hot steam resulting in useful work on the turning axle of the turbine. Finally, the exhaust steam completely condenses in the cooled condenser at constant temperature. (Cooling is necessary to absorb the heat of condensation.) Following condensation, the working fluid is pumped again into the boiler, thus entering a new cycle.

To calculate the efficiency of the cycle, work and heat associated with isotherms B–C and E–A, the isobar E–A, and the adiabat D–E are easy to calculate, but the change in energy of a liquid–vapor equilibrium system between A and B (along the bell-shaped curve) is not easy to describe. However, it can be replaced by calculating energy changes during an adiabatic compression A–B′ and a subsequent isobaric heating B′–B.

In Fig. 5.4, an imaginary Carnot cycle A′ – B – D′ – E between the temperatures of the Rankine engine boiler and condenser is also shown, as a rectangle containing dashed lines. To realize this cycle, we can see that a liquid–gas mixture should have been compressed from state A′ to B, which can only be done with complicated devices and important losses. Between states C and D′, an isothermal expansion of the steam should have been done which is also complicated to realize. (If there was not a superheating of the steam, it would have been introduced into the turbine in state C as saturated vapor and would liquefy during expansion into small droplets damaging turbine blades.) These technical complications and energy losses can all be avoided by the Rankine cycle at the price of a lower efficiency, even for an ideal operation without losses, compared to the Carnot cycle operating between the same two heat reservoirs. The theoretical efficiency of a Carnot engine operating between a 600°C and a 20°C heat reservoir is 66.4 %. A Rankine engine working with 600°C superheated water steam and a 20°C condenser has only 44.1% theoretical efficiency. However, energy losses are so small for this engine that there exists a power plant working at 39% effective efficiency.

5.4.2 Refrigerators and Heat Pumps Based on the Rankine Cycle

Domestic compressor refrigerators usually operate on a Rankine cycle. The actual device – whose schematic diagram is shown in Fig. 5.5 – operates almost in an identical cycle to the Rankine engine, except for its reverse direction. The most striking difference is the throttling valve between states E and D in place of the

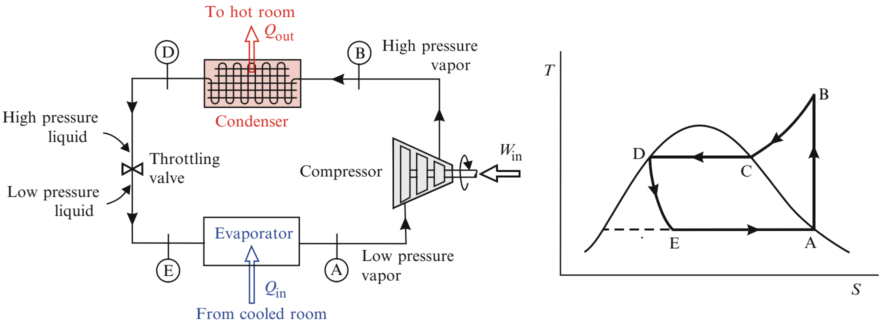

Fig. 5.5 Schematic diagram of a refrigerator working on a Rankine vapor compression cycle, and the T–S diagram of the cycle. The heat absorbed from the cooled room is used to produce vapor from liquid in the evaporator. The compressed vapor rejects heat to the hot room during condensation. *Letters* in the schematic diagram indicate states in the T–S diagram. The flow direction of the working fluid is indicated by *arrows*

turbine. (The throttling valve may be a small orifice on a plate, a porous ceramic filter, or a capillary within the tube. The gas expands across the throttle and its pressure drops.) The reason for this change is clear from the *T*–*S* diagram; the liquid expanding from state D partly evaporates. This would lead to the technical problems mentioned above in the operation of the turbine, and the liquid part of the mixture would produce much less work while expanding than the vapor. In this case, it is not worth recycling; it will take the form of losses. Another difference is that, having reversed the direction of the engine cycle, it is not the liquid to be pumped but the vapor to be compressed.

The refrigeration cycle begins with compressing the vapor by an adiabatic compressor from the low-pressure state A into the high-pressure state B, the entrance point of the condenser coil. The vapor is condensed inside the coil and the heat released is dissipated to ambient air. The high-pressure liquid formed (state D) expands through the throttling valve and forms a low-pressure liquid–vapor mixture (state E) to enter the evaporator. There, its liquid content evaporates at constant temperature, withdrawing the necessary heat of evaporation from the cooled room. After evaporation, the fluid is once again in the vapor state A; thus, the cycle is closed and it starts over by compression.

