

Chapter 8

Thermodynamics and Heat engines

We have now developed the microscopic foundation of thermodynamics. We have demonstrated the arrow of time and basic concepts such as entropy and free energy and how to calculate them based on a microscopic theory. We can, for example, calculate the entropy of a microcanonical system or the Helmholtz free energy for a canonical system, and then find other state variables through derivatives of these quantities. However, there are many ways we can determine the state variables and the equations of state for macroscopic systems: It can indeed be through a microscopic theory, it can be through simulations, or it can be through direct, experimental measurements. Thermodynamics addresses how we can describe macroscopic systems when we assume that the basic laws of thermodynamics are known as well as equations of state for all the systems involved.

In this chapter, we will review thermodynamics, and then see how we can apply thermodynamics to discuss heat machines, such as steam engines, diesel engines, stirling engines, and heat exchangers. We will place particular emphasis on the stirling engine, which is elegant in design and frequently used for solar energy applications. Indeed, the best solar energy stirling machines have efficiencies around 30 percent – which is quite amazing given the primitivity of a mechanical machine compared with high technology approaches such as solar cells.

8.1 Thermodynamics

In thermodynamics we discuss the behavior of a **system**, which is a part of the universe, which is separated from the rest of the universe, which we call **the environment**. The system may be **thermal contact** with the environment, if it is allowed to exchange energy with the environment, or it may be **thermally insulated**, if there is no energy exchange with the environment. An isolated system has no types of interactions with the environment, neither through changes in shape of the system through changes in the number of particles in the system, or through changes in the

energy in the system. For an isolated system the energy, E , volume, V , and number of particles, N , are constant.

Two systems are in thermal equilibrium with each other if they are in thermal contact with each other and we have waited for a long time. What characterizes thermal equilibrium? In thermal equilibrium (or thermodynamic equilibrium), the two systems have the same temperature. For two systems A and B in thermal equilibrium, we know that $T_A = T_B$. The **zeroth law of thermodynamics** states that if two systems are in equilibrium with a third system, they are also in thermal equilibrium with each other. If the two systems A and B both are in thermal equilibrium with system C, this means that $T_A = T_C$ and $T_B = T_C$, and therefore $T_A = T_B$ – they are therefore also in thermal equilibrium with each other.

We describe thermodynamic system with **state variables**, which describe the macroscopic state (macro-state) of a system. State variables can be variables such as energy, E , pressure, p , volume, V , entropy, S , number of particles, N , chemical potential, μ etc. There are two types of state variables: **extensive** and **intensive** variables. Extensive variables depend on (are proportional to) the number of particles, N , such as energy, E , entropy, S , and, of course, the number of particles, N . Intensive variables do not depend on the number of particles, such as the density, ρ , the pressure, p , the temperature, T , and the chemical potential, μ .

We describe the behavior of a thermodynamic system through **equations of state**, which are equations that relate various state variables. For example, for the ideal gas, we know that there is an equation relating pressure, P , volume, V , the number of particles, N , and temperature, T . In general, we can write this equation of state as

$$f(P, V, N, T) = 0, \quad (8.1)$$

where $f()$ is some function. For the ideal gas, we know how this function looks – we know the equation of state:

$$PV - NkT = 0. \quad (8.2)$$

We will develop many similar equations of state for other systems throughout this text.

It is important to notice that any state variable, depends on the state of the system, but not on how the system got to this state. If we say that the energy $E(S, V, N)$ is a state variable, we know that it is always the same for the same set of values for S , V , and N – independent of how the system got there. This is different for the work performed on a system or the thermal energy transferred to a system – these depend on how the system moves from one state to another state, and are therefore not state variables.

Changes in the state of the system occur through **processes**, which correspond to changes in the state variables of the system. We can sketch such changes in various ways, as illustrated in fig. 8.1. We can describe the state of a system in P, V -space – as we will often do for machines. The state of the system is then given by a pair P, V of coordinates. (We have then typically assumed that N is constant). Or we can describe the system in S, T space. A process is then a path from one state to another

state in the system, as shown as lines in the sketch. The two processes R_1 and R_2 which take the system from state 1 (P_1, V_1) to state 2 (P_2, V_2) are shown in the figure. If we want to determine the work done on the system in each of these processes we need to calculate the integrals over the curves of PdV , so that the work for the two processes are:

$$W_{R-1} = \int_{R_1} PdV, \quad W_{R-2} = \int_{R_2} PdV, \quad (8.3)$$

and these two quantities are generally not equal. (For the given figure they are clearly different, since the integrals correspond to the areas under the $P(V)$ curves for the two processes). Also notice that a process does not need to be described as function $P(V)$, but is more generally described as a curve that may not have a one-to-one correspondence between P and V or other state variables.

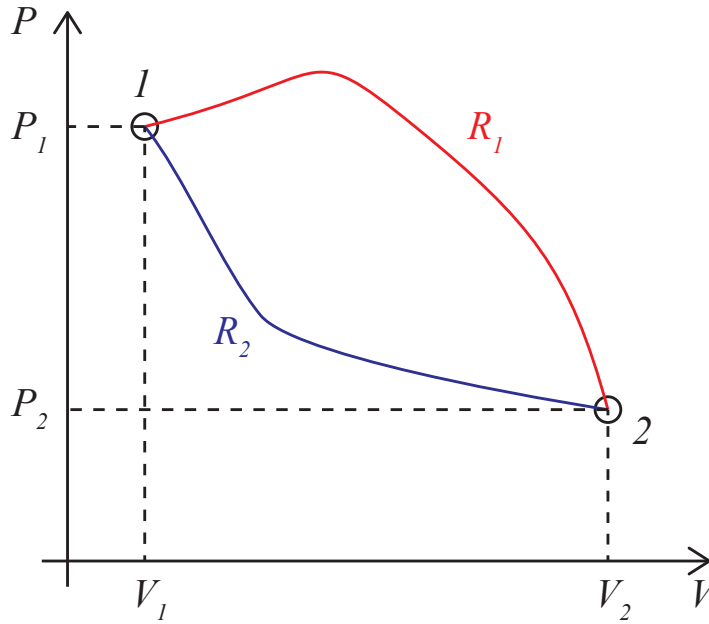


Fig. 8.1 Sketch of two processes R_1 and R_2 in a P - V diagram. Each point in the P, V space corresponds to a state of the system.

