KPK

The Karlsruhe Physics Course

for the secondary school A–level

Thermodynamics

The Karlsruhe Physics Cours

A textbook for the secondary school A-level

███ Electrodynamics
███ **Thermodynamics**
███ Oscillations, Waves, Data
███ Mechanics
███ Atomic Physics, Nuclear Physics, Particle Physics

TABLE OF CONTENT

1 HEAT

The science of heat is about the description of phenomena in connection with an object being warmer or colder. Similar to our study of momentum balances in mechanics, the science of heat will make us deal again and again with heat balances.

The science of heat is about the description of phenomena in connection with an object being warmer or colder. Similar to our study of momentum balances in mechanics, the science of heat will make us deal again and again with heat balances.

It is important to understand natural phenomena and technical devices and machines.

Life on Earth is only possible thanks to a huge heat flow that comes from the Sun. Climate and weather on Earth are essentially determined by thermal processes. ("Thermal" means "concerning heat".)

A very large number of machines work by taking advantage of the laws of heat: the car engine, the steam turbines in power plants, the heat pump of the fridge.

The heat loss of each house and the procurement of heat by the heating can be quantitatively described with the resources of the science of heat.

The important role that heat plays for chemical reactions should also be kept in mind.

1.1 Entropy and temperature

Just as each time we introduce a new field of physics, we first need to familiarize ourselves with our main tools: the physical quantities that we will work with. In mechanics, we started out with two quantities in order to describe the state of motion of an object – with velocity and momentum. Accordingly, we introduce the science of heat with two quantities, which describe the thermal state of an object.

One of these quantities, the temperature, you already know. It is abbreviated with the Greek letter ϑ (pronounced "theta") and measured in the unit °C (pronounced "degrees Celsius"). Hence, the phrase "the temperature amounts to 18 degrees Celsius" can be abbreviated as

$$\vartheta = 18 \,°\text{C}.$$

Most likely, you also know the second quantity that we need, although by a name that differs from the one used in physics. We are referring to what is colloquially known as "quantity of heat" or simply "heat". Its physical name is entropy, its symbol S and its measurement unit Carnot, abbreviated Ct. Consequently, if the entropy content of an object amounts to 20 Carnot, we can write

$$S = 20 \,\text{Ct}.$$

The measurement unit is named after Sadi Carnot (1796 — 1832), a physicist who contributed substantially to the invention of entropy.

To illustrate the difference between entropy and temperature, we will make a simple experiment, Fig. 1.1. In a glass A, there is 1 l of water with a temperature of 80 °C. We fill half of this water in another, empty glass B. What happens to temperature and what to entropy in the process? The temperature of the water in each of the glasses A and B after the filling pro-
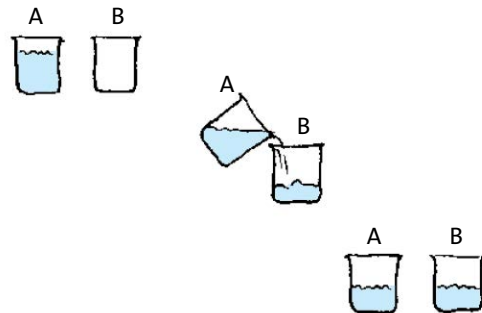
Fig. 1.1 Half of the water in recipient A is filled into recipient B.

cess is equal to the temperature of the water in A prior to filling. The entropy, in contrast, dispersed to the glasses A and B during the filling process. If there were originally 100 Carnot in A, there will be 50 Carnot in A and 50 Carnot in B at the end.

Hence, the temperature characterizes the state of being warm (or also of being cold) of an object, regardless of its size. The entropy, in turn, is something that is contained within the object.

As soon as we explore the properties of the quantity entropy in the following, you simply have to bear in mind that entropy is what we colloquially call heat.

Let us compare the two glasses of water from Fig. 1.2. Both contain the same quantity of water. The water in the glass on the left is hot, it has a temperature of 70 °C; the water in the glass on the right is cool, its temperature amounts to 10 °C. Which glass contains more entropy? (Which glass contains more heat?) The one on the left, of course.

> The higher the temperature of an object, the more entropy it contains.

Now we compare the glasses of water from Fig. 1.3. Their temperatures are equal, but the mass of the water on the left and on the right are not the same. Which glass of water contains more entropy? Again the one on the left.

> The greater the mass of an object, the more entropy it contains.

Finally, we compare the two glasses of Fig. 1.4. The temperature is the same in the glass on the left and the one on the right, and so is the mass. However, the glasses contain different liquids: the one on the left contains water, the one on the right alcohol. (As the density of alcohol is lower than the density of water, the volume of the alcohol in the recipient on the right is greater.) In spite of an equal mass and temperature, the entropy contents are not equal: one kilogram of water contains slightly more entropy than one kilogram of alcohol.

> The entropy contained in an object depends on the material of the object.

We will analyze how the entropy depends precisely on temperature, mass and material at a later time.

Now, we will have another look at the experiment of Figure 1.1. Glass A contains 1 l of water with an entropy content of 4000 Ct. We fill 1/4 of the water, i.e. 250 ml, in the other, empty glass B. How much entropy is con-
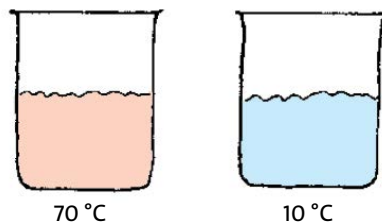
Fig. 1.2 The water in the glass on the left contains more entropy than the one in the glass on the right.
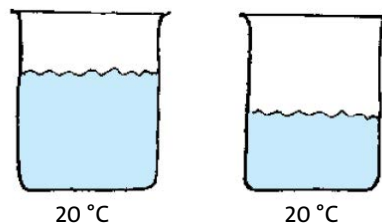
Fig. 1.3 The water in the glass on the left contains more entropy than the one in the glass on the right.
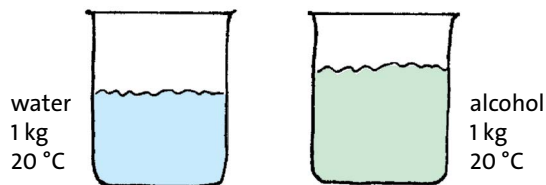
Fig. 1.4 One kilogram of water with a temperature of 20 °C contains slightly more entropy than one kilogram of alcohol with 20°C.

tained in A, and how much in B after this process? During the process, the entropy was divided in the same ratio as the quantity of water. Consequently, 1000 Ct were poured in glass B while 3000 Ct remained in A.

What can be understood by 1 Carnot? Is it much or little entropy? 1 Carnot is a relatively handy unit: 1 cm^3 of water with a temperature of 25 °C contains 3.88 Ct. Or as a rough standard rule:

> 1 cm^3 of water at a normal temperature contains approximately 4 Ct.

▬ Exercises ▬▬▬▬▬▬▬▬▬

1. The air in a room A with a volume of 75 m^3 has a temperature of 25 °C. The air in another room B with a volume of 60 m^3 has a temperature of 18 °C. Which room contains more entropy?
2. The coffee in a full coffee pot contains 3900 Ct. Then, equal quantities of coffee are poured in three cups. After that, the pot is half full. How much entropy is contained in the pot after pouring? How much is contained in each cup?

1.2 Temperature difference as a driving force for an entropy current

We dip a recipient A with hot water into a recipient B with cold water, Fig. 1.5. We would like to observe what happens and subsequently explain the observation.

Let us start with the observation: the temperature of the water A decreases, the one of the water in B increases. The temperatures approach each other and finally become equal. Temperature in B increases, but not beyond temperature in A.

Explanation: entropy flows from A to B until the temperatures have become equal.

The experiment can be repeated with other recipients, Fig. 1.6a and b.

The water in both recipients always takes on the same temperature. In the case of Fig. 1.6a, this final temperature is closer to the initial temperature of B; in Fig. 1.6b, it is closer to the initial temperature of A. In both cases we have:

$$\vartheta_A = \vartheta_B.$$

Of course, it is possible to start in a way that the inner recipient A has the lower, and the outer recipient B the higher temperature. Also in this case, the temperatures approach each other and finally adjust to the same value. We conclude:

> Entropy flows by itself from places of higher temperature to places of lower temperature.

A temperature difference $\vartheta_A - \vartheta_B$ can consequently be interpreted as a driving force for an entropy flux.

> A temperature difference is a drive for an entropy flux.

Now, it is easily understandable that the entropy current in the experiments of Figures 1.5 and 1.6 eventually stops to flow: as soon as the temperatures become equal, the driving force for the entropy current will disappear.

The state of temperature equality that is reached at the end is called *thermal equilibrium*.

In front of you, there is a cup of tea. The tea is still too hot to be drunk. Hence, you wait until it has cooled down. But what has happened during cooling? As the temperature of the tea is initially higher than that of the air and the table, an entropy current flows from the
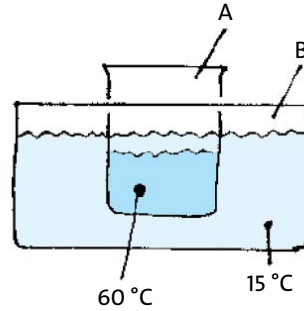
Fig. 1.5 Entropy flows from the inner recipient A to the outer recipient.
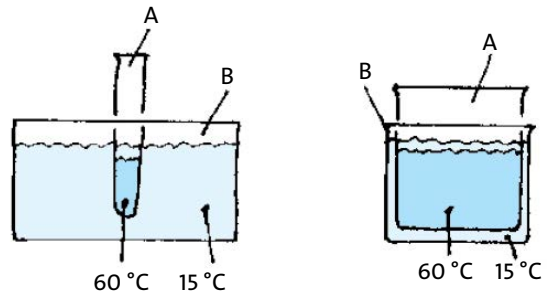
Fig. 1.6 In both cases, the entropy flows from the inner into the outer recipient.

tea to the environment. Does the environment heat up in the process? Very strictly speaking, yes. But the entropy that comes from the tea dilutes so much that it practically cannot be noticed anymore.

We touch different objects in the classroom. Some of them feel cool: the metal of the desks, the concrete posts. Others seem to be less cool, e.g. the wood of the desks. Some are almost cozily warm: a wool glove or a piece of styrofoam. The temperature of an iron object seems to be lower than the one of a wooden object. This observation should make you wonder as we have just formulated: "entropy flows by itself from places of higher temperature to places of lower temperature." Consequently, entropy would have to flow continuously from the wooden parts into the iron parts of the desk. In this process, the iron would become warmer and the wood cooler until…? Until the temperatures are equal.

Instead of wondering, we should measure the temperatures of different objects in the classroom with a thermometer so that we do not have to rely on our gut. The result is surprising. All temperatures are equal. Iron, wood and styrofoam all have the same temperature, provided that objects have been in the same room long enough for their temperatures to become equal.

Only in winter, the objects that are located higher up in the room will have a slightly higher temperature than those that are located further down. This is due to the fact that the warm air from the heating rises upwards. Hence, the establishment of the thermal equilibrium is constantly hampered by the heating. In summer, by contrast, the equilibrium can generally be established easily. Let us conclude for now: our gut feeling for "warm" and "cold" misled us. In one of the following sections you will learn how this illusion could emerge and why it is actually not an illusion.

Exercises

1. (a) During cooking, entropy goes from the hotplate into the pot. Why? (b) The pot is placed upon a coaster on the table. Then, entropy goes from the pot into the coaster. Why? (c) A cooled bottle of coke is put on the table. The table becomes cold at the place where the bottle is located. Why?
2. A big metal block A has a temperature of 120 °C, a small block made of the same metal has a temperature of 10 °C. The blocks are brought in contact so that entropy can flow from one to the other. From which to which does the entropy flow? Will the final temperature be closer to 120 °C or closer to 10 °C?
3. In front of you there is a small hot metal block and a big cool one. (a) Can you tell which one of the two has more entropy? (b) You bring the blocks in contact with one another. What happens to temperature and entropy? (c) Which block contains more entropy at the end?
4. Three objects A, B and C consist of the same material, A and B have the same volume, C is bigger. A has the same temperature as C, B is cooler. (a) Compare the entropy contents. (b) A and B are brought in contact so that new temperature and entropy values emerge. Compare them to each other and to the original values. (c) Now C is brought in contact with A. Compare the new temperatures and entropies with each other as well as with the values from (a) and (b).

1.3 The heat pump

The fact that the entropy flows by itself from the object with a high temperature to the object of a low temperature does not mean that it could not flow in the opposite direction at all, i.e. from cold to hot. It is possible, but not "by itself". To achieve this, some "force" needs to be applied: a pump for the entropy is needed. The name *heat pump* has become popularly used for such a device. Nowadays, everybody has a heat pump at home: it is part of the fridge and is used to transport the entropy from the inside of the fridge to the outside. Prior to looking at the fridge in detail,
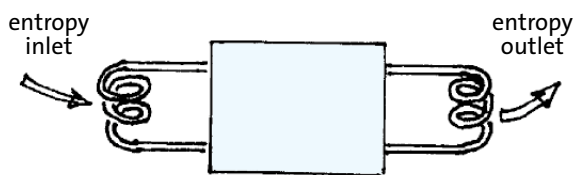
Fig. 1.7 The heat pump has an input and an entropy output for entropy.

we need to learn about some fundamental aspects of the heat pump.

Just as any other pump, the heat pump has two connections for the "stuff" to be pumped: an input and an output. A water pump has an input and an output for water, a momentum pump has an input and an output for momentum. Accordingly, the heat pump has an input and an output for entropy, Fig. 1.7.

Both the input and the output are made of a coil through which flows a liquid or a gas. This is how the entropy is transported into the pump and out of it.

> A heat pump transports entropy from places of lower temperature to places of higher temperature.

Cooling an object means depriving it of entropy; heating an object means feeding it with entropy. Fig. 1.7 shows that a heat pump can be used for cooling as well as for heating. Heat pumps are actually used for both purposes.

Let us take a closer look at the fridge, Fig. 1.8. The heat pump itself is located at the bottom, in the rear of the fridge. The entropy output can also be seen from the rear: a coil that occupies a great part of the back of the fridge. In order to ease the transfer of the entropy to the air, there is a metal grid between the pipes. Here, you recognize the release of the entropy from the fridge due to the coil being warm as long as the fridge is running. The entropy input is located inside the fridge. In older
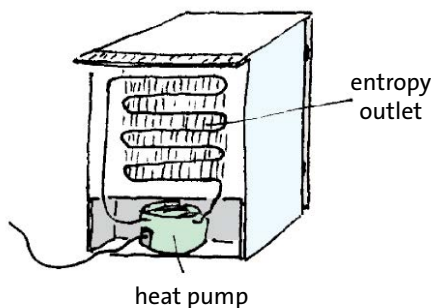
Fig. 1.8 Rear view of the fridge. The figure shows the heat pump and the coils through which the entropy entropy leaves the fridge.

fridges, this coil is still very visible; in modern fridges, it is integrated in the wall of the freezer.

Some houses are heated with a heat pump. Here, the entropy is taken from the outside air or, if available, from a stream or river close by. Also, the water in some swimming pools is heated in this way.

Another device in which a heat pump is used is the air conditioner. An air conditioner sets a certain temperature and a certain humidity inside a building. Therefore, it also needs to cool the air of the building, among others, which is done by means of a heat pump. Fig. 1.9 shows a simple air conditioning unit that can only cool the air inside the room.

Fig. 1.9 Simple air conditioning unit. The blowers inside and outside help improve the heat exchange with the air.

=== **Exercises** ===

1. Examine the fridge at your home. Look for the heat pump, the input and the output for entropy. Touch the coils of the entropy output.
2. What happens to the entropy when the door of the fridge is left open for a longer time?

1.4 The absolute temperature

How much entropy can be pumped out of an object?

How much entropy does it contain?

At first, we need to understand that these are two different questions.

If there is only positive entropy, only as much entropy as an object contains can be pumped out of it. Just as it is impossible to pump more air out of a recipient than it contains.

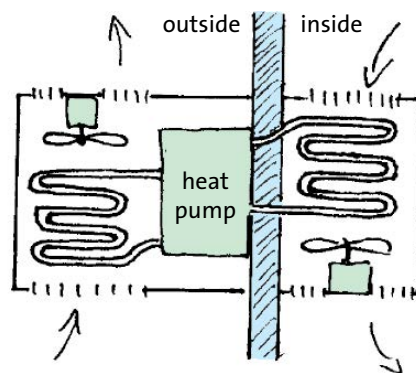It would be different if there were also negative entropy. Then, entropy could still be pumped out of an object if its entropy content were zero Carnot. If, for example, further 5 Ct were pumped out, the object would contain minus 5 Carnot afterwards. We know that this is possible for momentum: momentum can be withdrawn from a body at rest, i.e. an object with the momentum zero Huygens; then, its momentum will become negative.

Therefore, we can replace the initial questions by another one: does negative entropy exist? (Then, we could possibly say that negative entropy is what we colloquially call "cold" or "quantity of cold".)

In principle, the answer to this question is easy to find. All we need is a very good heat pump. We take any object, such as a brick, and pump entropy out of it as long as possible. Let us have a first try with the fridge. This way the temperature of the brick might de-

crease to – 5 °C. We cannot go any further because the heat pump of the fridge is not able to do better. However, more entropy could be taken off the brick by putting it in the freezer. The temperature will then decrease to –18 °C. But there are even better (and, of course, more expensive) heat pumps. With them, even lower temperatures can be achieved. Such heat pumps are called refrigerating machines.

There are refrigerating machines that could reduce the temperature of our brick to –200 °C. The air is already liquid at that temperature. Such machines are actually used to liquefy air; and there are refrigerating machines that could take out even more entropy from our brick. It could be recognized by the fact that the temperature would fall even further. This is how –250 °C, then –260 °C and –270 °C and, with even more effort –271 °C, –272 °C, –273 °C could be reached. –273,15 °C is the limit though. In spite of the greatest efforts and the use of all possible means, temperature cannot become any lower.

The explanation is simple:
- At this temperature the brick contains no more entropy.
- Entropy cannot admit negative values.

The lowest temperature a body can have is –273.15 °C. At that temperature, it does not contain any more entropy.

For ϑ = –273.15 °C is S = 0 Ct.

After discovering that there is a lowest temperature, it was logical to introduce a new temperature scale. This new *absolute temperature scale* is shifted against the Celsius scale in a way that its zero point is at –273,15 °C. The symbol for the absolute temperature is T, the measuring unit Kelvin, abbreviated K. Fig. 1.10

shows how the two scales are related. Please bear in mind that a temperature difference of 1 °C is equal to one of 1 K. The boiling temperature of water on the Celsius scale is

$$\vartheta = 100 \text{ °C}$$

and

$$T = 373.15 \text{ K}$$

on the absolute scale.

> The zero point of the absolute temperature scale is at –273.15 °C. The measuring unit of the absolute temperature is Kelvin.

Exercises

1. Convert the following Celsius temperatures to absolute temperatures:
   0 °C (melting temperature of water)
   25 °C (normal temperature)
   100 °C (boiling temperature of water)
   –183 °C (boiling temperature of oxygen)
   –195.8 °C (boiling temperature of nitrogen)
   –268.9 °C (boiling temperature of helium)
   –273.15 °C (absolute zero point)
2. Convert the following absolute temperatures to Celsius temperatures:
   13.95 K (melting temperature of hydrogen)
   20.35 K (boiling temperature of hydrogen)
   54.35 K (melting temperature of oxygen)
   63.15 K (melting temperature of nitrogen)

Fig. 1.10 Celsius scale and absolute temperature scale

Fig. 1.11 Entropy is generated in the flame.

1.5 Entropy production

A heat pump can be used to heat a room. Entropy is transferred into the house from the outside. However, most indoor heating systems actually work differently. A fuel such as heating oil, coal, wood or an combustible gas, is burnt. Combustion is a chemical reaction in which the fuel and oxygen are transformed into other substances, mostly into carbon dioxide and (gaseous) water. But where does the entropy, which is released by the flames during combustion, come from? It was neither contained in the fuel nor in the oxygen prior to combustion because both substances were cold. Apparently, it sis produced during combustion. *Entropy is produced in the flame*, Fig. 1.11.

Another heating type is the electric heating. A strong electric current is sent through a thin wire. The wire heats up in the process. *Entropy is generated in the wire*, Fig. 1.12. Many electric devices work on the basis of this principle: the hotplate, the iron, the immersion heater, the night storage heater, the heating system of the hair dryer, the light bulb.

You also know a third method to create entropy: mechanical friction. When you slide down a climbing

pole, you feel the entropy emerging in an uncomfortable way. You can also feel it when drilling with a blunt drill or sawing with a dull saw. *Entropy is generated on the contact area of the bodies rubbing against each other.*

During all these processes, entropy is really created anew and not brought along from somewhere else.

> Entropy can be produced
> - in a chemical reaction (e.g. combustion);
> - in a wire in which an electric current is flowing;
> - by mechanical friction.

All these processes can be regarded as a sort of friction. Every time something flows through a connection or a wire, in which a resistance works against the respective current, friction takes place. In the case of mechanical friction, momentum flows from one body to another via a connection that hardly conducts the momentum. In electric heaters, electricity flows through a wire in which a resistance opposes the electric current. And also during a chemical reaction, a type of frictional resistance, the so-called reaction resistance, has to be overcome.

We have discussed the question of where we can obtain the entropy to heat a room or a body. Now we would like to explore the opposite problem: a body needs to be cooled. We already know one method. Entropy can be pumped out of a body by means of a heat pump.

A second method works in cases where the body is warmer than its environment (when its temperature is higher). What do we do when the tea is too hot? We just wait. The entropy flows to the environment by itself.

In both cases, i.e. with and without a heat pump, the entropy that disappears from the body to be cooled emerges again at a different place. Wouldn't it be possible though to eliminate the entropy in a definite way? Couldn't we make it disappear in a way that it will not emerge again at another place? Couldn't it be destroyed? Haven't we seen earlier that it can be generated?

Many inventors and many scientists have tried this – without success. Nowadays, we are strongly convinced that entropy cannot be destroyed.

> Entropy can be created but not destroyed.

In this occasion we should think of some other physical quantities: energy, momentum and electric charge. These three physical quantities can neither be created nor destroyed and we have always taken this fact for granted. Whenever the amount of energy in-

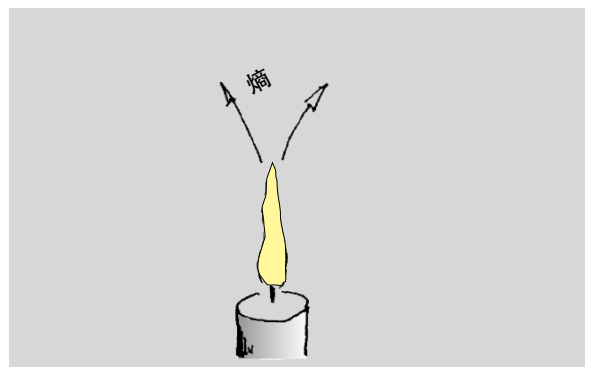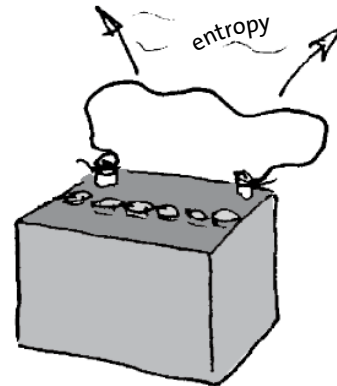**Fig. 1.12** An electric current flows through the wire. Entropy is created in the process.

creases at some place, it needs to decrease at another place, and whenever it decreases somewhere, it needs to increase somewhere else. The same applies for momentum and electric charge.

> Energy can neither be created nor destroyed.
> Momentum can neither be created nor destroyed.
> Electric charge can neither be created nor destroyed.

The possibility to create entropy leads us to interesting questions and has peculiar consequences.

Here a first problem. Entropy can be produced and is indeed produced in countless processes that take place on Earth. Combustion processes are particularly efficient sources of entropy. Please bear in mind that combustion processes do not only take place in furnaces, boilers and car engines, but to a much greater extent in nature: in all living creatures, from microbes to mammals, continuous oxidation, i.e. combustion, processes take place during which entropy is created. Would the amount of entropy on Earth not have to keep increasing, i.e. would the world not have to become increasingly warmer under these circumstances? In fact, the temperature on Earth has remained constant for millions of years, leaving minor variations aside. Explanation: looking at the Earth alone is not enough. First, the Earth constantly receives new entropy with the sunlight. (Also in this case, the entropy flows from the high to the low temperature. The surface of the Sun has a temperature of approximately 6000 K, the temperature of the surface of the Earth amounts to approximately 300 K.) Second, the Earth constantly radiates entropy into space. (Again, the en-

tropy flows from the high to the low temperature: space has a temperature of approximately 3 K.) Also the entropy that is radiated by the Earth is carried by light, albeit by invisible infrared light. This infrared light brings just enough entropy away as to keep the temperature at a nearly constant level. Of course, there is still the question of what will happen to the universe if its entropy is constantly increasing. This question has not been answered up to present. However, it only raises a small issue compared to the other unanswered questions about structure and development of the universe.

The fact that entropy can be created but not destroyed has another peculiar consequence. Someone projects a video (without sound) but without telling you whether the video runs forward or backward. Can you tell in which direction the video runs? The "video" from Fig. 1.13 shows, if played in the correct direction, a burning candle. If played incorrectly, it shows something that does not exist in reality: a candle that grows by itself. Thus, the video shows an *irreversible* process. Why is this process irreversible? Because it generates entropy. A reversal would mean the destruction of entropy – which does not exist.

Another irreversible is shown by the images from Fig. 1.14: a person slides down a climbing pole. This process is also irreversible because it generates entropy.

However, there are processes that can run in a forward and backward direction: any processes that do no generate entropy. Fig. 1.15 shows a ball that is flying past a window. Did the ball fly from the left to the right as shown by the video? Or does the video run in the wrong direction and the ball actually flew from the right to the left?

> Processes in which entropy is created are irreversible.

— Exercises —

1. A lamp is connected to a battery. The lamp lights up and the battery empties slowly. Explain the corresponding reverse process and assume that it is not forbidden to destroy entropy.
2. Explain in detail which processes will take place if the process "driving car" would run backwards and if it were not forbidden to destroy entropy.
3. A cyclist brakes. What would happen in detail if the process took place in a reverse way? Assume that entropy could be destroyed.

Fig. 1.13 Burning a candle is an irreversible process.
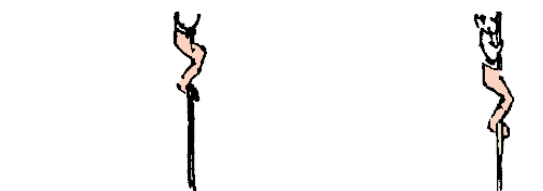
Fig. 1.14 Are the images arranged in a correct order?
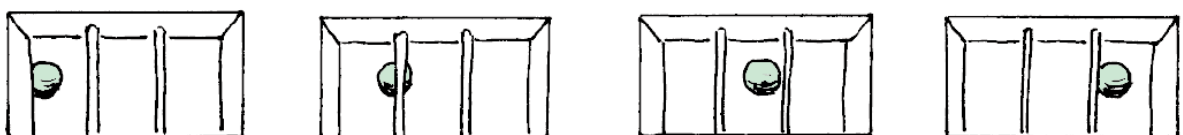
Fig. 1.15 The process of a ball flying past is reversible.

1.6 The entropy current

The metal bar in Fig. 1.16 is heated at its left end and cooled at the right end. In other words: entropy is transferred to the bar on the left and withdrawn from it on the right.

Entropy flows in the bar from the left to the right, from the higher to the lower temperature. We say there is an entropy current. The *entropy current* I_S at any cross-section of the bar is understood as the amount of entropy ΔS, which flows past it during a period of time Δt, divided by this period of time:

$$I_S = \frac{\Delta S}{\Delta t}. \tag{1.1}$$

The measuring unit for the entropy current is "Carnot per second", abbreviated as Ct/s.

Fig. 1.16 An entropy current flows from the hot to the cold end of the bar.

1.7 Entropy conductivity

What does the entropy current between two places A and B depend upon? Let us have a look at Fig. 1.17. In the upper arrangement, the temperature difference between body A and body B is greater than in the lower one. Otherwise, the upper and the lower parts are identical. As the drive for the entropy current is greater in the upper part than in the lower part, the current is also greater there.

> The higher the temperature difference between two places (the greater the drive), the greater the entropy current that flows from one place to the other.

If the temperature difference ΔT between the ends of a heat conductor not too high, the entropy current is proportional to the temperature difference, i.e.

$$I_S \sim \Delta T \tag{1.2}$$

Two entropy currents, however, even though the temperature differences are the same. This is because it not only depends on the temperature difference but also on the kind of connection.

Fig. 1.18 shows two entropy conductors (a) and (b) with the same temperature difference of 20 K between their ends.

However, the cross-sectional area of conductor b (4 cm^2) is twice that of conductor (a) (2 cm^2), see Table 1.1.

Fig. 1.17 In the upper part, the temperature difference between body A and body B is higher.
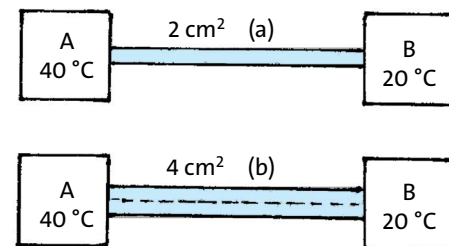
Fig. 1.18 A greater entropy current flows through the thicker conductor.

	A	ΔT	I_S
(a)	2 cm^2	20 K	0.5 Ct/s
(b)	4 cm^2	20 K	1 Ct/s

Table 1.1

	d	ΔT	I_S
(a)	10 cm	20 K	1 Ct/s
(b)	20 cm	20 K	0.5 Ct/s

Table 1.2

Now, in each half of conductor b (in the upper and in the lower one) flows as much entropy as in conductor (a), i.e. twice as much as in conductor (a) in both halves together. Consequently, at an equal temperature difference the entropy current is proportional to the crosssectional area A of the heat conductor:

$$I_S \sim A \qquad (1.3)$$

Fig. 1.19 again shows two conductors whereby conductor (b) is twice as long (20 cm) as conductor a (10 cm). See Table 1.2.

We see that there is a temperature difference of 10 K on each of the two halves of (b). This means that the entropy current flowing through (b) must be half of the one flowing through (a). Consequently: in the case of equal temperature differences, the entropy current is inversely proportional to the length d of the heat conductor:

$$I_S \sim \frac{1}{d}. \qquad (1.4)$$

The three proportionalities (1.2), (1.3) and (1.4) can be summarized as just one:

$$I_S \sim \frac{A}{d}\Delta T. \qquad (1.5)$$

Finally, Fig. 1.20 shows two conductors that the same length and the same cross-sectional area. In addition, there is the same temperature difference between their ends. Nevertheless, the entropy current flowing through b is smaller than the one flowing through a, because b is made of wood and a of copper.

We take this into account by adding a factor σ_S to relation (1.5). This factor has a characteristic value for each material:

$$I_S = \sigma_S \frac{A}{d}\Delta T.$$

σ_S is high for a material that conducts the entropy well, and low for a material that has bad conducting properties. σ_S is called the *entropy conductivity*. As measuring unit for σ_S, we find:

$$\frac{Ct}{s \cdot m \cdot K}$$

We now analyze a few materials to find out whether they have a high or a low entropy conductivity; whether they are good or bad heat conductors. We hold a small bar made of a given material with the fingers on one end and hold the other end into a flame, Fig. 1.21. Depending on the conductivity of entropy, we feel more or less quickly with our fingers that it is becoming hot.
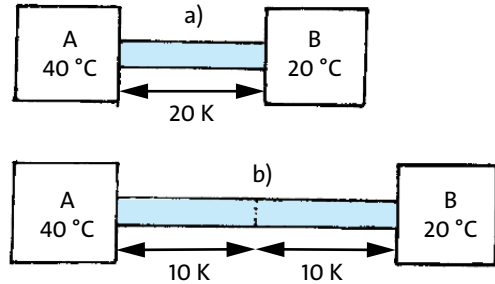
Fig. 1.19 A greater entropy current flows through the shorter conductor.
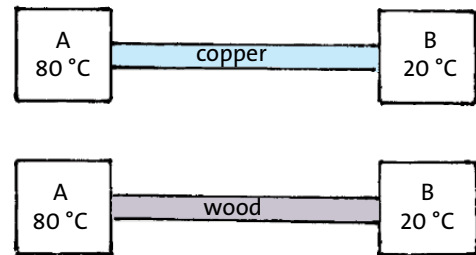
Fig. 1.20 The entropy current flowing through the copper bar is greater than that flowing through the wooden bar.
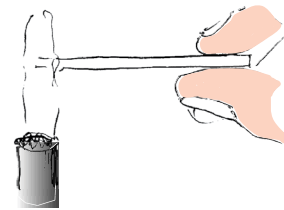
Fig. 1.21 Depending on the entropy conductivity of the little bar, it heats up more or less quickly on its right end.

We find that the entropy conductivity of wood and glass is rather low whereas metals have a high entropy conductivity of and hence are good heat conductors. Air and other gases have a very low entropy conductivity. This is why materials that contain a lot of air are used for heat insulation of buildings: bricks with cavities, aerated concrete blocks, foamed plastics and fiber insulation materials. But also a woolen pullover keeps us warm because the wool contains so many cavities (filled with air). Table 1.3 shows a list of the σ_S values for some materials.

Now we can also explain why a metal body feels colder than a wooden one.

At first, we would like to point out that this observation does not apply for high temperatures though. We put a piece of wood and a piece of metal into boiling water so that both bodies reach a temperature of 100 °C.

We then pull the bodies out of the water and touch them with our fingers. This time, the metal body feels hotter than the wooden one. How can this be explained?

If we touch a piece of wood and a piece of metal which both have a temperature of 10 °C with our fingers having a temperature of 25 °C, entropy will begin to flow from our fingers to the body, Fig. 1.22. But then, the wood will quickly heat up at the contact area, it takes on the temperature of our fingers because the entropy cannot flow away. In the metal, by contrast, the entropy flows away from the contact area to the inside of the body and the contact area heats up only slightly.

