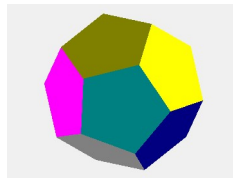


The first and second law of Thermodynamics

This is an article from my home page: www.olewithansen.dk



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1. The first law of thermodynamics

We shall not justify the first law of thermodynamics, since it is the most general formulation of the conservation of energy.

The first law of thermodynamics: For an arbitrary physical system, which can exchange energy with the surroundings, it holds good without reservations that the sum of the work W done on the system plus the heat Q added to the system is equal to ΔE , the signed change of the energy of the system.

$$(1.1) \quad W + Q = \Delta E \quad \text{where} \quad \Delta E = \Delta E_{kin} + \Delta E_{pot} + \Delta E_{internal}$$

The energy consists of 3 parts: Kinetic, potential and internal energy (not to be confused with heat). To the equation (1.1) we need to add that all quantities are signed. If the work W is negative it means that the system is doing work on the surroundings, and if Q is negative it means that the system submits heat to the surroundings. If ΔE is negative it means that the system loses energy to the surroundings.

If the work done is work done by pressing the piston inward, caused by an external pressure P , then the work done is equal to.

$$(1.2) \quad W = -P \Delta V \quad (\Delta V = V_2 - V_1)$$

The minus sign is because ΔV becomes negative, as the piston moves inwards, and A should be positive according to the first law, but if the piston moves outward then $\Delta V > 0$, the work done by the gas on the surroundings is $W_{gas} = P \Delta V$.

But as the gas performs a work on the surroundings this work should be counted negative in the first law, so that $W = -W_{gas} = -P \Delta V$.

Since this is the same expression as in (1.2), then (1.2) is valid whether the piston moves in or out.

For this reason, the work done due to an expansion or compression against an outer constant pressure the first law of thermodynamics takes the form.

$$(1.3) \quad W + Q = \Delta E \quad \text{og} \quad W = -P \Delta V \quad \text{giver} \quad Q = \Delta E + P \Delta V$$

If the pressure is not constant, one has to split the process up into small intervals where the pressure may be considered as constant, which is the same as writing the first law in differential form:

$$(1.4) \quad dQ = dE + PdV$$

For an ideal gas, the energy depends only on the temperature T . This is a consequence of the prerequisites for the kinetic theory of gasses. However, it would not be the case, if the molecules interacted by medium range forces.

One main result from the kinetic theory of gasses is that the internal energy of an ideal gas can be expressed as.

$$(1.5) \quad E = \gamma n_M RT$$

$\gamma = c_V$, is the molar heat capacity, at constant volume ($\gamma = 3/2$ for an one-atomic gas). n_M is number of moles in the gas. $R=8,31 \text{ J/mol K}$ is the gas constant, and T is the absolute temperature. Inserting $E = \gamma n_M RT$ in (1.3), we have:

(1.6) $dQ = \gamma n_M R dT + PdV$

2. Isothermal and adiabatic change of state

Isothermal change of state

We shall first consider an isothermal change of state, which means that $T = \text{const}$, so that $dT = 0$, which again for an ideal gas means that $E = \text{const}$. We therefore have:

(1.7) $dQ = PdV$ (isothermal change of state)

From which we notice, that a isothermal change of state, is always accompanied by a exchange of heat with the surroundings. (Since dQ is always non-zero)

Hereafter on can easily calculate the exchange of heat, which occur by isothermal change of state, where the volume changes from V_1 to V_2 . The calculation is done by integrating using (1.7):

$$Q = \int dQ = \int_{V_1}^{V_2} PdV \wedge PV = n_M RT \Rightarrow Q = \int_{V_1}^{V_2} \frac{n_M RT}{V} dV$$

(1.8) $Q = n_M RT \int_{V_1}^{V_2} \frac{1}{V} dV = n_M RT \ln\left(\frac{V_2}{V_1}\right)$

Adiabatic change of state

Adiabatic means heat isolated, so that an adiabatic change of state is equivalent to $dQ = 0$. When this is inserted in the first law, we get: $dE + PdV = 0$, which for ideal gases becomes:

(1.9) $\gamma n_M R dT + PdV = 0$

From which is seen, that an adiabatic change of state is always accompanied by a change in the temperature of the gas.

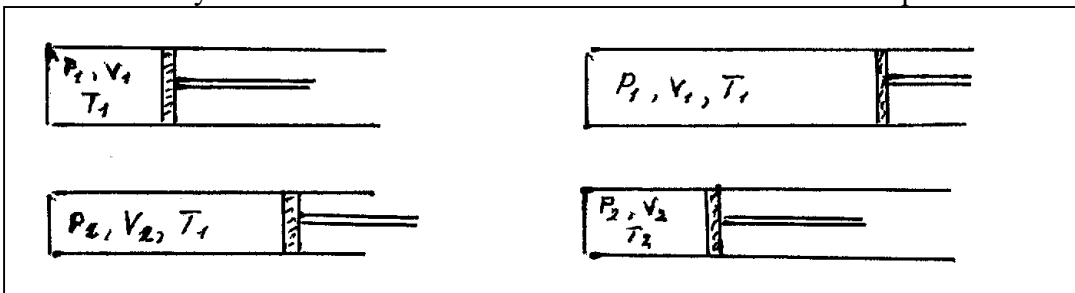
Illustration of isothermal and adiabatic change of state

$T = \text{const}$: Isothermal change.

$Q = 0$: Adiabatic change.

Establishes Boyle-Mariottes law.

Establishes the adiabatic equations.