Processes may be **reversible** or **irreversible**. A reversible process is just that – a process that can be reversed. This must, for example, mean that the entropy change in the process must be zero. For a reversible process there cannot be any friction forces, since such forces would ensure that we do not return to the same state if we reverse a process.

Often, we want to specify processes where the system is always very – infinitesimally – close to equilibrium. We call such processes **quasi-static** processes. All reversible processes are necessarily quasi-static. We must always be very close to

equilibrium for a process to be reversible. However, there can be quasi-static processes that are not reversible, for example, processes where the internal friction in the system is non-negligible.

8.2 Engines

It is now time to address some of the consequences of thermodynamics. Thermodynamics was developed before we had a good microscopic understanding. Instead, it was developed partly out of necessity - because we needed the tools to develop and understand **engines**.

What is an engine? A **heat engine** is an engine that absorbs energy and converts (some of) it into mechanical work. Only part of the thermal energy can be converted into mechanical energy.

In general, heat and work are two different ways to transfer energy – and to change the internal state of a system: $\Delta E = W + Q$. Heat is the thermal transfer of energy between systems in thermal contact. Work is the mechanical transfer of energy to a system by changes in the external parameters (volume, pressure, magnetic field, gravitational potential).

Indeed, we can argue that the conversion of heat into energy is one of the most important processes in our society. It was the basis of the industrial revolution where in particular the steam engine was important. Still, steam engines and steam turbines are important and used to convert heat from burning gas or coal into electric energy – in today's power plant. Indeed, the use of hot water from solar heating or geological systems is one possible way to produce renewable energy from our environment.

There is a fundamental difference between heat and work related to the transfer of entropy. For reversible, quasi-static processes we know that $TdS = dE + pdV + \mu dN$ and $dE = Q + W$, therefore when $W = 0$ we know that $Q = TdS$. (Notice that the entropy does not change in a quasistatic, adiabatic process).

How can we use this relation to understand engines? The idea of an engine is to convert thermal energy transferred into a system into mechanical energy (work) done by the system, and then returns to its initial state. (Otherwise we could not continue to do this process).

Now, if we transfer thermal energy $Q = TdS$ into the system, the source of the thermal energy must decrease its entropy. However, if all the thermal energy was converted into work - which may be done adiabatically - we do not have any other change in entropy - and we would have a net decrease in entropy. This is not possible - from the second law of thermodynamics. We therefore also need to transfer entropy in addition to doing work - and this is done through the transfer of some of the energy that was not converted into work.

8.2.1 A simple piston

Let us now see how we can create a *heat engine* – a machine that converts heat to mechanical work. The simplest machine we can imagine consists of a single piston filled with a gas, as illustrated in fig. ???. We are going to heat up the gas in the piston. What happens to the system? How does the system behave?

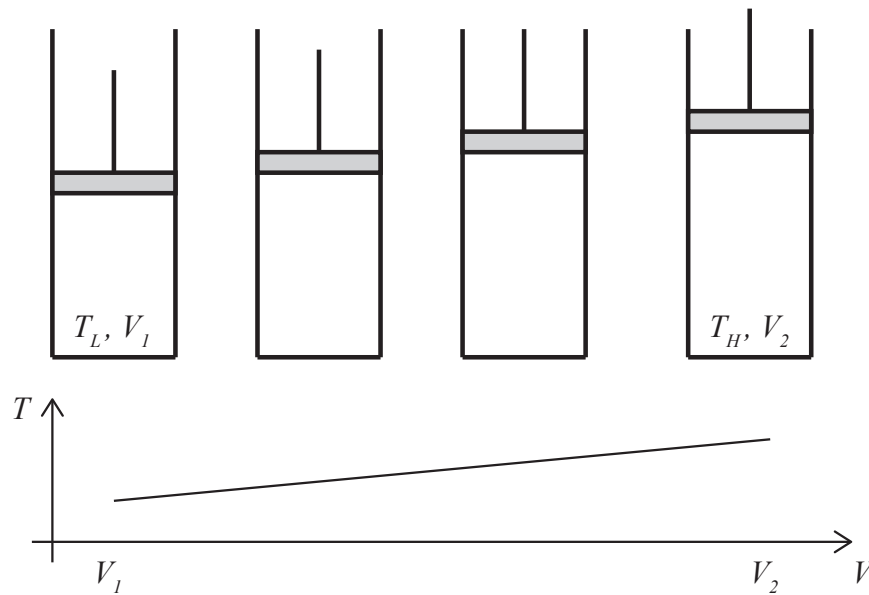


Fig. 8.2 Illustration of a piston which is supplied a heat Q so that the piston increases its temperature and expands, doing work on the environment in the process.

What do we expect to happen if all we know is that we add a thermal energy Q – heat – to the system. We expect the temperature in the gas to increase and the pressure in the gas to increase. As the pressure increases, we will expect the pressure to push on and move the piston, so that the system expands – which subsequently will lead to a cooling of the gas and a lowering of the pressure.

This process is a bit too unspecified. Let us be more precise in how we describe the process. Let us assume that the gas starts at some temperature T_L (the Low temperature) and is then suddenly put in contact with a reservoir with temperature T_H (the High temperature). The temperature in the gas will then gradually increase, until it reaches the temperature T_H , and the piston will move, changing the volume of the system from some initial volume V_1 to a final volume V_2 .

We can be even more specific. Let us divide this process into two parts. First, we place the gas in thermal contact with a reservoir with temperature T_H so that the gas increases its temperature to T_H , but we keep the volume constant. Then we allow the volume to change, while the gas still is in thermal contact with the reservoir, so that

the temperature is constant in the subsequent process, where the volume increases from V_1 to V_2 . Now, the piston is expanded, and the temperature inside the piston is high. The machine has performed work with the motion of the piston, but only once. If we want the machine to continue to produce work, we need to be able to repeat the process – we need the machine to return to its initial state, so that we can add heat yet again and produce more work. We need to have a **cyclic process**, corresponding to a loop in the P, V diagram for the process. We therefore need to compress the piston back to a volume V_1 and reduce the temperature to T_L . However, if we first return the volume to V_1 while the system is at the high temperature, the work done will be exact the same as was done to expand the gas – and the net work done will be zero. However, if we instead first cool the gas to T_L , and then push the piston back at the lower temperature and pressure, we will do less work on the piston to return it to its original position and the machine will be able to perform a net work.