Exercises

1. How does a house have to be built to achieve the lowest possible heat loss (entropy loss)?
2. In a radiator of the central heating system, the entropy should flow as easily as possible from the water inside the radiator to the outside. Which measures can be applied to achieve this? Mention other bodies for which a good heat transfer is advantageous.
3. Compare the loss of entropy through the windows of a heated room with that through the walls. Assume the following: surface of the windows: 0.75 m²; thickness of the glass: 5 mm; surface of the walls that are not covered with glass: 120 m². The walls are insulated with styrofoam boards that have a thickness of 5 cm. Assume that they only consist of styrofoam. Internal temperature: 20 °C; external temperature: 10 °C. How can the heat loss be reduced best?
4. Styrofoam boards with a thickness of 5 cm are fixed on a brick wall with a thickness of 12 cm. By how much will the heat loss decrease? Hint: a) Assume that the temperature difference between the inside and the outside is 20 K. Calculate the entropy current per area I_S/A for the noninsulated wall. b) Assume for the insulated wall that the entropy current flowing through the brick (I_S, Brick) is equal to that which flows through the styrofoam (I_S, Styrofoam). Equate the respective terms. Use the fact that the temperature difference over the brick wall plus the temperature difference over the styrofoam is 20 K. Calculate the temperature difference over the bricks. c) Calculate the entropy current per area for the bricks. Compare with a).

1.8 Entropy transfer by convection

A temperature difference is a driving force for an entropy current. If we were to transfer entropy from a point A to another point B, it is sufficient to ensure that A has a higher temperature than B. This type of entropy transfer is called heat *conduction*. In other words, it is the normal way to transport entropy from A to B.

material	σ_S in Ct/(s·m·K)
Silver	1.54
Copper	1.43
Iron	0.29
Bricks	0.003
Glass	0.002 7
Wood	0.000 47
Styrofoam	0.000 13
Water	0.000 9
Air	0.000 088

Table 1.3 Entropy conductivity
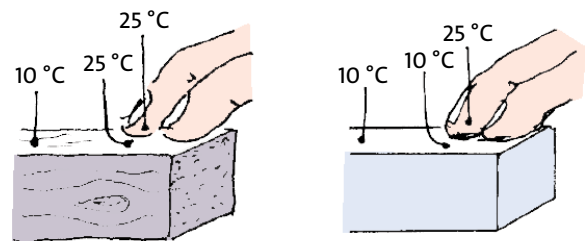
Fig. 1.22 Prior to touching, both bodies have the same temperature. After, the temperatures change.
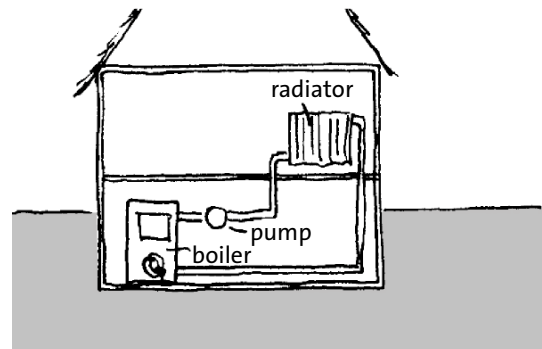
Fig. 1.23 Central heating system. The entropy flows convectively from the boiler to the radiators.

However, when careful observing our environment, we notice that most entropy transfers, and especially entropy transfers over long distances, do not happen this way. There is yet another method to transfer entropy: the *convective* entropy transfer or *convection*.

A liquid or a gas is heated and transferred from A to B – for instance by means of a pump. Then, the entropy is simply taken along by the flowing substance. No temperature difference is needed as a driving force; however, there must be a driving force for the flow of the liquid or the gas instead.

An example for a convective entropy transfer is the central heating system, Fig. 1.23. Within the boiler,

that is mostly located in the basement of the house, water is heated, for example through combustion of fuel oil. The warm water is pumped through pipes to the radiators in the different rooms of the house. In the radiators, it gives a part of its entropy away and then flows back to the boiler via a return duct.

Convective entropy transfers can be realized more easily than conventional ones, i.e. those that are driven by temperature differences. The reason: there are no really good heat conductors. Even copper as a relatively good heat conductor is essentially still a very bad heat conductor. For example, it would be impossible to transport the entropy from the boiler of the central heating system to the various rooms of the house by means of copper bars. In contrast, it is no problem at all to transport water or air, together with its entropy, over long distances.

> Convective entropy transfer: the entropy is taken along by a flowing liquid or a flowing gas. No temperature difference is needed for a convective entropy transfer.

Nature and technology provide many examples for convective entropy currents.

In a heated room, the entropy from the radiator or stove should spread out in the entire room. How can this be reached, being air such a bad heat conductor? The entropy is transferred convectively with the air. By the way, air flows without a pump in this case. At the heater or the stove, the air rises because warm air has a lower density than cold air, Fig. 1.24.

Each car engine must be cooled; i.e. entropy must be taken away from the engine, Fig. 1.25. Most car engines are water-cooled: the entropy is transported with water from the engine to the cooler, just as in the central heating system. The cooling water pump ensures circulation of the water. In the cooling system, the entropy is released into the air that flows past.

Also the great entropy transfers in nature, which determine our weather, are convective transfers. In the atmosphere, entropy is transported with the wind, i.e. with moving air, over very long distances.

Another interesting example of a convective entropy transfer is the Gulf Stream. It transports entropy from the Caribbean to Europe, Fig. 1.26. As a consequence, the European climate becomes milder than it would be due to its geographical latitude alone.

We would like to contrast the entropy transfer through conduction of heat again with the convective transfer by tracking the path of the entropy in a house with a central heating system. In the boiler, the entropy
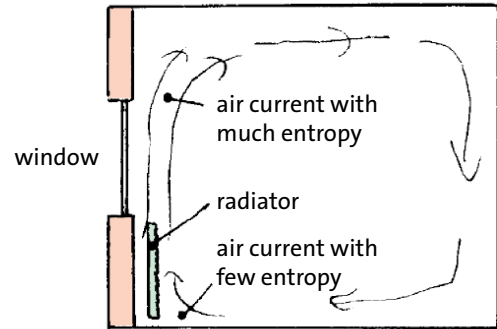
Fig. 1.24 The entropy is spread in the room by means of convection.
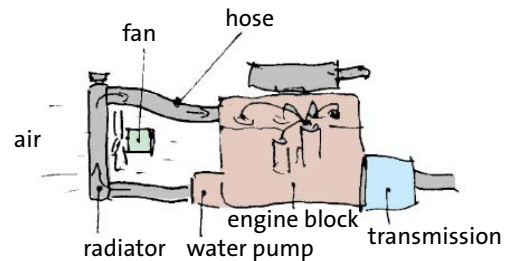
Fig. 1.25 Cooling the car engine. The entropy flows convectively from the engine to the cooler.

Fig. 1.26 The Gulf Stream. Entropy is transported with a water current from the Caribbean to Europe.

created in the flames flows convectively to the outer wall of the water tank. It flows through this wall in a normal way, i.e. driven by a temperature difference. Next, it flows convectively with the water to the radiators. Through the wall of the heater, it needs to flow again in the usual way. From the outer surface of the heater, it will eventually get convectively with the air to the different places of the room. It can therefore be seen that, on the long way from the flames of the boiler to the room to be heated, only tiny distances, i.e. just a few millimeters, are bridged by conventional heat conduction.

> Entropy transfers over long distances are mostly convective.

1. Describe the ways in which a house loses heat. Which losses are based on heat conduction? And which ones on convection?
2. Describe the way of the entropy from the inside of a car engine up to the ambient air. On which parts of the way does the entropy flow due to a temperature difference? On which parts does it flow convectively?
3. How does the car heating work? Describe the path of the entropy.

1.9 Entropy as an energy carrier

We will consider the laws of balance for an electric heating unit. An electric heater is nothing more than a wire through which electricity flows, making it warm. As you know, this type of heating has many applications: hot plates, irons, light bulbs...

We know that a heater produces entropy. While it is running, the heater gives up entropy. We also know that a heater "uses" energy, meaning that the energy flows into the heater through the electric cable. The carrier for the energy flowing in is electric charge.

The energy flowing continuously into the device with electric charge must come out again. We ask the question we have asked so often before: What is the carrier of this energy?

The answer is self-evident. Along with the energy, entropy flows out of the heater. This entropy is the carrier we are seeking. We can make a general statement about this: Wherever and whenever an entropy current flows, an energy current is flowing.

Entropy is an energy carrier.

Electric heaters belong to the category of devices that we earlier called energy transfer devices or energy exchangers. The energy goes into the appliance with the carrier electric charge. Entropy is produced in the appliance, and the energy leaves it with this entropy. The energy is transferred from electric charge to entropy. Fig. 1.27 shows a schematic of our heater.

Notice that energy and electric charge both have an inlet and an outlet, while entropy has only an outlet. Another way of saying this would be: In an electric heater, energy is transferred to the newly produced entropy.

We had learned about an energy exchanger where energy is transferred from electric charge to entropy,
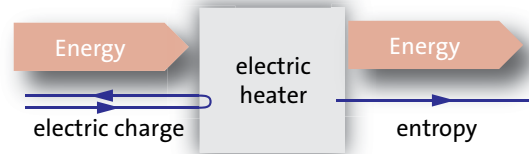
Fig. 1.27 Energy flow chart of an electric electric heater
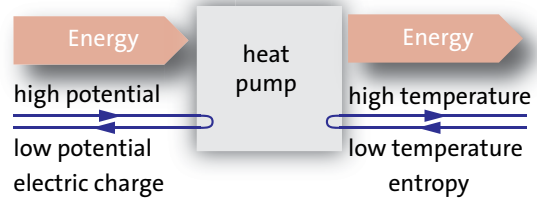
Fig. 1.28 Energy flow chart of a heat pump

and where the entropy is not created: the heat pump. The flow chart is shown in Fig. 1.28.

Entropy enters the heat pump at low temperature. Within the pump it takes over the energy that is delivered by the electric charge, and it leaves the heat pump at a higher temperature, together with the additional energy.

We conclude, that entropy carries the more energy, the higher its temperature is.

The higher the temperature, the more energy is transferred with the entropy.

1. Sketch the energy flow diagram for an oil heater.
2. Sketch the energy flow diagram for the process of friction in Fig. 1.29. Hint: The "energy exchanger" is the bottom of the crate rubbing against the floor.
3. A tower of building blocks collapses. During which part of this process is entropy produced? Where does the energy needed for this come from?
4. Sketch the energy flow diagram for the inverse of a heat pump. What is the resulting device good for?

Fig. 1.29 For exercise 2

1.10 The relationship between energy and entropy current

Each entropy current is accompanied by an energy current. How are the intensities of these two currents related?

Prior to analyzing this question with scientific rigor, we would like to try to guess the result. The method we are using in this process is a conclusion by analogy: we know a problem that has a very similar structure, and we know its solution. We would like to try to derive the solution of our current problem from this solution.

Earlier, we learned about the electric charge as an energy carrier, and we found a relationship between the energy current and the electric current:

$$P = \Delta\varphi \cdot I.$$

The energy current is proportional to the current of the energy carrier. The proportionality factor is the electric potential difference $\Delta\varphi$, i.e. the physical quantity that is the driving force of the electric current.

Then, if the energy carrier is not the electric charge but the entropy, we can expect P to be proportional to I_S and the proportionality factor to be the physical quantity that is the "driving force" of the entropy current, i.e. the temperature difference. Consequently, we could say:

$$P = \Delta T \cdot I_S. \tag{1.6}$$

This is indeed the correct formula. If the way in which we have obtained it looks suspect to you, please read the slightly more precise derivation that follows.

We look at a given heat pump. It is designed in a way as to raise of 5 Ct per second by a temperature difference of $\Delta T = 20$ K. When doing so, the heat pump has a certain energy consumption that we would like to call P_0. We now connect two such heat pumps "in parallel" and consider the pair of pumps as a single, larger pump, Fig. 1.30.

This new pump pumps 10 Ct/s over the same temperature difference and consumes $2 \cdot P_0$. Hence, we can conclude that the energy current is proportional to the entropy current, whereby we have kept the temperature difference constant:

$$P \sim I_S \text{ for } \Delta T = \text{const} \tag{1.7}$$

Next, we set up a "series circuit" of two heat pumps and again consider the pair of pumps as a single pump, Fig. 1.31. The new pump still pumps 5 Ct/s but up on a higher temperature level, i.e. $\Delta T = 40$ K. The energy
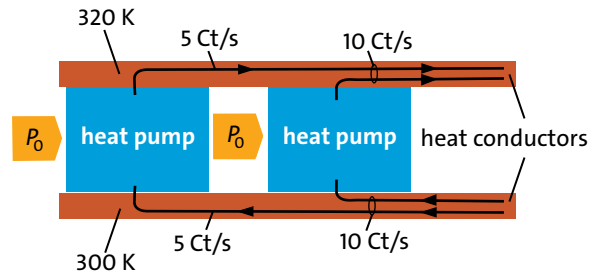
Fig. 1.30 Two heat pumps connected in parallel pump twice as much entropy and consume twice as much energy as a single one.
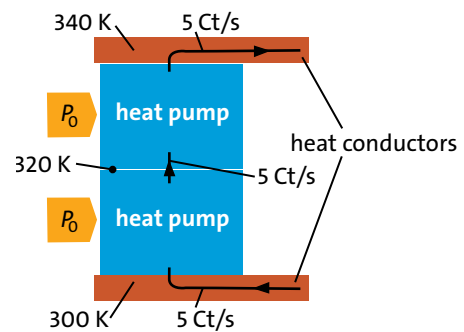
Fig. 1.31 Two heat pumps connected in series pump the entropy over a temperature difference that is twice as high as a single one and consume twice as much energy.

consumption is again $2 \cdot P_0$, i.e. that of two single pumps. Consequently, the energy current is proportional to the temperature difference whereby we have kept the entropy current constant this time:

$$P \sim \Delta T \text{ for } I_S = \text{const} \tag{1.8}$$

The two proportionalities (1.7) and (1.8) can be summarized in a single one:

$$P \sim \Delta T \cdot I_S.$$

This is almost equation (1.6). The fact that the proportionality factor is "one" is due to the appropriate choice of the measuring units of temperature and entropy. Actually, we can write:

$$P = \Delta T \cdot I_S \tag{1.9}$$

In words:

The heat pump consumes more energy
- the more entropy it needs to haul
- the higher the temperature difference it has to overcome

By means of equation (1.9) we can calculate the energy consumption of a heat pump. But the equation tells us even more. Let us first write it at in another form:

$$P = (T_A - T_B) \, I_S$$

We have called $\Delta T = T_A - T_B$, where T_A is the high temperature at the entropy output and T_B the low temperature at the entropy input.

$$P_B = T_B \cdot I_S$$

is the energy that the entropy carries into the heat pump at the low temperature, and

$$P_A = T_A \cdot I_S$$

is the energy that the entropy carries out of the heat pump at the high temperature.

We see that two entropy currents of the same intensity can carry different amounts of energy. The one that enters the heat pump carries little, and the one that comes out carries much energy.

In general, the following applies:

$$P = T \cdot I_S \qquad (1.10)$$

In words:

An entropy current I_S carries an energy current $T \cdot I_S$.

The equation also shows that the temperature can be interpreted as follows:

The temperature indicates how much an entropy current is charged with energy.

Example

A heat pump that is used to heat a house brings per second 30 Ct from the outside into the house. The outside temperature is 10 °C, the temperature in the house 22 °C. What is the energy consumption of the pump?

Here, we do not need to convert the Celsius temperature into absolute values because the differences are equal on both scales. Hence, $T_A - T_B = 12$ K. We therefore obtain

$$P = (T_A - T_B) \, I_S = 12 \text{ K} \cdot 30 \text{ Ct/s} = 360 \text{ W}.$$

We now assume that the same house is heated with a common electric heating, i.e. the entropy is not pumped in from the outside but produced within the house. Of course, the temperature in the house should again be 22 °C, and of course we need again 30 Ct/s in the house as the house loses this quantity through the walls. We calculate the energy current that comes out of the electric heating with equation (1.10), whereby $T = (273 + 22)$ K = 295 K and $I_S = 30$ Ct/s:

$$P = T \cdot I_S = 295 \text{ K} \cdot 30 \text{ Ct/s} = 8850 \text{ W}.$$

According to our calculation, the energy consumption of the common electric heating is much higher than that of the heat pump. In reality, the difference is not as high because some entropy is also created in each heat pump.

Exercises

1. A house that is heated up to a temperature of 20 °C by means of a fuel heater has a heat loss of 35 Ct/s. What is the energy consumption of the heater?
2. The radiator of a car, whose temperature is 90 °C, releases 60 Carnot per second to the air. What is the energy current that leaves the radiator to the air?
3. The temperature at the bottom of a 1000 W iron is 300 °C. How much entropy is released from the iron per second?
4. A swimming pool is heated with a heat pump. The heat pump takes the entropy from a stream flowing past. The temperature of the water in the stream is 15 °C, the temperature of the water in the swimming pool 25 °C. The water in the swimming pool constantly loses entropy to the ambient, precisely 500 Ct per second. To keep its temperature, the heat pump constantly needs to supply new entropy. What is the energy consumption of the heat pump?
5. (a) A house is heated with a heat pump. The outside temperature is 0 °C, the temperature in the house 25 °C. The heat pumping is at a rate of 30 Ct/s. What is its energy consumption? (b) The same house is heated with a conventional electric heating, i.e. the 30 Ct/s are not pumped in from the outside, but produced within the house. What is its energy consumption now?

1.11 Entropy production by entropy currents

An entropy current flows through a bar that is made of a material which is a good heat conductor, Fig. 1.32. The current is sustained by means of a temperature difference. The bar is thermally insulated towards its sides so that no entropy is lost there. At the beginning of the experiment, the temperature can still change at the different points of the bar. These

changes will though stop after a while: a steady state will be reached.

The equation relating the entropy and energy current to each other leads us to a surprising statement here.

We look at three different points of the bar: the right, cold end, the center and the left, hot end. We mark the values of physical quantities referring to these three spots with "1", "2" and "3". An energy current P_3 flows into the bar at the left. As the steady state is reached, there is no accumulation of energy and the energy current must have the same value everywhere throughout the bar:

$$P_3 = P_2 = P_1 \tag{1.11}$$

Now we know that the energy current P is related to the entropy current I_S by

$$P = T \cdot I_S \tag{1.12}$$

We replace the energy currents in equation (1.11) by means of equation (1.12) and obtain:

$$T_3 \cdot I_{S3} = T_2 \cdot I_{S2} = T_1 \cdot I_{S1} \tag{1.13}$$

Now we know that the temperature T_3 is greater than T_2 and that T_2 is greater than T_1:

$$T_3 > T_2 > T_1 \, .$$

In order for equation (1.13) to be valid, we must have

$$I_{S3} < I_{S2} < I_{S1}$$

The entropy current increases towards the right. More entropy flows out of the bar on the right, at the cooling water, than on the left where it has entered next to the flame. Consequently, entropy must have been produced in the bar. How is that possible?

Basically, this result is not as surprising as it might seem at first. We discovered earlier that entropy is produced whenever there is some type of frictional process, whenever a current flows against a resistance. This is exactly what happens here as well. However, the flowing substance is neither a liquid or a gas, nor momentum or electricity, but the entropy itself. Consequently, entropy is also created by the flow of entropy through a resistance.

In our minds, we can divide the entropy at the output of the bar, i.e. on the right end, in two portions: the
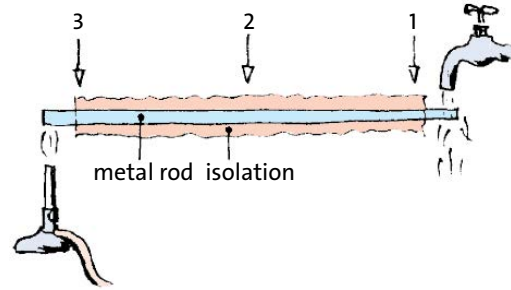
Fig. 1.32 More entropy comes out at the right end of the rod than flows in at the left.

portion that has flown in on the left, and the one that has been created on the way from the left to the right. Hence, we can write

$$I_{S1} = I_{S3} + I_{S\,produced}$$

$I_{S\,produced}$ represents that part of the entropy current that is produced in the bar.

> If entropy flows through a thermal resistor, additional entropy is produced.

Example

The heating wire of a 700-W immersion heater, Fig. 1.33, is at 1000 K (727 °C).

The entropy current flowing out of the wire is

$$I_S = \frac{P}{T} = \frac{700 \text{ W}}{1000 \text{ K}} = 0.7 \frac{\text{Ct}}{\text{s}}.$$

On its surface, the immersion heater has the same temperature as the water. We assume that the water temperature is 350 K (77°C).

Hence, the entropy current at the outer wall of the immersion heater is:
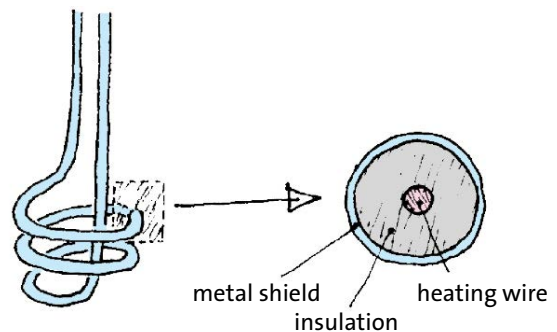
Fig. 1.33 An immersion heater. A cross section on the right (simplified and enlarged).

$$I_S = \frac{P}{T} = \frac{700 \text{ W}}{350 \text{ K}} = 2\frac{\text{Ct}}{\text{s}}.$$

Over the short distance from the heating wire to the surface of the immersion heater

$$(2 - 0.7)\text{Ct/s} = 1.3 \text{ Ct/s}$$

are created. 0.7 Ct/s are created in the wire by the electric current. More is produced by the entropy on its way to the outside than is created by the electric current.

— **Exercises** —

1. A house is heated with 20 kW. The internal temperature is 20 °C, the outside temperature –5 °C. (a) What is the outward-flowing entropy current on the inner wall of the house? (b) What is its value on the outer wall? (c) How much new entropy is produced per second as the entropy is flowing out?
2. The heating wire of a 1000 W hotplate has a temperature of 1000 K. (a) How much entropy is created per second in the heating wire? (b) On a hotplate, there is a pot with hot water; the water temperature is 373 K. How much entropy flows in the water per second? (c) How much entropy is generated on the way from the heating wire to the water?

1.12 Heat engines

A thermal engine can be best explained by means of an energy flow chart, Fig. 1.34: an energy exchanger that receives energy with the carrier entropy and that releases it with the energy carrier angular momentum. The fact that the angular momentum is the carrier of the energy at the output of the machine means that the energy comes out through a rotating shaft; the purpose of the machine is to drive something.

The category of thermal engines includes:

- the steam turbine
- the piston steam engine
- all combustion engines (gasoline or diesel engines)
- jet engines
- other, less common engines.

We will see how each of these engines works at a later time. For now, we only look at the common features of all heat engines. Let us start with a little detour.

Fig. 1.35 shows the energy flow chart of a water turbine, i.e. of a device that is not a heat engine.

Water with a high pressure flows into the turbine and back out with a low pressure. The water with the high pressure transports much energy, the one with the low pressure transports little energy. While the water in the turbine "goes down" from the high to the low pressure, it discharges energy. This energy leaves the turbine via the shaft with the carrier angular momentum.

Now, a comparison of Fig. 1.35 with Fig. 1.34 shows that the heat engine has something essential in common with the water turbine. Entropy flows into the heat engine on a high temperature, i.e. entropy that carries much energy. The same entropy flows back out of the machine on a low temperature, i.e. with little energy. While the entropy in the machine "goes down" from the high to the low temperature, it discharges energy, and this energy also comes out via a rotating shaft, i.e. with the energy carrier angular momentum.

> In a heat engine, energy changes its carrier. It enters the engine with the carrier entropy and leaves it with angular momentum.

We calculate the energy that a heat engine releases per second. The machine receives the energy current $T_A I_S$ at the entropy input at the high temperature T_A and releases an energy current $T_B I_S$ at the entropy output at the low temperature T_B. The difference is the the energy which is tranferred to the angular momentum. With the angular momentum, an energy current

$$P = T_A I_S - T_B I_S = (T_A - T_B)\, I_S$$

leaves the engine.
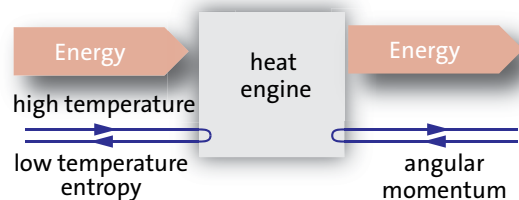
Fig. 1.34 Energy flow chart of a thermal Heat engine
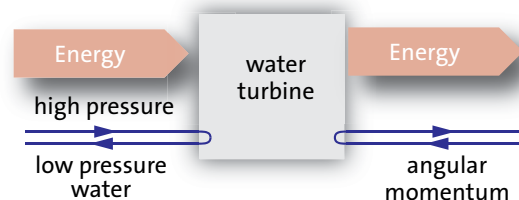
Fig. 1.35 Energy flow chart of a water
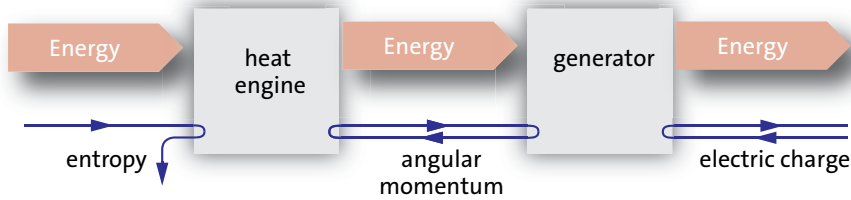
Fig. 1.36 Energy flow chart of a thermal power plant
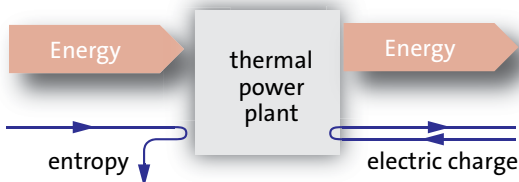
Fig. 1.37 Energy flow chart of a thermal power plant. Turbine and generator are indicated by only one symbol.
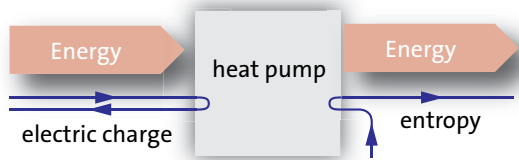
Fig. 1.38 Energy flow chart of a heat pump

With the abbreviation $\Delta T = T_A - T_B$, we obtain

$$P = \Delta T \cdot I_S$$

This is our old equation (1.9).

> A heat engine releases the more energy with the angular momentum
> - the greater the entropy current that flows through the machine;
> - the greater the temperature difference that the entropy current flows down within the machine.

In most power plants, the generator is driven by a heat engine. The flow chart of the two interconnected machines is shown in Fig. 1.36.

The two energy exchangers can also be represented symbolically with a single box, Fig. 1.37.

Compare this flow chart with the one of an electric heat pump, which is shown again in Figure 1.38. (It is the same as in Figure 1.28.)

Each input in one flow chart becomes the output in the other, and vice versa. The entropy enters the power plant on a high temperature and comes out of the heat pump on a high temperature.

Hence, the power plant does just the opposite of what the heat pump does. While the electric heat pump transfers energy from electricity to entropy, the energy is transferred from entropy to electricity in the power plant of Fig. 1.37.

A thermal power plant is a complicated and very big installation. There are devices which do exactly the same as such a power plant but which are very small and handy and robust at the same time: the *thermocouples*.

A thermocouple can even be operated inversely: as a heat pump. Hence, it is at the same time a simple, affordable and very compact heat pump.

Unfortunately, thermocouples have high energy losses and are therefore only suitable for applications in which losses do not play a major role.

1.13 Entropy sources for heat engines

There are always two problems to solve when a heat engine is to be operated:
- A source of entropy at a high temperature is needed.
- It must be possible to get rid of the entropy at a lower temperature. There must be a so-called "trash dump" for the entropy.

These problems can be solved in different ways.

Natural entropy sources

This is the solution least damaging to our environment: Natural sources of entropy at high temperatures are exploited.

There are places on Earth where hot steam is contained in layers of rock at depths that are not too great. This steam is allowed to flow to the Earth's surface through drilled holes and can be used to drive power plants. Unfortunately, there are not many such sources of this *geothermal* energy.

The huge amounts of entropy at very high temperatures received by the Earth with sunlight provide another possibility. This entropy is being exploited in solar power plants. Although this entropy source is inexhaustible, it presents us with some problems that are not easy to solve. One of these is that sunlight is thinly distributed. This means that the entropy, and the energy with it, is strongly diluted. It must therefore be "collected" on large surfaces that the Sun shines upon. This collecting can be accomplished by erecting mirrors so that the light is concentrated on a boiler. Another problem related to solar energy is that the Sun does not always shine. It does not shine at all in the night, and in winter, when energy is most needed, it shines only weakly.

Artificial entropy sources

Most of the entropy used to drive heat engines today is acquired in a less elegant manner: It is produced by burning fuels or by nuclear fission.

Heat engines are widely used, and present not only the problem of how to acquire entropy but also the problem of "thermal trash". We will see how these problems are solved for the most important heat engines.

Thermal power plants

Most power plants operate with steam turbines. In coal-fired power stations, entropy is produced in a steam boiler by burning coal. Entropy is produced in nuclear power plants by splitting the atomic nuclei of uranium and plutonium.

When entropy leaves the power plant, its temperature is only slightly higher than the temperature of the surrounding environment. The entropy is mostly released into the water of a large river. If no river is available, or if a river's water does not suffice, the entropy is given up to the air in cooling towers.

Combustion engines

Entropy is created by burning gasoline or diesel oil inside an engine. Most of it leaves the engine with the exhaust fumes. The flow diagram in Fig.1.34 doesn't actually describe a combustion engine because the entropy is not introduced to the engine from outside.

Piston steam engines

These were the most important engines before electric and combustion engines were invented. They were used in steam locomotives, steam ships, steam rollers, and steam plows. They also drove threshing machines.
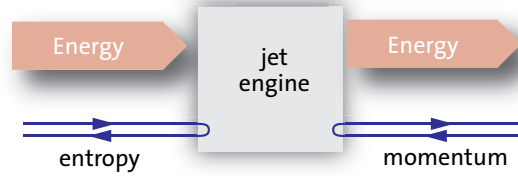
Fig. 1.39 Energy flow chart of a jet engine

Piston steam engines were used to drive the machines in many factories as well.

Entropy was produced for these engines in the boiler by burning coal. The steam driving the engine was commonly allowed to escape into the air after it had done its job. The entropy escaped to the air with the steam.

Jet engines

These are used to drive almost all large airliners. Jet engines do not exactly satisfy our definition of a heat engine. They don't give up their energy through a shaft with angular momentum, but together with momentum, Fig. 1.39. These engines "pump" momentum out of the air and into the airplane.

As with combustion engines, the entropy is produced in the engine by burning fuel, and it leaves the jet engine with the exhaust gases.

— Exercises

1. An entropy current of 100 Ct/s flows through a heat engine. At the entrance, the temperature is 150 °C, at the exit it is 50 °C. How much energy per second does the engine emit with the energy carrier angular momentum?
2. A power plant gives off an energy current of 1000 MW with electricity. The temperature of the steam at the entrance to the turbine is 750 K, at the exit it is 310 K. What is the entropy current that flows away with the cooling water? What is the energy current carried by this entropy current?
3. Think of some possibilities for applications of entropy with high temperature found in nature. Also discuss possibilities you might consider unrealistic.

1.14 Energy loss and efficiency

On the way from the faucet to the nozzle, Fig. 1.40, water is lost. 2 liters per second come out of the faucet but only 1.8 liters per second get to the nozzle.

The difference, i.e., 0.2 liters per second, flows out of the hole in the hose. We have a loss of 0.2 l/s. Usu-

ally, loss is expressed as a fraction of the initial quantity. The loss is symbolized by V. Therefore, in our case we get

$$V = \frac{0.2 \text{ l/s}}{2 \text{ l/s}} = 0.1.$$

In most devices, where energy is transferred from one carrier to another, and in most conductors for transferring energy, energy gets lost. What does this mean? Energy cannot be destroyed! It is similar to the water in Fig. 1.40. A part of the energy does not get where it should go. It seeps out, so to say.

Energy loss is almost always connected to creation of entropy. We consider a water turbine. So far, we have sketched the flow chart of a water turbine like the one shown in Fig. 1.41 (also see Fig. 1.35).

This is actually a perfect, idealized turbine as we would never see it in the real world because in every real turbine, entropy is produced unintentionally. This happens at various locations: by friction created by the water rubbing against the walls of the pipe, by water rubbing against itself ("fluid friction") and by friction in the bearings of the turbine shaft. The entropy produced also leaves the turbine by various paths: partly in the water flowing away and partly into the surrounding air.

Energy flows away with this entropy. Fig. 1.42 shows the energy flow chart of a real turbine. The strengths of the currents are indicated by the thicknesses of the energy arrows.

The value of the energy current due to loss is called P_V. The relation between the produced entropy and the lost energy is then

$$P_V = T_0 \cdot I_{S \text{ produced}} \tag{1.14}$$

Here, T_0 is the ambient temperature. The loss V of the machine is defined as the quotient

$$V = \frac{P_V}{P_{\text{in}}}. \tag{1.15}$$

The energy current flowing into the engine is indicated by P_{in}.

Hence, the loss is the fraction of the arriving energy that is released to the ambient together with the created entropy, i.e. the portion that is lost.