We are now able to derive the two asserted connections between temperature T , pressure P and volume V from an isothermal change of state, and from an adiabatic change of state. From the first law:

$$(2.1) \quad dQ = dE + PdV \quad \text{and} \quad dE = \gamma n_M R dT \quad \text{and} \quad dQ = 0 \quad \Rightarrow \quad \gamma n_M R dT + PdV = 0$$

Furthermore we have the equation of state for ideal gasses:

$$PV = n_M R dT.$$

Dividing the first term in the first law (2.1) by the right hand side of the equation of state and the second term by the left hand side of the equation of state, we have:

$$\gamma \frac{dT}{T} + \frac{dV}{V} = 0$$

and integrating the equation:

$$\begin{aligned} \gamma \int_{T_1}^{T_2} \frac{dT}{T} + \int_{V_1}^{V_2} \frac{dV}{V} &= 0 \quad \Rightarrow \quad \gamma \ln \frac{T_1}{T_2} + \ln \frac{V_1}{V_2} = 0 \quad \Rightarrow \\ \ln \left(\frac{T_1}{T_2} \right)^\gamma + \ln \frac{V_1}{V_2} &= 0 \quad \Leftrightarrow \quad \ln \left(\frac{T_1^\gamma V_1}{T_2^\gamma V_2} \right) = 0 \quad \Leftrightarrow \end{aligned}$$

| |
|---|
| $(2.2) \quad \frac{T_1^\gamma V_1}{T_2^\gamma V_2} = 1 \quad \Leftrightarrow \quad T_1^\gamma V_1 = T_2^\gamma V_2$ |
|---|

The relation (2.2) above is then the first one of the adiabatic equations.

We obtain the second relation by inserting $T = \frac{PV}{n_M R}$ from the equation of state.

$$T^\gamma V = \text{const} \quad \text{then gives :} \quad \left(\frac{PV}{n_M R} \right)^\gamma V = \text{const} \quad \Rightarrow \quad P^\gamma V^{\gamma+1} = \text{const} \quad \Leftrightarrow \quad \frac{P^\gamma}{V^{\gamma+1}} = \text{const}$$

Resulting in the analogous law to the Boyle-Mariotte law, but for adiabatic changes of a gas.

| |
|---|
| $(2.3) \quad P^\kappa V = \text{const} \quad \text{where} \quad \kappa = \frac{\gamma}{\gamma+1}$ |
|---|

Example

The increase in temperature and pressure, by an adiabatic compression

a) Calculate the increase in temperature of a gas, when the volume is reduced to 1/5, $t_0 = 20^\circ\text{C} = 293\text{ K}$.

The gas is two atomic, so $\gamma = 5/2$.

Solution

$$\frac{V_1}{V_2} = 5 \quad \text{so} \quad T_2^\gamma V_2 = T_1^\gamma V_1 \quad \Rightarrow \quad \frac{T_2^\gamma}{T_1^\gamma} = \frac{V_1}{V_2} = 5 \quad \Leftrightarrow \quad \frac{T_2}{T_1} = 5^{\frac{1}{\gamma}} = 5^{\frac{2}{5}} = 1,90 \quad \Rightarrow \quad T_2 = 558\text{ K}$$

Thus, it is quite a large increase in temperature, as a result of a fast compression of a gas. The most well known application of this is, as you may know, in the Diesel engine, which has no electric ignition.

Then we calculate the increase in pressure, by the same adiabatic compression, where we apply the second one of the adiabatic equations.

$$\frac{V_1}{V_2} = 5 \quad \text{and} \quad P_2^\kappa V_2 = P_1^\kappa V_1 \Rightarrow \left(\frac{P_2}{P_1}\right)^\kappa = \frac{V_1}{V_2} = 5 \Leftrightarrow \frac{P_2}{P_1} = 5^{\frac{1}{\kappa}} = 5^{\frac{7}{5}} = 9,52 \Rightarrow P_2 = 9,52 \text{ atm}$$

However by an isothermal compression the pressure will only increase to 5 atm from Boyle-Mariotte's law.

Finally we can calculate from the first law, the work done by an adiabatic process.

$$dQ = 0 \Rightarrow \gamma_M R dT + P dV = 0$$

$$(2.4) \quad W = \int_{V_1}^{V_2} P dV = -\gamma_M R \int_{T_1}^{T_2} dT = \gamma_M R (T_1 - T_2) = \gamma (P_1 V_1 - P_2 V_2)$$

3. The second law of thermodynamics

The second law comes in two formulations which, however can be shown to be equivalent. The first formulation refers to daily life experiences, which are known even by a child.

(a) Heat can not be transferred by itself from a colder body to a warmer one. (Clausius)
Or.

If you bring a colder body in contact with a warmer body, it is *impossible* that the warmer body get hotter and the cold body get colder, (although it does not conflict with energy conservation).

(b) It is impossible to construct a periodically working machine, which consumes a heat Q and converts it to mechanical energy, without other changes. (Kelvin-Planck).

Or.

Heat cannot without limitations be converted to mechanical energy, (although the opposite is certainly possible).

That the two formulations of the second law are in fact equivalent may be seen from the following line of argument.

Heat-power engines operate most often in a manner, where a gas consuming a heat Q_1 , from a reservoir at a high temperature expands and perform some work W . To return to the initial state the gas is compressed, and delivers a heat $Q_2 = Q_1 - W$ in a reservoir at a lower temperature.

The compression of the gas requires less work, than the gas delivered by the expansion, and according to (a) it is impossible to get the heat back to the reservoir with high temperature by itself, therefore (b) is valid.

On the other hand, because (b) is valid, you can not extract heat from a reservoir, convert it to work And again convert it to heat with the higher temperature, so (a) is valid.

A machine that does work without supplying energy is called a *perpetuum mobile* (perpetual motion machine) of the first kind.

Although it is probably one of the most frequently proposed inventions in the last 100 years it does not (do) work.

A machine which does not comply with the second law is called a *perpetuum mobile* of the second kind.

For example the oceans contains an infinite reservoir of heat, which without the constraints of the second law could be fetched, converted to work, and thereby only lowering the temperature of the oceans, but this would be regained from the sun.

Notice, however, that a *perpetuum mobile* of the second kind does not conflict with energy conservation.

The second law of thermodynamics gets another mathematical guise, as one invents a new thermodynamic concept, a state function, called the *entropy*. By the aid of the concept of entropy one may extend the first law also to comply with the second law.

4. Reversibility

That a process is reversible means that it can proceed both ways without intervention. Daily life is certainly not a reversible process (although you may sometimes wish it was), but all motions (without friction) that are guided from Newton's second law in conservative fields are in fact reversible.