Let us look at the various steps in this process in detail. The system starts in state 1, where the temperature is T_L and the volume is V_1 . This state is illustrated in fig. 8.3. The system then comes in contact with a reservoir with temperature T_H so that the temperature increases from T_L to T_H without any change in volume in the system. This process takes us from a point 1 at (P_1, V_1) in the diagram to a point 2 at (P_2, V_1) . We call such a process an **isochor** process, since it is a process without any change in volume.

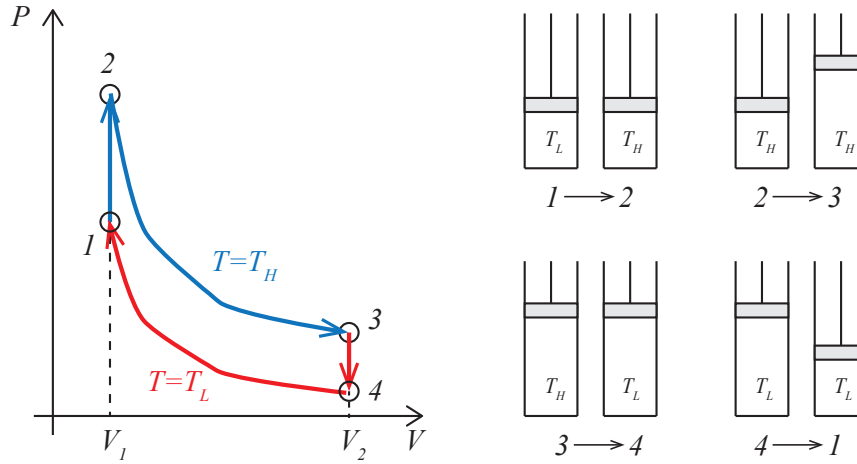


Fig. 8.3 Illustration of an engine as a sequence of processes in a $P-V$ -diagram.

1 \rightarrow 2: an isochor heating. The process is illustrated in fig. 8.3. The work done by the system on the environment is zero, since the volume does not change. This means that the change in energy is just due to the thermal energy transferred. From the first law, we have $\Delta E_{1,2} = -W_{1,2} + Q_{1,2} = Q_{1,2}$, when $W_{1,2} = 0$. (Notice that we have changed the sign of work when we discuss engines – we prefer to work with

positive work when the machine does work on the environment). We can therefore find the thermal energy transferred (the heat) from the change in energy. For an ideal monoatomic gas, the energy is $E = (3/2)NkT$, and the change in energy is therefore $\Delta E_{1,2} = (3/2)Nk(T_H - T_L)$, which is also the heat transferred to the system in this process.

2 → 3: an isothermal expansion. In the next step of the process, the gas expands while keeping the temperature constant. We call processes at constant temperature **isothermal processes**. How does this process look in the P, V diagram? We can find how P depends on V from the equation of state for the ideal gas: $PV = NkT$, and since this process occurs at $T = T_H$, we have $P = (NkT_H)/V$. We can therefore find the work done by the system on the environment in this step:

$$W_{2,3} = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{NkT_H}{V} dV = NkT_H \ln \frac{V_2}{V_1}. \quad (8.4)$$

If we perform work on the environment, but keep the temperature in the gas constant, thermal energy must be transferred from the reservoir. This is also evident from the first law, because $\Delta E_{2,3} = -W_{2,3} + Q_{2,3}$. For an ideal (monoatomic) gas, we know that $E = (3/2)NkT$. For a process with constant T there is therefore no change in energy, and $\Delta E_{2,3} = 0$, hence $Q_{2,3} = W_{2,3}$: all the energy used to perform the work is taken from the reservoir.

3 → 4: an isochor cooling. Now, we cool the system to the initial temperature T_L by putting the system in contact with another reservoir at a lower temperature T_L . The discussion for this process is similar to the isochor heating: The heat $Q_{3,4}$ corresponds to the change in energy because the work is zero (since there is no change in volume). We therefore have $Q_{3,4} = \Delta E_{3,4} = (3/2)Nk(T_L - T_H)$. Now, this is a negative value, indicating that this heat is transferred out of the system and not into the system.

4 → 1: an isothermal compression. Finally, the system is brought back to the beginning by compressing the system back to the starting volume V_1 . This is again an isothermal process at $T = T_L$ and we can find the work by integrating $P(V) = NkT_L/V$:

$$W_{4,1} = \int_{V_2}^{V_1} \frac{NkT_L}{V} dV = NkT_L \ln \frac{V_1}{V_2}, \quad (8.5)$$

and this work corresponds to the heat $Q_{4,1} = W_{4,1}$. Both the work and the heat are negative, indicating that heat is transferred out of the system and work is done on the system in this process.

8.2.2 Net work and efficiency of the machine

We have now described a complete cycle of the machine. The cycle is illustrated in fig. 8.3.

We see that the work performed from 2 to 3 is the integral of $P(V)$ with respect to V , and we can interpret this as the area under the curve of the $P(V)$ curve from 2 to 3. Similarly, the work performed from 4 to 1 is (minus) the area under the $P(V)$ curve from 4 to 1. The net work done in the whole cycle is therefore the area enclosed by the $P(V)$ curve for the entire, cyclic process.

The **net work** is the sum of all the works done in each subprocess. This corresponds to the area enclosed by the curve in the P - V diagram. You can see this by realizing that the system does positive work when the system moves to the right along the $P(V)$ curve. The area under this part of the curve is therefore the positive work done. The system does negative work when the system moves to the left along the $P(V)$ curve. If we subtract these two areas – as illustrated in fig. 8.4 – we get the net work, which corresponds to the enclosed area.