The fraction of P_{in}, that can be used, is called the efficiency η of the machine or of the conductor:

$$\eta = \frac{P_{\text{in}} - P_V}{P_{\text{in}}} = 1 - V \tag{1.16}$$

Both loss and efficiency can also be expressed in percent. Thus we may have:
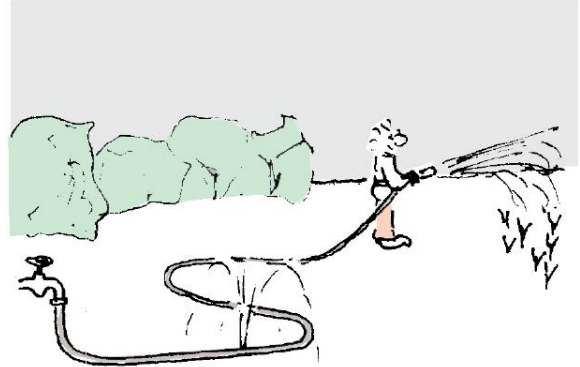
Fig. 1.40 Water gets lost through the hole in the hose.
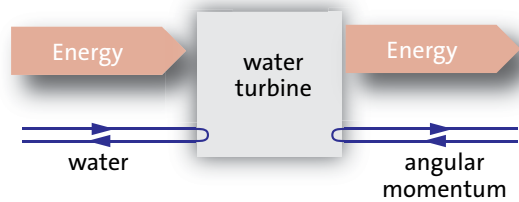
Fig. 1.41 Energy flow chart of an ideal water turbine
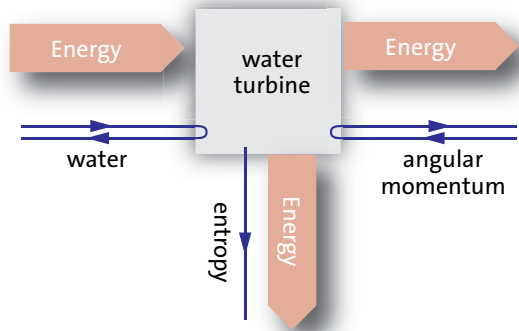
Fig. 1.42 Energy flow chart of a nonidealized water turbine

$$V = 0.1 = 10 \text{ %}$$

In this case the efficiency would be:

$$\eta = 0.9 = 90 \text{ %}$$

Fig. 1.43 shows the energy flow diagram of a real (not idealized) electric motor. Here as well, entropy is created unintentionally. A part of this entropy is created in the wires (entropy is always produced when an electric current flows through a wire). Another part is created in the bearings.

The energy loss in a simple electric motor is also calculated with Equation (1.15).

We have seen that energy loss depends upon entropy production. Of course one would wish to avoid this loss. Therefore remember:

Avoid creating entropy.

The loss in some energy exchangers is very large. Table 1.4 shows some typical values.

You probably wonder about the high losses in power plants. This is due only to a small extent to the losses in steam turbines and the generator. They occur mostly because of the entropy produced in the burner or in the reactor.

Exercises

1. An automobile engine releases 20 kW through its shaft. Only 18 kW reach the wheels because entropy is produced (by friction) in the bearings and the gearbox. What is the percentage loss?
2. An electric motor with a loss of 40 % uses 10 W. How much energy does it release with angular momentum? How much entropy is produced per second? (The ambient temperature is 300 K.)
3. A generator with a loss of 8 % gives up an energy current of 46 kW with the electricity. What is the energy current that flows over the engine shaft into the generator? What is the energy current due to loss? What is the current of the produced entropy? (Ambient temperature is 300 K.)

1.15 The efficiency of combustion processes

Combustion processes are the main cause of energy losses in industrial plants and households. That is why they offer the highest potential for energy savings. For this reason, we would like to learn about the efficiency of combustion processes in a broad sense. It can be the heating system of your house, the firing system of a power plant, the combustion process in a car engine, and also the reactor of a nuclear power plant.

We will see that the loss and the efficiency of the firing system can be expressed by means of only two temperatures: 1. the temperature T, at which the firing system supplies the created entropy, and 2. the ambient temperature T_0, i.e. the temperature at which the entropy is "disposed of".

To calculate V, we first need the energy consumption of the firing system P_{in}. The firing system receives
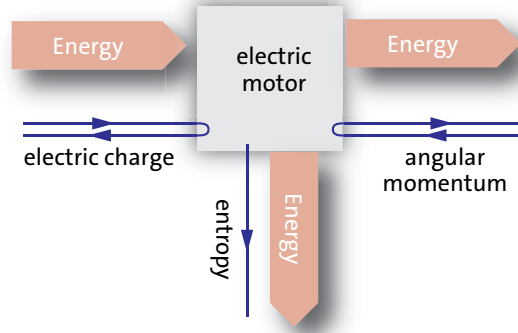
Fig. 1.43 Energy flow diagram of a nonidealized electric motor

	loss
Large steam turbine	10 %
Large electric motor	10 %
Toy electric motor	40 %
Solar cell	90 %
Coal fired power plant	57 %
Nuclear power plant	67 %

Table 1.4 Typical values of energy loss

this energy with the fuel (+ oxygen) and releases it with the created entropy. We can write:

$$P_{in} = T \cdot I_{S\ produced}$$

The lost energy is the energy that is needed to dispose of the created entropy, equation (1.14):

$$P_V = T_0 \cdot I_{S\ produced}$$

Hence, we obtain:

$$V = \frac{P_V}{P_{in}} = \frac{T_0 \cdot I_{S\ produced}}{T \cdot I_{S\ produced}}.$$

We thus get for the loss:

$$V = \frac{T_0}{T}. \tag{1.17}$$

and the efficiency

$$\eta = 1 - V = 1 - \frac{T_0}{T} = \frac{T - T_0}{T}. \tag{1.18}$$

Equation (1.17) tells us that the loss is smaller the higher the temperature T at which the entropy is supplied. This is the reason why nuclear power plants have a significantly lower efficiency than coalfired power plants: the temperature of the steam, which a nuclear reactor produces, is considerably lower than the steam temperature in a coal-fired power plant.

From equation (1.17) we can conclude that there is even a "heating" process which has a loss of 100 %: a process that does not heat up although it releases entropy. How does this work? The combustion process simply needs to run at ambient temperature, for example in the following way: wood is left outside until it becomes rotten. In that process, entropy is generated – slowly but over the time in large quantities. Since this entropy is generated at ambient temperature, we need to replace T by T_0 in equation (1.17) and we obtain $V = 1$.

These considerations confirm what we have already understood earlier: the creation of entropy comes along with a loss of energy. What we have discovered in addition is the fact that energy losses are the bigger the lower the temperature at which the entropy is generated.

However, why are technical processes applied, in which entropy is generated on purpose? Why is coal burnt in order to get energy that is carried by electricity? Can't the energy be transferred from the fuels to the electricity, without entropy as a "detour"? In fact, this is possible. Devices that are capable to do this are called fuel cells. A fuel cell works similar to a battery. It is substantially a battery in which the materials that are being consumed are constantly supplied anew. So far, however, *fuel cells* only work with very pure, liquid and gaseous fuels and not with coal. In addition, its lifespan is not yet long enough to compete with the conventional power plants.

▬ Exercise ▬▬▬▬▬▬▬▬▬▬▬▬▬▬

1. The reactor in a nuclear power plant releases the created entropy at a temperature of 550 K to the steam that is used to run the turbine. What is the efficiency of the reactor? Compare with a coal-fired power plant that supplies entropy at a temperature of 800 K.

1.16 Measuring entropy

How much entropy is contained in 2 kg of iron, 3 mol of sodium chloride, 0.5 liters of water at a normal temperature? A simple method to answer this
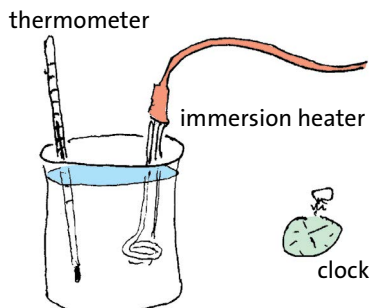
Fig. 1.44 To measure the entropy, we need a heater (e.g. immersion heater), a thermometer and a clock.

question: looking it up in a table. In the table, we find the values for 1 kg or for 1 mol or for 1 liter. We multiply with the mass, the quantity of substance (= number of moles) or the volume and obtain the desired value. Maybe you are not satisfied with such an answer though. How were the figures from the table established? It must be measurable somehow. This is the topic we will explore in the following.

We start with a method that does not yet solve the problem completely. At first, we hold back our expectations a bit and do not ask questions about the overall entropy contained in an object, but only about the change of the entropy content when the temperature of the object changes. Consequently, there is –for instance– the following measurement task:

In front of us, there is a recipient with 10 liters of water at 10 °C and another one with 10 liters of water at 50 °C. How much more entropy is contained in the warm water compared to the cold one? The measurement principle is as follows: start with 10 liters of water at 10 °C and heat it up to 50 °C, e.g. with an immersion heater. Measure the entropy ΔS that you supply during heat-up, Fig. 1.44.

How do we obtain ΔS? From equation (1.1), we get

$$\Delta S = I_S \cdot \Delta t \tag{1.19}$$

Hence, we need to measure the intensity of the entropy current I_S, which we use for heating, and the time Δt that we need for the heatup.

The following heat-up time is measured in our case:

$$\Delta t = 2\,100 \text{ s}.$$

We obtain I_S from the energy current and the temperature:

$$I_S = \frac{P}{T}.$$

Let us assume that we heat up the water with a 800 W immersion heater. (We should check whether the immersion heater really supplies 800 W. The indication on the device is generally not very accurate.) Hence,

$$P = 800 \text{ W} .$$

To calculate I_S, we need to divide P by the temperature. However, the temperature changes during the heat-up. This means that also the entropy current will change. At the beginning of the heating process, the entropy current is greater than at the end, see Table 1.5. To calculate the entropy ΔS supplied in total, we consequently first determine the average value of I_S.

$$\overline{I}_S = \frac{2.84 + 2.48}{2} \text{Ct/s} = 2.66 \text{Ct/s}.$$

Using equation (1.19) we obtain the entropy:

$$\Delta S = I_S \cdot \Delta t = 2.66 \text{ Ct/s} \cdot 2100 \text{ s} = 5586 \text{ Ct}.$$

The measurement you have just learned about is so simple that it can be realized with household equipment: a clock, a thermometer and an immersion heater.

When using this method to calculate ΔS, we made an assumption that is fulfilled only approximately: to determine the time average of I_S, we simply calculated the average of the initial and the final value. However, this will give the time average only if the change of I_S between these two points is linear in time. In the small temperature range from 283 K to 323 K, this condition is fairly met. If we were to determine ΔS with greater accuracy, we could do the following: we divide the total heat-up time Δt into many small, equal time intervals and measure the temperature for each of these time intervals. We then calculate the average entropy current for each time interval, from temperature and energy current, and subsequently the entropy supplied in the time interval. Finally, we add up all these entropy values.

We would like to apply the method to our 10 liters of water. Starting from water with a temperature of 10 °C, we measure the temperature in intervals of 5 min = 300 s; see first and second columns of Table 1.6.

With $I_S = P/T$, we calculate the entropy current at the different instants of time, Column 3. Next, we calculate the average value of I_S, from the initial and final value of each of the 7 time intervals, Column 4. Column 5 contains the entropy supplied during the time

ϑ in °C	T in K	P in W	$I_S = P/T$ in Ct/s
10	283	800	2.84
50	323	800	2.48

Table 1.5 Current of entropy of an immersion heater at 10 °C and at 50 °C

t in s	T in K	I_S in Ct/s	$\overline{I}_S$ in Ct/s	ΔS_i in Ct
0	283.0	2.83		
			2.80	840
300	288.7	2.77		
			2.745	823
600	294.5	2.72		
			2.69	807
900	300.2	2.66		
			2.635	790
1200	306.0	2.61		
			2.59	777
1500	311.7	2.57		
			2.545	764
1800	317.4	2.52		
			2.50	750
2100	323.2	2.48		
				ΔS = 5551 Ct

Table 1.6 Table of values to measure the entropy

interval ΔS_i . The sum of all these entropy contributions is the total entropy that has been supplied, in our case:

$$\Delta S = \sum_i \Delta S_i = 5551 \text{ Ct}.$$

The deviation from the value that we have obtained with the simplified method (5586 Ct) is less than 1 %, i.e. very small.

The total entropy contained in an object can be measured, in principle, in the same way, although the procedure is technically much more demanding. Imagine what it would be like to determine the total entropy that is contained in a piece of copper at 20 °C.

One would proceed as follows:
1) The piece of copper is cooled down to 0 K.
2) Then, it is heated up to 20 °C = 293 K and the entropy, which is supplied in the process, is measured.

Step 1) is technically difficult because it requires a very expensive "refrigerating machine" (= heat pump).

It is easier to explain the entropy measurement, if differential and integral calculus are available. If you know them, please keep reading. If not, skip the rest of this section.

Since the entropy current is equivalent to the time derivative of the amount of entropy, i.e.

$$I_S(t) = \frac{dS(t)}{dt}$$

the entropy can be obtained by integrating over the entropy current:

$$S(t_2) - S(t_1) = \int_{t_1}^{t_2} I_S(t)dt.$$

We insert

$$I_S(t) = \frac{P}{T(t)}$$

and obtain

$$S(t_2) - S(t_1) = P\int_{t_1}^{t_2} \frac{dt}{T(t)}.$$

Hence, the function $T(t)$ must be measured, i.e. the temperature as a function of time. The integration can be done by a computer.

Exercises

1. Measure the entropy that needs to be supplied to one liter of water in order to raise its temperature from 50 °C to 60 °C. Repeat the experiment with salt water (20 g/liter).
2. Suggestion for an entropy measurement method: the meter is a recipient filled with water that ends with a small tube at the top, Fig. 1.45. The higher the water level in the tube, the more entropy is contained in the water. The device is calibrated in a way that the entropy contained in the water can be read from the water level. Now, the entropy that is needed to increase the temperature of a given object from 30 °C to 100 °C is to be measured. The measurement is started by heating the object up to 100 °C. Then, it is brought in thermal contact with the calibrated entropy meter until its temperature has decreased to 30 °C. The entropy difference is read on the tube of the entropy meter. What is the inherent disadvantage of the method?

1.17 The heatability

The entropy contained in a body depends on:
1. the mass of the body;
2. the temperature of the body;
3. the material the body is made of.

We would like to examine these three dependencies. We start with the relation between entropy and temperature. If entropy is supplied to a body, its temperature will increase. This applied at least for the objects we have seen so far. The relation between the entropy content and the temperature, however, is not linear as we might hope or assume. The T-S graph has a complicated shape and is even different for each substance. Fig. 1.46 shows the T-S relation for 1 mol of copper as an example.
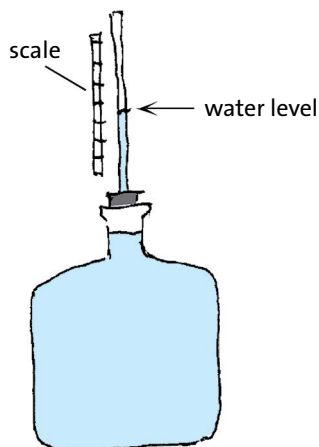
Fig. 1.45 Suggestion for an entropy meter. Why does the device not work well?

The steeper the curve of the T-S diagram, the smaller the entropy needed to achieve a given temperature increase, i.e. the easier is it to heat up the substance.

Fig. 1.47 shows the curve for 1 mol of water. This water graph contains two horizontal sections. These are the areas in which the water changes its state of aggregation, or its "phase". We will analyze such processes in greater detail later.
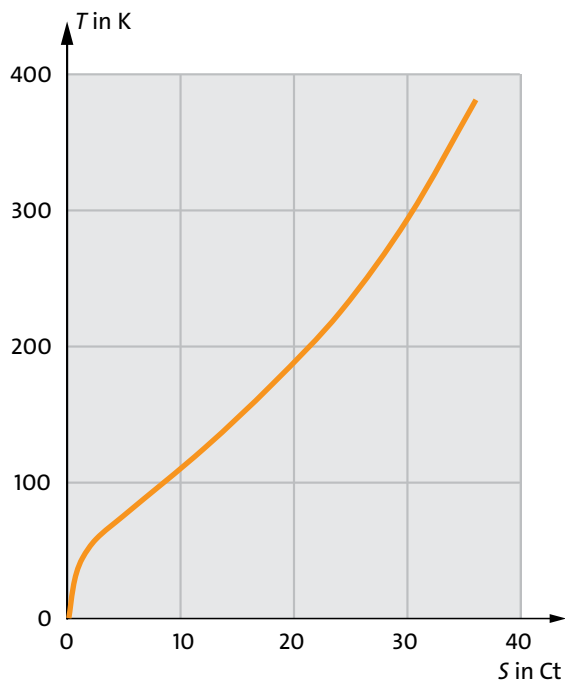
Fig. 1.46 T-S relation for 1 mol of copper
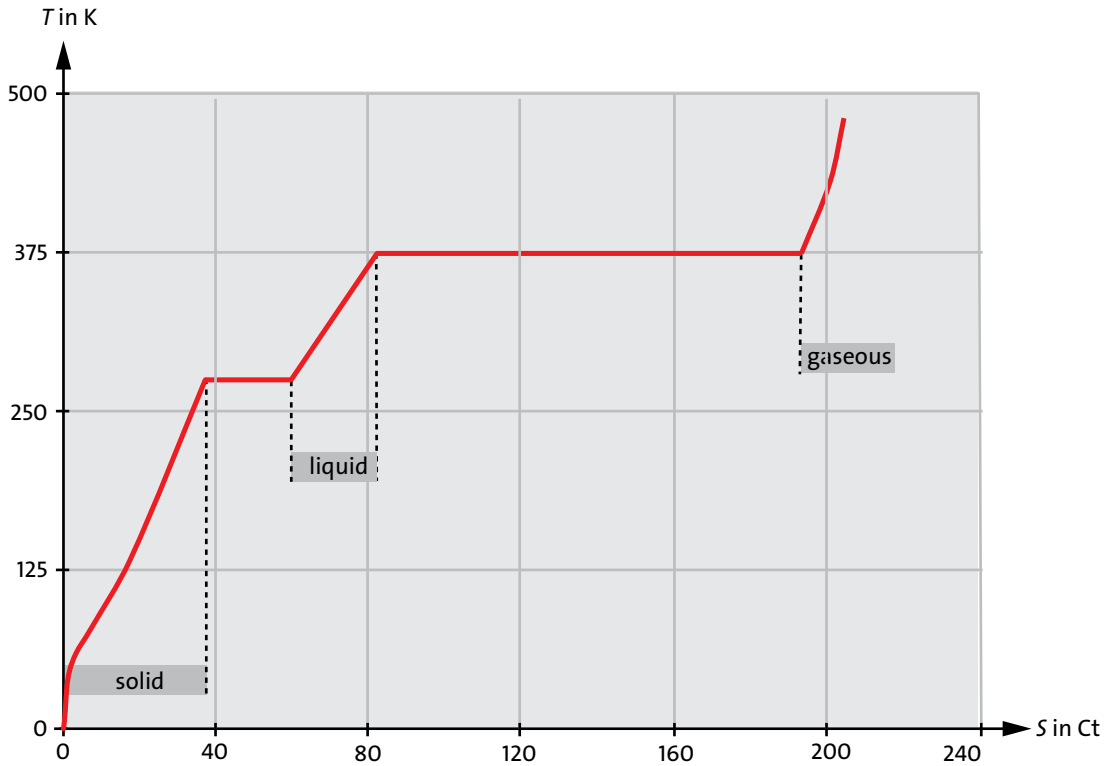
Fig. 1.47 *T-S* diagram for 1 mol of water
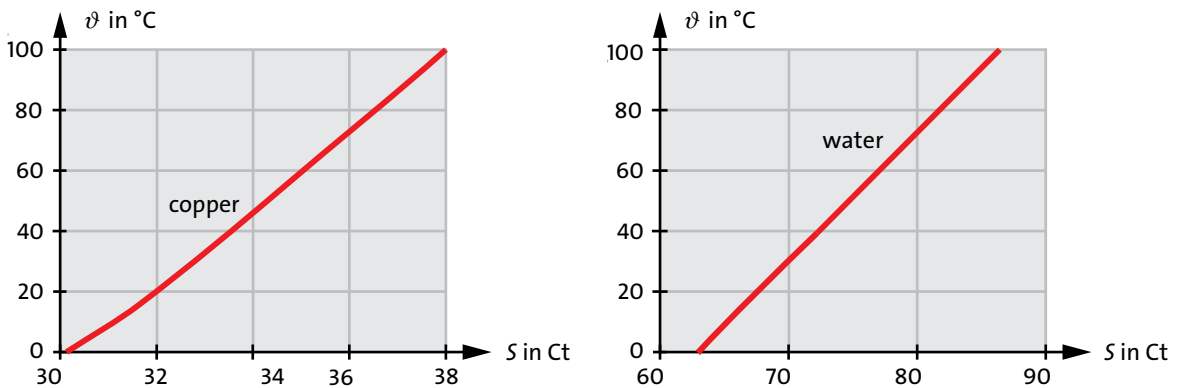
Fig. 1.48 *T-S* relationship for 1 mol of copper and 1 mol of water. The entropy scales do not start with the value *S* = 0 Ct. The temperature scales do not start with the absolute zero point but with the zero point of the Celsius scale.

If we only look at what happens in the normal ambient temperature range, a diagram whose temperature axis does not start at 0 K will be more helpful: an enlarged section of the previous figures. Fig. 1.48 shows such diagrams for 1 mol of copper and 1 mol of water.

As the relation between entropy increase and temperature change is nearly linear in the range of ambient temperature, we can write:

$$\Delta S \sim \Delta T \tag{1.20}$$

Now, let us talk about the entropy as a function of the mass of the body. Since a piece of iron of 2 kg contains twice as much entropy as a piece of iron of 1 kg (provided that the temperatures are equal), we can write

$$S \sim m$$

From this, we conclude that the entropy portion ΔS, that is needed to increase the temperature by ΔT, is also proportional to m:

$$\Delta S \sim m \qquad (1.21)$$

Here, we have indicated the amount of iron in kg, i.e. we have used the mass as a measure of the amount of iron. However, there are other possibilities to measure the amount of a substance. From everyday life you know that an amount of something is sometimes indicated in liters (e.g. when you buy milk or gasoline) and sometimes in pieces (when you buy melons or cabbage). The respective physical quantities are the volume V and the amount of substance n. (The SI unit of amount of substance is the mol. 1 mol $= 6.022 \cdot 10^{23}$ pieces.)

For our comparison of temperature changes during the supply of entropy, the amount of substance is more suitable than the mass. The reason will be explained later. However, we would like to switch from mass to amount of substance already now. As mass and amount of substance are proportional to each other for a given substance, we can simply replace m by n in (1.21):

$$\Delta S \sim n \qquad (1.22)$$

Now we merge the two proportionalities (1.20) and (1.22) into a single one:

$$\Delta S \sim n \cdot \Delta T$$

and divide by n:

$$\Delta T \sim \frac{\Delta S}{n}.$$

In words: the temperature increase is proportional to the entropy supplied per amount of substance.

The proportionality will become an equation if a proportionality factor is introduced:

$$\Delta T = \alpha \frac{\Delta S}{n}. \qquad (1.23)$$

α is a physical quantity that characterizes the material. A great value of α means that the material reacts to the entropy supply with a high temperature increase. A small α means that the material is difficult to heat up. Hence, we call α the *heatability*.

We now bring α on one side:

$$\alpha = n \frac{\Delta T}{\Delta S}. \qquad (1.24)$$

In the T-S diagram for 1 mol, α indicates the slope of the curve. This does not only apply for the case where the correlation is linear, such as in Fig. 1.48, but also at each point of Figures 1.46 and 1.47. Therefore, the heatability of a substance can change from one temperature to the other.

Table 1.7 shows a list of the α values for different substances at normal temperature. It is seen from the table that the heatabilities of the metals are nearly equal although their other properties, such as density or heat conductivity, are very different from each other. We now understand why it was clever to use the quantity "amount of substance" as a measure for the amount of the substances: if equation (1.24) contained the mass instead of the amount of substance, the heatability defined in this way would vary greatly from one metal to the other.

At the end of this section, we will come back to the different possibilities to indicate the amount of copper, water, sulfur, sugar, etc. We got to know three measures for the amount:
- mass m (measuring unit: kg)
- volume V (measuring unit: m^3)
- amount of substance n (measuring unit: mol)

There is often the problem of converting one measure into another.

The conversion of volume to mass and vice versa is done with recourse to the *density ρ*:

$$\rho = \frac{m}{V}.$$

Hence,

substance	α in mol·K/Ct	ρ in g/cm^3	M in g/ mol
Al	11.93	2.7	27.0
Ag	11.55	10.4	107.9
Au	11.53	19.3	197.0
Cu	12.11	8.96	63.5
Fe	11.67	7.86	55.8
Na	10.44	0.97	23.0
Pb	10.96	11.34	207.2
Si	14.65	2.42	28.1
water	3.89	1.00	18.0
ethanol	2.62	0.789	46.0

Table 1.7 Heatability, density and molar mass of some substances at normal temperature

$$m = \rho \cdot V$$

The conversion of amount of substance to mass and vice versa is done with recourse to the *molar mass M*:

$$M = \frac{m}{n}.$$

Therefore,

$$m = M \cdot n \qquad (1.25)$$

The molar mass of the elements is usually indicated in the periodic table of the elements. We have also listed the density and the molar mass in Table 1.7.

— Exercises —

1. Read the heatability of copper at 100 K and at 300 K from Fig. 1.46.
2. What is the heatability of water at point P in Fig. 1.47? Try to explain.
3. 80 Ct are added respectively to one kilogram of copper and to one kilogram of aluminum with an initial temperature of 20 °C. By how much will the heat of the two metals increase? By which factor do the temperature changes differ? (For α, use the value at normal temperature.)
4. How much entropy is needed to heat up 100 l of water from 20 °C to 100 °C? (For α, use the value at normal temperature.)

1.18 The relation between energy supply and temperature change

Whenever we want to heat up water, entropy must be added. Together with the entropy, however, energy will flow into the water because every current of entropy is accompanied by an energy current. The relation between the currents of energy and entropy is

$$P = T \cdot I_S$$

If we insert

$$P = \frac{\Delta E}{\Delta t}$$

and

$$I_S = \frac{\Delta S}{\Delta t}$$

and multiply by Δt we obtain

$$\Delta E = T \cdot \Delta S \qquad (1.26)$$

Together with the portion of entropy ΔS, we add a portion of energy $T \cdot \Delta S$ to the water.

Most people probably know that energy is needed to heat something up: we know that heating up water costs money and that this money is paid for energy.

In the following, we will determine the energy that is needed to heat up 1 kg of water in order to raise its temperature by 1 °C. In mathematical symbols:

$$\frac{\Delta E}{m \cdot \Delta T}$$

We insert equations (1.26), (1.25) and (1.24):

$$\frac{\Delta E}{m \cdot \Delta T} = \frac{T \cdot \Delta S}{m \cdot \Delta T} = \frac{T \cdot \Delta S}{n \cdot M \cdot \Delta T} = \frac{T}{M \cdot \alpha}.$$

With

$T = 293$ K,
$M = 0.018$ kg/mol
$\alpha = 3.89$ mol·K/Ct

we obtain

$$\frac{\Delta E}{m \cdot \Delta T} = \frac{293 \text{ K}}{0.018 \dfrac{\text{kg}}{\text{mol}} \cdot 3.89 \dfrac{\text{mol} \cdot \text{K}}{\text{Ct}}}$$

$$= 4180 \frac{\text{J}}{\text{kg} \cdot \text{K}}.$$

The result can also be written as follows:

$$\Delta E = c \cdot m \cdot \Delta T$$

with

$$c = 4180 \frac{\text{J}}{\text{kg} \cdot \text{K}}.$$

The equation allows us to calculate the energy ΔE that must be added to water of mass m in order to raise its temperature by ΔT. It is valid for temperatures around ambient temperature, i.e. 20 °C. However, it is sufficiently accurate for the whole range of liquid water, i.e. from 0 °C to 10 °C, for many purposes.

c is called the *specific heat capacity* of the examined substance. Of course, we could have calculated c for any other substance as well.

1.18 The relation between energy supply and temperature change

▬ Exercises ▬

1. Half a liter of water should be heated up from 25 °C to 100 °C with a 500 W immersion heater. How much time is needed?

2. What is the energy consumption for a shower of five minutes? Calculate first how many liters of hot water are approximately consumed during the 5 minutes. Assume that 0.1 l of water flow out of the tap per second during the shower. Also assume that the water flows into the hot boiler at a temperature of 15 °C and comes back out of it at 45 °C.

3. Calculate the specific heat capacity of copper. (Use values from Table 1.7.)

4. The warm water tap is open. Which costs are higher: the water bill or the energy charges?

5. 0.1 liters of water flow through a solar collector of 20 m^2 per second. The collector collects 200 W per m^2. By how many °C will the water heat up while flowing through the collector?

2 GASES

2.1 Gases and condensed substances

Substances can be solid, liquid or gaseous.

The liquid and the gaseous phase have something in common: both liquid and gaseous substances can flow. When there is wind, or when a ventilator or a hair dryer runs, air is flowing. Water flows in rivers and streams, in the seas and of course as soon as the tap is opened. As liquid and gas flows have much in common, liquids and gases are sometimes summarized as a single class of substances: they are called *fluids*. Consequently, fluids are the opposite of solid substances.

On the other hand, there are also some common features of solid and liquid substances. Properties that distinguish them from the gases. Liquid and solid substances have a much higher density than gases. Consequently, solid and liquid substances are also summarized as one class: they are called *condensed substances*. Condensed substances are the opposite of the gases, Fig. 2.1.

In the following, we want to look at further properties that distinguish the gases from the condensed substances.

The tendency to disperse

We pump the air out of a glass recipient and let some water drop into it, Fig. 2.2. The water falls to the bottom, just like in a nonevacuated recipient. We repeat the experiment but let air enter the recipient instead of water. In order to see where the air goes, we first let it flow through a cigarette. (You see, cigarettes can even be helpful.)
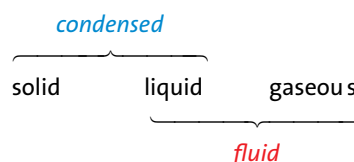
Fig. 2.1 Two types of classification of substances
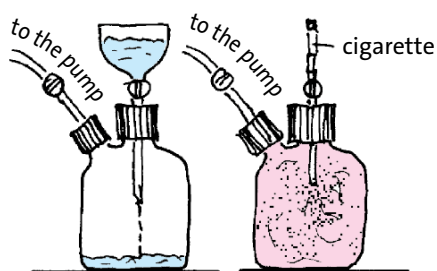
Fig. 2.2 Gases spread out and take up the whole available space. Liquids do not.

These experiments show:

Gases fill the entire space available to them, condensed substances do not.

To summarize something with a short formula, simplifications are often necessary. The sentence above is such a simplification. It applies for most cases, but not always. For example, it is not valid for the air above the surface of the Earth seen as a whole. In theory, this air could disperse into all of outer space but it does not leave the Earth. Why?

Compressibility

There is air in a cylindrical recipient with a movable piston. If the piston is pushed into the cylinder, the air will be compressed, Fig. 2.3a. If, however, there is water in the cylinder instead of air, Fig. 2.3b, the piston cannot be pushed inside; water is not compressible. By taking a closer look, we can observe a change of the volume for water, which can be neglected for many practical purposes though.

Even if a solid body can be put into the cylinder together with the water, Fig. 2.3c, the piston cannot be moved because solid bodies are (almost) not compressible either. Some solid bodies give us the impression that they would be easy to compress, foam for example. However, what is actually compressed in case of the latter is not the solid material itself, but only the air in its pores.

We can summarize our observations as follows:

Gases can be compressed, condensed substances hardly at all.

Compression means reducing the volume of a determined portion of substance while keeping its mass constant. Consequently, the formula $\rho = m/V$ implies that the density of the material increases through compression. It is possible to increase the density of a compressible substance by raising the pressure. If a substance is incompressible, raising the pressure will not result in any change of density. We can summarize this as follows:

The density of gases increases with increasing pressure, the density of condensed substances does (almost) not.

This fact has interesting consequences, for example: the density of the water in a lake hardly increases towards the bottom in spite of an increased pressure. The density of the water is practically the same at all levels of depth, i.e. 1000 kg/m^3. A very different behavior can be observed in the air above the surface of the Earth. The pressure decreases in an upward direction, and so does the density. This is why breathing becomes increasingly hard when we climb up a mountain.

Thermal expansion

Gases and condensed substances also react differently when entropy is added to them.

If a solid body is heated, its volume will almost not change. The same applies for liquids. Gases, by contrast, behave very differently. If we heat up the air in a
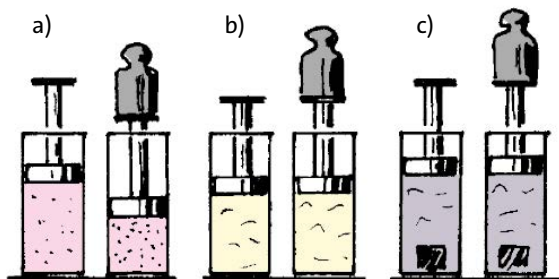
Fig. 2.3 Gases (a) are compressible, liquids (b) and solid substances (c) are not.
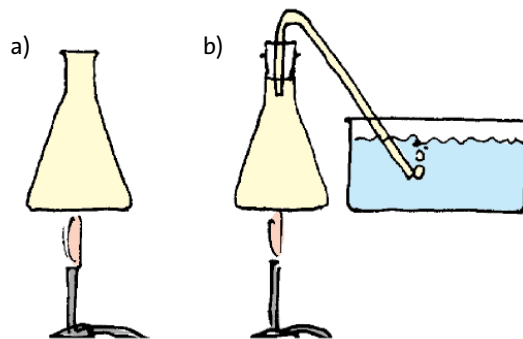
Fig. 2.4 Gases expand when entropy is added to them (a). In the right experiment (b), the overflow of the recipient is visualized.

recipient that is open at the top, Fig. 2.4a, it will greatly expand and "overflow". Since air is invisible, this overflow cannot be seen. With an easy trick, it can be visualized though, Fig. 2.4b.