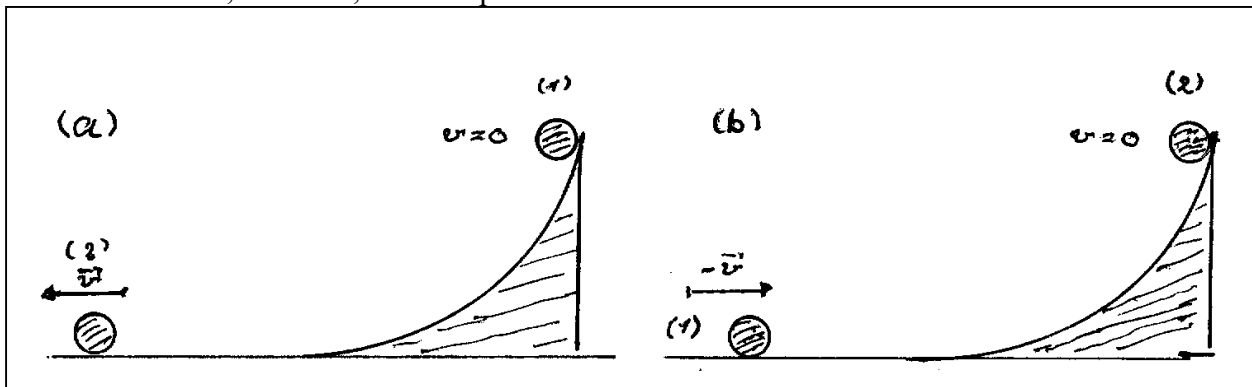
If you look at a movie rolling backwards of a reversible process it will not look unnatural. The reason for this is that Newton's second law.

$$(4.1) \quad F_{res} = m \frac{d^2x}{dt^2}$$

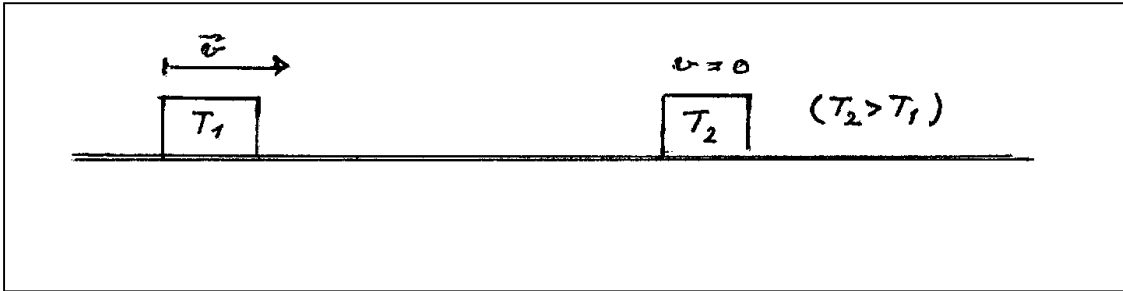
The second law is a differential equation of second order in time, so if you replace t with $-t$ (the time run backwards) the equation is unchanged, and the resulting motion is only determined by the initial conditions.

You may think of a motion, where a ball is running down a hill with increasing velocity, and ends having a velocity v . If you roll the movie backwards, then the ball will have the initial speed v , and (as a consequence of conservation of energy) it will stop at the top with speed 0.

Both motions are, however, in correspondence with Newton's 2. law.



If we on the other hand look at a block with initial velocity v , sliding on a horizontal surface with friction, then the motion is clearly irreversible. It is inconceivable that the block could use the consumed heat to regain its speed. The kinetic energy is inevitably converted to heat.



We now intend more formally to introduce the concepts of reversibility and (useful) work, as the second law of thermodynamics is apt to be formulated with these concepts.

In the classical mechanics a motion is characterized by the position, velocity and acceleration.

In thermodynamics on the other hand the state of a system is determined by the physical quantities temperature, T , pressure P , volume V and energy E , which completely describe the state of the system.

The variables of state T , P are V are the same all over the system. Should there be a difference in temperature or pressure within the system, it will quickly be cancelled by exchange of heat or material approaching *thermodynamic equilibrium*.

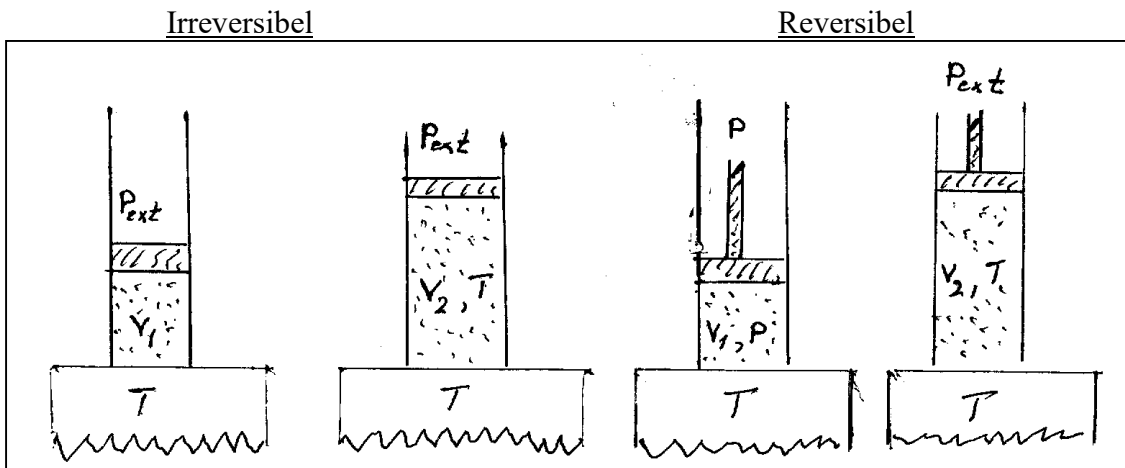
A spontaneous countervail towards thermodynamic equilibrium will always be irreversible.

A relevant question is therefore whether it is possible at all to conceive a reversible process in thermodynamics.

In the following we shall show that it is possible, but it is an idealization, which however has fundamental theoretical impact, in the same sense as mechanical motion without friction.

We shall therefore consider a reversible and an irreversible change of state of an ideal gas

The gas being confined in a cylinder with pressure P and temperature T . The cylinder is placed on a heat reservoir having temperature T .