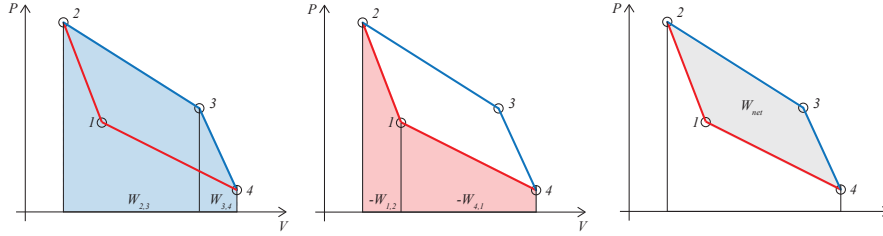


Fig. 8.4 Illustration of work done by the system on the environment for a complete cycle of a machine.

The **net heat** is the sum of all the heats transferred in each subprocess. The **added heat** corresponds to the sum of the positive heats ($Q > 0$). We can apply the first law to a complete cycle. In this case, the change in energy is zero, since the energy at the beginning and end of the cycle must be the same since the energy is a state variable. Hence, the net work must correspond to the net heat added to the system: $W_{net} = Q_{net}$ and $\Delta E_{net} = 0$.

What is the efficiency, e , of this machine? It is reasonable to call the efficiency how much work you get out for each unit of heat you put into the system:

$$e = \frac{W_{net}}{Q_{add}}. \quad (8.6)$$

We can calculate the efficiency of the machine we have described, by inserting the values we have found for work and heat. We notice that the added heat corresponds to the heat added in process $1 \rightarrow 2$ and $2 \rightarrow 3$, that is $Q_{net} = Q_{1,2} + Q_{2,3}$. The efficiency is therefore

$$e = \frac{W_{net}}{Q_{net}} = \frac{NkT_H \ln V_1/V_0 - NkT_L \ln V_1/V_0}{NkT_H \ln V_1/V_0 + Nk(T_H - T_L)} . \quad (8.7)$$

This is a nice result. And as we shall soon see – the machine we have described here corresponds to a Stirling machine, which is used for example for solar array systems.

8.2.3 Limits on efficiency

We have found a particular efficiency in this case. But how good is this machine? To answer that we need to know of efficient a machine can be – is there a theoretical maximum in efficiency for a heat engine? The answer is yes – and we can find this maximum.

Let us look at this more systematically. We can sketch an engine as in figure 8.5.

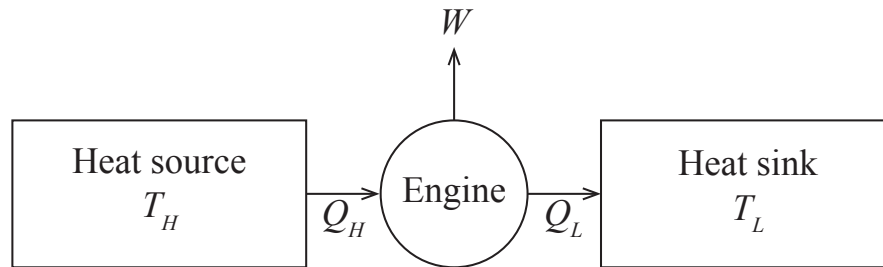


Fig. 8.5 Sketch of a heat engine.

This engine works between a heat source at T_H and a heat sink at T_L .

- The engine performs a cycle that should end in the engine coming back to the state it started from (not microstate, of course, but the same macrostate).
- In this cycle a thermal energy Q_H is transferred into the engine.
- The engine does work W .
- And the engine transfers a thermal energy Q_L out of the engine and into the heat sink.
- The heat source and heat sink are so large that their temperatures do not change in this process.

We have so far defined the work done *on the system* as positive, but for an engine we are usually more interested in the work done *by the system*. We will therefore

use the common convention Q_H , Q_L and W all are positive. In this notation, the first law of thermodynamics is

$$\Delta E = Q_H - Q_L - W , \quad (8.8)$$

where W is the net work done in a complete cycle, Q_H are all the heats that are added to the system – this may occur in more than one of the processes – and Q_L are all the heats that are removed from the system – again this may occur in more than one processes. Notice that we have changed the sign in front of the work, because the work W is now the work done by the system on the environment. For a complete cycle, the change in E must be zero, because E is a state variable and therefore will be the same in the first and the last point in the cycle, because these are the same states. The first law of thermodynamics for this system is therefore

$$W = Q_H - Q_L , \quad (8.9)$$

the net work W is equal to the net thermal energy (heat) added during a complete cycle.

What is the efficiency of such a machine: It is what we get out (net work) divided by what we put in (heat in Q_H):

$$e = \frac{W}{Q_H} . \quad (8.10)$$

Ok. But what is the maximum efficiency we can get? It is limited by the laws of thermodynamics. From the first law of thermodynamics, we see that $Q_H = W + Q_L$. The efficiency is therefore:

$$e = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} . \quad (8.11)$$

We can use the second law to relate Q_L and Q_H . From the second law we know that

$$dS = dS_H + dS_L = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0 , \quad (8.12)$$

which gives:

$$\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H} . \quad (8.13)$$

and therefore

$$e = 1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H} . \quad (8.14)$$

(Notice that we have here assumed that the heat is deposited to the low temperature and taken from the high temperature). When the cycle is reversible, we know that the equality holds, and in this case the efficiency is:

$$e = 1 - \frac{T_L}{T_H} . \quad (8.15)$$

This is the maximum efficiency of an engine. A reversible engine of this type is called a *Carnot engine*. Notice that this means that all engines that operate between the same two temperatures (and that are reversible) have the same efficiency – independent of how they are constructed.

However, in practice, no real engine reaches the theoretical efficiency, and differences in the actual implementation is therefore important - typical engines reach about 30-40% of the theoretical limit, often even less.

Clicker example of cycles

8.3 The Carnot cycle

Let us show an example of a cycle – a heat engine – that achieves the theoretical limit in an idealized setting. The Carnot cycle consists of four steps. It starts from a state 1 with a temperature T_H . (It is in contact with a heat bath with this temperature).