Gases expand as entropy is supplied; condensed substances only expand very little.

To analyze and describe gases, we need the following physical quantities:
- volume V,
- pressure p,
- entropy S,
- temperature T.

Pressure and volume are physical quantities that are normally used in mechanics. Hence, we will use the two mechanical quantities V and p, and the two thermal quantities S and T, in the following.

The last emphasized sentence can also be written as follows: in gases, the mechanical and thermal quantities influence each other. This property makes them particularly interesting for physicists.

It is not always easy to get an overview of the relationships between four different physical quantities. We will only make a first step in the following section:

we will explore qualitative relationships. Consequently, we will not ask for the corresponding mathematical formulas. Instead, we will only ask questions like this one: if the volume is kept constant and entropy is added to the gas, will the temperature increase or decrease, and will the pressure increase or decrease?

Such questions can be answered relatively easily. Only in the subsequent section, we will include a quantitative, i.e. mathematical, description.

=== **Exercises** ===

1. Why do bicycles have tires filled with air? Why are the tires not filled with water?
2. Fig. 2.5 shows a hot-air balloon. The balloon is open at the bottom. The air in the balloon is heated by means of a gas flame. Why does the balloon rise?

Fig. 2.5 Hot-air balloon (For Exercise 2)

2.2 Qualitative relationships between *S*, *T*, *V* and *p*
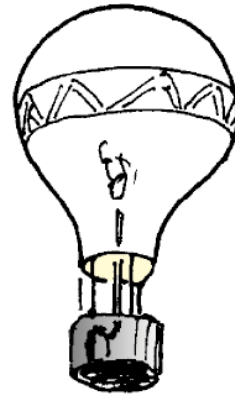
Prior to looking at the interaction of mechanical and thermal quantities, we need to formulate a rule. We experiment with a certain amount of a gas. We can ensure that the gas will have a given temperature, e.g. 320 K, and a given volume, e.g. 12 liters, that it will have a given pressure, e.g. 2.5 bar or that it will contain a given amount of entropy, e.g. 8.2 Ct.

How many of these values can be fixed at the same time? Couldn't it be that pressure, volume and temperature are defined unambiguously as soon as we have decided, that the gas should contain an entropy of 8.2 Ct? Or can we adjust the values of all four physical quantities arbitrarily? We find the answer by looking at a precise example.

We fill a defined quantity of gas into a recipient whose volume can be changed: a cylinder with an movable piston. In addition, it is possible to heat up the, i.e. to supply entropy to it. At the beginning, all four quantities have any values. Now, we would like to change these values.

Let us assume that the gas has an initial volume of 9 liters but we would like it to have $V = 12$ liters. To achieve this, we simply have to move the piston to set the volume to the desired value. Then, the piston will be fixed so that the volume cannot change any more.

But can we still set a value for a second physical quantity? Yes, of course. Assume that the temperature is 310 K but we would like it to be 320 K. We only need to heat a little bit, i.e. to supply entropy, until 320 K is reached.

Being it so simple, we try with a third physical quantity: the pressure is 2 bar, but we want it to be 2.5 bar. How could this value be reached? Either we press the piston a bit further into the cylinder – then, the pressure will grow but the volume will change at the same time (and we do not want it to change) – or we heat a little bit more. The latter will lead to the desired pressure increase but it will lead to an undesired temperature increase. Hence, it is impossible. We cannot choose an arbitrary value for the pressure anymore.

We could have tried all other possibilities. Every time we would have found that: as soon as the values of two physical quantities are defined, the remaining two are also defined. We could also say:

> The state of a gas is defined as soon as the values of two quantities are defined.

"The state is defined" means that "all physical quantities have well-determined values".

In the following, we will examine a series of processes, i.e. transitions from one state to another. To keep the processes simple and clear, we work through the following steps:
- 1. We keep one of the four physical quantities constant. (Hence, we determine the value of one of the four quantities.)
- 2. We change a second one of the four quantities. (Hence, we dispose of a second one of the four quantities.)
- 3. and 4. We observe how the values of the two remaining quantities behave. Will they increase or decrease?

2.2 Qualitative relationships between S, T, V and p

Process with constant pressure (Fig. 2.6)

What we do:
- 1. We keep the pressure constant by means of the weight on the piston.
- 2. We increase the entropy content through heating.

What we observe:
- 3. The temperature increases.
- 4. The gas expands, i.e. its volume increases.

Process with constant volume (Fig. 2.7)

What we do:
- 1. We keep the volume constant by using a recipient with a fixed volume.
- 2. We increase the entropy content through heating.

What we observe:
- 3. The temperature increases.
- 4. The pressure of the gas increases.

Process with constant temperature (Fig. 2.8)

What we do:
- 1. We keep the temperature constant.
- 2. We reduce the volume by moving the piston.

Under normal conditions, the compression would cause a temperature increase. However, if we press very slowly and if the gas is not thermally insulated from the environment, the temperature of the gas can constantly balance with the ambient: entropy will flow from the gas to the ambient. Therefore, at the end there will be less entropy in the gas than before.

What we observe:
- 3. The pressure increases.
- 4. The entropy decreases.

Process with constant entropy (Fig. 2.9)

What we do:
- 1. We keep the entropy constant.
- 2. We reduce the volume by moving the piston (compression of the gas).

To keep the entropy constant during compression, the cylinder must be equipped with a good thermal insulation and the compression must be done fast. This way, the entropy has no time to escape to the ambient.

Fig. 2.6 If entropy is supplied to a gas at constant pressure, it will expand.

Fig. 2.7 If entropy is supplied to a gas at constant volume, its pressure increases.

Fig. 2.8 If a gas is compressed at constant temperature, its entropy content will decrease.
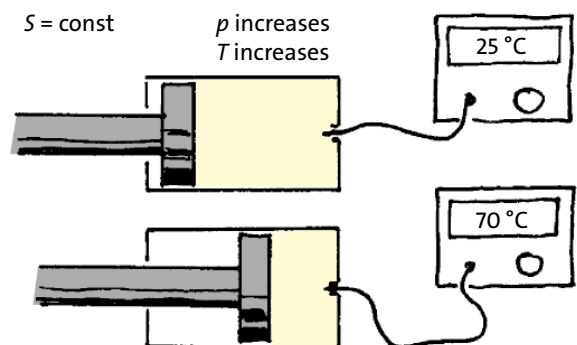
Fig. 2.9 If a gas is compressed at constant entropy, its temperature will increase.

What we observe:
- 3. The pressure increases.
- 4. The temperature increases.

This behavior of the air is plausible: the compression also entails the compression of the entropy that is contained in the air, i.e. its concentration to a smaller space. Much entropy in a small space translates into a high temperature though.

We can express these results symbolically by indicating for each physical quantity whether its values decrease, remain constant or increase.

The lines of Table 2.1 describe four different processes that can be realized with gases.

Of course, these statements also apply in a reverse order. The reversal of the first line is:

p = const $S\downarrow$ $T\downarrow$ $V\downarrow$

■ Exercises

1. We need: a bottle that can be tightly closed and a bowl with warm water and another one with cold water (you can use the two sections of the kitchen sink). (a) The air in the open bottle is cooled by means of the cold water. The bottle is closed and pushed under water in the hot water bowl. The lid of the bottle is slightly loosened so that it does not seal the bottle completely anymore. What happens? Explanation? (b) The air in the open bottle is heated by means of the hot water. The bottle is closed and pushed under water in the cold water bowl. The lid of the bottle is slightly loosened. What happens? Explanation?
2. Two recipients contain an equal quantity of the same gases at the same temperature. Now, the same quantity of entropy is added to both gases. In one, the volume is kept constant, in the other the pressure. Are the temperature changes equal for both gases? If not, which gas has the greater temperature change? Does the temperature increase or decrease? Explain!
3. How can we make the temperature of a gas decrease although entropy is supplied?

2.3 Quantitative relations between *S, T, V* and *p*

The complete relationships between all four physical quantities are complicated and somewhat confusing. Instead of analyzing them systematically, we take a different path: we limit our efforts to the relationships that can be measured easily.

1. The gas law

Three of our four quantities are particularly easy to measure: the temperature with a thermometer, the pressure with a manometer and the volume with a ruler. Hence, it is also particularly easy to determine the quantitative relationship between these three quantities in an experiment.

The result could not be simpler:

$$p \cdot V = n \cdot R \cdot T$$

We will to discuss the gas law step by step.

1. On the right side, there is a measure of quantity: the amount of substance n. This is logical because there is also a measure of quantity on the left side: the volume. If we produce a "copy" of a given amount of a gas and place it next to the initial one, the quantities pressure and temperature will not change, but the volume on the left side of the equation will double. Hence, in order to double the right side as well, there must also be a measure of a quantity.

2. R is a physical constant. It amounts to

$$R = 8.3144 \ \text{Ct/mol}.$$

We could have expected the equation to contain a "constant" that has a different value for each kinds of gases. The fact that this is not the case reflects the fact that this equation is a very fundamental one.

3. The relationship between T and V, as well as between T and p is the simplest one we can think of: it is linear.

We would like to see what the gas equation tells us about the processes that we have discussed in qualitative terms in the previous section.

We always tag the values of the physical quantities in their initial state with the index 0; in the final state, they do not have an index.

Initial state: $p_0 \cdot V_0 = n \cdot R \cdot T_0$ (a)
Final state: $p \cdot V = n \cdot R \cdot T$ (b)

Our first process was "heating at constant pressure", Fig. 2.6. The condition of maintaining the pressure constant is taken into account by writing p_0 also in the

p = const	$S\uparrow$	$T\uparrow$	$V\uparrow$
V = const	$S\uparrow$	$T\uparrow$	$p\uparrow$
T = const	$V\downarrow$	$p\uparrow$	$S\downarrow$
S = const	$V\downarrow$	$p\uparrow$	$T\uparrow$

Table 2.1

2.3 Quantitative relations between S, T, V and p

	β
Air	0.4
Steam	0.3
Carbon dioxide	0.29
Helium	0.63

Table 2.2

equation for the final state.

Consequently, equations (a) and (b) become now:

Initial state: $\quad p_0 \cdot V_0 = n \cdot R \cdot T_0$ (a)
Final state: $\quad\ \ p_0 \cdot V = n \cdot R \cdot T$ (b)

We divide equation (b) by equation (a) and obtain:

$$\frac{V}{V_0} = \frac{T}{T_0} \text{ if } p = const$$

In words:

> At constant pressure, the volume is proportional to the temperature.

Our second process was "heating at constant volume", Fig. 2.7. The condition of maintaining a constant volume is taken into account by setting $V = V_0$ in our equation for the final state. Equations (a) and (b) now become:

Initial state: $\quad p_0 \cdot V_0 = n \cdot R \cdot T_0$ (a)
Final state: $\quad\ \ p \cdot V_0 = n \cdot R \cdot T$ (b)

We divide equation (b) by equation (a) and obtain:

$$\frac{p}{p_0} = \frac{T}{T_0} \text{ if } V = const$$

In words:

> At constant volume, the pressure is proportional to the temperature.

The third process was a compression at constant temperature, Fig. 2.8. The condition of maintaining a constant temperature is taken into account by writing $T = T_0$ in the equation for the final state. Equations (a) and (b) are read now:

Initial state: $\quad p_0 \cdot V_0 = n \cdot R \cdot T_0$ (a)
Final state: $\quad\ \ p \cdot V = n \cdot R \cdot T_0$ (b)

Now the right side of (a) is equal to the right side of (b). Hence, the left sides are also equal:

$p \cdot V = p_0 \cdot V_0$ if $T = const$.
In words:

> At constant temperature, the product of pressure and volume is constant.

4. Finally yet a simple rule: by inserting 1 mol for the amount of substance in the gas equation, and 1 bar = 10^5 Pa and 25 °C = 298 K for pressure and temperature, we can calculate the volume:

$$V = \frac{n \cdot R \cdot T}{p} = \frac{1 \text{ mol} \cdot 8.3144 \text{ Ct/mol} \cdot 298 \text{ K}}{100\,000 \text{ Pa}}$$

$$= 0.02478 \text{ m}^3 \approx 25 \text{ Liter}$$

> One mol of any gas has a volume of 25 liters at $p = 1$ bar and $T = 298$ K.

2. Processes with constant entropy

Keeping the entropy constant is not difficult in principle: we must be careful that no entropy can flow in from outside or flow out from inside by means of a good thermal insulation of the container of the gas. However, precisely this can be a practical problem. Moreover, we need to ensure that the entropy generated by friction will be kept at a minimum. If all this is considered, we will find

$$\frac{T}{T_0} = \left(\frac{V_0}{V}\right)^{\beta} \text{ if } S = const \qquad (2.1)$$

where the exponent β is a material constant. However, the value of β does not change significantly from one material to another, Table 2.2.

Equation (2.1) tells us how the temperature of a gas increases when it is compressed and the entropy is maintained constant.

By means of the gas law

$$p \cdot V = n \cdot R \cdot T$$

another interesting equation can be derived from (2.1) (Exercise 7):

$$\frac{T}{T_0} = \left(\frac{p}{p_0}\right)^{\frac{\beta}{\beta+1}} \text{ if } S = const \qquad (2.2)$$

It tells us how the temperature increases when the pressure is increased and the entropy is kept constant.

Fig. 2.10 shows the *V-T*-relationship and the *p-T*-relationship for air.

Exercises

1. The air in a spherical hot-air balloon with a diameter of 12 m is heated to 200 °C. It still floats above the surface of the Earth. (The density of the air is 1.29 kg/m³.) The outside temperature is 20 °C. What is the overall mass of the balloon and the passengers?
2. A 10 liter gas bottle contains hydrogen. The manometer indicates a pressure of 90 bar. Its temperature is always 25 °C. How much hydrogen is left in the bottle? Indicate the result (a) in liters at 90 bar; (b) in liters, after the pressure of the hydrogen is reduced to normal pressure; (c) in kg; (d) in mol.
3. Use a quantitative approach to answer question 1 from section 2.2. Assume that the temperature of the cold water is 15 °C and that of the warm water is 40 °C. The bottle has a volume of 1 liter. What is the excess pressure or negative pressure? Which percentage of the air flows out, and how many ml of water flow in?
4. A car tire with a volume of 8 liters was pumped up so that the air pressure amounts to 3 bar. (Caution: not an excess pressure of 3 bar). The temperature is 20 °C. When driving, the air in the tire heats up to 80 °C. What will be its pressure?
5. Your living room is heated from 15 °C to 22 °C. How much air flows out in the process?
6. Steam with a temperature of 400 °C and a pressure of 15 bar flows into a steam turbine. In the turbine it expands to 2 bar. At which temperature will the steam leave the turbine?
7. Derive equation (2.2) from equation (2.1), making use of the gas law. $R = 8.3144$ Ct/mol.

Fig. 2.10 During expansion (increasing volume, decreasing pressure), the temperature of the air decreases. During compression, it increases. Upper: temperature as a function of the volume. Lower: temperature as a function of the pressure.

2.4 The operating mode of thermal engines

We learned in section 1.12 that in a thermal engine entropy goes from a high to a low temperature while it "drives" something – just as water in a water turbine goes from a high to a low pressure while driving something.

Though, how is it possible to bring entropy from a high to a low temperature in order to set something in motion?

Bringing entropy from a high to a low temperature without driving anything is no problem. It mostly happens all by itself: we simply let the entropy "slide down" from the high to the low temperature through a heat conductor (see also section 1.11). The energy that one would like to transfer to a useful energy carrier, angular momentum, for example, goes away along with the newly produced entropy. It is wasted.

How do we then bring entropy from the high to the low temperature without producing new entropy?

Fig. 2.11 (a) Entropy is introduced into a compressed gas. (b) The gas expands, its temperature goes down and it supplies energy. (c) The entropy is given away at a lower temperature.

Since we have learned about the thermal properties of gases, this is no problem for us anymore. Fig. 2.11 shows how it can be done.

2.4 The operating mode of thermal engines

The entropy is brought into a compressed gas. Then, the gas can expand. The process is the reversal of the one from line (4) in Table 2.1: the piston is pushed outwards, i.e. the volume increases. According to Table 2.1, the temperature decreases in the process. The energy, that is released by the gas, flows away through the piston rod and to a crank that causes the rotation of a shaft.

> A gas is allowed to expand in a heat engine. In the process, the pressure and temperature of the gas go down and the gas supplies energy.

This is the basic idea behind all heat engines. There are a number of various technical implementations of this idea: steam engines, steam turbines, gasoline engines, diesel motors, jet engines, and more.

We will take a closer look at two of these machines: first, the piston steam engine, because it has played an important role in the past; and second, the gasoline engine, because most of the cars are driven by it.

The steam engine

The biggest problem to be solved in the realization of a machine built upon the principle of Fig. 2.11, is getting the entropy into and out of the machine *quickly*. It will work by no means as implied by Fig. 2.11, i.e. by letting the entropy flow into the working cylinder by means of conventional heat conduction. This process would be much too slow. However, we already know a trick to transport entropy quickly from one place to another: through convection. This is how the steam engine works.

The gas is heated up outside the cylinder and then filled into the cylinder. There, it expands and supplies energy to the piston at the same time. Then, it is let out of the cylinder again.

Fig. 2.12 shows the details of this process for a steam engine.

Steam is used as a working gas. The steam is generated in the boiler and subsequently "overheated". The steam input and output of the cylinder is controlled by the slide valve (not shown in Fig. 2.12). The piston is at first located on the very left, image part a. From the left, hot steam flows into the left part of the cylinder. As soon as the piston has moved slightly to the right, image part b, the steam input is closed. The steam pushes the piston further to the right and expands in the process, pressure and temperature decrease. The piston reaches the reversal point on the right, image part c, and starts moving back. In the meantime, the outlet has been opened. The expanded, cooled steam is pushed out along with its entropy.
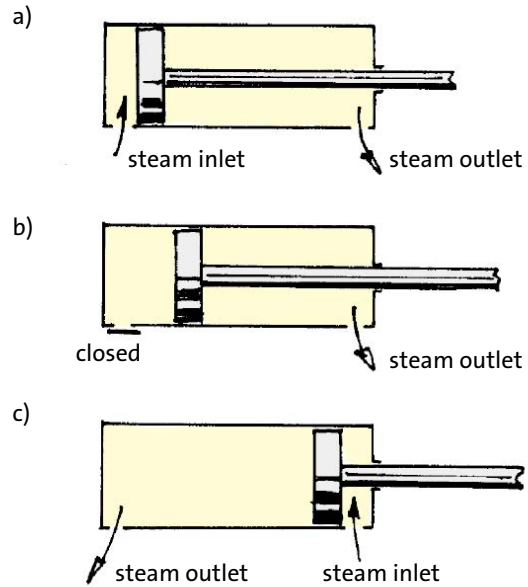
Fig. 2.12 Steam engine at three different times
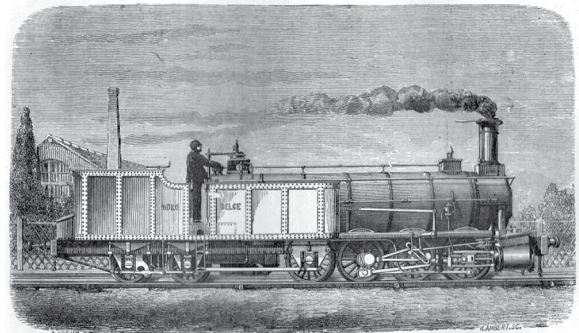
Fig. 2.13 A steam locomotive

The respective processes also occur on the right side of the piston. The steam on the right side pushes the piston to the left.

The parts of such a steam machine are easily recognizable in a steam locomotive, Fig. 2.13.

The gasoline engine

Here, the trick to fill the cylinder fast with entropy consists in creating the entropy in the cylinder itself, through combustion of a mix of gaseous gasoline and air. The combustion is an explosive process, i.e. it is very fast.

Therefore, the cylinder needs to be filled with the inflammable mix of gasoline and air, whereby the piston has to be in a position such that the volume of the gas very small. This is ensured by letting the engine initially work as a pump for one revolution.

Each half revolution of the crank shaft is called a *stroke*. Hence, the charging process of the engine, the

a) intake strole   b) compression stroke   c) firing   d) working stroke e) exhaust stroke

valve

valve

intake

exhaust

charging of the engine
with a mixture of
gasoline and air

Fig. 2.14 An gasoline engine at five phases of its working cycle

pumping process takes two strokes: during the *aspiration stroke*, the mix of gasoline and air is sucked into the cylinder, Fig. 2.14, image part a. In the *compression stroke*, it is compressed, image part b. Now, the piston is located in the upper dead center position and it is ready to work, image part c. The mix of gasoline and air is inflamed by means of an electric spark produced by the ignition plug. It practically burns instantly. Entropy is created during the combustion process. Temperature and pressure strongly increase. Now the hot gas pushes the piston downwards. Temperature and pressure decrease in the process. This stroke is called the *working stroke*, image part d. Then, in the *exhaust stroke*, the exhaust gases are pushed out through the exhaust pipe together with their entropy, image part e.

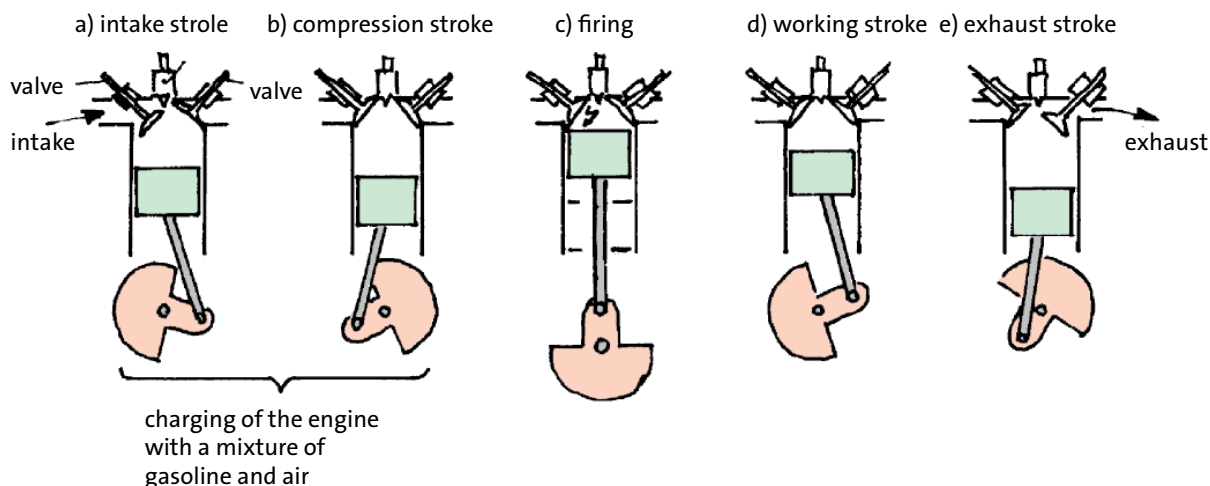Such a single-cylinder engine works, as we can see, only during a quarter of the time, i.e. during the working stroke. During the remaining three strokes, it keeps running thanks to the momentum. A gasoline engine runs "more smoothly" if it has several cylinders that work in an alternating manner. Most car engines have four cylinders. When such an engine runs, one of the cylinders has its working stroke at any moment.

Also, a series of auxiliary devices are part of a gasoline engine:

- the carburetor; it vaporizes the gasoline and mixes it with air;
- the gasoline pump; it transports the gasoline from the tank to the carburetor;
- spark coil and interrupter; they generate the high electric voltage for the ignition spark;
- the ignition distributer; it sets the high voltage each time at the right spark plug.

― Exercises ―

1. Imagine the "working substance" in the heat engine of Fig. 2.11 is not a gas but a liquid. Would the engine work? Give reasons!
2. A diesel engine is built very similarly to an Otto engine. The difference: It has no spark plugs. The diesel fuel/air mixture ignites by itself. How is this possible?
3. Instead of closing the steam inlet of the cylinder of a reciprocating steam engine after it has moved a little to the right, it could be left open until the piston has moved all the way to the right. The engine would be stronger and would give off more energy. This mode of operation is possible in steam locomotives. It is used to start motion and to move uphill. What is the disadvantage of this mode of operation?

2.5 Why the air above the Earth's surface gets cooler with altitude

On a high mountain, it is colder than in the valley. The higher we go up, the lower the temperature becomes. The temperature decreases by approximately 0.6 °C per hundred meters of altitude. On a plane, the impressively low value of the outside temperature is shown on screens. For a plane that flies at an altitude of 10 000 m, the temperature is −55 °C.

How can these low temperatures be explained? Should the temperature difference between above and below not reach an equilibrium? As we know, the entropy flows from places of higher temperature to places of lower temperature. There is still an obstacle though. The entropy will only flow if the thermal resis-

tance is not too great. And air is, as we know, a very good insulation material. A few millimeters of air between the glass panes of a double-glass window are already very effective. Between the upper and the lower part of the Earth's atmosphere, we have an air layer of many kilometers. Consequently, a temperature adjustment based on heat conduction is practically impossible.

But how does the temperature difference come about? We need to use our knowledge of the thermal properties of gases. The air in the Earth's atmosphere is constantly moving. We will learn the reason in the following section. For now, let's just imagine that someone is constantly stirring the air.

We look at a determined portion of air that is currently moving downwards. As the pressure increases in the downward direction, it contracts. Since the entropy content of the portion of air remains constant, its temperature must increase according to line (4) in Table 2.1.

Just the opposite happens to another portion of air that is currently moving upwards: its temperature decreases.

Therefore, a given portion of air changes its temperature when it is moved upwards or downwards. Further up it is colder, further down warmer. There is a well-defined temperature for each altitude.

— **Exercise**

1. Air of 20 °C rises from sea level to an altitude where the pressure amounts to only 800 Hectopascal. What will be its temperature there?

2.6 Thermal convection

Warm air rises, as everyone knows. Why is this? The explanation is easy now that we have become experts on the thermal properties of gases. We consider the radiator of a central heating unit. The air near the radiator is heated and expands (see section 2.2). In the process, its density becomes less than that of the unheated air around it. The heated air tends to move upward. That is basically all there is to it.

However, something else happens to our air after it has risen: it gradually releases its entropy to the colder ambient air and to the bodies in the room and cools down in the process. Consequently, its density increases again and it is displaced by the freshly heated, rising air: it flows back downwards and replaces the warm, rising air there. In short: a cycle has developed, Fig.

2.15. Such a permanent flow is called *thermal convection*.

Thermal convection is responsible for many entropy transfers in nature and technology. We have just talked about a relevant example: thermal convection ensures the distribution of the entropy that is released by a radiator in the entire room.

Even for the development of wind, thermal convection plays an important role. Although some wind systems are formed in a very complicated way, thermal convection is the simple cause in other cases.

An example is the sea breeze. It is the wind that blows at the coast during the day from the sea towards the land. Due to solar radiation, the temperature of the Earth strongly increases on the land, and only slightly on the water (because entropy flows to a much greater depth in the water). The air on the land consequently expands, reduces its density and rises, Fig. 2.16. From the sea, above which the air expands only slightly, air flows towards the land. At a few hundred meters elevation, the air from the land flows back to the sea in order to come down again over the sea.
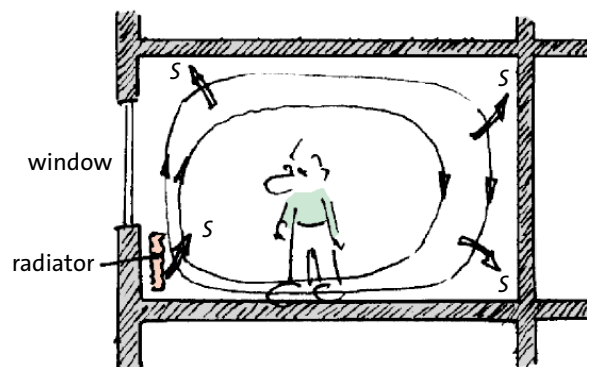

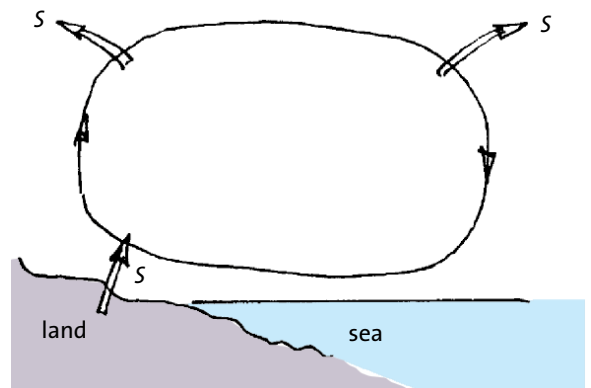**Fig. 2.15** Thermal convection in a heated room

Fig. 2.16 The Sun heats up the land mass greatly, but the ocean only a little. Convective currents are created.
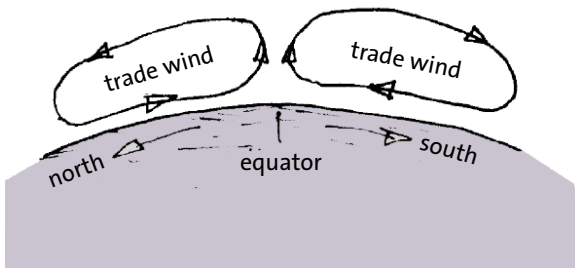
Fig. 2.17 How the trade winds are created

The surface of the Earth heated by the Sun is equivalent to the radiator in the case of the convection flow from our previous example.

Temperature differences that lead to different heating of air are not only to be found between land and ocean, but on many other places on the surface of the Earth. Wherever there is a place where the Earth is warmer than its surroundings, an updraft occurs. If the place is cooler than its surroundings, there is a downdraft.

The ascending air currents that develop in warm places (the so-called thermals) are often used for rising by birds and glider pilots.

Also, the trade winds are an example of a thermal convection flow, Fig. 2.17. In the equator region, the air is strongly heated. It rises, flows in a high altitude southwards and northwards, i.e. in areas where it is colder. In the area around the 30th degree of latitude (North and South), it descends and flows back to the equator at a low altitude. This reflux towards the equator is the trade wind.

We would now like to look at the thermal convection from a different perspective. Air absorbs entropy at a low altitude and rises. The temperature of the air decreases in an upward direction because the density of the air decreases. Then, it gradually releases entropy because it still has a higher temperature than its environment. However, it releases the entropy at a temperature that is lower than the one at which it has absorbed the entropy.

Thus, the same happens to the air as to the working gas in a heat engine: absorption of entropy at a high and release of entropy at a low temperature. Consequently, each thermal convection could be considered a heat engine in which air is set in motion instead of a rotating shaft.

Finally, energy is often taken out of moving air by windmills, wind turbines, and sailboats. The energy of convective flow in a room could be used to turn a pin wheel.

Exercises

1. Liquids expand only very slightly when entropy is added to them. However, this slight expansion is enough to set thermal convective flows in motion. Give an example. Where is entropy added to the liquid, and where is it removed?

2. Why does the flame of a candle point upward from the wick and not downward?

2.7 Irreversible processes with gases

As we discover that a given process runs only in one direction and never reversely, we can conclude that entropy is produced in that process. The reversal of the process would mean that entropy is destroyed – and that is not possible.

Expansion into the vacuum

Fig. 2.18 shows such a process: the recipient consists of two compartments. First, air (or another gas) is only in the compartment on the left; the one on the right has been emptied by means of a pump. Then, the dividing wall is pulled out. The air immediately spreads out in both compartments. Without any doubt, this process is not reversible. If we put the dividing wall back in, the air will not do us the favor of retracting to the compartment on the left.

The experiment looks a bit distant from real life, but it is essentially the same as a bicycle tire that loses its air. The tire will not pump itself back up either.

Hence, entropy must have been produced during the "expansion into the vacuum" in the experiment from Fig. 2.18. And this additional entropy must be contained in the air.

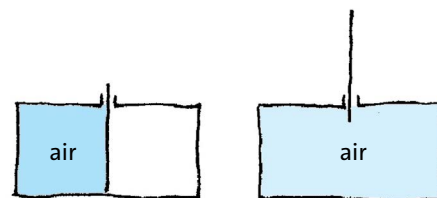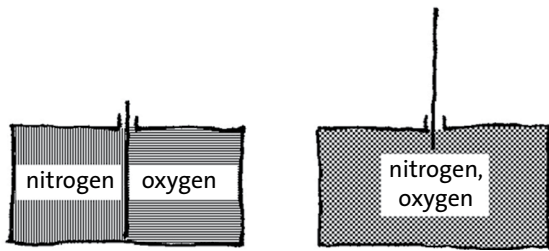> Entropy is produced during the expansion of a gas into a vacuum.

Fig. 2.18 The process is irreversible. Entropy is produced during the expansion into the vacuum.

Fig. 2.19 The process is irreversible. Entropy is produced when gases are mixed.

This leads us to the following interesting question: does the air become warmer or colder during the expansion? Here you find arguments in favor of both options:

- Entropy was produced. If entropy is supplied to a gas, its temperature will rise.
- We learned earlier that the temperature of the gas decreases as soon as the gas expands – provided, however, that the entropy remains constant.

In our case, there are both effects. One seeks to increase the temperature while the other is trying to decrease it. It is hard to predict which one will override the other. What will actually happen can either be calculated or discovered through an experiment. However, the calculation is complex and the experiment very involved. This is why we only indicate the result:

The temperature of a gas does not change during expansion into the vacuum.

Apparently, the two effects neutralize each other. We could regard this as a coincidence. There are gases that respect the gas equation only vaguely, not accurately. For these gases, we cannot hold that the temperature remains constant during expansion into the vacuum.

Mixing gases

Now, there are two different gases in the recipient with two compartments: nitrogen on the left and oxygen on the right, Fig. 2.19.