The throttling valve between states E and D is usually a thin capillary. The change of state across the valve is an *isenthalpic* expansion. During this process, the entropy increases and the liquid partially evaporates. This part of the cycle is essentially different from the Rankine engine cycle.

The coefficient of performance of a Rankine vapor compression cycle is somewhat lower than that of a Carnot refrigeration cycle. In domestic refrigerators, there are also important losses. As a result, a common domestic refrigerator usually has a coefficient of performance of about 2.5, while a deep-freezer unit is only slightly higher than 1. The coefficient of performance of heat pumps operating between moderately large temperature differences is around 4.

5.4.3 Isenthalpic Processes: The Joule–Thompson Effect

As mentioned in the previous section, expansion through a throttle has a great practical importance. Apart from refrigerators, this procedure is also used in devices to liquefy gases. The first realization of a throttling expansion (see Fig. 5.6) was done by Joule[5] and Thomson; thus, it is also called a *Joule–Thomson process* (or Joule–Kelvin process). Their original throttle was a silk tissue, later changed for sea sponge. Actual devices are small orifices on a plate, thin capillaries or glass membrane filters of small pore diameter.

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[5] James Prescott Joule (1818–1899) was a Scottish brewer and hobby scientist. His scientific activity was most fruitful in experimental studies of energy transformations. The SI unit of energy is named after him.

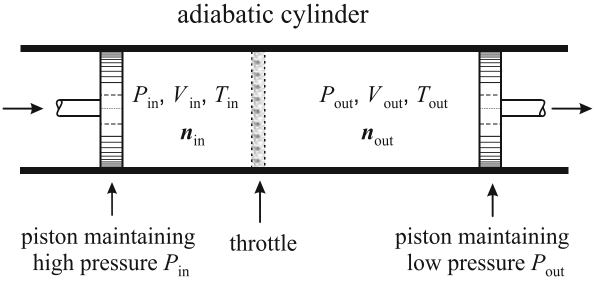

Fig. 5.6 Schematic diagram of a device for a Joule–Thomson process. The gas at high-pressure P_{in} seeps across the throttle while expanding to the low-pressure P_{out}. The flow of the gas across the throttling is low enough so that equilibrium is maintained at both sides

Let us describe the change when $\boldsymbol{n}_{\text{in}}$ mol of the gas is compressed across the throttle at constant pressure P_{in} on the high-pressure side and P_{out} on the low-pressure side; i.e., $\boldsymbol{n}_{\text{in}} = \boldsymbol{n}_{\text{out}}$. Both pistons and the cylinder are adiabatic; thus, the energy of the gas can only change by the work $P_{\text{in}}V_{\text{in}}$ done by the left, and $P_{\text{out}}V_{\text{out}}$ done by the right piston:

$$U_{\text{out}} = U_{\text{in}} + P_{\text{in}}V_{\text{in}} - P_{\text{out}}V_{\text{out}}. \tag{5.13}$$

By rearranging, we get

$$U_{\text{out}} + P_{\text{out}}V_{\text{out}} = U_{\text{in}} + P_{\text{in}}V_{\text{in}}, \tag{5.14}$$

which is equivalent to the equality $H_{\text{out}} = H_{\text{in}}$, showing that the enthalpy did not change during the process. This is the reason to call it an *isenthalpic process*.

The change in temperature during the process can be given by integrating

$$\mathrm{d}T = \left(\frac{\partial T}{\partial P}\right)_{H,\boldsymbol{n}} \mathrm{d}P, \tag{5.15}$$

and the result – apart from the difference in pressure – depends on the *Joule–Thomson coefficient* $\left(\frac{\partial T}{\partial P}\right)_{H,\boldsymbol{n}}$. This coefficient can be calculated from the measurable quantities introduced in Sect. 4.4.2. To perform the calculations, suppose that the composition does not change, and let us relate all quantities to $\boldsymbol{n} = 1$ mol; thus, the variable $\boldsymbol{n}$ is no more necessary to write. Using the cyclic rule (F1.23), the Joule–Thomson coefficient can be written as follows:

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \tag{5.16}$$

We have identified the measurable quantities as the second derivatives of the function $G(T, P, \boldsymbol{n})$. Thus, based on the definition of enthalpy

$$H = G + TS, \tag{5.17}$$

we can write

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial S}{\partial P}\right)_T \tag{5.18}$$