Step 1 ($1 \rightarrow 2$) – Isothermal expansion: First, it executes an isothermal expansion from $1 \rightarrow 2$. The system expands while in contact with the heat source. This means that heat is transferred into the system. For a gas this corresponds to the gas pushing on a piston turning a crank to produce work. Since the system stays at the same temperature, the engine must get thermal energy from the heat bath. (We assume that heat is flowing into the system, even though the system and the bath are at the same temperatures - for example by expanding the system in very small steps, so that we are always infinitesimally close to equilibrium).

We could then compress the system isothermally to return to state 1. This would complete the cycle, but exactly the same work would be needed to push the piston back - we would not have done any net work! We therefore need a few more steps - we could reduce the pressure in the system, so that we could return the piston at a lower pressure, which would require less work. But then we would need to increase the pressure again before returning to the initial state. We could also lower the pressure by doing an adiabatic expansion, and this is what we do:

Step 2 ($2 \rightarrow 3$) – adiabatic expansion. We now isolate the system (remove the thermal contact). The volume continues to increase, but no heat is added. Then both the pressure and the temperature decreases. The temperature decreases all the way to T_L .

We also perform work in this part of the cycle - but now the energy that goes into the work comes from the internal energy of the system, $\Delta E_{2,3} = W_{2,3}$, since the system is thermally isolated.

Now, we can restore the system to its initial condition, starting at a lower pressure. First, we perform an isothermal compression at T_L .

Step 3 (3 \rightarrow 4) – Isothermal compression. Work is done on the system by pressing the piston back in. This would increase the temperature of the system, but instead thermal energy is flowing out of the system and into the heat sink (T_L).

Finally, we need to increase the temperature of the system back to its original state.

Step 4 (4 \rightarrow 1) – Adiabatic compression. We now need to increase the temperature (and pressure) of the system back to its original state. We remove the contact with the heat sink, and compress the system without any thermal energy flowing into it - this is done until the temperature is back at T_H (and the pressure is back to its initial state).

8.3.1 Carnot cycle for ideal gas

Let us look at the Carnot cycle for an ideal gas in detail. The cyclic process is sketched in the $P(V)$ diagram in fig. 8.6.

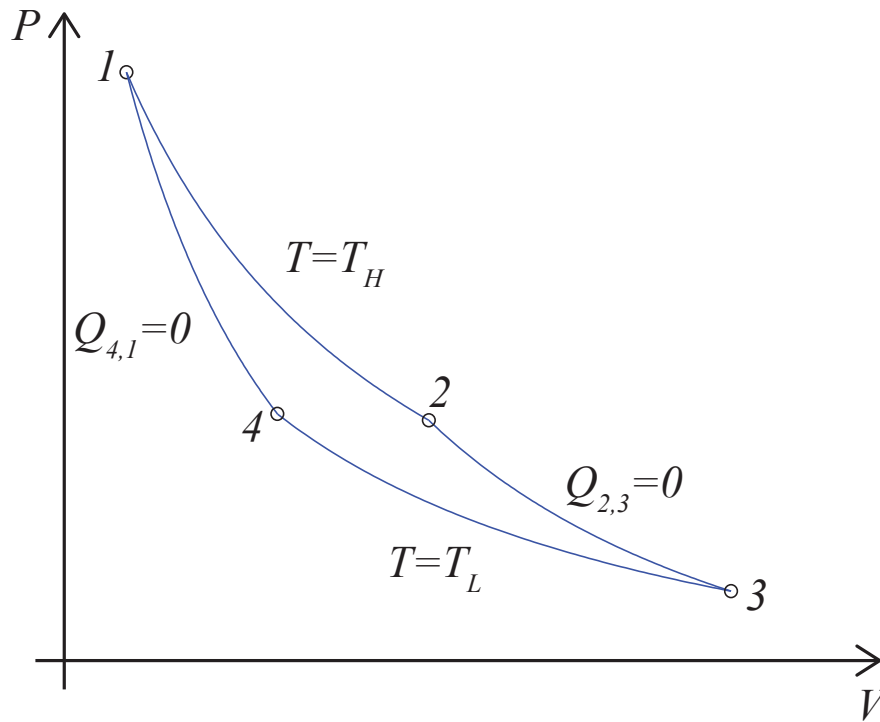


Fig. 8.6 Illustration of the Carnot cycle for an ideal gas.

Isothermal expansion ($1 \rightarrow 2$). The gas starts at $T_1 = T_H$ and V_1 . The gas expands isothermally to V_2 . First, how does this curve look like in the diagram?

If the temperature is constant, we know that $pV = NkT$, and hence we know that

$$p = \frac{NkT}{V} \quad (8.16)$$

for this curve.

Since the temperature is constant, and the energy U for an ideal gas is linear in temperature, we know that $dU = 0$ for this process, hence $Q = W$. The heat transferred is therefore given by the work:

$$W = \int_{V_1}^{V_2} p dV = NkT \int_{V_1}^{V_2} \frac{1}{V} dV = NkT \ln \frac{V_2}{V_1}, \quad (8.17)$$

(Notice, that you would have found the same by using that the heat is $Q = TdS$ for this process and that the entropy is $S = Nk \ln V + f(N, U)$, which would give the same result for the heat).

We can draw the curve from 1 to 2 in a pV diagram, and notice that the work is the area under the curve from 1 to 2.

Adiabatic expansion ($2 \rightarrow 3$). Now, the gas is disconnected from the bath at T_H and thermally isolated - so that the work is given as the change in internal energy of the system. The work done in this process is simple to find from $dU = Q + W$, where now $Q = 0$, and therefore $dU = W$, where $U = (3/2)NkT$ for a monatomic ideal gas and $((f+3)/2)NkT$ for a general ideal gas. The work is therefore simply

$$W_{23} = \frac{3}{2}Nk(T_H - T_L). \quad (8.18)$$

What does the curve $P(V)$ look like for this process?