For the sake of simplicity, we just assume that pressure and temperature are equal on the left and on the right side. As soon as we pull out the division wall, the gases merge. Again, the process is irreversible because the gases will not separate again if we put the wall back in. Entropy must have been produced in the mixing process and this entropy must be contained in the mix of gases. Concerning the entropy balance, each of the two gases behaves as if the other one was not there:

each gas makes a separate expansion into the vacuum whereby entropy is created. The quantity of entropy that is produced in the mixing process is equal to the sum of these two individual entropies.

Entropy is produced when gases are mixed.

Exercises

1. The expansion into the vacuum corresponds to one of the lines in Table 2.1. Which one?
2. The expansion process into the vacuum can be made a bit easier if the wall is not removed completely but if it is just equipped with a small aperture with a flow resistance. How does the temperature of the gas in the compartment on the left behave? What happens to the temperature of the gas in the compartment on the right? Which temperature will there be in case a thermal equilibrium develops between the left and the right side?
3. A problem that has kept researchers busy for a long time. We mix two gases that are not completely different from each other, such as nitrogen and oxygen, but two that are very similar, e.g. a nitrogen isotope on the left and another isotope one on the right. In the mixing process, the same quantity of entropy is generated as in cases where the gases are very different. Now, we assimilate the gases more and more until they are not different anymore. The produced amount of entropy should remain constant. However, we know that no entropy will be produced if the two gases are equal. The problem has long been solved. What do you think?

3 SUBSTANCE-LIKE QUANTITIES

Over time, you have learned about different sub-fields of physics: mechanics, electricity, thermodynamics, maybe some optics, atomic physics or nuclear physics.

You have gotten to know so many details in the process that it is time to put things in an order now.

The following is not part of any of those fields in particular. Rather, it is part of all of them. To get an overview, we are going to jump back and forth among a variety of physical topics. At the beginning, we will organize the many physical quantities that we have encountered so far.

3.1 Substance-like quantities

Someone tells you that he has measured and found the entropy value:

$S = 50\ 000\ \text{Ct}.$

In case you are interested in the matter, you will maybe ask: which entropy do you mean and where did you measure it? The answer could be: in this room, in this water recipient or in this body, Fig. 3.1.

What matters is the fact that an entropy value refers in any case to an extended body, to a *region of space*: the region of the room, the water recipient or the body.

This observation is remarkable because it does not apply for all physical quantities.

Let's look at another situation: someone tells you that he has measured and found a temperature:
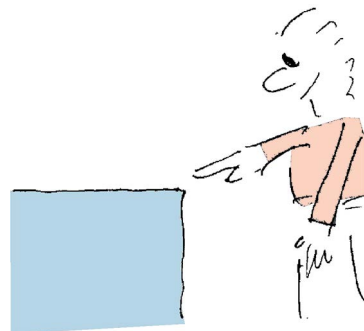
$\vartheta = 17.42\ °\text{C}$

If you ask again "but where?", the answer could be: "at this point of the room", or in the top right corner of the radiator, Fig. 3.2.

Hence, a temperature value does not refer to a region of space but to a *point*.

Fig. 3.1 How much entropy is contained in this region of space?
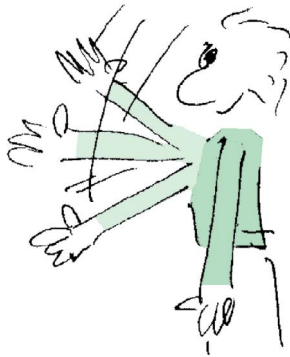

Fig. 3.2 What is the temperature at this point?

Fig. 3.3 How much entropy flows through this surface?

Values refer to	
point	temperature velocity electric potential pressure density
surface	entropy current momentum current electric current energy current
region of space	entropy momentum electric charge mass energy

Table 3.1

There is also a third possibility: someone has measured an entropy current and found

$$I_S = 12 \text{ Ct/s.}$$

To which geometrical object does this value refer? To the *surface* through which the entropy current has flown, Fig. 3.3.

We thus have found a classification system for physical quantities. Most quantities refer to a point, a surface or a region of space.

Before you keep reading: try to classify as many as possible of the physical quantities you know. You can compare your result with Table 3.1.

Apart from these three types of physical quantities, there are others that do not fit into the pattern, see Exercise 2.

At the moment, we are particularly interested in the physical quantities that refer to a region of space: entropy, momentum, electric charge, mass and energy, because they comfortably allow us to treat them like

$$I_S = \frac{S}{t}$$

$$\vec{F} = \frac{\vec{p}}{t}$$

$$I = \frac{Q}{t}$$

$$I_m = \frac{m}{t}$$

$$P = \frac{E}{t}$$

Table 3.2

materials. This is what we have already done so far, without explicitly mentioning it. Due to this property, these physical quantities have a special name: we call them *substance-like quantities*.

> The values of the physical quantities energy, mass, momentum, electric charge and entropy refer to a region of space. We call these quantities substance-like quantities.

We can say that they are contained in a region (a body, a recipient). They can move or *flow* from one place to another. This is why to each of them a current or current intensity is defined. In any case, the definition

$$\text{current} = \frac{\text{substance-like quantity}}{\text{time interval}}$$

applies.

These definitions are listed in Table 3.2 for the entropy S, the momentum $\vec{p}$, the electric charge Q, the mass m and the energy E.

Apart from the mass current I_m, we had encountered all of them previously.

There is one physical quantity that refers to a region of space but that we do not want to include in the category of substance-like quantities: the volume. It does not make any sense to say that the volume is contained in a body.

Exercises

1. There are physical quantities whose values refer to two points. Which ones?
2. Mention physical quantities that do not fit into the pattern of Table 3.1.

3.2 The driving force for currents

Again we will put together a few things that we have encountered in very different contexts.

Each substance-like quantity is associated with a current and a respective current intensity. A current is generally hampered: there is a sort of friction, a resistance. Hence, if something is meant to flow, there must be a *driving force*. So far, we have seen three relevant examples.

1. Electric charge flows through an electric conductor that is not perfect. The current is hampered by the resistance of the conductor. There must be a "driving force" to make electric charge flow through the "resistor" of Fig. 3.4: an electric potential difference. It is created by a battery or another "electricity pump".

2. Entropy flows outside through the building wall. The building wall is a thermal resistor, i.e. a resistor for the entropy current. The entropy flows because there is a driving force: a temperature difference. The temperature inside the house is higher than outside, Fig. 3.5. A temperature difference can be generated in two ways:
- By creating entropy. Where it is created, temperature rises.
- By means of a heat pump.

3. A momentum current flows between the bodies that rub against each other. Because of the friction, the momentum current has to overcome a resistance. The momentum will only flow from one body to the other if the bodies move with a different velocity, Fig. 3.6. Hence, the velocity difference is the driving force for the momentum current. The velocity difference is generated, for example, by means of a motor.

These findings are summarized in Table 3.3.

In the previous section, we put together five substance-like quantities. Apart from electric charge, entropy and momentum, there were mass and energy. Do such rules also apply for mass and energy?

We will deal with this question in the following sections. We would like to anticipate the answer though. For the energy, it is "no", for the mass "yes".
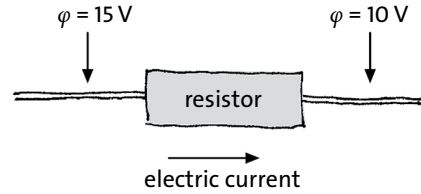
Fig. 3.4 A driving force is needed to make the electric charge flow through the resistor: an electric potential difference
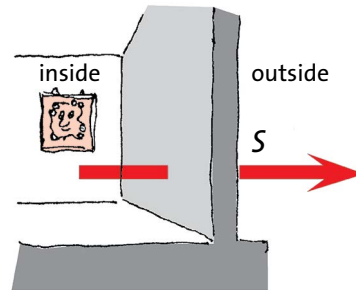
Fig. 3.5 The entropy flows through the thermal resistor (the building wall) because there is a driving force: a temperature difference.
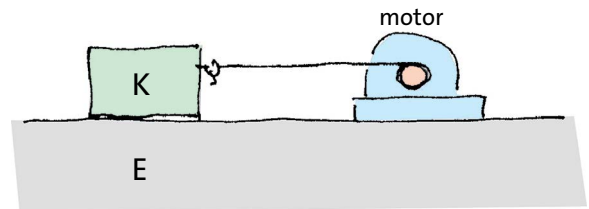
Fig. 3.6 Friction between body K and Earth E means that there is a momentum resistor between K and E. A momentum current flows through this resistor because there is a driving force: a velocity difference.

substance-like quantity	entropy S	momentum $\vec{p}$	electric charge Q
current	entropy current I_S	momentum current (force) $\vec{F}$	electric current I
resistance	thermal resistance	friction, momentum resistance	electric resistance R
driving force	temperature difference $T_2 - T_1$	velocity difference $\vec{v}_2 - \vec{v}_1$	electric potential difference $\varphi_2 - \varphi_1$
"pump"	heat pump	motor, engine	battery, generator, solar cell

Table 3.3

3.3 Energy currents

Earlier, we referred to the substance-like quantities entropy, momentum and electric charge as energy carriers. This was because the current of each of the three physical quantities is related with the energy current in the same way. This can be expressed by the following three equation that are very similar among themselves:

$$P = T \cdot I_S$$
$$P = \vec{v} \cdot \vec{F}$$
$$P = \varphi \cdot I$$

The formulas tell us:
- whenever there is a current of entropy, there is also a current of energy.
- whenever there is a current of momentum, there is also a current of energy.
- whenever there is an electric current, there is also a current of energy.

Often, the energy carrier quantity flows in a closed circuit. Then, we have a go-and-return line and the net energy transfer becomes:

$$P = (T_2 - T_1) \cdot I_S \tag{3.1a}$$
$$P = (\vec{v}_2 - \vec{v}_1) \cdot \vec{F} \tag{3.1b}$$
$$P = (\varphi_2 - \varphi_1) \cdot I \tag{3.1c}$$

Here, we see that no separate driving force for the energy current is needed. The energy will always flow as soon as one of the other substance-like quantities flows. The energy is always taken along by one of the other substance-like quantities. This is why we also referred to these quantities as energy carriers.

▬ Exercises ▬▬▬▬▬▬▬▬▬▬

1. Mention examples for energy transfers that are described by the equations 1a, 1b and 1c.

3.4 Mass and gravitational potential

We look at the water wheel of a water mill, Fig. 3.7. (The turbine of a modern hydraulic power plant would have also been a valid example. However, the illustration of such a power plant would not be as transparent as the one of a water mill).

Our problem: how much energy can be obtained from the water? We track the portion of water with mass m on its ways through the water wheel. On this way, from the altitude h_2 to the altitude h_1, it releases the amount of energy

$$E = m \cdot g \cdot (h_2 - h_1) \tag{3.2}$$

to the water wheel. However, not only this portion flows through the wheel, but a continuous water current and consequently a continuous mass current

$$I_m = \frac{m}{t}. \tag{3.3}$$

And the water is not supplied with only one portion of energy, but with a continuous energy current

$$P = \frac{E}{t}. \tag{3.4}$$

With the equations (3.3) and (3.4), equation (3.2) becomes:

$$P = g \cdot (h_2 - h_1) \cdot I_m \tag{3.5}$$

Finally, a note about naming: we call the product of g and h the *gravitational potential* and abbreviate it with the Greek letter ψ (say "psi"). We can therefore write:

$$\psi = g \cdot h \tag{3.6}$$

Thus, equation (3.5) becomes

$$P = (\psi_2 - \psi_1) \cdot I_m$$

This is again an equation of the type of the equations (1a) to (1c) in the previous section.
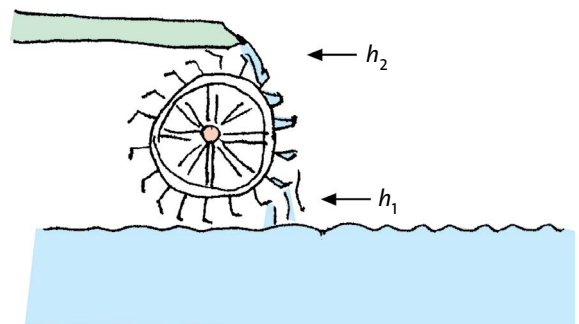
Fig. 3.7 Water wheel. While the water descends from the altitude h_2 to the altitude h_1, it supplies energy to the water wheel.

We compare it to

$$P = (T_2 - T_1) \cdot I_S$$

Here, the difference $T_2 - T_1$ was a driving force for the entropy current that flows through a thermal resistor. If our newly discovered equation is of the same type, we could expect $\psi_2 - \psi_1$ to be a driving force for a mass current. A mass current needs a driving force if it is hampered, i.e. if the pipe in which it flows contains a resistor. Such a pipe is the tube in Fig. 3.8. There, the mass obviously flows from the top to the bottom. Does it thereby flow from the high to the low gravitational potential? Yes, because the gravitational potential is higher at the top than at the bottom. The greater the difference in altitude $h_2 - h_1$, the greater becomes the energy current.

But what does the gravitational field strength g in equation (3.6) stand for? If the pipe from Fig. 3.8 was located on the Moon, the water would flow more slowly and the drive would be weaker.

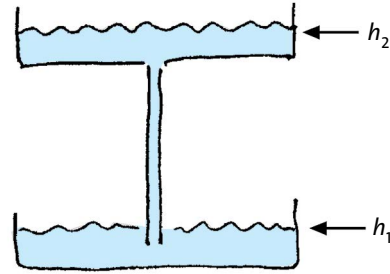The arrangement from Fig. 3.8 looks a bit absurd. In fact, however, it is basically the same as a very normal river or stream. A river also flows from a higher to a lower altitude while being slowed down by the riverbed. The riverbed is the resistor.

Fig. 3.8 The water flows from the altitude h_2 to the altitude h_1. The difference of the gravitational potential is the driving force.

— **Exercises** —

1. There is a power plant at the Iffezheim barrage on the Rhine. During the regular season, approximately 900 m^3 of water are flowing there per second. The barrage has a height of 11 m. How many MW does the power plant supply?

2. In the mountains, the differences in altitude, which can be used for a power plant, are much greater. A water current of 10 m^3/s is led through pipes to the turbines located 300 m further down. What is the energy current produced by the power plant?

4 AMOUNT OF SUBSTANCE AND CHEMICAL POTENTIAL

One substance-like physical quantity was not mentioned in the last chapter: the amount of substance. It is the most important measure for an amount of something in chemistry. Though, this does not mean that it does not play a role in physics. In any case, there is the question of how it fits into the systematic pattern of the other substance-like quantities. We will see that the amount of substance behaves in a way that is very similar to entropy, momentum, electric charge and mass: there is also a driving force quantity for the amount of substance. It is called *chemical potential*, its symbol is μ.

4.1 The amount of substance

As the name suggests, the quantity 'amount of substance' with the symbol n measures the quantity or the amount of a substance. Its measuring unit is the *mol*.

A portion of substance of 1 mol contains $6.022 \cdot 10^{23}$ smallest particles.

It is not always easy to decide what the smallest particles of a substance are.

Often, molecules are the smallest particles. 1 mol of gaseous hydrogen contains $6.022 \cdot 10^{23}$ H_2 molecules. In some substances, for example in helium gas, atoms are the smallest particles. One mol of helium contains $6.022 \cdot 10^{23}$ He atoms. The situation is a bit more complicated for most solid substances. A common salt crystal could basically be regarded as a single giant molecule, i.e. the crystal would consist of one single "smallest" particle. In this case, however, it is standard to refer to a Na ion together with a Cl ion as the smallest particle. Strictly speaking, such a "NaCl formula unit" is not a molecule though. When we talk about

1 mol of common salt in the future, we actually mean $6.022 \cdot 10^{23}$ of such NaCl formula units.

Instead of saying that a substance consists of smallest particles, we could also say that there is a smallest portion for it, whose quantity can be expressed in mol. We refer to the smallest possible amount of substance as *elementary amount*. The following applies:

$$6.022 \cdot 10^{23}\,\text{particles:} \quad 1\,\text{mol}$$

$$1\,\text{particle:} \quad \frac{1}{6.022 \cdot 10^{23}}\,\text{mol}$$

or:

$$= 1.66 \cdot 10^{-24}\,\text{mol}$$

Elementary amount $= 1.66 \cdot 10^{-24}$ mol.

You remember that there is also a smallest portion for the electric charge: the *elementary charge*:

Elementary charge $= 1.602 \cdot 10^{-19}$ C

To measure the values of the amount of substance, we do not have a simple meter as for the measurement of mass values. To determine an amount of substance, we need to make a detour: in the periodic table of elements, the mass of a mol is indicated for each chemical element. The upper one of the two numbers on the left of the element symbol describes the masse per amount of substance, i.e. the quotient of mass and amount of substance. Caution: the value is not stated in kg/mol, but in g/mol. Copper, for example, has the following values:

$$^{63.546}_{29}\,\text{Cu}$$
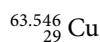
Hence, for copper we obtain

$$m/n = 63.546 \text{ g/mol}.$$

This means that 1 mol of copper weighs 63.546 g, or in other words: a portion of copper, whose amount of substance is 1 mol, has a mass of 63.546 g.

To determine the mass of one mol of a chemical compound, we need to add up the m/n values of the elements that the compound consists of. In cases where there are two, three, etc. atoms of the same type in a compound, the respective m/n values must be counted twice, three times, etc.

Example

What is the mass of 1 mol of Fe_2O_3?
For iron, the periodic table of elements says

$$^{55,847}_{26} Fe$$

and for oxygen:

$$^{15,999}_{8} O$$

Hence, the mass of 1 mol of Fe_2O_3 is

$$m = 2 \cdot 55.847 \text{ g} + 3 \cdot 15.999 \text{ g} \approx 159.7 \text{ g}.$$

Just as for any other substance-like quantity, there is a current, the *substance current* I_n. It is

$$I_n = \frac{n}{t}.$$

The measuring unit of the substance current is mol/s.

Exercises

1. What is the mass of 1 mol of the following substances?
   H_2O (water)
   O_2 (oxygen)
   CO_2 (carbondioxide)
   Ag_2S (silver suphide)
   $Pb(NO_3)_2$ (lead nitrate)
   $C_{12}H_{22}O_{11}$ (cane sugar)
2. How much sugar is contained in 100 g of candies? (Candies are practically made of 100 % cane sugar).
3. What is the amount of substance of 1 l of water?
4. A gas bottle contains 12 kg of propane (C_3H_8). How much is that in mol?

4.2 The chemical Potential

Just as a temperature difference drives an entropy current or as an electric potential difference drives an electric current, the chemical potential difference is a driving force for a substance flow. First, we would like to get a feeling for this new physical quantity.

We consider two points A and B. Between A and B, there should be

- no temperature difference
- no electric potential difference,
- no velocity difference and
- no gravitational potential difference.

Hence, all these driving forces are zero. We could assume that no current will flow from A to B either. If we were to find out that there is indeed something flowing from A to B, it would mean that there must be a driving force that we have not mentioned yet. In fact, there are countless situations in which there is a current although none of the four mentioned driving forces exists. Here are some examples:

If a piece of rusk is kept together with fresh bread in the bread box, the rusk will become soft and flexible after some time. It absorbs water from the bread. Water has moved from the bread (A) to the rusk (B).

An orange is peeled. After a short time, the whole room smells of orange. The aromatic substances have "spread".

The aromatic substances of freshly ground coffee escape, just as the solvents of the glue or the water of the ink shortly after writing.

In all these cases, the transfer of a substance was driven by a difference of the chemical potential.

> A difference of the chemical potential acts as a driving force for a substance flow.

4.3 What the chemical potential depends upon

If we were to predict whether a substance flows or moves, we would have to know on which factors the chemical potential depends. Please remember: in case of the gravitational potential ψ it was easy – as long as the gravitational acceleration is constant, ψ only depends on the altitude.

We should expect things to be more complicated when it comes to the chemical potential. We try to find out what μ depends on, only on the basis of common sense. Only after, we will deal with the quantitative dependences.

Dependence on the concentration

One dependence is obvious: we look at a layer of paint that is about to dry, Fig. 4.1

The solvent – let's assume it is water – moves from the bottom to the top, from A to B. The technical term for this process is diffusion. We say that the water diffuses from A to B.

But how does the water know in which direction it needs to diffuse? How do the positions A and B differ? In the concentration of the water. By concentration we mean the ratio of the amount of substance n to the volume V.

$$c = \frac{n}{V}$$

As long as the concentration of the water at A is higher than at B, it diffuses from A to B. Hence, we conclude:

> The chemical potential grows with an increasing concentration.

In most cases, we only notice a diffusion process in an indirect way – something dries slowly, some smell expands. But diffusion could also be observed. Fig. 4.2 shows an experiment that is very easy to realize.

Some drops of water are put on a glass plate. A small crystal of potassium permanganate, a salt with a strong purple color, is put into the water. A second glass plate is pressed upon the water with the crystal. The result can be watched best in a projection: starting from the small crystal, the permanganate ions diffuse to the outside. The second glass plate is necessary to avoid convection, i.e. a water flow.

Dependence on pressure

Just as obvious is the dependence on the pressure. Fig. 4.3 shows a section of a pipe in which air flows from the top left (A) to the bottom right (B).

All of the four driving forces mentioned in the previous section are not an option. Earlier we would have said that the difference of pressure is the driving force. This statement is certainly not wrong, but we can also make the following conclusion:

1. As a substance is flowing, there must be a chemical potential difference.

2. The chemical potential difference depends on the pressure.

The chemical potential is higher where the pressure is higher as well. This statement is actually not different from saying that the chemical potential increases with the concentration, because we can conclude from
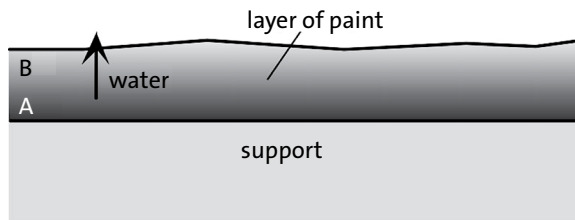
Fig. 4.1 Strongly enlarged view of a layer of paint. The solvent water diffuses from A to B as long as the water concentration is higher at A than at B.
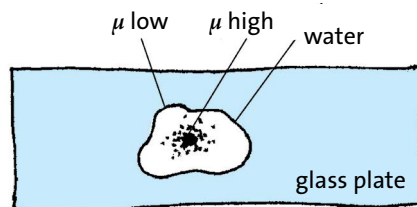
Fig. 4.2 The permanganate ions diffuse away from the $KMnO_4$ crystal to the outside.
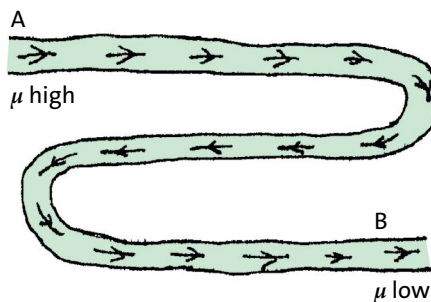
Fig. 4.3 The air flows from A (high pressure) to B (low pressure). We conclude that the chemical potential increases with growing pressure.

the gas equation that the concentration n/V (in case of a constant temperature) is proportional to the pressure:

$$c = \frac{n}{V} = \frac{p}{RT}$$

> The chemical potential grows with an increasing pressure.

At the moment, it still looks like the chemical potential is actually not quite needed. We could simply say that a concentration difference is the driving force for a substance flow. However, we will see later that there are situations in which the substance flow moves from the low to the high concentration. This means

that the concentration cannot be the right measure for the driving force.

Dependence on the nature of the substance

For the gravitational potential we could say: the potential is high at one point, and low at another one – regardless of the substance at the two points: water, stones or air. This does not apply for the chemical potential: at the same point, the chemical potential of one substance can be high and the one of another substance low. This is how two different substances can diffuse in opposite directions, Fig. 4.4.

Hence, we conclude:

The chemical potential depends on the nature of the substance.

Dependence on the phase of the substance

You have also observed this dependence very often, even at times when you did not know anything about chemical potential. The water disappears from the freshly cleaned blackboard after a few minutes – it evaporates. We conclude that the chemical potential of the gaseous phase is lower than that of the liquid phase, Fig. 4.5. However, the opposite could possibly be the case as well. If the concentration of the water in the air is not high enough, the chemical potential of the vapor can become higher than that of the liquid water. As a consequence, the vapor condenses.

This is an example for a process in which a chemical potential difference drives the substance flow from the low to the high concentration.

Sometimes liquid water freezes, and sometimes ice melts. In the first case, the chemical potential of the liquid water is higher than the one of the solid water; in the second case, the chemical potential of the ice is higher than that of the liquid water. Hence, the water always goes into the physical state in which the chemical potential has the lower value. Apart from the solid, the liquid and the gaseous phase, there are countless other phases. There are, for instance, solid substances with a variety of crystal structures. The chemical potential has a different value for each of these phases.

The chemical potential depends on the phase.

Dependence on the surrounding material

This dependence is not as obvious as the ones discussed so far. It makes sense to distinguish between the following two cases:

1. Dependence of the chemical potential of the dissolved substance on the nature of the solvent
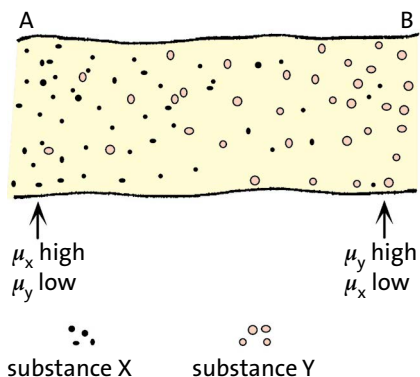
Fig. 4.4 Substance X diffuses from A to B, substance Y from B to A. The chemical potential has different values for different substances.
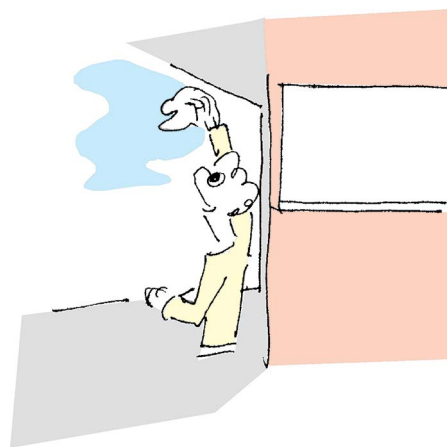
Fig. 4.5 The blackboard dries. The water evaporates because its chemical potential in the liquid phase is higher than in the gaseous phase.
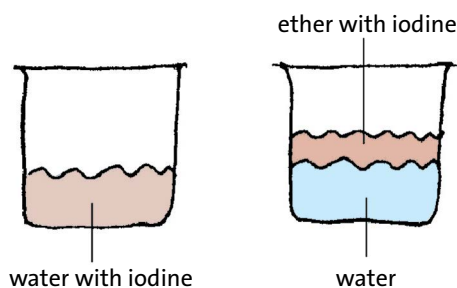
Fig. 4.6 (a) The water is brown due to the dissolved iodine. (b) Most of the iodine has moved to the ether as its chemical potential there is lower than in the water.

We dissolve some iodine in water, Fig. 4.6. The solution has a brown color. Now, we carefully pour some ether over the water, stir to mix the water with the ether and wait. The ether moves back to its position above the surface of the water. However, the water has

become clear and the ether is brown. The iodine has moved from the water to the ether during the stirring process. We conclude that the chemical potential of the iodine is lower in the ether environment than in the water environment.

> The chemical potential depends on the surrounding material.

This effect is often taken advantage of. For example, silica gel can be used to dry air. Silica gel absorbs the water from the air because the chemical potential of the water in the silica gel is lower than in the air.

2. Dependence of the chemical potential of the solvent on the concentration of the dissolved substance

A glass recipient is divided into two compartments by means of a porous wall. The wall is permeable for water, but not for sugar molecules as the latter are bigger than the pores, Fig. 4.7. On the left of the wall, there is pure water; on the right, there is water with dissolved sugar.

We observe that the water permeates the porous wall; it flows from the left to the right. The driving force for this flow must be a chemical potential difference again. We conclude that the chemical potential of the pure water is higher than the chemical potential of the water in which the sugar is dissolved. We have already seen that a chemical potential difference leads to a concentration balance. This is also the case here, as we can see, although what flows is not the dissolved substance but the solvent.

The potential difference in this case only depends on the difference between the concentrations of the dissolved substances on the right and on the left of the wall. It neither depends on the nature of the solvent, nor on the nature of the dissolved substance.

Such walls, that are only permeable for certain substances, play an important role in biological systems.

As the porous wall has a high resistance for the flow of the substance, the process is quite slow. However, this does not make it less important.

Dependence on the temperature

Finally, we should mention that the chemical potential is also dependent on the temperature. The examination of this dependence is more complicated than the dependences we have seen so far, because – as soon as we have a temperature differences – there is also a thermal driving force besides the chemical one, and it is not easy to differentiate between these two driving force. We will get back to the dependence of μ on temperature later.
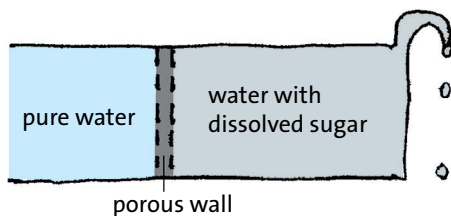

Fig. 4.7 The pure water (left) has a higher chemical potential than the water with the dissolved sugar (right). It flows through the porous wall to the right.

To finish off, we would like to introduce an important term that we will need very frequently in the subsequent sections: *chemical equilibrium*. We have seen that the reason of a substance flow from A to B is that the chemical potential at A is higher than at B. If the chemical potential at B is higher than at A, there will be a flow from B to A. If the values of the chemical potential at A and B are equal, no substance will flow and we have chemical equilibrium.

Chemical reactions

A chemical reaction is also driven by a chemical potential difference. We look at the reaction

$$3\,H_2 + N_2 \rightarrow 2\,NH_3$$
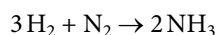
The chemical potential has a well-defined value for each of the two sides of the chemical equation. As the chemical potential of $3\,H_2 + N_2$ is higher than that of $2\,NH_3$, the reaction runs from left to right. If the chemical potential were higher on the right side, the reaction would proceed from right to left. If the left and the right side have the same potential, no reaction takes place, i.e. there is chemical equilibrium. However, we will not discuss how to handle such reactions.

We have now seen a series of processes in which the chemical potential works as a driving force. However, we still need to understand how to determine the values of the chemical potential. In addition, we have not yet seen any equation in which the chemical potential appears. You will get the missing information in the following section.

> A difference of the chemical potential acts as a driving force for phase changes and chemical reactions.

— **Exercise** ——————————————

1. Give examples for substance flows that are driven by a difference of the chemical potential.

4.4 Amount of substance as an energy carrier

Substances carry energy, regardless of whether they are in the gravitational field, whether they are warm or cold, or whether they are electrically charged or not. A substance carries energy because it is that particular substance, i.e. different substances carry different amounts of energy. As a measure for much or little substance, we have introduced the *amount of substance*. Hence, we can say:

Amount of substance is an energy carrier.

One mol of a substance can carry more or less energy. The energy current and the substance current are consequently connected by a factor of proportionality which is different for each substance and whose value also depends on the state of the substance. This proportionality factor is the physical quantity that we have just studied – the chemical potential. Hence, we can say:

$$P = \mu \cdot I_n$$

In other words: if a substance flows through a pipe, there is also an energy current.

(The substance flow generally comes with a current of entropy, and sometimes also with a current of electric charge, etc. Therefore, there are yet other contributions to the total energy current.)

If there is a go-and-return line, we have:

$$P = (\mu_2 - \mu_1) \cdot I_n \tag{4.1}$$

whereby μ_2 is the chemical potential of the go line and μ_1 that of the return line.

We have not yet defined the chemical potential in the previous section. In fact, equation (4.1) can be regarded as the defining equation of the chemical potential. It will also help us calculate the relation between the chemical potential and the pressure.

From equation (4.1) we obtain the measuring unit of the chemical potential: Joule per mol = J/mol, for which we use an acronym: Gibbs (G). Josiah Williard Gibbs (1839 – 1903) is the inventor of the chemical potential. Just as for the electric potential, we can define the zero point of the chemical potential arbitrarily. Thereby, we need to bear in mind that the chemical potential depends on the phase of the substance.

We define:

$\mu = 0 \, G$ for the most stable phase at $\vartheta = 25 \,°C$ and $p = 1 \, bar$

The most stable phase is that phase for which the chemical potential is lowest.

4.5 The relation between chemical potential and pressure

We will establish this relationship by looking at a compressed air machine, Fig. 4.8 – a sort of engine that can be used to drive something. A compressed air machine is very similar to a piston steam engine. Instead of an input and an output for steam, it has an input and an output for air. At the input, air enters with a high pressure, the so-called compressed air, and expanded air, i.e. air with a low pressure, leaves the machine at the output. Compressed air drives are used in many construction machines. The air does not necessarily have to generate a rotary movement, it can also be a back-and-forth movement. An example you certainly know is the pneumatic hammer.

Now, we would like to explain the operating mode of the machine from Fig. 4.8. We start with the state in which the piston is located on the far left, Fig. 4.8a. The
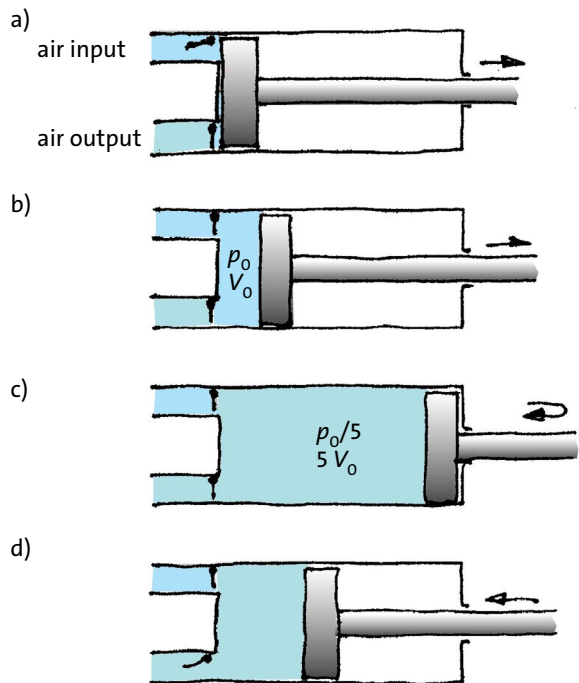

Fig. 4.8 Compressed air machine

air output is closed, the air input open. The compressed air pushes the piston a bit to the right. As soon as it has made a fifth of the way, the air input is closed, Fig. 4.8b. However, the piston keeps moving whereby the air expands. The volume of the compressed air increases fivefold, the pressure is reduced to a fifth, Fig. 4.8c. We assume that the thermal balance with the cylinder walls is as good as to prevent a reduction of the temperature. Then, the exhaust valve opens and the air is pushed out, Fig. 4.8d. The process can start again.