Irreversible change of state: The gas expands freely, having a constant temperature T , from a volume V_1 against a constant external pressure P_{ext} , until the piston comes at rest at a volume V_2 . In an irreversible change of state, we just have to notice that a work has been done.

$$W_{irr} = P_{ext}(V_2 - V_1)$$

We shall next proceed to do the change of state from the same initial state to the same final state, but this time reversibly. Theoretically this can only be done by maintaining thermodynamic equilibrium during the entire process.

This may be done if we let the counter pressure P_{ext} against the piston be equal to the gas pressure P , and perform the expansion so slow (actually infinitely slow) that the overall gas temperature T is the same during the expansion.

Back in (1.8) we have already calculated the added heat Q , which is equal to the work done by the gas in an isothermal expansion.

$$A_{rev} = Q = n_M RT \int_{V_1}^{V_2} \frac{1}{V} dV = n_M RT \ln \left(\frac{V_2}{V_1} \right)$$

This work is, however, reversible, since it is precisely equal to the work which has to be done to bring the gas back to its initial state, releasing the heat Q to the external reservoir.

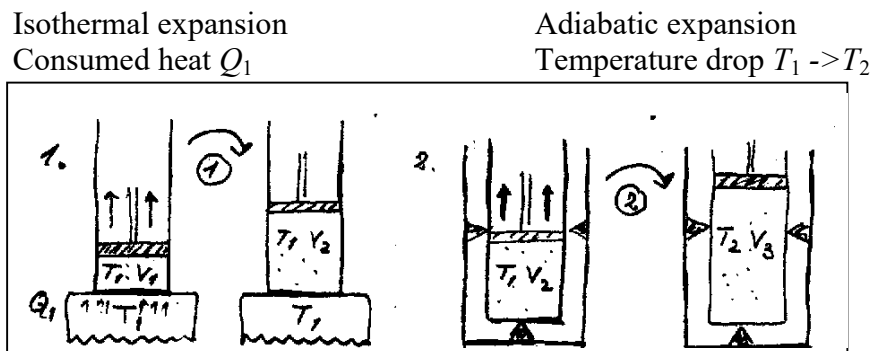
It is rather easy to convince yourself that $W_{irr} < W_{rev}$. Thus if we let the external pressure P_{ext} be less than the pressure P of the gas, then the work done will also be less. If $P_{ext} = 0$ the work done is also equal to 0. There is no work done by letting a balloon fuse in the air.

So the best we can do is to let the outer pressure constantly be equal to the gas pressure.

By an irreversible change of state the system cannot be brought back to the original state, without doing work.

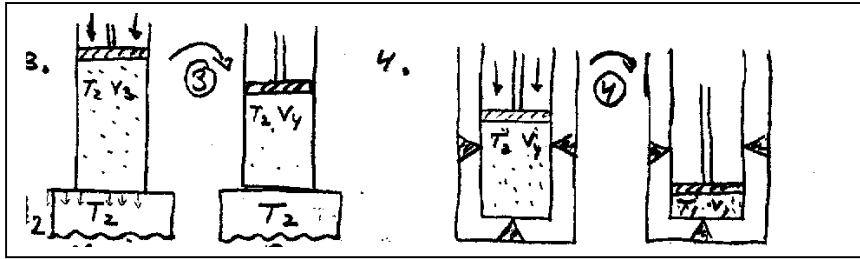
This example (piston work on a gas in a cylinder) indicates however that a more general notion that the maximum work, that can be extracted from a system is achieved, when the change of state is done reversibly. We shall proceed to give a theoretical argument for this assessment, a consideration that leads to a more formal formulation of the second law of thermodynamics.

Thus we shall discuss how much work one can extract from a (theoretical) machine, which is working between two heat reservoirs with temperatures T_1 and T_2 where $T_1 > T_2$, performing a cycle, where a heat Q_1 is consumed at temperature T_1 and a heat Q_2 is delivered at a temperature T_2 . If the machine works reversibly, then there is done a work which according to the first law is $W = Q_1 - Q_2$.



Isothermal compression at T_2 .
Delivered heat Q_2

Adiabatic compression
Temperature T_2 rises to T_1



The most primitive cycle is the so called Carnot process (named after the French engineer Sadi Carnot 1824), which consists of the following processes displayed above.

- 1) Isothermal expansion at the temperature T_1 .
- 2) Adiabatic expansion, where the temperature drops from T_1 to T_2 .
- 3) Isothermal compression at temperature T_2 .
- 4) Adiabatic compression where T_2 rises to T_1 .

The processes (1) to (4) are considered to be performed so slowly that the system at any time is in thermodynamic equilibrium.

According to (3.3) the work done by the system is: $W = Q_1 - Q_2$.

By the *efficiency* ε of the “machine”, one should understand the performed work W divided by the consumed heat Q_1 at the higher temperature T_1 .

$$(4.4) \quad \varepsilon = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

According to the second law (Kelvin Planck formulation) $Q_2 > 0$, so that $\varepsilon < 1$.

We shall then proceed to show that it is impossible to extract more work from a machine than from a reversible one.

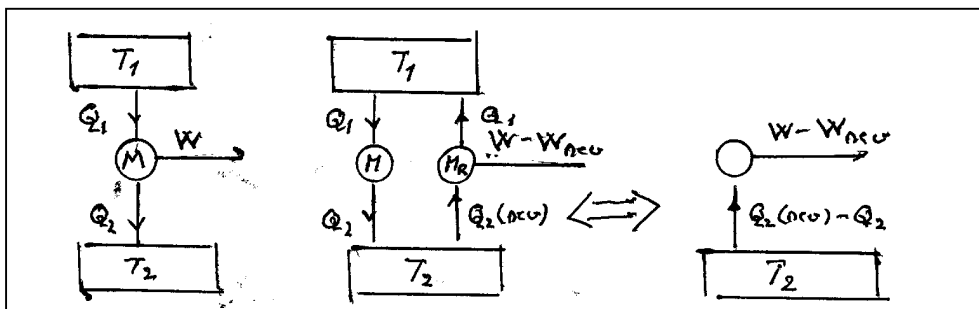
Firstly we emphasize that when the machine is reversible the process can be reversed, so that the machine consumes a heat Q_2 at temperature T_2 and delivers a heat Q_1 at temperature T_1 , at the same time as an amount of work $W = Q_1 - Q_2$ is done.