For a quasistatic, adiabatic process the entropy is constant. The entropy for an ideal gas is given by the Sackur-Tetrode equation:

$$S = Nk \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{4\pi m U}{3Nh^2} + \frac{5}{2} \right), \quad (8.19)$$

where

$$U = \frac{3}{2}NkT, \quad (8.20)$$

and therefore

$$S = Nk \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{2\pi mkT}{h^2} + \frac{5}{2} \right). \quad (8.21)$$

Constant S therefore means that $\ln VT^{3/2}$ is constant, and therefore that $VT^{3/2}$ is constant. We can use this to find the volume at the end of the expansion:

$$T_L V_3^{2/3} = T_H V_2^{2/3}, \quad (8.22)$$

that is

$$V_3/V_2 = (T_H/T_L)^{3/2} . \quad (8.23)$$

And we can also find the shape of the $P(V)$ curve - which we often simply call an adiabat, by inserting $T = pV/Nk$ into $VT^{3/2} = \text{const.}$, which gives $V^{5/2}p^{3/2}$ is constant, or $PV^{5/3}$ is constant, and the curve is $P = C/V^{5/3}$, which we can sketch.

Isothermal compression ($3 \rightarrow 4$). The gas is now in contact with the bath at T_L and compressed isothermally to the volume V_4 . How should we choose V_4 ? We must choose V_4 so that we can go along an adiabat from 4 to 1, and therefore V_1, T_H , and V_4, T_L must be connected by an adiabat, therefore

$$V_4 T_4^{3/2} = V_1 T_H^{3/2} \Rightarrow V_4/V_1 = (T_H/T_L)^{3/2} , \quad (8.24)$$

where we again have that $(T_H/T_L)^{3/2} = V_3/V_2 = V_4/V_1$.

What work is done on the gas? We find the work by integrating

$$W_{34} = \int_3^4 p dV = NkT_L \ln \frac{V_3}{V_4} = NkT_L \ln \frac{V_2}{V_1} . \quad (8.25)$$

A corresponding energy is transferred into the system as heat, since the internal energy does not change for an ideal gas during an isothermal process. The heat is therefore

$$Q_{34} = Q_L = W_{34} . \quad (8.26)$$

Adiabatic compression ($4 \rightarrow 1$). Finally, the gas is isolated thermally again, and the gas is compressed along an adiabat from 4 to 1. The work done in this process is:

$$W = \frac{3}{2} Nk (T_H - T_L) , \quad (8.27)$$

which cancels the work done during the isentropic expansion from 2 to 3.

The net work done by the whole cycle can be read from the pV -diagram. Look at the area below the curve from 1 to 2, 2 to 3, 3 to 4 and 4 to 1, and see that the net work corresponds to the area enclosed by the curve. This net work is

$$W_{\text{net}} = Q_H - Q_L = Nk (T_H - T_L) \ln \frac{V_2}{V_1} . \quad (8.28)$$

Efficiency: We can put this back into the efficiency, and find that the efficiency is

$$e = \frac{W_{\text{net}}}{Q_H} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} . \quad (8.29)$$

8.4 Carnot refrigerator

A refrigerator is a heat engine that works in reverse - it uses work to cool a system down. It takes heat from the low temperature region – inside the refrigerator – and combines it with work, and dumps heat at a high temperature bath - outside the refrigerator.

In this case the efficiency depends on Q_L and W , but we call it the coefficient of performance (COP):

$$\text{COP} = \frac{Q_L}{W} . \quad (8.30)$$

Again, we can use the first law to relate the three energies:

$$Q_H = Q_L + W , \quad (8.31)$$

which gives

$$\text{COP} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1} . \quad (8.32)$$

What are the limits for the efficiency of a refrigerator? The second law gives us:

$$\frac{Q_H}{T_H} \geq \frac{Q_L}{T_L} \Rightarrow \frac{Q_H}{Q_L} \geq \frac{T_H}{T_L} . \quad (8.33)$$

(Notice that the inequality is in reverse compare to before because the entropy is flowing in the opposite direction). This gives:

$$\text{COP} \leq \frac{1}{T_H/T_L - 1} = \frac{T_L}{T_H - T_L} . \quad (8.34)$$

The coefficient may be higher than 1 - indeed it will usually be. For example, for a kitchen fridge we may have $T_H = 298\text{K}$ and $T_L = 255\text{K}$, which gives $\text{COP} = 5.9$. Notice that COP goes to infinity as the temperature difference goes to zero! Also notice that we can make a Carnot cycle refrigerator - but this is not how things are done in practice since the cycle would take too long time. We will address a few more realistic processes in the following.

8.5 Realistic model for Stirling Engine

We can gain more insight into how real engines work by developing a realistic model for a Stirling engine. Here, we will work on a model engine used in the 2.670 class at MIT, inspired by a report by M. Byl in 2002. The Stirling engine we will model is sketched in fig. ???. This engine consists of two connected chambers. One chamber on the left, where the displacement piston is working. The volume of the gas in this chamber remains constant throughout the process, but the portion that is in contact with the hot temperature, T_H , and the portion that is in contact with the cold region,

T_L , varies in time. We will assume that the whole gas has the same temperature $T(t)$. This means that the temperature will vary in time, but we assume that the temperature in the gas is the same everywhere along the machine.

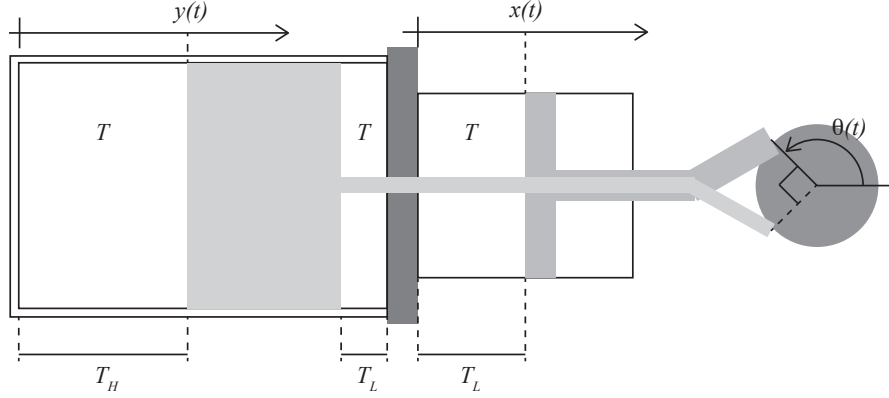


Fig. 8.7 Illustration of a realistic Stirling engine using air as the gas medium.