We have looked at a machine in which the air is expanded to a fifth, e.g. from 5 bar to 1 bar. Of course, the position of the valves could also be arranged in a way that the air expands only to half or to a twentieth of the initial value. In practice, the air is usually expanded to match the pressure of the ambient. In this case, the maximum quantity of available energy is extracted from it.

The air at the input of the machine has a high pressure and consequently also a high chemical potential; the air at the output has a low pressure, i.e. a low chemical potential. In the following, we will examine the relationship between the two physical quantities.

We assume that we have several compressed air machines at our disposal. They all have the same structure, i.e. the same size and they all expand the air to half of the pressure. This means that one liter of air of 20 bar is expanded to two liters of 10 bar, or that one liter of air of 2 bar is expanded to 2 liters of 1 bar.

Now, let's assume to have a source of compressed air to supply air with a pressure of 8 bar. We would like to gain the greatest benefit of this compressed air. Therefore it should be expanded from 8 to 1 bar. (We cannot expand it further because the ambient pressure is 1 bar.) What can we do? Remember that we only have machines that ensure expansion to half of the pressure. We expand in several steps, Fig. 4.9.

The first step is simple: air of 8 bar is led into one of the machines – we call it M1. At the output of M1, the air has a pressure of 4 bar. Hence, it can still be used to drive other compressed air machines. But we cannot just build a further machine behind the first because the volume of the air has doubled in M1. While 2 liters of air enter the M1 per second, 4 l/s come out of it. If the subsequent machines have to run as fast as the first one, we will need to connect two machines M2a and M2b in parallel. Then, the air current from M1 spreads to M2a and M2b, whereby each of them receives 2 l/s. We imagine M2a and M2b to be a single machine M2, as indicated by the dashed box in Fig. 4.9.

You see what happens next. The air at the output of M2 has a pressure of 2 bar. We can expand it once
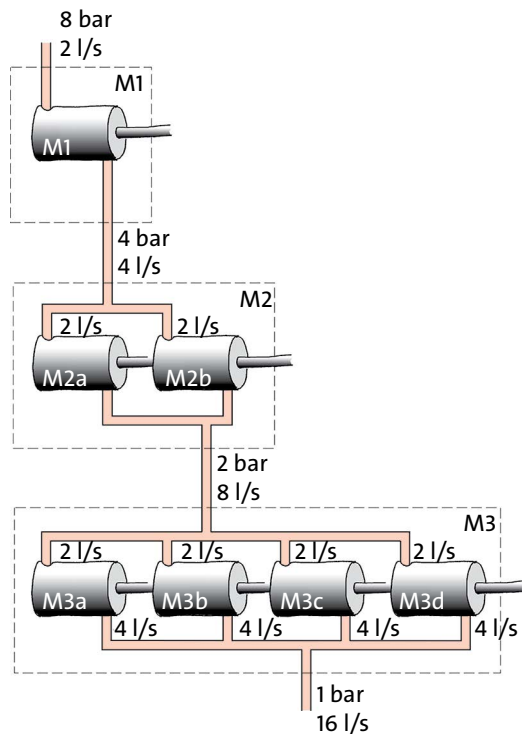
Fig. 4.9 Each time the air is expanded to half of its pressure, it releases the same amount of energy.

again. This time, we need to connect four machines, M3a to M3d, in parallel. All four machines together are called M3.

Now we ask how much energy is supplied by the machines; more precisely: how much is supplied by M1 compared to M2 and M3?

We first compare the energy supplied by M1 with the energy supplied by M2a. The energy current that a machine releases through the piston rod is calculated according to

$$P = v \cdot F$$

Now we know that

$$F = p \cdot A$$

(A = piston area, p = pressure).
Thus

$$P = v \cdot p \cdot A$$

In the respective positions of the piston, the pressure in M2a is always exactly half as high as in M1. Hence, the energy current supplied by M2a is half of

the one supplied by M1 (because v and A are equal for both machines).

M2a and M2b together consequently supply the same amount of energy as M1. This means that M2 supplies as much energy as M1:

$$P_1 = P_2$$

We conclude from the respective comparison of M2 and M3 that M2 and M3 also supply equal amounts of energy. We thus have:

$$P_1 = P_2 = P_3$$

During the expansion from 8 bar to 4 bar, the air supplies as much energy as during the expansion from 4 to 2 bar or from 2 bar to 1 bar. This is an important result. It allows a conclusion about the value of the chemical potential.

> Whenever a gas is expanded to half of its initial pressure at a constant temperature, it supplies the same amount of energy.

We remember equation (4.1):

$$P = (\mu_2 - \mu_1) \cdot I_n$$

Since the same substance current In flows through the three machines M1, M2 and M3, there must be the same chemical potential difference between the input and the output of all three machines.

Assuming that the chemical potential at the output of M3, i.e. for the air of 1 bar, is 0 kG, and that the chemical potential for air of 2 bar is 1.5 kG, we know that the chemical potential for the air of 4 bar must be 3.0 kG, and that of 8 bar must be 4.5 kG, Table 4.1.

> Whenever the pressure of a gas increases by the same *factor*, the chemical potential increases by the same *summand*.

This is our result. However, it is still formulated in an uncommon way. Normally, it should be formulated mathematically. What type of function is $\mu(p)$?

Fig. 4.10 shows μ as a function of p. This is the graph of the logarithm function. We have therefore discovered that the chemical potential is proportional to the logarithm of the pressure.

Deriving this result, we have not paid attention to other factors in the μ-p relationship. This would have made the argumentation more complicated. Hence, we

p in bar	μ in kG
1	0
2	1.5
4	3
8	4.5

Table 4.1
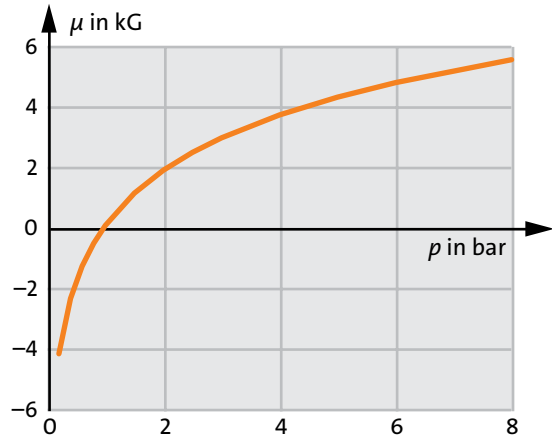
Abb. 4.10 The chemical potential of a gas is proportional to the logarithm of the pressure.

simply indicate the complete result

$$\mu(p) - \mu(p_0) = R \cdot T \cdot \ln\left(\frac{p}{p_0}\right) \qquad (4.2)$$

On the left, there is the difference of the chemical potentials in two states with the different pressures p and p_0. On the right, there is the logarithm of the quotient of the two pressures. Ahead of them, there are the gas constant R and the temperature, both as factors. Bear in mind that the equation is valid for a constant temperature: the temperature in the states with p and p_0 must be equal.

We would like to get a feeling of how the formula works:

1. At first, we insert $p = p_0$, i.e. the initial and the final state are identical. Then, we have on the right side of the equation (2)

$$\ln\left(\frac{p}{p_0}\right) = \ln 1 = 0$$

On the left side, we have

$$\mu(p_0) - \mu(p_0) = 0,$$

as expected.

2. Now we look at the difference of the chemical potentials of two gases of which one has a pressure of 100 bar and the other of 50 bar:

$$\mu(100 \text{ bar}) - \mu(50 \text{ bar}) = R \cdot T \cdot \ln 2$$

And now the difference between two gases with 2 bar and 1 bar:

$$\mu(2 \text{ bar}) - \mu(1 \text{ bar}) = R \cdot T \cdot \ln 2$$

Hence, the result is the same. The chemical potential difference for two states is consequently always the same if the quotient of the pressures in the states is equal. The formula expresses correctly what we have already found out by means of the compressed air machines.

3. We will often have to deal with processes that run at a normal temperature. Therefore, it is useful to memorize the factor ahead of the logarithm for that case:

$$R \cdot T = 8.3144 \text{ Ct/mol} \cdot 298 \text{ K} = 2477.7 \text{ G}$$

or

$$R \cdot T \approx 2.5 \text{ kG}$$

4. We have already derived from the gas equation that pressure and concentration are proportional to each other. Hence,

$$p = R \cdot T \cdot c$$

For a process, in which the pressure changes from p to p_0 but in which the temperature remains constant, the quotient is

$$\frac{p}{p_0} = \frac{R \cdot T \cdot c}{R \cdot T \cdot c_0} = \frac{c}{c_0}$$

This means that we can replace p/p_0 in equation (4.2) with c/c_0:

$$\mu(c) - \mu(c_0) = R \cdot T \cdot \ln\left(\frac{c}{c_0}\right) \tag{4.3}$$

This equation does not only apply for gases, but also for dissolved substances.

We summarize:

> The chemical potential of gases and dissolved substances is proportional to the logarithm of the concentration.

Exercises

1. In two steel cylinders, there is helium gas of 60 bar and 110 bar. Calculate the difference of the chemical potentials.
2. The components of a mixture of gases do not mutually influence their chemical potentials. This means that pure oxygen has the same chemical potential as oxygen that is mixed with nitrogen as long as its concentration is the same. Calculate the chemical potential of the oxygen and of the nitrogen in normal air.
3. A recipient is connected to a vacuum pump. Then, the pump is switched on. What will happen to the pressure and what to the chemical potential if the pump runs longer and longer?
4. A few drops of alcohol are brought into a recipient filled with water. Describe in qualitatively what the alcohol (a) will do right at the beginning and (b) some time after having spread out in the water. What kind of process takes place?
5. The chemical potential of CO_2 that is dissolved in water is 8.36 kG for a one-molar solution. (a) For which concentration will the chemical potential be 0 kG? (b) A bottle of mineral water, that has not yet been opened, contains CO_2 with a pressure of 1.5 bar in the small gas chamber above the surface of the water. What is the concentration of the CO_2 in the mineral water?
6. In a bottle, there is water and – above the surface of the water – CO_2 with a pressure of 2 bar. CO_2 has dissolved in the water so that there is a chemical equilibrium for the CO_2 in the water and outside. The pressure of the CO_2 is now increased to 6 bar. By which factor will the CO_2 concentration in the water increase?

4.6 Chemical resistance

A chemical potential difference leads to a substance flow. The substance flow tries to reduce the potential difference. The intensity of the flow can be high, but it can also be low or very low.

It is similar to a current of entropy, that is driven by a temperature difference, or to an electric current, that is caused by an electric potential difference: the substance flow is hampered as well, there is a "chemical" resistance. The smaller this resistance, the faster chemical equilibrium is reached.

A diffusion process, such as shown in Fig. 4.2, runs very slowly; the chemical resistance is high. Later, we will look at phase transitions – transitions between the solid, liquid and gaseous states. For them, the resistance is very low.

To get a feeling for such resistances, we experiment with some water and carbon dioxide, Fig. 4.11.
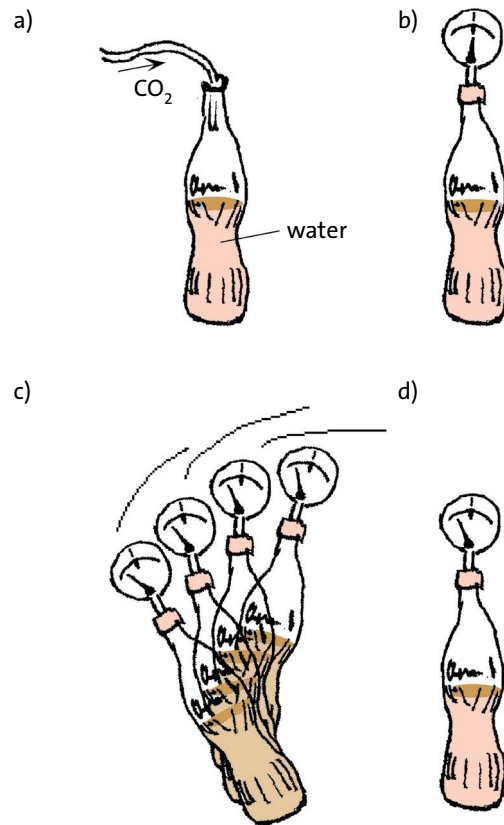
About half of a bottle is filled with tap water. The other half is filled with CO_2. If the CO_2 can simply flow

in, it will have the same pressure as the ambient air, i.e. 1 bar. Then, we close the bottle carefully and subsequently reopen it. Nothing happens, just as you might have expected. We close it again, shake it strongly and reopen it. We can hear a clear hissing noise. If a manometer were fixed in the lid, we could observe the process even better.

Our shaking has caused a vacuum in the bottle; CO_2 was dissolved in the water. In other words, the chemical equilibrium was established between the CO_2 dissolved in the water and the CO_2 in the gaseous phase. In the process, CO_2 from the gaseous phase has dissolved. The resistance for this process is very high though. It was reduced by shaking.

▬ Exercise

1. Half of the content is poured out of (or drunken from) a bottle of mineral water. The bottle is closed, shaken and reopened. What happens? Explain and make statements about the chemical equilibrium.

Abb. 4.11 (a) In the lower half of the bottle, there is tap water; the upper half is filled with CO_2. (b) The CO_2 pressure is 1 bar. (c) If the bottle is shaken, chemical equilibrium will establish: CO_2 will be dissolved. (d) The CO_2 pressure has decreased.

4 AMOUNT OF SUBSTANCE AND CHEMICAL POTENTIAL

5 PHASE TRANSITIONS

5.1 What is a phase?

We have already used the term. It is a generalization of the term "physical state" or "state of aggregation". Hence, we refer to the solid, the liquid and the gaseous phase of a substance.

In many cases, there is no continuous transition between two phases. This is obvious, for instance, for the transition from solid to liquid water. Ice is hard, liquid water not. And there is no water with a hardness somewhere in between. Boiling water passes from the liquid to the gaseous phase. The density changes sharply in the process – the density of liquid water is 1 kg/liter, that of the steam is 0.78 g/liter.

However, there are many substances for which the phase transition is continuous. If glass is heated, it passes smoothly from the solid to the liquid state. When heating it first is rather viscous but then it becomes more and more fluid.

The transition from the liquid to the gaseous phase can also be continuous. This is the case when the pressure is very high.

The most interesting phase transitions, however, are the discontinuous ones. We would like to deal exclusively with them in the following. Such a phase transition is basically the same as what we have called a chemical *reaction*. It is the simplest case of a reaction: a substance A is transformed into a substance B, e.g. ice (A) into liquid water (B).

A note about the wording: the gaseous phase is also called vapor. Hence, vapor is gaseous water. There are also well-defined terms for the transitions between the phases:

- solid → liquid: melting
- liquid → solid: freezing
- liquid → gaseous: vaporizing
- gaseous → liquid: condensing

Not only water appears in different phases, but also other substances. You certainly know that metals can be melted. But they can even be vaporized as well. All materials that are normally gaseous can be liquefied and brought into the solid phase.

The solid, the liquid and the gaseous state are the three best known phases of substances. However, there are many other phases, i.e. all solid materials also appear in several different crystal structures which are also referred to as different phases of the respective material. An example is carbon. One solid phase is graphite, the other one is the diamond.

When a solid material is dissolved in a liquid, it passes to another phase: from the solid to the dissolved phase.

Also, the transition to the supra-conductive phase is abrupt. Hence, we talk about the normal conductive and the supra-conductive phase. Apart from this, there are countless phases in which the substances have different magnetic properties.

5.2 The driving force for phase transitions

Why does water vaporize? Sometimes it vaporizes, but in other cases it condenses. Why?

We are already used to formulating such questions in a different way. What is the driving force for such a process?

In our particular case, we already know the answer – a difference of the chemical potential. If the chemical potential of the substance in the gaseous phase is higher than in the liquid phase, the substance will condense; if the chemical potential in the liquid phases is higher, the substance will vaporize. If the potentials are equal, nothing will happen, there is *chemical equilibrium*.

	μ in kG
water, H_2O	
liquid (1 bar)	0
solid (1 bar)	0.59
gaseous (1 bar)	8.59
carbon dioxide, CO_2	
gaseous (1 bar)	0
aqueous solution (1-mol)	8.36
chlorine, Cl_2	
gaseous (1 bar)	0
aqueous solution (1-mol)	6.9
hydrogen	
H_2 gaseous (1 bar)	0
H gaseous (1 bar)	203.26
oxygen	
O_2 gaseous (1 bar)	0
O gaseous (1 bar)	231.75
O_3 (ozone) gaseous (1 bar)	163.18
carbon, C	
graphite	0
diamond	2.9
sulfur, S	
rhombic	0
monoclinic	0.04
tin, Sn	
white	0
grey	0.13

> $\mu_{\text{gaseous}} > \mu_{\text{liquid}}$ The substance condenses.
> $\mu_{\text{gaseous}} < \mu_{\text{liquid}}$ The substance vaporizes.
> $\mu_{\text{gaseous}} = \mu_{\text{liquid}}$ Chemical equilibrium.

The same applies for all other phase transitions.

Table 5.1 lists the chemical potential for different phases of a few materials at 25 °C.

As the chemical potential depends on temperature and pressure, a temperature or pressure change can lead to a change of phase.

Table 5.1 Chemical potential of some substances in different phases at 25 °C. For one of the phases, the chemical potential was arbitrarily set to zero.

Phase transition by means of temperature change

Liquid water, that is put into a freezer, turns to ice. Ice, that is left in a warm environment, melts.

The chemical potential decreases with increasing temperature, and that for all substances and for all phases. The extent to which it decreases depends on the nature of the substance and on the phase. The decrease is generally stronger for gases than for liquids, and stronger for liquids than for solids. For this reason, the μ-ϑ-curves of any two substances must have an intersection.

Fig. 5.1 shows the dependencies for solid and liquid water. They intersect at 0 °C. At this temperature the chemical potential of the solid water is equal to that of the liquid water. Both phases coexist, there is a chemical equilibrium.

The same applies for the transition between the liquid and the gaseous phase.

The equilibrium temperature for the transition from solid to liquid is also called *melting temperature*; the one for the transition from liquid to gaseous is called *boiling temperature*.

As the chemical potential also depends on the pressure, the situation of the intersection of the μ-ϑ-curves

also depends on the pressure. This means that the melting and the boiling temperature depend on the pressure. In Table 5.2, both equilibrium temperatures are listed for some substances at normal pressure.
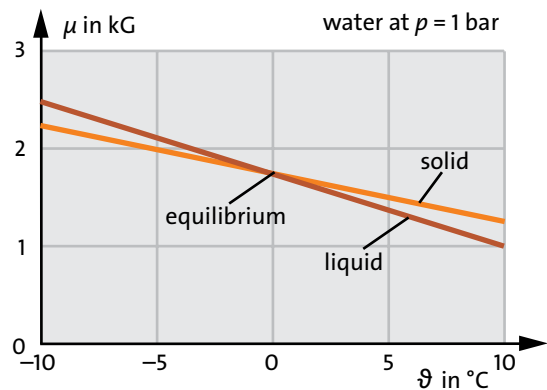
Fig. 5.1 The μ-ϑ-curves of two phases intersect at one point. Here, the two phases are in chemical equilibrium.

substance	melting temperature in °C	boiling temperature in °C
aluminum	660	2450
copper	1083	2590
iron	1535	2880
water	0	100
ethanol	−114.5	78.3
oxygen	−218.8	−183
nitrogen	−210	−195.8
hydrogen	−259.2	−252.2

Table 5.2 Equilibrium temperature solid-liquid (= melting temperature) and equilibrium temperature liquid-gaseous (= boiling temperature) at $p = 1$ bar

Phase transition by means of pressure change

In a transparent lighter, we can see the liquid fuel, the butane. If it is let flow out, it vaporizes quickly. There is a higher pressure in the lighter than outside.

The chemical potential increases with growing pressure for all substances and for all phases. (We had already examined the dependence for gases.) Again, the degree of the increase is different for the various phases, so that also the μ-p-curves of two different phases must have an intersection. Fig. 5.2 shows the curves for liquid and gaseous butane. They intersect at approximately 2 bar. At this pressure the chemical potentials of the liquid and of the gaseous butane are equal. Both phases coexist; there is chemical equilibrium. This is the state inside the lighter.

In the case of equilibrium between the liquid and the gaseous phase, the pressure at which the μ-p-curves intersect is called *saturation pressure*. We will explain the reason for this peculiar name later.

Table 5.3 lists the saturation pressures for some substances at normal temperature.

Just as the equilibrium temperature depends on pressure, the equilibrium pressure depends on temperature.
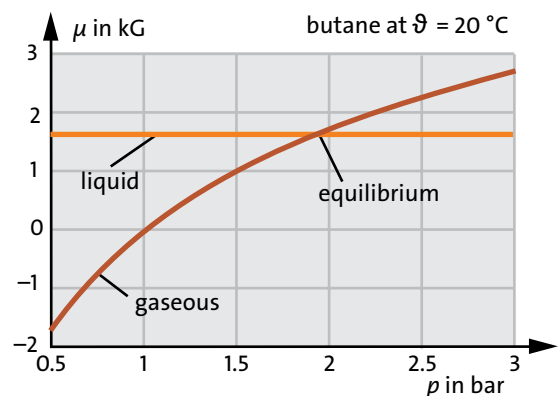
The equilibrium curve

In the following, we limit our explanations to the transitions between the liquid and the gaseous phase, and we refer exclusively to water. All our results can though be applied accordingly to other phase transitions and other substances.

We have seen that the equilibrium pressure depends on the temperature, and that the equilibrium temperature depends on the pressure. Hence, for the state of equilibrium, it should be possible to express the pressure as a function of the temperature in a graph. In fact, the measurement of this function $p(\vartheta)$ is not difficult. We fill some water into a recipient that can stand

high pressures and that allows to measure pressure and temperature and heat it up, Fig. 5.3.

We just need to overcome one obstacle prior to the experiment: above the surface of the liquid in the recipient, there is at first not only water vapor, but also air. Consequently, the pressure that we measure would not be the pressure of the water vapor, but the pressure of the mixture of air and water vapor – which is not interesting for us. Before starting the measurement, we would therefore have to pump out the air. This can easily be done with a vacuum pump.

Fig. 5.2 The μ-p-curves of the phases intersect at one point. Here, the two phases are in chemical equilibrium.

substance	saturation pressure in bar
water	0.023
carbon dioxide	57.3
mercury	0.000 001 63
ethanol	0.0587
propane	7.9
butane	2.01

Table 5.3 Equilibrium pressure liquid-gaseous (= saturation pressure) at $T = 293$ K.
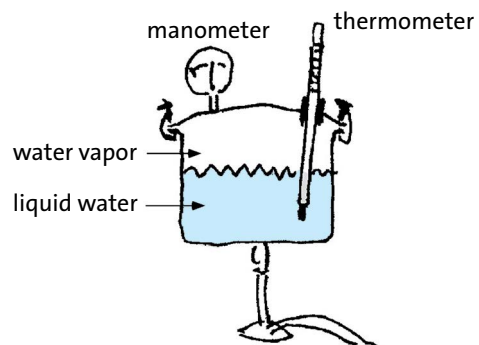
Fig. 5.3 Liquid water and steam are in chemical equilibrium. The equilibrium pressure is measured as a function of the temperature.

The result of the measurement can be found in Table 5.4.

The graph is shown in two scales in Fig. 5.4. Such a figure is also called *phase diagram*. The name is reasonable because each point in the p-ϑ plane characterizes a phase of the water.

In the states that are on the *equilibrium curve $p(\vartheta)$*, the liquid and the gaseous phase are in chemical equilibrium. Both phases coexist. In the states above the curve, the chemical potential of the gaseous phase is higher than the one of the liquid phase. Gaseous water is not stable here – the water is liquid. Below the curve, the chemical potential of the liquid water is higher than that of the gaseous water. Here, the water is in the gaseous phase.
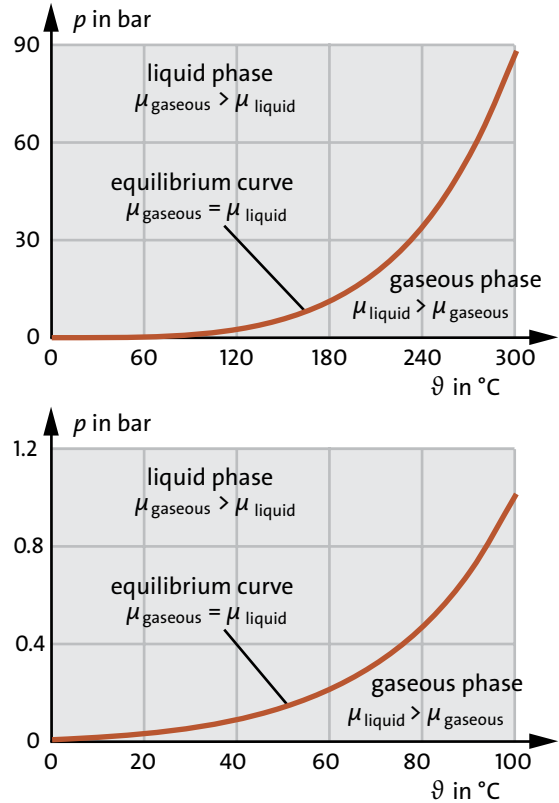
5.3 The heat balance for phase transitions

We put an immersion heater in a glass beaker with water, switch on the heater and measure the temperature of the water, Fig. 5.5. While the immersion heater supplies entropy to the water, the temperature increases – at least at the beginning. Then, however, when the temperature reaches 100 °C, the water starts boiling and the temperature does not increase any further although the immersion heater continues to supply entropy. Why?

During the boiling process, liquid water passes to the gaseous state. The water vapor has the same tem-

Fig. 5.4 Phase diagram of water in two different scales. The curve $p(\vartheta)$ refers to states in which the liquid and the gaseous phase are in a chemical equilibrium.

perature as the liquid water: 100 °C. The entropy we supply to the water is obviously used to vaporize the water. We conclude that water vapor contains more entropy than liquid water.

Subsequently, the vapor can be heated up even further. It is led through a pipe while heating the pipe from outside, Fig. 5.6.

In Fig. 5.7, the temperature of 1 kg of water is displayed above the entropy content of the water. (The

ϑ in °C	p in bar
0	0.006107
20	0.02337
40	0.07374
60	0.1992
80	0.4736
100	1.013
120	1.9853
140	3.614
160	6.18
180	10.027
200	15.551
220	23.201
240	33.48
260	46.94
280	64.19
300	85.92

Table 5.4 Pressure as a function of temperature for the equilibrium between liquid and gaseous water
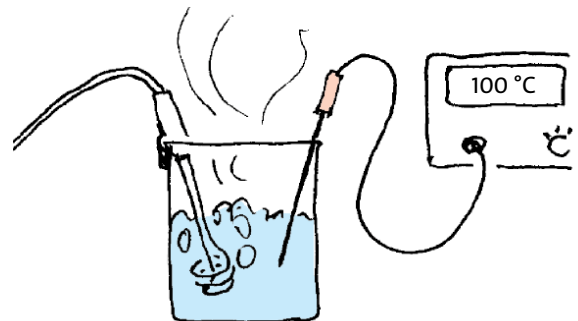
Fig. 5.5 In spite of a continuing entropy supply, the temperature stops increasing at 100 °C.

Fig. 5.6 The water vapor, which has an initial temperature of 100 °C, is heated further.

figure is substantially the same as Fig. 1.47; in Fig. 5.7, we simply used one kilogram instead of one mol.) We can derive from the curve that 1 kg of vapor contains approximately 6000 Ct more than 1 kg of liquid water. The exact value is 6048 Ct.

> The entropy content of 1 kg of water vapor is approximately 6000 Ct higher than that of 1 kg of liquid water.

The diagram also shows that there is a similar phenomenon during the transition solid → liquid. Liquid water contains 1222 Ct more than solid water, i.e. ice.

To transform 1 kg of ice of 0 °C into 1 kg of liquid water of 0 °C (i.e. to melt 1 kg of ice), an amount of entropy of 1222 Ct must be supplied. Accordingly, 1222 Ct must be withdrawn to transform 1 kg of liquid water into 1 kg of ice.

> The entropy content of 1 kg of liquid water is approximately 1200 Ct higher than the one of 1 kg of ice.

The same applies for other substances and other phase transitions. Only the numbers change accordingly.

— Exercises —

1. Derive from Fig. 5.7 how much entropy is contained in 1 kg of water vapor at 100 °C and in 1 kg of liquid water at 100 °C. By which factor is the value for the vapor higher than that of the liquid?
2. How much entropy is needed to transform 10 l of liquid water at 90 °C into vapor of 100 °C?
3. 6000 Ct are needed to melt an ice block. What is the mass of the ice block?
4. A quarter of a liter of mineral water is cooled from 20 °C to 0 °C by means of ice cubes. How much ice is melting in the process?
5. A glass of milk (0.2 l) is heated from 15 °C to 60 °C by means of the steam jet of an espresso machine. How many grams of vapor are needed? (Milk essentially consists of water.)
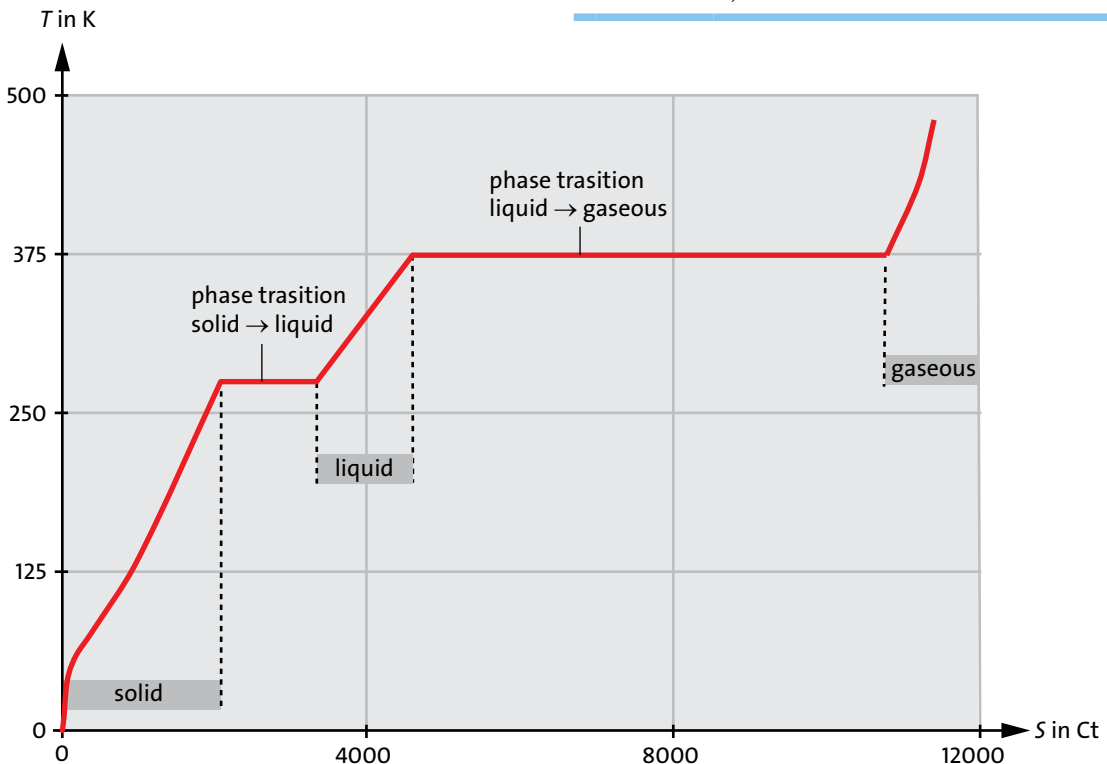
Fig. 5.7 *T-S*-relationship for 1 kg of water

5.4 Phase transition in a thought experiment

In the previous section, we examined the heat balance of the liquidgaseous phase transition, but under slightly complicated conditions. We heated up the water and observed that it vaporizes at 100 °C. In fact, however, water already vaporizes at temperatures below 100 °C as we know; it "evaporates". This process, however, is so slow that we could neglect it in our previous observations. In contrast to the evaporation, we call the vaporization at 100 °C "boiling". The fact that there are these two different vaporization processes is due to the condition that there is air besides the water. To clarify the role of the air, we would like to look at the heat balance of a phase transition again in absence of the air, i.e. under slightly simpler conditions.

We realize a phase transition in two different ways: once at constant pressure and another time at constant temperature. (We have already made this differentiation in section 5.2.)

Our descriptions here refer to so-called thought experiments. A thought experiment is an experiment that could in principle be carried out, i.e. without violating any physical laws, but whose implementation fails because of technical difficulties. In our case, the technical problems consist in the impossibility of having a piston that is perfectly sealed on one hand and that should move very smoothly on the other hand.

Phase transition at a constant pressure

The piston of the recipient from Fig. 5.8 can be moved freely. It is so light that we can neglect its weight. This ensures the pressure on the inside to be always equal to the outside pressure. We assume that it is 101 300 Pa. We now will supply entropy to the water and observe what happens.

We start with a temperature of 20 °C, Fig. 5.8a. The phase diagram tells us that the water at this temperature is liquid. You might think you would have also known this without the phase diagram, but bear in mind that water, which is not locked inside a recipient, evaporates, i.e. that it does not necessarily have to be liquid. However, our water is locked, it has a pressure of 1 bar and is therefore liquid.