This is precisely what happens in a heat pump, which is also the mechanism in a refrigerator, where the difference basically is that the two heat reservoirs are switched.

5. Reversible machines and maximum work

Let us assume that we have an – not necessarily reversible – machine that works between the two temperatures T_1 and T_2 , and where there is an exchange of heats Q_1 and Q_2 respectively.

The machine performs a work W , and let us tentatively assume that $W > W_{rev}$. Fig (5.1)



In the figure above is shown a machine M , which does the work W . The machine consumes the heat Q_1 at temperature T_1 , and let out the heat Q_2 at temperature T_2 , performing the work W .

Assuming that $W > W_{rev}$, we intend to show that it leads to a contradiction to the second, law in the Kelvin-Planck formulation.

The Machine M is now thought to be coupled to a *reversible* machine M_{rev} , working backwards between the same two reservoirs, and therefore delivers the heat Q_1 at the higher temperature. According to the premise that $W > W_{rev}$, the efficiency ε , which is equal to W/Q_1 must be greater than ε_{rev} , in other words $\varepsilon > \varepsilon_{rev}$, but that means that the machine M , besides running the machine M_{rev} , is able to do some useful work $W - W_{rev}$.

The net result is that we have designed a machine that consumes a heat $Q_{rev} - Q_2$ from the reservoir at temperature T_2 , which is completely transformed to work.

But this is impossible according to the second law in Kelvin-Planck formulation.

Therefore $W - W_{rev} < 0$ implying that $W < W_{rev}$.

Thus it is a consequence of the second law of thermodynamics that the maximum work you can get from a machine is when it operates reversibly.

One should notice, however, that this arguments rest on the assumption of the existence of a (theoretical) machine M_{rev} that can operate both ways with the same turnover ratio between work and heat.

Although far from the real world, this is theoretically important, especially because we have acquired a simple formula for the maximum efficiency of a heat-work machine.

$$(5.2) \quad \varepsilon_{rev} = \frac{A_{rev}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

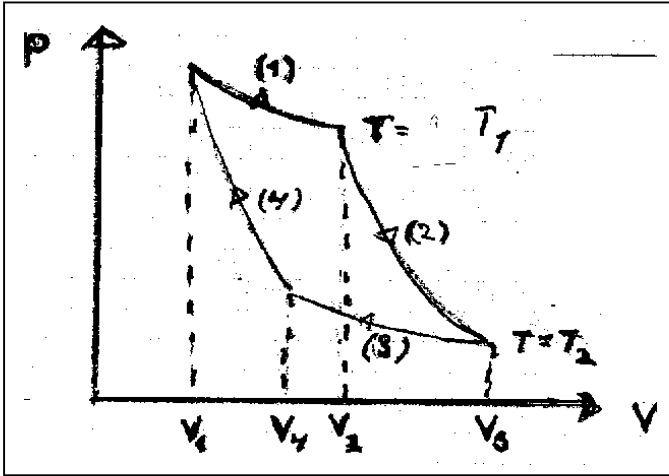
ε_{rev} is obviously a fundamental theoretical quantity, which signifies the largest efficiency of a machine working between the reservoirs with temperatures T_1 and T_2 .

From the reasoning above it is seen that ε_{rev} neither depends on the construction of the machine, if it is reversible, nor of the gas, fluid, refrigerant which implements the cycle process.

As a matter of fact ε_{rev} can only depend on the temperatures T_1 and T_2 , and if we manage to compute ε_{rev} for just one type of reversible machine, it must be the same function of T_1 and T_2 for any other reversible machine. Theoretically the simplest machine is the one sketched on page 8, where the working fluid is a ideal gas.

6. Carnot process. Maximum efficiency

If the working fluid is an ideal gas the cycle process (named the Carnot – process) can be illustrated as sketched below in a $P - V$ diagram.



1. Isothermal expansion. Consumed heat Q_1
2. Adiabatic expansion $Q = 0$
3. Isothermal compression $Q = - Q_2$
4. Adiabatic compression $Q = 0$

The isothermal expansion (1), adds heat Q_1 . In the two adiabatic processes (2) and (4) no heat is added or consumed. In the isothermal process (3) the heat Q_2 is let out.

The efficiency is:

$$(6.2) \quad \varepsilon_{rev} = \frac{Q_1 - Q_2}{Q_1}$$

As the efficiency for a reversible machine is the same as for all reversible machines, we may settle for calculating it for a cylinder containing an ideal gas and working between two reservoirs with temperatures T_1 and T_2 , as shown on page 3 and 8. For an isothermal expansion, we have:

$$A_{rev} = Q = n_M RT \int_{V_1}^{V_2} \frac{1}{V} dV = n_M RT \ln \left(\frac{V_2}{V_1} \right)$$

(1) \rightarrow (2) isothermal expansion: $V_1 \rightarrow V_2$ and $T_2 = T_1$:

$$Q_1 = n_M RT_1 \int_{V_1}^{V_2} \frac{1}{V} dV = n_M RT_1 \ln \left(\frac{V_2}{V_1} \right)$$

(3) \rightarrow (4) isothermal compression: $V_3 \rightarrow V_4$ og $T_4 = T_3 = T_2$

$$Q_2 = n_M RT_2 \int_{V_3}^{V_4} \frac{1}{V} dV = n_M RT_2 \ln \left(\frac{V_4}{V_3} \right)$$

For the relation between $\frac{V_2}{V_1}$ and $\frac{V_4}{V_3}$ the adiabatic equations hold good (page 3).

$$T_1^\gamma V_1 = T_2^\gamma V_2 \quad \Leftrightarrow \quad \frac{V_2}{V_1} = \frac{T_1^\gamma}{T_2^\gamma}$$