We can substitute from (4.38) αv in place of $(\mathrm{d}S/\mathrm{d}P)_T$. From (4.51), we know that $(\mathrm{d}G/\mathrm{d}P)_T$ is the volume; thus, we can replace it by the molar volume v. Taking this into account, the numerator in (5.16) becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = v - \alpha T v. \tag{5.19}$$

The denominator (as it is also related to 1 mol) is the molar heat capacity c_P. Using these results, the Joule–Thomson coefficient can be given as follows:

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{v}{c_P}(1 - \alpha T). \tag{5.20}$$

The pressure decreases when the gas passes across the throttling (i.e., $\mathrm{d}P < 0$); thus, the process results in a decrease in temperature if the Joule–Thomson coefficient is positive ($\alpha T > 1$). Conversely, in case of a negative coefficient ($\alpha T < 1$), it results in an increase in temperature. The switching between the two regimes depends on the value of the coefficient of thermal expansion α. The temperature at which the Joule–Thomson coefficient changes sign (and it is zero) is called the *inversion temperature*. It is clear from the above results that it can be calculated from the equation

$$\alpha T_{\text{inversion}} = 1. \tag{5.21}$$

The coefficient of thermal expansion for an ideal gas is easy to calculate:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{PV} = \frac{1}{T}. \tag{5.22}$$

We can see that the product αT is always 1 for an ideal gas; thus, its Joule–Thomson coefficient is zero and there is no change in temperature when it passes across a throttling. In case of real gases, there exists an inversion temperature depending on pressure, and there exists a pressure and temperature region within which they always get cooled when passing through a throttling. Hydrogen gas, for example, cools below 193 K (-100.16°C) at atmospheric pressure. All other gases – except for helium – have a higher inversion temperature.

In a liquefying device, gases are first cooled below their inversion temperature and then expanded across a throttle. During this expansion, a part of the gas becomes liquid. The rest is pressed again across the throttling, resulting in further liquefaction. A continuous liquefaction can be maintained in this way.

Problems

1. Electric energy delivered from a power company is used to provide heating to our apartment to a temperature of 25°C in an environment of -2°C. To what factor can we improve our cost–benefit ratio if we use electric energy to drive an ideal Carnot heat pump rather than directly heating with a resistor?

Solution: As a heating resistor transforms electric energy directly into heat, the "efficiency" of heating is exactly 1. A Carnot heat pump has a coefficient of performance

$$\varepsilon' = \frac{T_\mathrm{h}}{T_\mathrm{h} - T_\mathrm{c}},$$

according to (5.11). Upon substitution of $T_\mathrm{h} = 298.16$ K and $T_\mathrm{c} = 271.16$ K, we get $\varepsilon' = 11.04$. Thus, we have to pay 11 times less for heating. (In reality, the efficiency of existing domestic heat pumps is much less than this, due to different construction with respect to a Carnot device and eventual losses, but it is still close to a coefficient of performance of 5 at the given conditions.)

2. The so-called *air-standard Otto cycle* is a rough model approximation of the operation of actual four-stroke petrol fuel engines in cars. In this cycle, the working fluid is considered to be air only (for the sake of simplicity supposed to be a monatomic ideal gas), the combustion as a simple heat intake, and exhaustion as a simple heat rejection. Thus, the cycle contains the following steps:

(a) an adiabatic compression; (b) a constant volume heating; (c) an adiabatic expansion; and (d) a constant volume cooling to the initial state.

As the piston moves from the head-end dead center to the crank-end dead center, the working fluid has twice the minimum volume and twice the maximum volume during the cycle; i.e., $V_A = V_D$ and $V_B = V_C$.

Sketch the operation of the cycle in a *T–S* and a *P–V* diagram and show that the efficiency of the engine can be given as

$$\eta = 1 - \left(\frac{V_A}{V_B}\right)^{-2/3},$$

if V_A is the volume of the working medium before, and V_B is that after the adiabatic compression.