Now we heat it up – we provide it with entropy. The consequence: the temperature of the water increases, Fig. 5.8b. We supply more entropy – the temperature rises further, Fig. 5.8c, until we finally reach 100 °C. Then, the temperature stops rising in spite of further entropy supply. Instead, water vapor is produced, Fig.
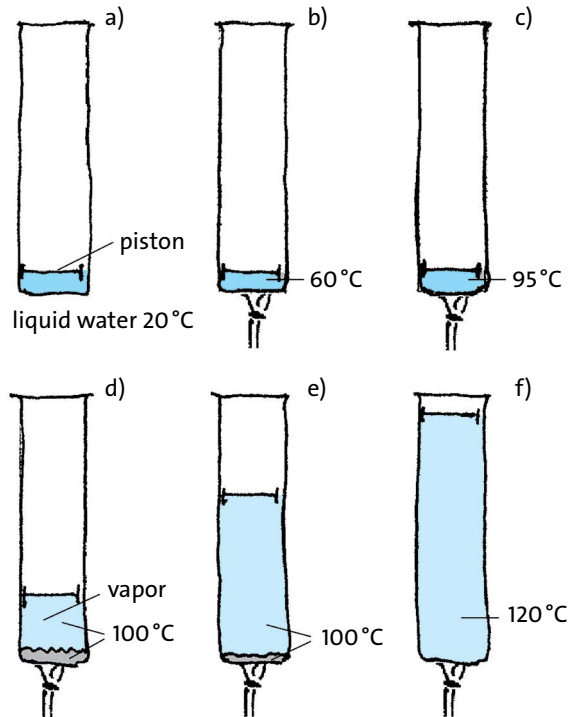
Fig. 5.8 Entropy is supplied to the water while the pressure is kept constant.

5.8d. We supply more entropy – more vapor emerges while the temperature remains 100 °C, Fig. 5.8e. Only when all the water is vaporized, the temperature continues to rise, Fig. 5.8f.

If we withdraw entropy from the water, we will pass through these phases again, but in a reverse order.

Phase transition at a constant temperature

The piston of the recipient from Fig. 5.9 cannot be moved freely anymore but is moved by *us*. This time, we imagine that the thermal contact with the environment is so good that there is a thermal equilibrium between the inside of the recipient and the ambient: even the slightest temperature increase or decrease on the inside creates a current of entropy that immediately balances the temperature difference. We assume that the temperature is 20 °C. We would like to change the volume of the water and observe what happens.

We start at a pressure of 1000 Pa, Fig. 5.9a. The phase diagram and Table 5.3 tell us that the water is gaseous at this pressure. Now we push the piston downwards. The consequence: the pressure of the vapor increases, Fig. 5.9b. We decrease the volume further – the pressure keeps increasing, Fig. 5.9c, until we finally reach 2337 Pa. Then, the pressure stops increas-

ing in spite of a further reduction of the volume. Instead, droplets are formed and the vapor starts to condense, Fig. 5.9d. We further reduce the volume – we obtain more liquid water while the pressure remains constant at 2337 Pa, Fig. 5.9e. Only when the entire vapor is condensed, the pressure continues to rise, Fig. 5.9f.

If we increase the volume, we pass through these phases again, but in a reverse order.

▬ Exercises ▬▬▬▬▬▬

1. Sketch the first experiment (phase transition at constant pressure) in a *T-S*-diagram and the second one (phase transition at constant temperature) in a *p-V*-diagram.
2. You make the experiment (constant temperature) with closed eyes. What do you feel when you push in the piston? Do you recognize which step of the process you are realizing?

5.5 Partial pressure and atmospheric humidity

In recipient A of Fig. 5.10 there are 3 mol of nitrogen; in recipient B, there are 2 mol of oxygen. Each recipient has a volume of 10 liters = 0.01 m^3. The temperature in both recipients is 20 °C = 293 K.

We can calculate the pressures by means of the gas equation

$$p_{nitrogen} = \frac{3 \text{ mol} \cdot 8.31 \text{ Ct/mol} \cdot 293 \text{ K}}{0.01 \text{ m}^3} = 7.30 \text{ bar}$$

$$p_{oxygen} = \frac{2 \text{ mol} \cdot 8.31 \text{ Ct/mol} \cdot 293 \text{ K}}{0.01 \text{ m}^3} = 4.87 \text{ bar}$$

In recipient C, that also has a volume of 10 liters, there are 3 mol of nitrogen as well as 2 mol of oxygen, i.e. 5 mol in total. The pressure can be derived from the gas equation

$$p_{mixture} = \frac{5 \text{ mol} \cdot 8.31 \text{ Ct/mol} \cdot 293 \text{ K}}{0.01 \text{ m}^3} = 12.17 \text{ bar}$$

The result is not surprising: the pressure of the mixture of nitrogen and oxygen is equal to the sum of the pressure that the nitrogen would have if it were alone in said recipient and the pressure that the oxygen alone would have:

7.30 bar + 4.87 bar = 12.17 bar

> The pressure of a gas mixture is equal to the sum of the partial pressures.
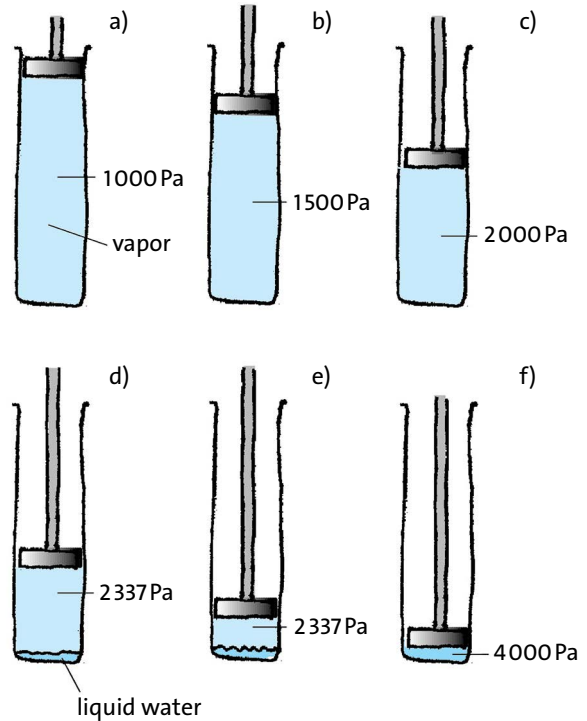

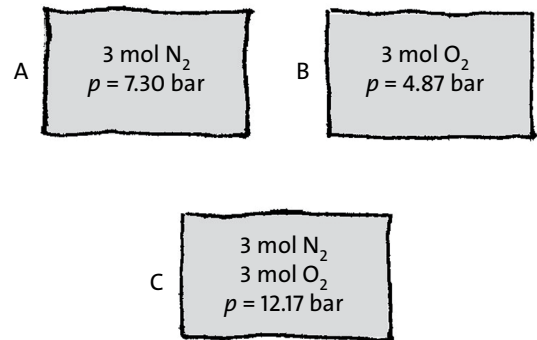Fig. 5.9 The volume of the water is reduced while temperature is kept constant

Fig. 5.10 The pressure in recipient C is equal to the sum of the pressures in recipients A and B.

We say that the nitrogen in recipient C has a *partial pressure* of 7.30 bar and the oxygen has a partial pressure of 4.87 bar.

Things become more interesting as soon as we add water. We make another thought experiment but we will see later that essentially the same process also takes place in nature.

The piston of the recipient from Fig. 5.11 has no weight and can be moved freely. Hence, the inside pressure is equal to the outside pressure. We assume it to be exactly 100 000 Pa. The temperature is 20 °C again.

In Fig. 5.11a there is air in the cylinder. (78.09 % of the amount of substance is nitrogen, 20.95 % is oxygen, 0.03 % is carbon dioxide and the remainder is made up by inert gases).

In the cylinder from Fig. 5.11b, there is also air, but this air contains some water vapor as it is common in normal air as well. The partial pressure of the steam is 1200 Pa. As the overall pressure is 100 000 Pa, there are 98 800 Pa left for the remainder, i.e. for nitrogen, oxygen, etc. together.

The cylinder from Fig. 5.11c contains some liquid water besides the air. In this case, we can conclude that the gaseous phase must contain water vapor because the liquid water is in chemical equilibrium with the water vapor in the air. The partial pressure of the water vapor must amount to 2337 Pa, see Table 5.4. We say that the air is *saturated* with water vapor. The air cannot contain more water vapor as it would condense immediately. It can, of course, contain less as it was the case in Fig. 5.11b. In most cases, the water content of the air is indicated as a percentage of the maximum water concentration. This value is called the *relative atmospheric humidity*. If the air is saturated with water vapor, the *relative atmospheric humidity* is 100 %.

> Relative atmospheric humidity: water concentration in the air as a percentage of the maximum concentration.

Exercise

1. Temperature 20 °C, relative atmospheric humidity 40 % (a) What is the partial pressure of the water vapor in the air? (b) Which percentage of the molecules in the air are water molecules? (c) How many grams of water are contained in one cubic meter of air?

5.6 Boiling and evaporation

We have seen that water boils at 100 °C, but that it already passes to the gaseous state at lower temperatures, just more slowly. This process is called "evaporation". Let's repeat the different terms: the transition liquid → gaseous is always called "vaporization". If vaporization takes place at the boiling temperature, i.e. fast, we also talk about "boiling". If vaporization takes place below the boiling temperature, i.e. slowly, we say that the water "evaporates".

But why is evaporation slow and boiling fast? What is the difference between the two processes? We look at a water surface at different temperatures, Fig. 5.12. The
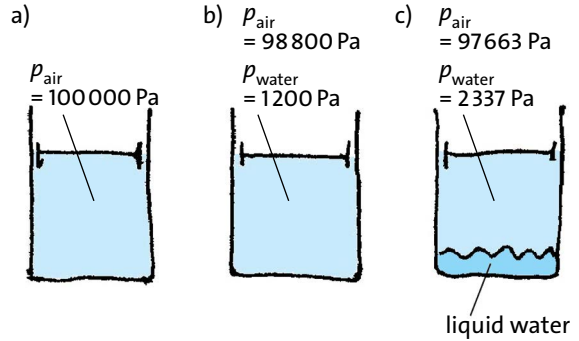
Fig. 5.11 (a) The air does not contain any water. (b) The air contains some water, the relative atmospheric humidity is lower than 100 %. (c) The air is saturated with water vapor, the relative atmospheric humidity is 100 %.
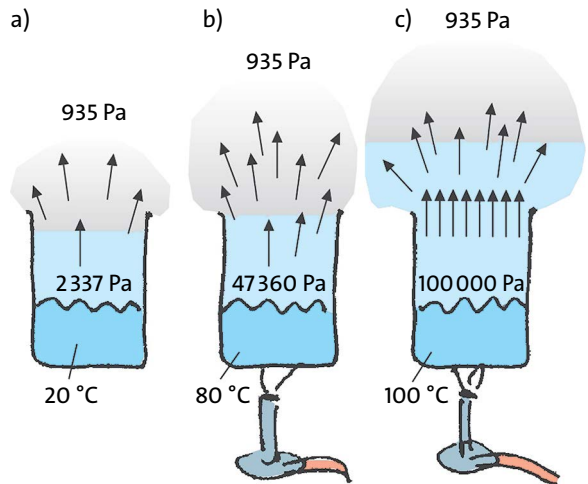
Fig. 5.12 (a) and (b): The water vapor, which forms at the surface of the liquid water, diffuses into the environment. (c) The partial pressure of the water vapor is equal to the atmospheric pressure. The water vapor pushes the air away like a piston.

atmospheric pressure is again 100 000 Pa. We start with 20 °C.

The air directly above the water surface is saturated with water vapor. The water vapor is in chemical equilibrium with the liquid water. The partial pressure of the water vapor is therefore equal to the saturation pressure at 20 °C (Table 5.4), i.e.

p_{water} = 2337 Pa.

The partial pressure of the remaining components of the air is

100 000 Pa − 2 337 Pa = 97 663 Pa

Far away from the water surface, the air has a lower humidity. Assume that the relative atmospheric humidity is 40 % (quite a typical value); hence, the partial pressure of the water vapor is equal to 40 % of the saturation pressure there, i.e.

$$2337 \ Pa \cdot \frac{40}{100} = 935 \ Pa \ .$$

The remaining components of the air have a pressure of

$$100\,000 \ Pa - 935 \ Pa = 99\,065 \ Pa \ .$$

Consequently, we have a downward slope in the partial pressure of the water between the water surface and the environment at a longer distance; i.e. a chemical potential difference. This means that the water vapor diffuses away from the surface. The missing water vapor above the surface is supplied anew as water vaporizes.

Hence, there is a continuous vaporization, which occurs very slowly though. The speed is limited by the slow diffusion process. Such a vaporization process is called *evaporation*. If the water is not heated, it takes the entropy necessary for vaporization from the ambient.

Now we heat up the water with a Bunsen burner. In the process, it is provided with more entropy than is needed for the evaporation. This is why the temperature of the water increases. We observe what will happen at a higher temperature, for example at 80 °C. Again, the partial pressure of the water vapor above the surface is equal to the saturation pressure, this time 47 360 Pa, see Table 5.4. The water vapor pressure difference to the outside is now higher than before and hence also the chemical potential difference. Consequently, the diffusion is faster and so is the evaporation of the water.

Something new will happen if the partial pressure of the water is equal to the overall atmospheric pressure. Then, no air will be left above the surface. As a consequence, the water vapor does not need to diffuse through the air anymore. It simply pushes the air away, as if it were a piston. In contrast to the diffusion, this process is no longer countered by a resistance. The vaporization process is no longer hampered by diffusion. From now on, it runs very fast, i.e. as fast as new entropy is supplied by the Bunsen burner. At this point, the entire amount of entropy is used for vaporization so that the water is not heated up any further. This vaporization, which is no longer hampered by the air, is called *boiling*.

> *Evaporation*: vaporization process whose speed is determined by diffusion
>
> *Boiling*: vaporization process whose speed is determined by the supply of new entropy

Now we can also understand an interesting phenomenon: if the atmospheric pressure is lower than 1 bar, water will boil at a temperature that is lower than 100 °C. If the atmospheric pressure is lower the water vapor coming from the surface of the liquid water will be able to displace the air completely at an earlier stage, i.e. at a lower temperature.

This phenomenon can be observed, for instance, in the mountains: on a high mountain, i.e. where the atmospheric pressure is lower, the boiling temperature of water is also lower than 100 °C.

— **Exercise** ————————————

1. In an altitude of 5400 m, the atmospheric pressure is approximately 0.5 bar. What is the boiling temperature of water?

5.7 The chemical resistance of phase transitions

The transitions between the solid, the liquid and the gaseous state mostly occur without any obstacles. The chemical resistance is zero. In the case of water, this is quite obvious: if we heat up a piece of ice, i.e. solid water, for example from −5 °C, we observe that the water remains solid at first. Exactly at 0 °C it starts melting. As long as the ice has not completely melted, the temperature does not rise above 0 °C. We have become so used to this behavior that we consider it as absolutely normal. But actually it is quite surprising. If the phase transition were hampered by a resistance, we would expect the ice to take on a temperature above 0 °C. It would only melt gradually. Equally, liquid water could also exist below 0 °C. Or liquid water above 100 °C and steam below 100 °C.

In fact, water can be heated up beyond 100 °C. However, this needs to be done with greatest care: the water must be distilled twice, the heating process is best done in an oil bath. This way, the water can be kept liquid up to a temperature above 110 °C although its chemical potential in the gaseous phase is lower.

In many other phase transitions, the chemical resistance works very differently: the transformation resistance is so high that the phase transition can practi-

cally not occur. An example is the transition from diamond to graphite. The chemical potential of graphite under normal conditions is 0 kG by definition. The chemical potential of the diamond is higher: 2.9 kG. Hence, diamonds would have to turn to graphite by themselves if the chemical potential were the only decisive factor. As we know, this does not occur. The reason: the chemical resistance is so high that the process is completely inhibited.

In some less common cases, the phase transition liquid → solid is strongly inhibited. The melting temperature of sodium thiosulfate, $Na_2S_2O_3 \cdot 5\,H_2O$, is 48.5 °C. If entropy is withdrawn from the melt, the temperature will steadily decrease, i.e. up to far below 48.5 °C, with no phase transition taking place. The chemical potential of this liquid is higher than the one of the solid substance at the same temperature, Fig. 5.13. The phase transition does not take place because the transformation resistance is "infinitely high".

However, the reaction can be "switched on" by putting a small crystal of sodium thiosulfate into the melt. Starting at this crystal, the liquid begins to solidify. Fig. 5.14 illustrates this process in the ϑ-S-diagram. We start at point A: the sodium thiosulfate is liquid, its temperature is above 48.5 °C. We withdraw entropy from the liquid, the temperature decreases up to far below 48.5 °C. If we put the crystal catalyst into the liquid at B, the system will quickly move into the state C: a part of the melt solidifies, the temperature increases until it reaches the equilibrium temperature. If more entropy is withdrawn, the development continues, via points D and E.

This effect is applied for thermal storage devices. As long as the solidification is not triggered, the entropy is stored in the non-solidified liquid phase and cannot escape. To release it, the solidification process can simply be triggered. Maybe you have already seen such a thermal storage device in the form of a "hand warmer".

5.8 Everything evaporates, everything dissolves

So far, we have paid little attention to one important phase transition. It takes place when a substance dissolves. If common salt crystals are put into water, they will dissolve. The solid state of the salt is one phase, the dissolved state another one. The dissolution process is very slow. Just as during evaporation: directly above the surface of the salt crystals, there is chemical equilibrium between the solid and the dissolved salt, Fig. 5.15.
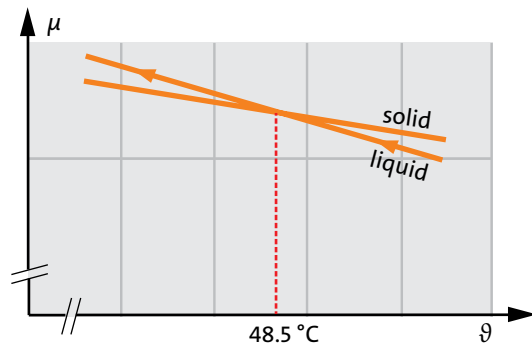

Fig. 5.13 The chemical potential of the liquid and the solid phase as a function of temperature. If cooled down below 48.5 °C, the sodium thiosulfate remains liquid even though the chemical potential of the solid phase is lower.
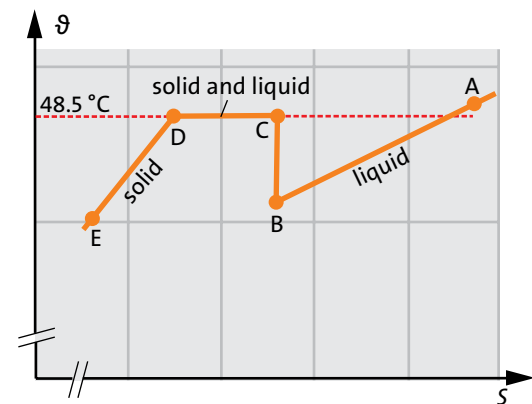

Fig. 5.14 If entropy is withdrawn, the sodium thiosulfate will first move from A to B. It remains liquid. In B, the solidification process is triggered. A part of the sodium thiosulfate solidifies. The left entropy causes a temperature increase up to the equilibrium temperature.
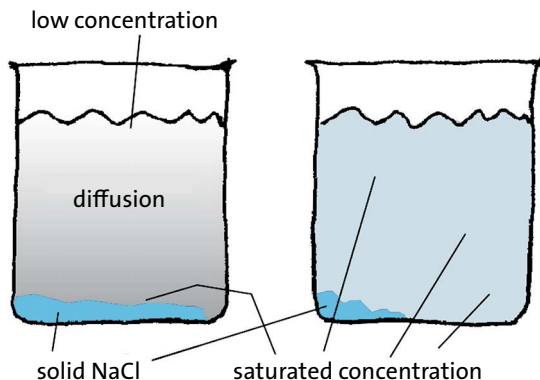

Fig. 5.15 (a) Above the surface of the common salt crystals, the salt solution is saturated: the chemical potential is equal to the one of solid sodium chloride. Farther away it is lower. Hence, the dissolved salt diffuses away. (b) The saturation concentration is reached everywhere. The phase transition has come to a halt.

5.8 Everything evaporates, everything dissolves

The concentration has the highest value that it could possibly have: the *saturation concentration*. The dissolved salt diffuses from there away to the places where the concentration is lower. Thereby space is created and further salt can dissolve. As the diffusion process is very slow, the dissolution is also slow. If enough salt is put into the water recipient, the dissolution process will stop at some point: when the salt solution is saturated everywhere. Now, the chemical potential of the NaCl has the same value everywhere, i.e. at all places of the solution and in the solid salt.

The saturation concentration for the well soluble NaCl in cold water is 6.1 mol/liter; for the hardly soluble calcium carbonate it amounts to 0.00014 mol/liter.

Let us now discuss an interesting question: there are obviously substances that cannot be dissolved in other substances at all. Glass does not dissolve in water, because a water glass does not dissolve in the water that we pour inside. The gasoline tank does not dissolve in the gasoline and the shot glass does not dissolve in alcohol. But these obvious statements are not compatible with what we have learned about the chemical potential. Why not?

We remember the equation that describes the chemical potential of a dissolved substance as a function of the concentration:

$$\mu(c) - \mu(c_0) = R \cdot T \cdot \ln\left(\frac{c}{c_0}\right).$$

Fig. 5.16 shows the respective graph once again.

We see that for $c \to 0$ the chemical potential goes towards negative infinity. This fact has an interesting consequence: if we put any solid substance A into a liquid substance B, the chemical potential of A in the solution will at first be infinitely low as its concentration is zero. This means, however, that there is a drive for the transition from the solid into the dissolved phase. Something of A must be dissolved. It is possible that a tiny amount is sufficient to bring the chemical potential of A in the dissolved phase to the value in the solid phase. But the concentration may not remain zero. In other words:

> Each substance dissolves in any othear substance.

The difference between a well soluble, a hardly soluble and an "insoluble" substance only consists in the saturation concentration. The saturation concentration of "insoluble" substances can be extremely low.

This finding can also be applied to other phase transitions.
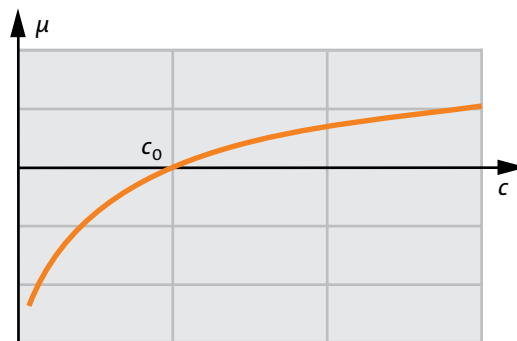
Fig. 5.16 As the concentration approaches zero, the chemical potential tends towards negative infinity.
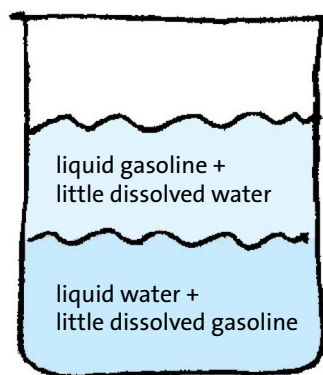
Fig. 5.17 Some water is dissolved in the gasoline (top), and some gasoline in the water (bottom).

There are liquids that evaporate easily, ether or alcohol for example. There are liquids that do not evaporate as easily, such as water. And there seem to be liquids that do not evaporate at all: viscous oil or mercury. In fact, they evaporate as well. Only their saturation concentration is so low that the evaporation process is hardly noticed.

There are liquids that appear not to mix with certain other liquids. If gasoline and water are poured together, a division level will emerge – the water at the bottom, the gasoline on top, Fig. 5.17.

In fact, some gasoline dissolves in the water, i.e. as much as to equalize the chemical potential of the gasoline above the division level and of the gasoline that is dissolved in the water. In addition, some water is dissolved in the gasoline above the division level for the same reason.

Fig. 5.18 shows a recipient with water that is open at the top.

So far, we have only looked at the water. There is water not only below the visible surface, but also above

it, in the gaseous phase. The air, i.e. the oxygen and the nitrogen, is located –as it appeared– only above the division level. Based on our new findings, this is not correct: oxygen and nitrogen must be dissolved in the water. Otherwise, the chemical potential of these substances would be minus infinite there and we would have no chemical equilibrium.

Of course, this applies for all places where water is in contact with air, i.e. also everywhere in nature. The water of the rain, of the rivers and the oceans contains oxygen, nitrogen, carbon dioxide and other gases that are part of the atmosphere. The oxygen that is dissolved in the water is essential for the fish.

For many purposes, ultra-pure substances are needed. Now we understand why it is impossible to produce absolutely pure substances.

▬ Exercise ▬

1. Normal air contains 0.03 % of CO_2 (content of the amount of substance). (a) Calculate the chemical potential of the CO_2 at normal temperature. The water of a lake is in a chemical equilibrium with the air. (b) What is the CO_2 concentration in the water?

## 5.9 Phase transitions in nature and technology

During a phase transition, a substance absorbs or releases entropy at a constant temperature – depending on the direction in which the phase transition takes place. This fact is often used in technology, and it is the explanation of several interesting natural phenomena.

The evaporative cooling effect

When you climb out of the swimming pool, and especially when the air is moving in addition, you feel cold. The water on your skin evaporates. Therefore, it needs entropy, which it takes from your body. The evaporation is particularly fast when the water, that has already evaporated, is carried away by the moving air.

Hot steam is more dangerous than hot water

It is by far not as dramatic to touch water of 100 °C as to touch steam of 100 °C. In both cases, entropy is transferred to the finger, which can burn the skin. The danger is much higher in case of the steam, because the steam condenses on the finger and releases an additional high amount of entropy to the finger.
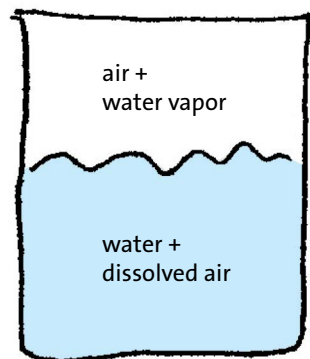
Fig. 5.18 Above the surface of the liquid water, there is water vapor. There is air, i.e. dissolved nitrogen and oxygen, in the liquid water.

Entropy storage

In summer, we would want to store abundantly available entropy for the winter.

There is a promising method based on a phase transition. A substance that has a phase transition solid → liquid at a suitable temperature is chosen. Approximately 50 °C would be a convenient. (It may not be a phase transition liquid → gaseous because gases take up too much space.) Then, a large quantity of the substance is melted in summer by means of solar energy. In winter, the entropy and energy are extracted to heat a building.

If the energy prices were to rise considerably in the future, this process to use solar energy might become competitive.

Cooling drinks with ice

To cool a coke, we could put it in the fridge. The heat pump of the fridge pumps the entropy out of the coke. But often we would like to cool a coke while it is on the table, or at least keep it cool. You know how to do that: by adding some ice cubes. However, why don't we just pour some cold water in the coke instead? The effect would be much weaker. The ice in the coke melts. To melt, it needs entropy, which it takes from the coke. Melting continues until the temperature of the coke reaches 0 °C (provided that there is enough ice).

Liquid nitrogen

If we wish to cool something down to a much lower temperature but if we do not have a refrigeration machine, we can use liquid nitrogen, which can be bought for a cheap price.

The boiling temperature of nitrogen is 77 K (–196 °C). But how can liquid nitrogen exist when the

ambient has a much higher temperature? The nitrogen is kept in a recipient with good heat-insulating walls. The little entropy that permeates the insulation entails continuous, very slow boiling of the nitrogen. The temperature of the remaining liquid nitrogen always stays at 77 K, just as boiling water keeps its temperature of 100 °C. This is how the liquid nitrogen can be stored for several days.

Entropy transfer with phase transitions

Earlier we could see that an entropy transfer through convection is much more effective than through heat conduction. Now there is a transfer process that works even better than the conventional convection, Fig. 5.19.

The substance in the pipes is vaporized at the source of entropy on the left. It absorbs much entropy in the process. Then, it flows through the upper pipe to the right. It condenses in the coil on the right and releases the entropy that it had previously absorbed in the process. Some time ago, central heating systems worked on the basis of this principle – the so-called steam heating systems. However, they had some disadvantages: they were difficult to regulate, and strange noises were caused by the condensation of the steam.

Nowadays, the method is used, inter alia, in heat pumps such as in the fridge. The cooling liquid vaporizes in the coil inside the fridge. In the process, it absorbs entropy. It condenses in the outer coil and thereby releases entropy. (In order to condense in the warmer place and to vaporize in the colder place, the pressure at the warmer place must be lower than in the colder place. This is ensured by a compressor.)

Also nature takes advantage of this entropy transfer process. Vaporization and condensation processes constantly take place in the atmosphere. If water vaporizes in one place, it becomes colder there. The water vapor is transported with the air to another place where it condenses. It becomes warmer there.

Freezing mixtures

We could see earlier that the chemical potential of a liquid decreases when another substance is dissolved in it. Salt water has a lower chemical potential than pure water. Hence, the entire μ-ϑ-curve of the water has a lower position the more salt is dissolved, Fig. 5.20. As a consequence, the intersection of the μ-ϑ-curves of the liquid and the solid phase moves to lower temperatures when salt is put into the water. This means that the melting point depends on whether and how much salt is dissolved in the water.
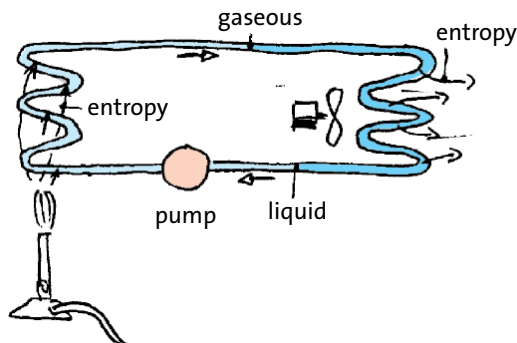
Fig. 5.19 A substance is vaporized on the left. It absorbs much entropy in the process. This entropy is released during condensation on the right.
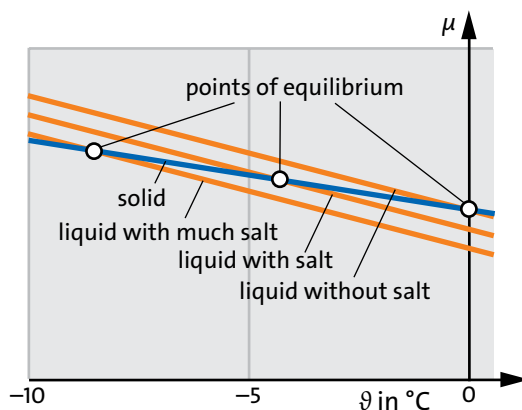
Fig. 5.20 The higher the salt concentration, the lower the position of the μ-ϑ-curve of the water.

If a foreign substance is dissolved in a liquid, the melting temperature will decrease.

This phenomenon is used when throwing salt on the road in winter. The ice on the road melts although the temperature is below 0 °C.

The effect can also be used to create low temperatures in a very comfortable way.

Mix liquid water and small pieces of ice or snow. As the solid and the liquid phase are in an equilibrium, the temperature is 0 °C. Then, add a larger amount of common salt and stir. The temperature will fall below −10 °C. By adding the salt, the chemical potential of the liquid water decreases. As a consequence, the ice melts. As more entropy is needed for this process and no entropy is supplied from outside, the temperature decreases. The temperature reduction leads to an increase of the chemical potential of the salt water. The melting process comes to a halt when the chemical potential of the salt water becomes equal to the chemical potential of the solid water.

6   COUPLED CURRENTS

6.1 One substance – several energy carriers

Energy is always linked to a carrier of energy. Hence, we have schematically displayed energy transfers as shown in Fig. 6.1: an arrow for the energy and another one for the energy carrier. The energy carrier is one of the substance-like quantities

- momentum p
- mass m
- amount of substance n
- entropy S
- electric charge Q.

So far, we have considered energy transfers in which only a single energy carrier plays a role, i.e. *either* momentum *or* entropy *or* electric charge ... The energy current was calculated according to one of the following equations:

- $P = v \cdot F$
- $P = \psi \cdot I_m$
- $P = \mu \cdot I_n$
- $P = T \cdot I_S$
- $P = \varphi \cdot I$.

We pretended that the entire process consisted exclusively of the flow of two physical quantities: energy and *one* energy carrier.

In fact, we have to expect that there is more than just one energy carrier; that all energy carriers contribute simultaneously to the energy current, Fig. 6.2.
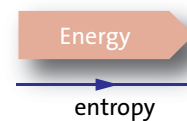
Fig. 6.1 Schematic illustration of an energy transfer: one arrow for the energy, one arrow for the energy carrier
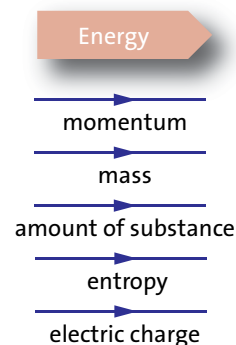
Fig. 6.2 In general, there are several energy carriers

Then, the energy current is the sum of the expressions $v \cdot F$, $\psi \cdot I_m$, etc.:

$$P = v \cdot F + \psi \cdot I_m + \mu \cdot I_n + T \cdot I_S + \varphi \cdot I. \qquad (6.1)$$

In fact, some or almost all summands are equal to zero in many cases of practical relevance. Such a summand can become zero in two ways: either because the current (the second factor) is zero, or because the driving force (the first factor) is zero.

Example: heat conduction in a metal bar

There is an current of entropy, the temperature is different from zero. Hence, the summand $T \cdot I_S$ in equation (6.1) is different from zero.