Let us start with a quantitative description of this machine. We will assume that there is a constant transport of heat from the surrounding reservoirs into the machine. There is a transfer of heat into the machine in the hot region and a transfer of heat out of the machine in the cold region. We will apply a simple law for heat conduction to estimate the *rate* at which thermal energy is transferred to the gas. The heat transfer from outside to inside the piston is proportional to the difference in temperature, $T_{out} - T_{in}$, the area of contact, A , and a constant, μ , that depends on the material properties of the cylinder wall. In the hot region, the only contact is through the large cylinder on the left. The heat transported through the wall and into the gas in a time interval Δt is then

$$Q_H = A_H \mu (T_H - T) \Delta t , \quad (8.35)$$

where $\mu = 100000 \text{ W/m}^2$ (calculated from the thermal conductance of steel and the thickness of the cylinder wall), and A_H depends on the position of the displacer piston.

How do we describe the positions of the displacer piston and the work piston? We notice that the two pistons are attached to a flywheel – through some mechanism that is not properly sketched in the figure – with the net effect that the pistons move a distance $2R$ back and forth along their axis, where R is the radius of the flywheel at the point of attachment. The position $x(t)$ of the work piston can then be written

$$x(t) = R(1 + \sin \theta(t)) , \quad (8.36)$$

with a proper choice of origin for θ . The position, $y(t)$, of the displacer cylinder should move with a phase difference of $\pi/2$, so that

$$y(t) = y_{max}(1 + \cos \theta(t)) , \quad (8.37)$$

where y_{max} is the maximum extension of the piston. If we know $x(t)$ and $y(t)$, we can find the surface areas A_H and A_L for the thermal conduction. At the hot end, the area A_H only depends on the maximum possible area, corresponding to the y_{max} multiplied with the circumference of the cylinder. We therefore find

$$A_H(t) = A_{H,max}(1 + \cos \theta(t)) . \quad (8.38)$$

where $A_{H,max} = A_0$ is the total surface area of the part of the large cylinder that contains gas.

For the cold end we need to include the heat transfer from the large cylinder and the transfer for the small cylinder:

$$A_L(t) = A_0(1 - \cos \theta(t)) + A_1(x) , \quad (8.39)$$

where $A_1(x) = A_{1,max}x(t)/x_{max}$ is the area of contact for the small cylinder to the right in the figure.

This means that in a short time interval Δt , the change in (internal) energy E of the gas in the system is

$$\Delta E = Q + W , \quad (8.40)$$

where $Q = Q_H - Q_L$, with $Q_H = A_H\mu(T_H - T)$ and $Q_L = A_L\mu(T - T_L)$. In addition, we need to include the work, W , done on the system. This work is done by the work piston, which has moved a distance $\Delta x = (\Delta x/\Delta t)\Delta t$ with a force $F = (P - P_0)A_p$ acting on the piston from the gas, where P is the pressure in the gas, P_0 is the outside pressure, and A_p is the area of the piston in contact with the gas. The work is therefore

$$W = -F\Delta x = -(P - P_0)A_p \frac{\Delta x}{\Delta t} \Delta t . \quad (8.41)$$

If we describe the position $x(t)$ through the angle $\theta(t)$, we see that

$$\frac{\Delta x}{\Delta t} = \frac{dR(1 + \sin \theta)}{dt} = R \frac{d\theta}{dt} \cos \theta = R\omega \cos \theta . \quad (8.42)$$

Now, we have a complete description of ΔE :

$$\Delta E = Q_H - Q_L + W = A_H\mu(T_H - T)\Delta t - A_L(T - T_L)\Delta t - PA_pR\omega \cos \theta \Delta t , \quad (8.43)$$

which gives a differential equation for $E(t)$:

$$\frac{dE}{dt} = A_H(t)\mu(T_H - T(t)) - A_L(t)(T(t) - T_L) - (P(t) - P_0)A_pR\omega(t) \cos \theta(t) . \quad (8.44)$$

In addition, we need to determine the motion of the flywheel. The flywheel has a moment of inertial I and is affected by a torque, τ , due to the force on the work piston. In addition, we will include a frictional effect due to friction in the flywheel as well as viscous damping due to gas motion in the displacement cylinder. The total

torque on the flywheel is then

$$\tau = FR \cos \theta - b\omega = (P - P_0)A_p R \cos \theta - b\omega, \quad (8.45)$$

where b is a viscous coefficient describing the effective damping in the system. This gives us the equation of motion for θ :

$$\frac{d^2\theta}{dt^2} = FR \cos \theta - b \frac{d\theta}{dt}. \quad (8.46)$$

We now have two equations, describing θ and E . In addition, we need to be able to calculate T , V and P in the system. We can find V from geometric considerations. The volume in the displacement cylinder is constant, V_c , but the volume in the work cylinder depends on x :

$$V(t) = V_c + A_p x, \quad (8.47)$$

where $A_p x$ is the volume of the gas in the work piston. We can now find the temperature through

$$E = C_V T \Rightarrow T = \frac{E}{C_V}, \quad (8.48)$$

where $C_V = c_V m$ is the heat capacity for the gas in the cylinder. And we find the pressure using the ideal gas law:

$$P = \frac{NkT}{V} = \frac{2}{5} \frac{E}{V}, \quad (8.49)$$

where we have used that $E = (5/2)NkT$ for the gas at realistic temperatures.

This completes the set of equations needed to determine the behavior of the machine. We can now model the machine by integrating the equations of motion for θ and the time development of E to find the behavior of the machine in a $P(V)$ diagram.

First, we need to know the values of the parameters for a realistic machine. We will use $T_H = 600\text{K}$, $T_L = 300\text{K}$, $R = 1.25\text{cm}$ (radius of flywheel), $A_0 = 40\text{cm}^2$ (surface area of active area of displacement cylinder), $A_p = 1.9\text{cm}^2$ (surface area of piston), $A_{1,max}/x_{max} = 4.9\text{cm}$ (perimeter of the work piston cylinder), $V_c = 40\text{cm}^3$ (volume of gas in displacement cylinder), $I = 4\text{kg} \cdot \text{cm}^2$, $b = 0.7 \cdot 10^{-3}\text{N/s}$ (damping constant representing viscous processes), $P_0 = 10^5\text{Pa}$ (trykk i omgivelsene), $C_V = 717\text{J/kg/K}$ (heat capacity for the gas), $\mu = 100000\text{W/m}^2$ (heat transfer coefficient for the cylinder wall), and ρ = (mass density for the gas).

