

# Heat engines

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# 1 Engines

We have now introduced some of the basic of thermodynamics and we have learned where thermodynamics comes from – we have developed a microscopic foundation for thermodynamics.

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:  $\Delta U = W + Q$ . 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 now all the thermal energy was converted into work – which may be done adiabatically – we 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.

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

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 is so large that the temperatures does 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 assume that  $Q_H$ ,  $Q_L$  and  $W$  all to be positive.

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

$$e = \frac{W}{Q_H} .$$

Ok. But what is the maximum efficiency we can get? Let us start from the first law of thermodynamics, which gives:  $Q_H = W + Q_L$ , and the efficiency is therefore:

$$e = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} .$$

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

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

which gives:

$$\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H} .$$

and therefore

$$e = 1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H} .$$

When the cycle is reversible, we know that the equality holds, and in this case the efficiency is:

$$e = 1 - \frac{T_L}{T_H} .$$

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. A pretty amazing result!

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

## 1.1 $PV$ diagrams of engine cycles

We can sketch cycles in a  $P, V$  diagram.

Notice that the cycle must be closed – the system must return to the same state as it started in.

The work done in the cycle can be seen as the area enclosed by the curves.

Clicker example of cycles

## 2 The Carnot cycle

Let us show an example of a cycle – a heat engine – that achieves the theoretical limit – of course 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).

First, it executes an isothermal expansion from  $1 \rightarrow 2$ .

The system expands while in contact with the heat source. This means that it will take a heat flux in.

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 they are at the same temperatures – for example 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 lower the pressure by doing an adiabatic expansion.

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,  $dE = W$ , 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  $T_L$ .

$3 \rightarrow 4$ : Isothermal compression. Work is done 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.

$4 \rightarrow 1$ : 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).

## 2.1 Carnot cycle for ideal gas

Let us look at the Carnot cycle for an ideal gas in detail.

We sketch the process in a  $PV$  diagram.

$1 \rightarrow 2$  Isothermal expansion.

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

$$p = \frac{NkT}{V}$$

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:

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

(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.

## 2 → 3 Adiabatic expansion.

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

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

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:

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

where

$$U = \frac{3}{2}NkT ,$$

and therefore

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

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:

$$T_L V_3^{2/3} = T_H V_2^{2/3} ,$$

that is

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

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.

## 3 → 4 Isothermal compression.

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

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

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 by integrating

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

This work is transferred as heat, since the internal energy does not change for an ideal gas during an isothermal process – the heat is therefore

$$Q_{34} = Q_L = W_{34} .$$

4 → 1 Adiabatic compression.

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:

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

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

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

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

$$e = \frac{W_{\text{net}}}{Q_H} = \frac{T_H - T_L}{T_H} = \frac{1}{T_H/T_L} - 1 .$$

### 3 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):

$$\text{COP} = \frac{Q_L}{W} .$$

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

$$Q_H = Q_L + W ,$$

which gives

$$\text{COP} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1} .$$

What are the limits for this? The second law gives us:

$$\frac{Q_H}{T_H} \geq \frac{Q_L}{T_L} \Rightarrow \frac{Q_H}{Q_L} \geq \frac{T_H}{T_L} .$$

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

$$\text{COP} \leq \frac{1}{T_H/T_L - 1} = \frac{T_L}{T_H - T_L} .$$

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.

## 4 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.

$S$ ,  $U$ , 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  $dU = W + Q$ , and the integral of  $dU$  around a complete loop is zero.

## 5 Heat and work at constant temperature and constant pressure

### 5.1 Isothermal work

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

$$W = dU - Q = dU - d(TS) = dF$$

In this case Helmholtz free energy is a proper energy.

### 5.2 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

$$W' = W + d(pV) = dU + d(pV) - Q = dH - Q ,$$

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  $Q = TdS = d(TS)$  and the effective work is

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

where we have introduced  $G = F + pV = U + pV - TS$ , 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.

## 6 Chemical Work

(Kittel, p 250)

## 7 Joule-Thompson effect

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