Which in the two cases (2) and (4) give:

$$(6.3) \quad \frac{V_3}{V_2} = \frac{T_2^\gamma}{T_3^\gamma} = \frac{T_1^\gamma}{T_2^\gamma} \quad \text{and} \quad \frac{V_4}{V_1} = \frac{T_1^\gamma}{T_4^\gamma} = \frac{T_1^\gamma}{T_2^\gamma}$$

From which we conclude $\frac{V_3}{V_2} = \frac{V_4}{V_1}$, and thus

$$\varepsilon_{rev} = \frac{Q_1 - Q_2}{Q_1} = \frac{n_M R T_1 \ln\left(\frac{V_3}{V_2}\right) - n_M R T_2 \ln\left(\frac{V_4}{V_1}\right)}{n_M R T_1 \ln\left(\frac{V_3}{V_2}\right)} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

$$(6.4) \quad \varepsilon_{rev} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

The relation (6.4) belongs to one of the most important results in theoretical thermodynamics, because it puts a theoretical upper limit for the work a machine can deliver, working between two heat reservoirs having temperatures T_1 and T_2 .

The theoretical upper limit is launched by a reversible machine (which is an idealization)

As an example, we shall calculate the efficiency of a stem engine, working between the temperatures $t_1 = 200^\circ\text{C}$ and $t_2 = 20^\circ\text{C}$.

$$\varepsilon_{rev} = \frac{T_1 - T_2}{T_1} = \frac{473 - 293}{473} = 0,38$$

Theoretically we can obtain an efficiency of 38% of the consumed heat Q_1 in such a machine, but in praxis the efficiency is much lower. For a good stem engine about 0.15.

7. The heat pump

A heat pump is an (ideally reversible) machine, doing a Carnot cycle, but in the opposite direction, as it consumes heat Q_2 at the lower temperature T_2 , and delivers the Q_1 at the higher temperature T_1 . According to the second law of thermodynamics this becomes only possible if some work W is done. If the heat pump works reversibly the following must hold: $W = Q_1 - Q_2$ or $Q_1 = Q_2 + W$.

The efficiency of the heat pump, the power factor η , is defined as the delivered heat Q_1 divided, by the invested work W . (This is the opposite of the efficiency of a reversible machine).

$$(7.1) \quad \eta = \frac{Q_1}{W}$$

For a reversible heat pump, we have according to (6.4).

$$(7.2) \quad \eta = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

If the heat pump is working in a geothermal environment with $T_2 = 283\text{ K}$ ($t_{earth} = 10^\circ\text{C}$), and is used to heat water from 10°C to 60°C ($T_2 = 333\text{ K}$), then we get a theoretical power factor

$$(7.3) \quad \eta_{\text{jord var me}} = \frac{T_1}{T_1 - T_2} = \frac{333}{333 - 283} = 6,7$$

This means that if we invest 1 Joule in work, e.g. in the form of electric energy, to operate the pump, we will get 6.7 J out of the system, in the form of heat. More than 6 times better, than using an electric heater.

There are however several reasons that one may not achieve such a high factor. Dependent of the working fluids applied, one may achieve a theoretical power factor ranging from 4 to 5.

The actual power factor lies for a good heat pump on about 2.5.

8. Entropy

Before we proceed to discuss reversible machines, we shall draw some more mathematical consequences of the theoretical considerations concerning these machines.

In our arguments we have several times used the second law, as this law establishes that some processes are irreversible.

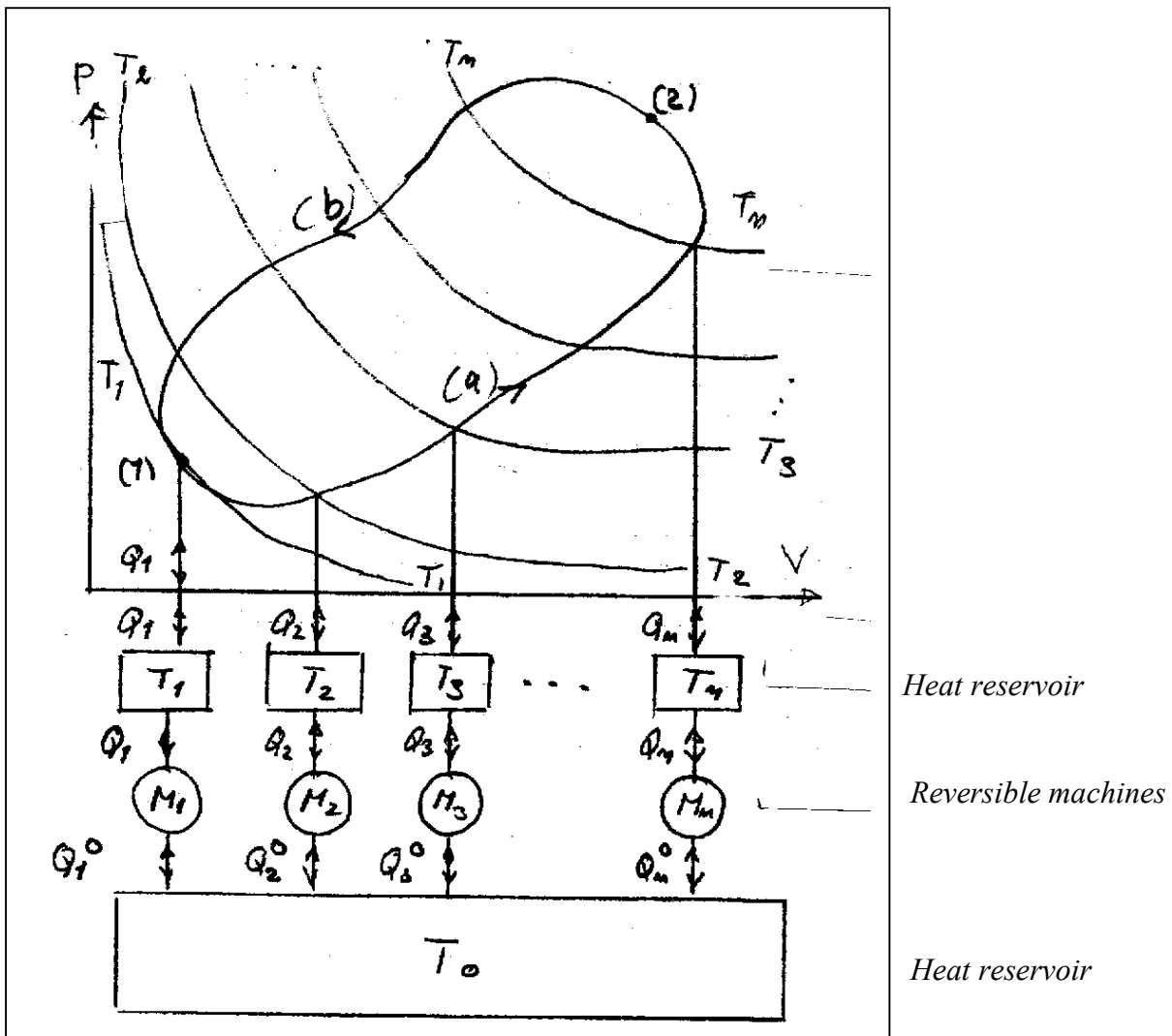
We are now ready to give a more concise mathematical formulation of the concept of reversibility, and this implies the introduction of a new thermodynamic quantity of state, which is called *entropy* and denoted S .