The motion of the cylinder is solved by the following implementation, where we have used Euler-Cromer for the time integration with a time step of $\Delta t =$.

The resulting behavior is illustrated in fig. 8.8. The simulation is for 5 seconds, but only the first second is shown for $x(t)$ and $T(t)$, because the behavior is completely regular after 1 second. We see that both the position and the temperature has a short transient behavior before they start having a periodic behavior. We can illustrate the behavior in the periodic part of the motion by plotting $P(T)$ and $P(V)$ for the last 2.5 seconds of the simulation. We see that the behavior of the machine

indeed is a closed loop in the $P - V$ diagram. However, the actual path in the $P - V$ diagram looks very different from the idealized case we used to model the behavior of the system.

We can estimate the efficiency of this – more realistic – Stirling engine: $e = W_{net}/Q_{in}$, by measuring the heat flow into the engine during a cycle and the net work done by the machine during a cycle. The net work corresponds to the area enclosed by the curve in the $P - V$ diagram, but in the model it is easier to calculate the net work done by the piston and the sum of the heat, Q_H , transferred into the system. Unfortunately, this results in a very low efficiency. (Something may be wrong with the calculation – can you find it?).

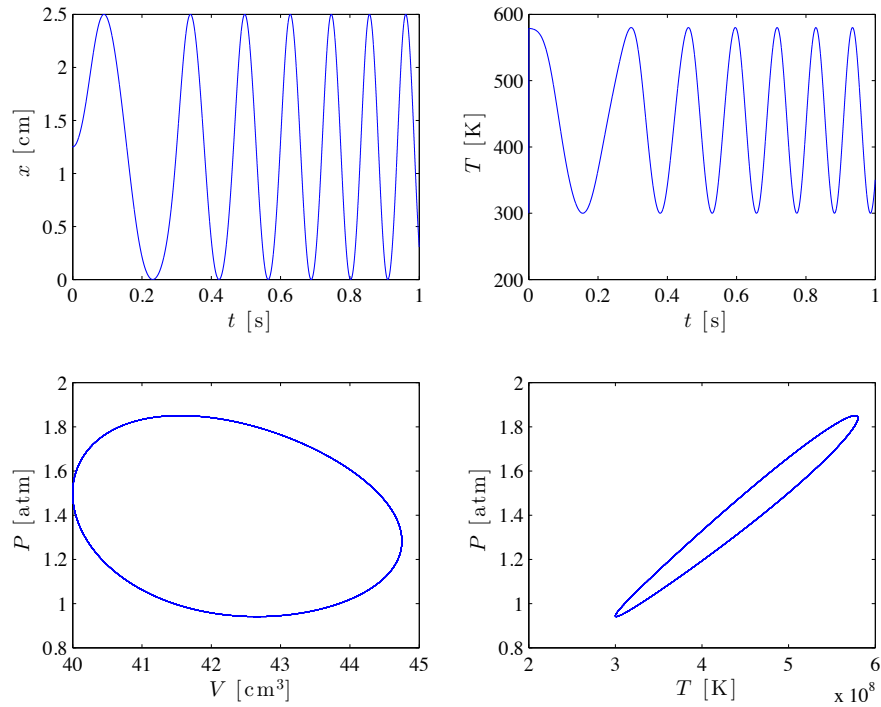


Fig. 8.8 Plots of the temporal behavior of the model Stirling engine.

8.6 Additional aspects of heat engines and thermodynamics (not relevant for exam)

8.6.1 Path dependence of Heat and Work

We need to be careful with how we write differences and differentials.

We have been careful not to write dW and dQ , since W and Q are not state functions.

S , E , etc are state functions and therefore form pure differentials.

If we go a complete loop, we will come back to the same value.

The integral over a closed loop is therefore zero.

But not so for W and Q . The integral around a complete loop of W is the net work done. And the integral around a complete loop of Q is the same - since they are related by $dE = W + Q$, and the integral of dE around a complete loop is zero.

8.6.2 Heat and work at constant temperature and constant pressure

Isothermal work. In a reversible, isothermal process T is constant and $TdS = d(TS)$, therefore $Q = TdS = d(TS)$ and

$$W = dE - Q = dE - d(TS) = dF \quad (8.50)$$

In this case Helmholtz free energy is a proper energy.

Isobaric work. Many processes occur at constant pressure - such as open processes in the atmosphere.

If we boil a liquid at constant pressure, the piston above a boiling system may move a distance dV , and the work due to this movement would be $-pdV = -d(pV)$. This work would be included in the total work done by the system. But if we compress the system, we get this work for “free” from the atmosphere, and if we expand the system we have to perform this work against the atmosphere, but this work cannot be used for anything else. It is therefore often useful to subtract $-d(pV)$ from the work, and only get the effective work performed on the system. We define this effective work as

$$W' = W + d(pV) = dE + d(pV) - Q = dH - Q, \quad (8.51)$$

where we have introduced the enthalpy $H = U + pV$. This plays the same role at constant P as U plays in processes at constant V .

The term pV is required to displace the surrounding atmosphere to get room for the system.

(We assume that there are other types of work in addition to this pressure work).

Two classes of constant pressure processes:

Processes with no effective work $Q = dH$ (no other work than the work needed to expand the system against the given pressure). Evaporation of a liquid - the heat of evaporation is the enthalpy difference between the liquid and gas phase.

Processes at constant T and constant p . Then $Q = T dS = d(TS)$ and the effective work is

$$W' = dF + d(pV) = dG, \quad (8.52)$$

where we have introduced $G = F + pV = E + pV - TS$, the Gibbs free energy. The effective work performed at constant pressure and temperature is equal to the change in Gibbs free energy. Useful for chemical reactions where the volume changes at constant pressure and temperature.

8.6.3 Chemical Work

(Kittel, p 250)

8.6.4 Joule-Thompson effect

(May use for exercise instead - process on van der Waals gas).