Solution: According to the above description, the operation of the four-stroke Otto cycle can be drawn in the two diagrams as seen below:

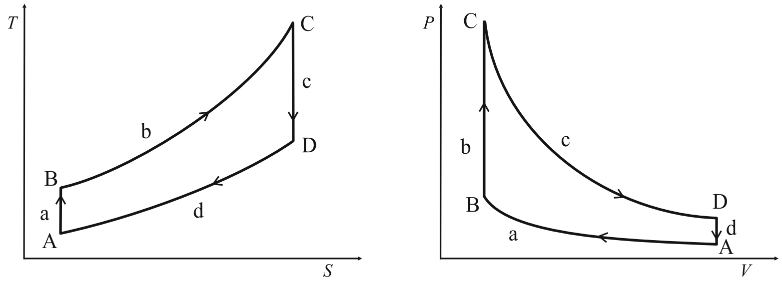

Fig. 5.7 The *T–S* and *P–V* diagram for the working fluid in the air-standard Otto cycle

According to (5.5), the efficiency of a heat engine can be expressed in the following way:

$$\eta = \frac{|Q_{\mathrm{in}}| - |Q_{\mathrm{out}}|}{|Q_{\mathrm{in}}|} = 1 - \frac{|Q_{\mathrm{out}}|}{|Q_{\mathrm{in}}|}$$

Heat is only absorbed in process b and rejected in process d, and both processes are at constant volume; thus we can write $Q_{\mathrm{in}} = C_V \Delta_{\mathrm{B}}^{\mathrm{C}} T$ and $Q_{\mathrm{out}} = -C_V \Delta_{\mathrm{D}}^{\mathrm{A}} T$, and

$$\eta = 1 - \frac{|Q_{\mathrm{out}}|}{|Q_{\mathrm{in}}|} = 1 - \frac{C_V(T_{\mathrm{D}} - T_{\mathrm{A}})}{C_V(T_{\mathrm{C}} - T_{\mathrm{B}})} = 1 - \frac{T_{\mathrm{D}} - T_{\mathrm{A}}}{T_{\mathrm{C}} - T_{\mathrm{B}}}.$$

To find the relation between temperature and volume during the isentropic processes a and c, when there is no heat exchange but only work exchanged with the surroundings, we can proceed similarly to the treatment of Sect. 4.4.2. Let us start from (2.26) written for a closed system (as we only consider air as a monatomic gas without chemical changes):

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V.$$

For the monatomic ideal gas, we can write

$$(\mathrm{d}U)_V = \frac{3}{2} nR\mathrm{d}T \quad \text{and} \quad \frac{P}{T} = \frac{nR}{V}.$$

Thus, we get

$$\mathrm{d}S = \frac{3nR}{2T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V.$$

As the first term is independent of V and the second one is independent of T, integration can be performed in the following way:

$$\Delta S = \frac{3}{2} nR \int_{T_A}^{T_B} \frac{1}{T}\mathrm{d}T + nR \int_{V_A}^{V_B} \frac{1}{V}\mathrm{d}V.$$

As a result, we get:

$$\Delta S = \frac{3}{2} nR \ln\frac{T_B}{T_A} + nR \ln\frac{V_B}{V_A}.$$

For the isentropic change, i.e., $\Delta S = 0$, this leads to

$$-\frac{3}{2} \ln\frac{T_B}{T_A} = \ln\frac{V_B}{V_A}.$$

Exponentiation of the two sides provides the searched-for relation of T and V:

$$\left(\frac{T_B}{T_A}\right)^{-3/2} = \frac{V_B}{V_A} \quad \text{or} \quad \frac{T_B}{T_A} = \left(\frac{V_B}{V_A}\right)^{-2/3}.$$

As $V_A = V_D$ and $V_B = V_C$, we can write the equalities:

$$\frac{T_A}{T_B} = \left(\frac{V_A}{V_B}\right)^{-2/3} = \left(\frac{V_D}{V_C}\right)^{-2/3} = \frac{T_D}{T_C}.$$

From the equality $T_A/T_B = T_D/T_C$, it follows that $T_D/T_A = T_C/T_B$. We may rewrite the equation from the efficiency to contain similar ratios:

$$\eta = 1 - \frac{T_\mathrm{D} - T_\mathrm{A}}{T_\mathrm{C} - T_\mathrm{B}} = 1 - \frac{T_\mathrm{A}(T_\mathrm{D}/T_\mathrm{A} - 1)}{T_\mathrm{B}(T_\mathrm{C}/T_\mathrm{B} - 1)}.$$

As we can see, the fraction reduces to T_A/T_B, which we can express from the above results as $(V_A/V_B)^{-2/3}$. Thus, we obtain the formula we had to prove:

$$\eta = 1 - \left(\frac{V_A}{V_B}\right)^{-2/3}.$$

Note that the efficiency of the Otto cycle improves with increasing compression ratio V_A/V_B. This is the reason to increase this ratio in modern engines up to 10, above which it is not worth to further improve the antiknocking properties of the fuel. Also note that for air, the efficiency is quite lower than the one calculated for the monatomic gas.

Further Reading

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