However, entropy differs from the other thermodynamic variables of state, as pressure, temperature and volume, in the sense that it bears no direct appearance in daily life.

With the introduction of entropy the second law of thermodynamic, may be formulated as:

For a closed system, the entropy, cannot decrease, and reversibility means that the entropy is constant

We shall then consider a system doing a (not necessarily reversible) cycle. The cycle can be plotted as a closed curve in a $P - V$ diagram, as shown below. (It is not a Carnot cycle).



The system consists of a common heat reservoir and n reversible machines. The i 'th machine M_i is working between the reservoir with temperature T_0 , and a reservoir with temperature T_i . While the system traverses the cycle, heat is exchanged with the surroundings. The single quantities of heat may in general be exchanged at various temperatures, such that the heat Q_i is exchanged with the reservoir at temperature T_i . We shall now use the second law to establish an inequality applicable for the exchanged amounts of heat at the indicated temperatures.

The system is considered to perform a work W by traversing the cycle. For the sake of the analysis every one of the designated heat reservoirs are thought to be connected via the reversible machines $M_1, M_2, M_3, \dots, M_n$, as they perform Carnot processes.

The reversible machines are constructed in such a manner, so they deliver the same amounts of heat Q_1, Q_2, \dots, Q_n to the n reservoirs, so that these reservoirs are unchanged after a cycle has been completed.

The machines themselves are supplied by the heat amounts $Q_{01}, Q_{02}, \dots, Q_{0n}$ from the reservoir at temperature T_0 .

For each of the reversible machines apply:

$$(8.1) \quad \varepsilon_{rev} = \frac{Q_{i0} - Q_i}{Q_{i0}} = \frac{T_0 - T_i}{T_0} \Rightarrow 1 - \frac{Q_i}{Q_{i0}} = 1 - \frac{T_i}{T_0} \Rightarrow \frac{Q_i}{Q_{i0}} = \frac{T_i}{T_0} \Rightarrow Q_{i0} = \frac{Q_i}{T_i} T_0$$

If we now consider the over all system, the net result of one cycle performed is that a heat

$$Q_0 = \sum_{i=1}^n Q_{0i} \text{ has been consumed from the reservoir at temperature } T_0, \text{ and a work } W = \sum_{i=1}^n W_{(i) rev},$$

where $W_{(i) rev}$ is the work, which has been supplied by the i 'th machine.

According to the second law (Kelvin Planck), this is possible, only if the work $W = \sum_{i=1}^n W_{(i) rev} = Q_0$

is negative. We then realize that:

$$(8.2) \quad Q_0 \leq 0 \Rightarrow \sum_{i=1}^n Q_{0i} \leq 0 \Rightarrow \sum_{i=1}^n T_0 \frac{Q_i}{T_i} \leq 0 \Rightarrow \sum_{i=1}^n \frac{Q_i}{T_i} \leq 0$$

The last inequality is indeed very important. It is called Clausius' inequality, and it expresses the fact that:

If a machine traverses a cycle, where it exchanges heat Q_i at temperatures T_i , then Clausius' inequality applies:

$$(8.4) \quad \sum_{i=1}^n \frac{Q_i}{T_i} \leq 0$$

If one split the cycle process in infinitesimal steps, the summation must be replaced by a curve integral along the entire cycle in the $P - V$ diagram.

If the amounts of heat become infinitesimal as well, they must be replaced by differentials dQ . However Clausius' inequality must still be valid.

$$(8.5) \quad \oint \frac{dQ}{T} \leq 0$$

Equality is, only valid when the cycle process is reversible.

The entropy S is defined by the equation:

$$(8.6) \quad dS = \frac{dQ_{rev}}{T}$$

Where dQ_{rev} means the reversible supplied heat at temperature T .

If a system is supplied reversibly with a heat dQ_{rev} at temperature T , the system has gained the entropy:

$$dS = \frac{dQ_{rev}}{T}$$

In a reversible process we therefore have:

$$(8.7) \quad \oint dS = \oint \frac{dQ_{rev}}{T} = 0$$

Since we made no reservations about the nature or direction of the process, then the change of entropy ΔS from a state (1) to a state (2) must be independent of how these states are reached.

The entropy depends only on the state of the system, but not on how the state is reached, and this implies that the entropy S is a state function in the same manner as pressure P , volume V , energy E and temperature T .

The difference between entropy and the other state functions P , V , T , are that the latter are commonly known daily life experiences, but this is in particular not the case with entropy, due to the rather intransparent theoretical concept of a reversible process.

Below is shown the formula to calculate the change in entropy from one state to another.

$$(8.7) \quad \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = S(2) - S(1)$$

Let us assume, that we have a cycle, where the process (1) \rightarrow (2) is spontaneous (irreversible), while (2) \rightarrow (1) is reversible. We then find, using Clausius' inequality:

$$(8.8) \quad \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ_{rev}}{T} < 0 \quad \Leftrightarrow \quad \int_1^2 \frac{dQ}{T} + S(1) - S(2) < 0 \quad \Leftrightarrow \quad \int_1^2 \frac{dQ}{T} < S(2) - S(1)$$

Especially, but rather fundamental, if the system is heat isolated, such that the process (1) \rightarrow (2) is adiabatic, then $dQ = 0$, and the last equation reads: $S(2) - S(1) > 0$.

In a closed heat isolated system, a spontaneous (non reversible) process always cause the entropy to increase:

$$(8.9) \quad S(2) > S(1)$$

Using the concept of entropy, we are now able to give another formulation the two laws of thermodynamics.

First law of thermodynamics: In a closed system the energy is conserved
 Second law of thermodynamics: In a closed system the entropy cannot decrease.

The entropy thus appears to be a concept of far reaching importance.

The entropy depends only on the state of the system. If one "measures" the entropy in two states of a closed system, one can in principle decide whether which was first, and which one followed. (Something you of course are aware of, if you have actually measured the entropy of the two states).

Entropy introduces an asymmetry in nature, which is not present in Newtonian mechanics, and one may speculate whether it is this asymmetry, which is the foundation of our notion of time, future and past.

We have hitherto applied the second law in Kelvin-Planck formulation to identify the concept of entropy. Formally we need to show that when the entropy increases in a closed system it has as its consequence the second law in Clausius' formulation. Spontaneously heat always moves from colder bodies to warmer bodies.

Suppose that we have two blocks with temperatures T_1 and T_2 which are brought in heat conducting contact with each other, but otherwise are isolated.

During the time interval dt the two bodies exchange spontaneously a heat dQ with each other.

Since the process is spontaneous:

$$dS = dS_1 + dS_2 > 0 \quad \Rightarrow \quad \frac{-dQ}{T_1} + \frac{dQ}{T_2} > 0$$

Assuming that $dQ > 0$, so that the heat flows from (1) til (2). (1 releases heat $-dQ$), we may write

$$\frac{-dQ}{T_1} + \frac{dQ}{T_2} > 0 \quad \Leftrightarrow \quad -\frac{1}{T_1} + \frac{1}{T_2} > 0 \quad \Leftrightarrow \quad T_1 > T_2$$

So the conjecture that the entropy always increases in a closed system, has the formal consequence that heat always moves from higher temperatures to lower temperatures. (Clausius)

Next we shall look at a typical situation, where a system is in contact with the surroundings, which has the temperature T_{ext} and the pressure P_{ext} .

If the system absorbs an amount of heat ΔQ , from the surroundings, it will result in an increase in entropy ΔS and the surroundings will get a change of entropy $\Delta S_{ext} = -\Delta Q/T_{ext}$. In any case:

$$\Delta S + \Delta S_{ext} > 0 \quad \Rightarrow \quad \Delta S - \frac{\Delta Q}{T_{ext}} \geq 0 \quad \Leftrightarrow \quad T_{ext} \Delta S \geq \Delta Q$$

According to the first law: $\Delta Q = \Delta E + P_{ext} \Delta V$. From which follows an inequality, which is also denoted Clausius' inequality

$$(8.8) \quad T_{ext} \Delta S \geq \Delta E + P_{ext} \Delta V$$

The equality holds only if thermodynamic equilibrium is maintained during the whole process, that is, only if the process is reversible. When such a process is conducted infinitely slow we have:

| |
|------------------------|
| (8.9) $TdS = dE + PdV$ |
|------------------------|

This equation comprises in an elegant way the contents of both the first and second law.

From the equation (8.9) one may for example calculate the entropy of an ideal gas. For such a gas the energy is given by $E = \gamma n_M RT$ and the equation of state is $PV = n_M RT$. From this we find by insertion in (8.9) followed by division by T .

$$dS = \gamma_M R \frac{dT}{T} + \frac{P}{T} dV$$

Inserting $P = \frac{n_M RT}{V}$ in the last term we find:

$$dS = \gamma_M R \frac{dT}{T} + \frac{n_M R}{V} dV$$

The change in entropy can then be calculated by integration.

$$(8.10) \quad \int_1^2 dS = \gamma_M R \int_1^2 \frac{dT}{T} + n_M R \int_1^2 \frac{dV}{V} \quad \Rightarrow \quad S(2) - S(1) = \gamma_M R \ln \frac{T_2}{T_1} + n_M R \ln \frac{V_2}{V_1}$$

9. Since the entropy is a state function dS is a total differential

In the mathematical analysis, the differential of a function $f(x_1, x_2)$ is defined as: (and we settle for two variables, although it is more general)

$$(9.1) \quad df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2$$

If f being twice differentiable, the sequence in which the second order differential quotients are evaluated is insignificant.

$$(9.2) \quad \frac{\partial^2 f}{\partial x_1 \partial x_2} = \frac{\partial^2 f}{\partial x_2 \partial x_1}$$

Conversely one may show that, if a differential form:

$$df = f_1(x_1, x_2) dx_1 + f_2(x_1, x_2) dx_2$$

has the property that:

$$(9.3) \quad \frac{\partial f_1}{\partial x_2} = \frac{\partial f_2}{\partial x_1}$$

Then f is a total differential, which again implies that f is a differentiable function: $f(x_1, x_2)$.

In mathematical analysis it is proved, that if you integrate a total differential from (a_1, a_2) to (b_1, b_2) , along a curve, then the integral is independent of the path chosen between (a_1, a_2) and (b_1, b_2) .

The opposite is also the case. If the integral of a differential form is independent of the path chosen, the differential form is a total integral.

That is what you call a state function in physics, for example the potential in a conservative field of force. You may apply this to derive some more formal relations between the state functions of thermodynamics.

We take our point of departure from (8.2):

$$TdS = dE + PdV,$$

and divide by T .

$$dS = \frac{1}{T}dE + \frac{P}{T}dV$$

From (9.1) it then follows: $\frac{\partial S}{\partial E} = \frac{1}{T}$ og $\frac{\partial S}{\partial V} = \frac{P}{T}$

And from (9.3) $\frac{\partial}{\partial V} \frac{1}{T} = \frac{\partial}{\partial E} \frac{P}{T}$

Frankly, I do not know, whether these relations have any practical importance, but they link the concept of total differential together with the concept of state function.