However, no mass, no momentum and no electric charge are flowing. That is why the summands $v \cdot F$, $\psi \cdot I_m$ and $\varphi \cdot I$ are zero. Actually, there is a substance flow because particles, the so-called phonons, are flowing with the entropy. Their chemical potential, however, is zero so that also the term $\mu \cdot I_n$ does not contribute to the energy current either.

But there is another reason for a simplification of equation (6.1). To understand it, we look at the energy supply of an electric device, i.e. a problem that we have already "under control", Fig. 6.3.

We do not only want to look at the current of the two physical quantities "electric charge" and "energy" at this point though. In the wires flows a current of negatively charged particles, the electrons. The electrons do not only transport electric charge and energy, they also have mass, amount of substance, entropy and momentum. Consequently, an entire "bundle" of currents is connected with the current of electrons:

- an energy current
- a current of electric charge
- a mass current
- a substance current
- an entropy current
- a momentum current.

To calculate the energy current that flows with the electrons, we first need to take into account all energy carriers that are taken along with the flow. All summands of equation (6.1) contribute to the energy current.

We can neglect the contribution of the mass current, as the mass of the electrons is very small, and the momentum current for the same reason. What remains to consider is the electric current (flow of electric charge), the substance current and the entropy current.
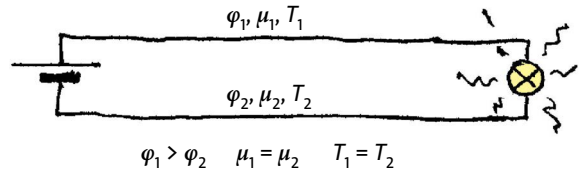
Now, there are two wires leading towards our electric device: the go and the return wire. Both must be taken into account when calculating the energy current. For the go wire we get

$$P_1 = \varphi_1 \cdot I + \mu_1 \cdot I_n + T_1 \cdot I_S$$

and for the return wire

$$P_2 = \varphi_2 \cdot I + \mu_2 \cdot I_n + T_2 \cdot I_S$$

The whole energy that is released to the device is the difference of the go and the return energy current:

Fig. 6.3 As the chemical potential and the temperature of the electrons in the go and return line are equal, the amount of substance and the entropy do not contribute to the net energy transfer.

$$P = P_1 - P_2$$
$$= (\varphi_1 - \varphi_2) \cdot I + (T_1 - T_2) \cdot I_S + (\mu_1 - \mu_2) \cdot I_n \quad (6.2)$$

But at the output of the device, the electrons have
- the same temperature
- the same chemical potential as at the input. Hence,

$$T_1 = T_2$$
$$\mu_1 = \mu_2$$

and

$$P = (\varphi_1 - \varphi_2) \cdot I$$

is what remains of equation (6.2), i.e. the well-known equation for the electric energy current.

Often, in one substance flow the energy is moved from one carrier to another. This can be seen clearly in the following example: the energy supply of a hydro-electric power plant that takes advantage of a difference in altitude, i.e. a power plant in the mountains,
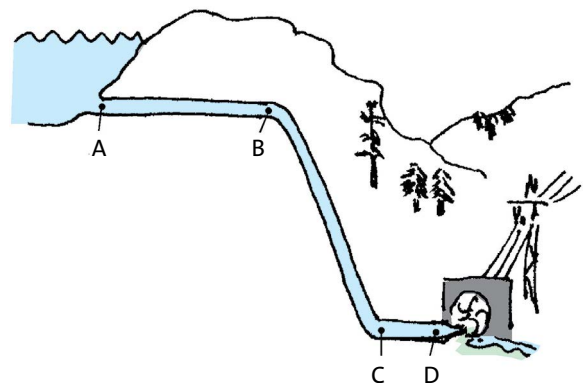
Fig. 6.4 Between A and B, mass is the energy carrier. Between B and C, the energy carrier is changed. Between C and D, the energy carrier is the amount of substance.

Fig. 6.4. We track the water on its way from the reservoir to the paddle wheel of the turbine.

As the temperature of the water remains unchanged, the entropy is not interesting for us. The electric charge does not play a role since the water is not electrically charged. Hence, only mass, amount of substance and momentum are relevant. Thus, equation (6.1) reduces to

$$P = v \cdot F + \mu \cdot I_n + \psi \cdot I_m \qquad (6.3)$$

On the way from A to B, the velocity of the water is low. As the pressure is low, the chemical potential is low as well. Only the gravitational potential is high as the duct is located at a high altitude. Hence, we can neglect the first two terms on the right side of equation (6.3) in relation to the third and obtain:

$$P = \psi \cdot I_m$$

The water carries energy between A and B as its gravitational potential is high. The energy carrier is the mass.

On the way from B to C, the gravitational potential of the water decreases. If we set the zero point of the altitude to the location of the power plant, the gravitational potential there is also zero. The velocity has not changed on the way from B to C, but the pressure and consequently the chemical potential has increased. Thus, equation (6.3) becomes

$$P = \mu \cdot I_n.$$

The water between C and D transports energy because its chemical potential is high. The energy carrier is the amount of substance.

We look at the remaining way of the water through the nozzle of the turbine, from D to E, in the enlarged view of Fig. 6.5. The water is accelerated in the nozzle. Its pressure decreases in the process. When it leaves the nozzle, the pressure has become equal to the normal ambient pressure. This can be neglected in relation to the pressure ahead of the nozzle.

Hence, equation (6.3) becomes

$$P = v \cdot F$$

The water transports energy from E to F because its velocity is high. The energy carrier is the momentum.

On its way from the reservoir to the turbine, the water has transported energy. In the process, the energy has had three different carriers. It has changed the carrier twice.
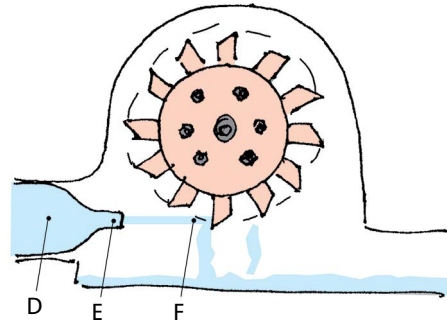

Fig. 6.5 Extract from Fig. 6.4. Between D and E, the energy carrier is changed. Between E and F, momentum is the energy carrier.

We can use the first of these carrier changes, the one between the points B and C, to derive an important general relationship: the chemical potential as a function of the pressure in liquids. (We have already learned about the respective relationship for gases: μ is a logarithmic function of the pressure.)

We track a portion of water with the mass Δm on its way from B to C. At B, it transports the energy

$$\Delta E = \psi \cdot \Delta m = g \cdot h \cdot \Delta m$$
(The gravitational potential is $\psi = g \cdot h$.)

When it arrives at point C, it carries the same energy, which is calculated as follows:

$$\Delta E = \mu \cdot \Delta n$$

We equate the two energy values:

$$g \cdot h \cdot \Delta m = \mu \cdot \Delta n$$

and move the chemical potential to the left side:

$$\mu = g \cdot h \cdot \frac{\Delta m}{\Delta n}.$$

We use the equation for the gravitational pressure to replace the altitude h by the pressure p. The gravitational pressure is

$$p = \rho \cdot g \cdot h$$

We also replace ρ by $\Delta m / \Delta V$.

$$\mu(p) = p \cdot \frac{\Delta V}{\Delta m} \cdot \frac{\Delta m}{\Delta n}$$

After canceling Δm, we obtain:

$$\mu(p) = p \cdot \frac{\Delta V}{\Delta n}$$

The chemical potential for liquids is proportional to the pressure. The proportionality factor is the molar volume $\Delta V/\Delta n$.

Exercises

1. Which substance-like quantities flow together with the water that drives a water mill? Which of these quantities is responsible for the energy transfer to the water wheel? Why do the other quantities not play a role?
2. Which "engine" discharges energy from the water so that only the velocity of the water changes? (There are such machines. If you do not know them, please try to invent them.) Which one is the pertinent energy carrier?
3. For the compressed air machine in chapter 4.5, only the chemical term $(\mu_1 - \mu_2) \cdot I_n$ had to be considered to calculate the exchanged energy. Why?
4. A pump presses 12 liters of water per second into a water supply network with an excess pressure of 4.5 bar. How much energy does the pump consume per second? (Calculate the substance flow as well as the chemical potentials at the input and the output of the pump first.)

and mass is tight. The mass of the water cannot move without carrying along the amount of substance. The entropy, in contrast, can simply "slide away" through the mass and the amount of substance. There seems to be no coupling. We will see later that there is also in this case a slight coupling. However, it is much weaker than the one between mass and amount of substance. For charged substances, such as electrons and ions, the coupling between amount of substance and electric charge is also tight.

We look at a concrete example. In a central heating system, entropy must be transported from the boiler to the radiators. Therefore, the water in the boiler is heated, i.e. it is charged with entropy. Then, the water must get to the radiators. This is ensured by means of a pump. The pump creates a pressure difference and hence a chemical potential difference. The latter act on the amount of substance and drives the water through the pipes. Entropy is taken along in the process. It would not be carried if there were no (i.e. not even a weak) coupling between amount of substance and entropy. As the coupling is weak, the entropy can be easily charged upon the water in the boiler and subsequently discharged it in the radiators.

6.2 Several driving forces

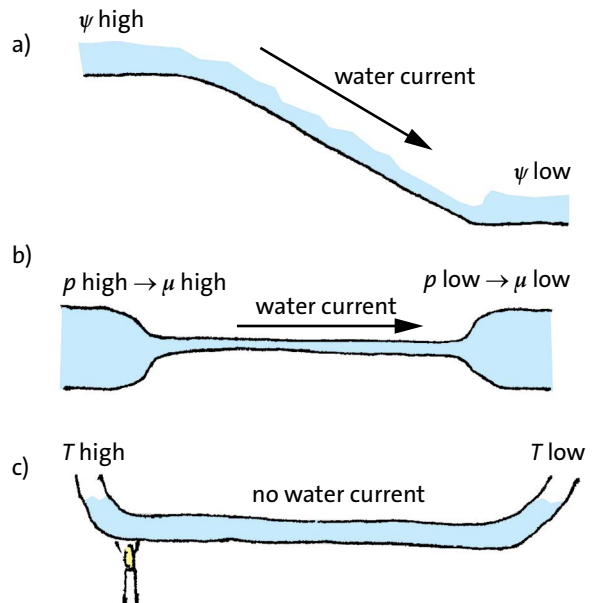To make a current flow while being hampered by a resistance, we need a driving force.

The electric potential difference is a driving force for an electric current; a temperature difference is a driving force for an entropy current, etc.

But what type of driving force is needed to drive a whole bundle of such currents? Let's look at water again. Water comes with mass, amount of substance, entropy and momentum as energy carriers. To move the water current, we can now "pull" at any of these quantities, or at least we can try. If we use, for example, the mass, Fig. 6.6a, it works: the water flows down the mountain because a gravitational potential difference pulls at the mass of the water. Or we use the amount of substance, which works as well, Fig. 6.6b: the water flows from the left, where the chemical potential is high (because the pressure is high) to the right, where it is low. Let's also try with the entropy, Fig. 6.6c. Although the temperature difference causes an entropy current, the latter simply flows through the water without carrying the water along.

This example shows that the different substance-like quantities are coupled with each other more or less strongly. The coupling between amount of substance

Fig. 6.6 (a) A gravitational potential difference pulls at the mass of the water. (b) A chemical potential difference pulls at the amount of substance of the water. (c) A temperature difference does not cause a water current.

6.3 Equilibria

Common equilibria

The equilibria we have seen so far were always associated with two partial systems A and B.

Whenever there is a heat-conducting link between two bodies A and B, there is a current of entropy until the two temperatures A and B have become equal. The state, which is reached in that case, is called *thermal equilibrium*.

Accordingly, we have defined what is meant by electrical and chemical equilibrium: the state in which two electric potentials or two chemical potentials have become equal.

However, we do not need to limit ourselves to two temperature values, electric potential values or chemical potential values. The bar from Fig. 6.7a has a different temperature at each point x. If we leave it up to itself for a while, the temperatures will become equal. At the end, all temperature values will be equal, Fig. 6.7b. There is a thermal equilibrium among all parts of the bar.

> thermal equilibrium: $T(x)$ = const

In the same way we can generalize the definition of the chemical and the electric equilibrium:

> chemical equilibrium: $\mu(x)$ = const
> electric equilibrium: $\varphi(x)$ = const

Also the gravitational potential tends to balance in such a way that an equilibrium results. We call it *gravitational equilibrium*.

> gravitational equilibrium: $\psi(x)$ = const

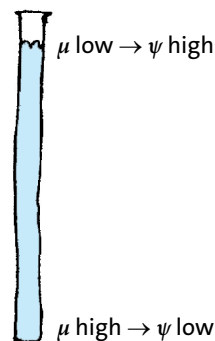### The gravito-chemical equilibrium

Defining the different equilibria, we have neglected that the different substance-like quantities are coupled to each other. This was allowed in the examples that we have seen. However, there are processes in which this coupling impacts on the formation of an equilibrium in a peculiar way.

Fig. 6.8 shows a recipient with water: a vertical pipe closed at the bottom. Why does the water in the pipe not flow to the top, being the pressure at the bottom higher than at the top? We could dismiss this question as nonsense. But the answer would still be missing. Bear in mind that we believe in the general validity of the physical laws.

The question can simply be answered with a second question: why does the water in the pipe not fall down,
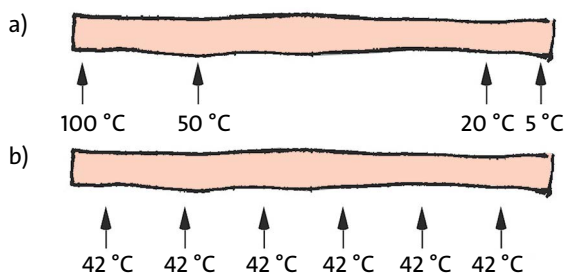
Fig. 6.7 (a) The bar has a different temperature at each point x. (b) After a while, the temperature is equal at all points.

Fig. 6.8 The chemical potential difference drags each portion of water to the top; the gravitational potential drags it to the bottom. The overall driving force is zero, there is gravito-chemical equilibrium.

being the gravitational potential higher at the top than at the bottom.

You see that both questions together provide the answer. Two driving forces are pulling at the water: the chemical potential difference pulls it to the top, the gravitational potential difference to the bottom. Both driving forces compensate each other. Each portion of water is neither in chemical nor in gravitational equilibrium. It is in a state of equilibrium that arises from the common action of gravitation and a chemical driving force. We say that the water is in the *gravitochemical equilibrium*.

For the gravito-chemical equilibrium, we can formulate a condition in the same way as we did for the simple equilibria at the beginning of this section:

> Gravito-chemical equilibrium:
> $\mu(x) + M \cdot \psi(x)$ = const

On the left side of the equation, there is essentially the sum of the chemical potential and the gravitational potential.

The factor $M = m/n$, the molar mass, ensures that the measuring units of the two summands become equal.

We apply the condition for the gravito-chemical equilibrium to the atmospheric air. Therefore we assume that the temperature is the same throughout the atmosphere. (This assumption is not very realistic. As we know, the temperature decreases towards higher altitudes. Nevertheless, the result is pretty good.)

We call the position coordinate h and formulate the equilibrium condition as follows:

$$\mu(h) + M \cdot \psi(h) = \mu(h_0) + M \cdot \psi(h_0)$$

Here, h_0 is the altitude value of the surface of the Earth. For the gravitational potential we insert
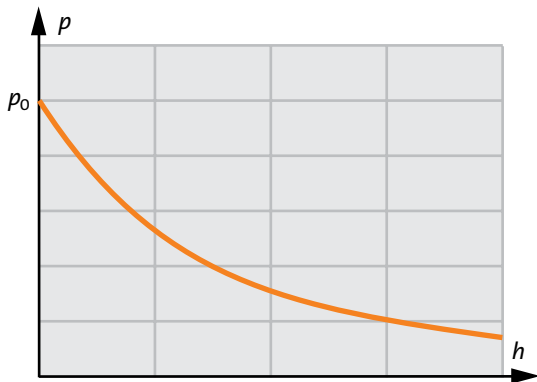
$$\psi(h) - \psi(h_0) = g \cdot (h - h_0)$$

and for the chemical potential

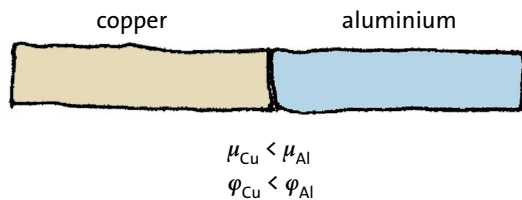$$\mu(h) - \mu(h_0) = \mu(p) - \mu(p_0) = R \cdot T \cdot \ln\frac{p}{p_0}$$

We obtain

$$R \cdot T \cdot \ln\frac{p}{p_0} = -M \cdot g \cdot (h - h_0)$$

Division by $R \cdot T$ results in

Fig. 6.9 The atmospheric pressure as a function of the altitude.

$$\mu_{Cu} < \mu_{Al}$$
$$\varphi_{Cu} < \varphi_{Al}$$

Fig. 6.10 The chemical potential of the electrons is lower in the copper than in the aluminum. Electrons flow from the aluminum to the copper until the electric driving force is balanced with the chemical driving force.

$$\ln\frac{p}{p_0} = \frac{-M \cdot g \cdot (h - h_0)}{R \cdot T}.$$

Now, we insert the left and the right side as an argument in the exponential function (we calculate "e to the power of the left side is equal to e to the power of the right side"):

$$e^{\ln\frac{p}{p_0}} = e^{\frac{-M \cdot g \cdot (h - h_0)}{R \cdot T}}.$$

Since the left side becomes p/p_0 we get:

$$\frac{p}{p_0} = e^{\frac{-M \cdot g \cdot (h - h_0)}{R \cdot T}}.$$

Now we take advantage of the fact that the zero point of the altitude coordinate can be chosen freely. We define the surface of the Earth to be the zero point of the altitude. Hence,

$$h_0 = 0.$$

In addition, we multiply the last equation with p_0 and finally obtain our result

$$p = p_0 \cdot e^{\frac{-M \cdot g \cdot h}{R \cdot T}}$$

The atmospheric pressure decreases exponentially with the altitude.

Fig. 6.9 shows the graph of $p(h)$.

The electro-chemical equilibrium

Fig. 6.10 shows two electric conductors that are in contact with each other. The one on the left is made of copper, the one on the right of aluminum. There are freely moving charge carriers in both conductors: the electrons.

Now, the chemical potential of the electrons in the two different environments is different, see Table 6.1: in the copper, it is approximately 15 kG lower than in the aluminum. But shouldn't be there a current of electrons from right to left, from aluminum to copper in this case?

Exactly this happens in the moment in which the copper is brought in contact with the aluminum – however, the current only flows for a very short time. As electrons flow from the originally neutral aluminum to the originally neutral copper, both metals are being electrically charged – the copper negatively, the aluminum positively. This, in turn, creates an electric potential difference, which pulls the electrons in the opposite direction of the chemical potential difference.

Electrons only flow from the aluminum to the copper until the emerging electric driving force is balanced with the chemical one. Although there is an electric voltage, no electric current is flowing. This type of electric voltage is called *contact voltage*.

Hence, a state of equilibrium results that is due to the combination of an electric and a chemical driving force. We can say that the electrons are in an *electro-chemical equilibrium*.

Again, we can establish an equilibrium condition.

> Electro-chemical equilibrium:
> $\mu(x) + q \cdot \varphi(x) = \text{const}$

On the left side, there is essentially the sum of the chemical and the electric potential.

The factor $q = Q/n$, the molar charge, ensures that the measuring units of the two summands are equal.

q is closely related to a physical quantity that you might know from chemistry class.

We look at an electrically charged substance whose particles carry a positive elementary charge, e.g. H^+ ions. For this substance, we have

$$q = \frac{\text{elementary charge}}{\text{elementary amount}}$$
$$= \frac{1.60 \cdot 10^{-19}\,\text{C}}{1.66 \cdot 10^{-24}\,\text{mol}} = 96\,500\ \text{C/mol}.$$

This constant is called

> Faraday constant: $F = 96\,500$ C/mol

For substances whose particles carry one negative elementary charge, such as electrons, we have

$$q = -F,$$

for substances whose particles carry 2 (positive) elementary charges, we obtain

$$q = 2\,F$$

etc. In general, we can write

$$q = z \cdot F$$

where z is a positive or a negative integer that indicates how many elementary charges are carried by the particles.

For electrons, $z = -1$, for H^+ ions, $z = +1$ and for Ca^{2+} ions, $z = +2$.

	μ in kG
Cu	0
Na	198
Mg	73
Al	14.4
Fe	8.68
Zn	15.4
Ag	9.65
Pb	38.6

Table 6.1 Chemical potential of electrons in different metals

We write the condition for the electro-chemical equilibrium by using the Faraday constant:

$$\mu(x) + z \cdot F \cdot \varphi(x) = \text{const} \qquad (6.4)$$

By means of this relationship, we can calculate the electric potential difference between two bodies that are in contact with each other, provided that we know the chemical potential difference.

— **Exercises** —

1. Describe a process in which $\mu(x) = \text{const}$ is established.
2. Describe a process in which $\varphi(x) = \text{const}$ is established.
3. Describe a process in which $\psi(x) = \text{const}$ is established.
4. Also, a motion equilibrium can be defined. What is the condition? Describe a process in which this equilibrium establishes.
5. Verify the validity of the condition for the gravito-chemical equilibrium in liquids. Use the formula for the dependence on pressure of the chemical potential at the end of section 6.1 as well as the equation for the hydrostatic pressure.
6. Sketch the atmospheric pressure as a function of the altitude. How does the graph $p(h)$ change for an atmosphere on another planet? (Assume that the pressure on the ground is the same as on Earth.) What would the graph look like if the atmosphere consisted of pure CO_2? (Assume again that the pressure on the ground is the same.) How does the graph change when the temperature increases? Answer these questions in a qualitative way.
7. Calculate the atmospheric pressure in an altitude of 4000 m.
8. Table 6.1 contains the chemical potential of electrons in different metals. The zero point of the chemical potential was set in a way that $\mu = 0$ for copper. Calculate the contact voltage between a piece of copper and a piece of sodium that are in contact with each other. Calculate the voltage between aluminum and lead.
9. Someone proposes a perpetuum mobile: a body made of copper and a body made of aluminum are brought in contact with each other. An electric contact voltage emerges between the two. Now, a small lamp is connected between the bodies. The lamp – as they say– will light up.
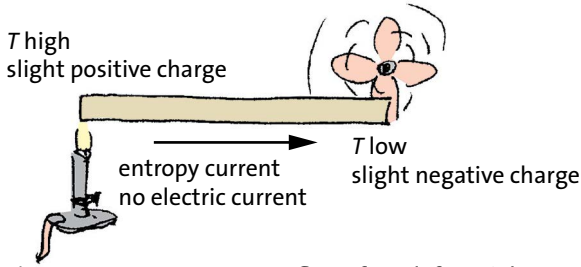
Fig. 6.11 An entropy current flows from left to right. While it "slides over the electrons", it slightly drags them to the right: the bar is charged negatively on the right end, and positively on the left end.
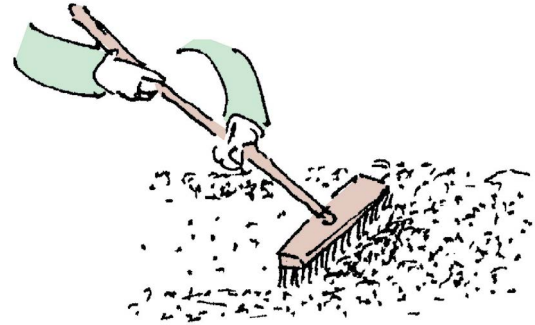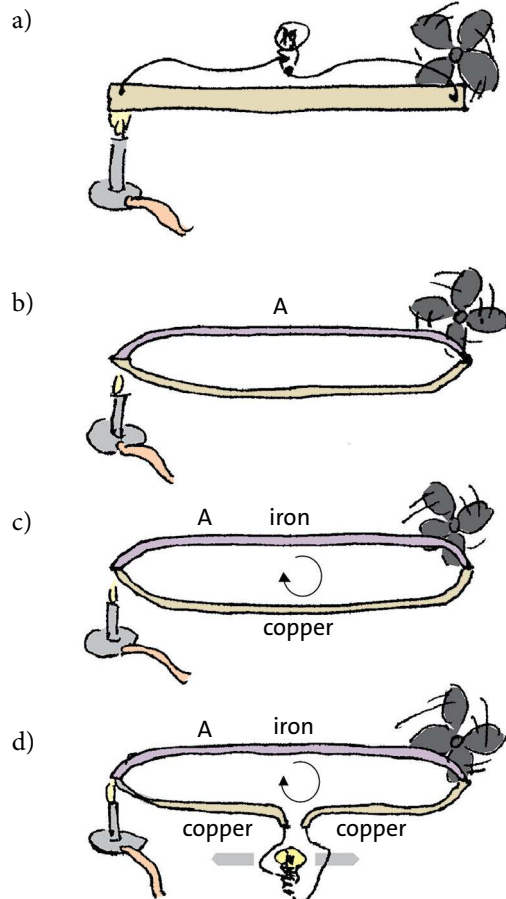
6.4 Thermoelectric energy exchangers

Whereas the amount of substance n, the mass m and the electric charge Q are tightly coupled to one another, the entropy can "slide" over the other quantities. But this does not mean that there is no coupling at all. It is coupled to mass and amount of substance – just not very firmly. The same is true for momentum. There are many phenomena that are based on such loose couplings. We will take a closer look at one of them: the *thermoelectric effect*.

An electric conductor is heated on one end and cooled on the other, Fig. 6.11. As a consequence, an entropy current flows from hot to cold. This entropy current is, albeit weakly, coupled to the electrons. It seeks to carry along the electrons together with their electric charge, mass and amount of substance.

The process can also be imagined as follows, Fig. 6.12: you are sweeping a somehow rough floor. The broom carries the dirt, but not completely. The "broom current" and the "dirt current" are coupled to each other, but the coupling is loose. Hence, you need to move the broom over the floor several times in order to remove all the dirt. Do you see the analogy? Broom ↔ entropy and dirt ↔ electric charge.

What will happen in the case of our electric conductor? The entropy first carries the electric charge to a certain extent. However, this leads to the creation of an electric potential difference between the ends of the conductor, which acts as a counter-driving force for the electrons. When thermal and the electric drive become equal, which happens after a very short time, the electrons stop moving. The entropy, in turn, continues to flow as it is not firmly coupled to the electrons.

We try to make something useful of this phenomenon: a source of electric energy. We could think that connecting two wires to both ends of the conductor

Fig. 6.12 The broom is only loosely coupled to the dirt. This is why it needs to be moved over the floor several times.

Fig. 6.13 (a) The electric circuit is closed. Does the lamp light up? (b) Electric circuit without a lamp. Both in the lower and in the upper arm of the electric circuit the electrons are driven to the right. There is no driving force that pushes the electrons in a circular direction. (c) The coupling between entropy and electric charge is stronger in iron than in copper. The electrons are carried along in a clockwise direction. (d) The lamp lights up.
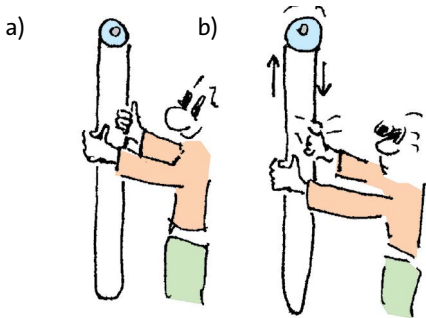
Fig. 6.14 The character pulls the rope with his hands on the right and on the left side. (a) The drag effect is equal on the right and on the left, the rope does not move. (b) On the right, the drag effect is stronger. The rope moves in a clockwise direction
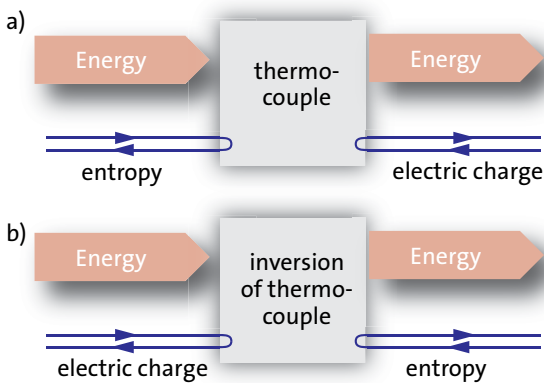
Fig. 6.15 The thermocouple (a) and its inversion (b) as energy exchangers.

that lead, for example, to a lamp would be sufficient to light up that lamp, Fig. 6.13a. Really?

First, we remove the lamp from the electric circuit, Fig. 6.13b, to obtain, a shorted electric circuit in which there should be an electric current – that at least is what we expect. However, this does not happen at all. In the lower connection B the same happens as in the upper connection A: the entropy tries to drag along the electric charge from left to right, i.e. from the hot to the cold end. In both parts A and B of the electric circuit, we have a driving force from hot to cold. The driving force in A tries to move the electrons in the electric circuit in a clockwise way. In B it tries to move them in a counter-clockwise direction. The two effects compensate themselves. The electrons gather a bit on the cold end but are not moved in a circular direction. Hence, our invention does not work.

But it takes only a little bit more to make it work. We only have to make the connections A and B of different metals, e.g. A of iron and B or copper, Fig. 6.13c. The driving forces in A and B are not equally strong anymore because the coupling of the entropy to the electric

charge is now different in the two materials. In our case, it is almost ten times stronger in the iron than in the copper. The entropy drags the electrons in the iron part of the way more strongly than in the copper part. The drag in the iron wire "wins" over that in the copper wire. The electrons move in a clockwise direction.

In case you have not yet fully understood this problem, please look at the comparison from Fig. 6.14. A closed rope is hanging on a roll. You try to set the rope in motion by letting your hands slide over the rope from the top to the bottom. You pull on both sides with the same effort. As you are pulling simultaneously on the left and on the right with the same force, the rope does not move.

Now, make the coupling between the hand and the rope different on the two sides by pulling a bit more strongly on the right. The drag effect by the right hand is now stronger and the rope starts moving in a clockwise direction.

Do you see the analogy? Hands ↔ entropy and rope ↔ electric charge.

The transportation effect between entropy and electric charge is called *thermoelectric effect*; the mechanism from Fig. 6.13d is called *thermocouple*.

The voltages that are created with a thermocouple, however, only amount to a few mV. To actually light up a lamp, many thermoelements need to be connected in series.

The thermocouple is an energy exchanger, Fig. 6.15a. The energy flows in with entropy and comes out with electric charge.

The device also works in the reverse direction, Fig. 6.15b: if an electric current is led through an electric circuit that consists of two parts of different materials, Fig. 6.16, one of the contacts will warm up and the other one will cool down. Hence, the arrangement works as a heat pump.

Thermocouples have some advantages in relation to other thermoelectric energy exchangers: they are easy to produce and they are robust. An important disadvantage is their low efficiency. They only reach 10 %.
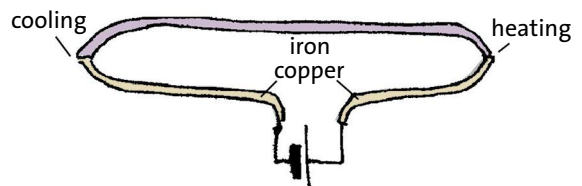
Fig. 6.16 The electric current tries to drag along the entropy. The coupling is stronger at the top than at the bottom. On the right contact, the entropy accumulates; from the left contact, the electron current pull entropy away.

The major application of the thermoelectric effect in the direction that is illustrated in Fig. 6.15a can be found in sensors for thermometers: one of the contacts is located on the ambient temperature that is assumed to be known, the other contact is the actual sensor. A great advantage compared to other thermometers is the fact that such a contact of two wires is resistant to very high and also very low temperatures.

There are also applications for the reverse version, Fig. 6.15b. The thermoelectric effect is used for cooling. If only a light cooling effect is required, the unfavorable efficiency can be disregarded. The advantage is that the device needs is cheap, works silently and without requiring any care.

— **Exercise** —

1. There are electric conductors whose charge carriers are positively charged. (They are the so-called defect electrons that you might have already seen in another occasion.) This fact can be used to build better thermocouples than the ones described in the text. Why?

6.5 Electrochemical energy exchangers

Electrochemical cells are devices that transfer the energy from the carrier amount of substance to electric charge, or from electric charge to amount of substance, Fig. 6.17. They exist in countless versions with different names. If such a cell works as shown in Fig. 6.17a, it is called electrolytic cell. When working as in Fig. 6.17b they are called battery or fuel cell, etc. Some of these devices are operated in one or the other direction in an alternating way. An example is the storage battery in the car.

All these devices or "cells" have a slightly different structure. The essence of their functioning, however, is the same in all cases. In the following, we try to understand it by means of a system that is hard to realize for technical reasons but that provides a clear illustration of the functional principle.

This cell uses the chemical potential difference through which of a gas –in our case hydrogen– when it expands, Fig. 6.18.

In one reservoir, there is hydrogen at a high pressure such as 10 bar. In a second one, the hydrogen pressure is 1 bar.

On its left end, the cell has an input for the hydrogen at a high pressure, and an output for the hydrogen at a low pressure on its right end. Due to the pressure

difference and hence the chemical potential difference, the hydrogen tries to flow through the cell. However, it is hampered in this attempt.

Behind the input, there is a platinum wall, a so-called electrode. A similar electrode is located at the side of the output.

One characteristic of platinum is its ability to absorb hydrogen. There is not enough space for the relatively large hydrogen molecules between the platinum atoms, but the hydrogen molecules disintegrate into electrons and protons as soon as they enter, and these particles can move relatively freely in the platinum.

Between the platinum electrodes there is an acid, e.g. sulphuric acid, and this acid is not permeable for the hydrogen, at least not without a trick. We need to consider the following property of acids:

Acids are conductors for protons and insulators for electrons.

The hydrogen tries to move from the left to the right. Each hydrogen atom contains one proton and one electron. In the platinum, the proton and the
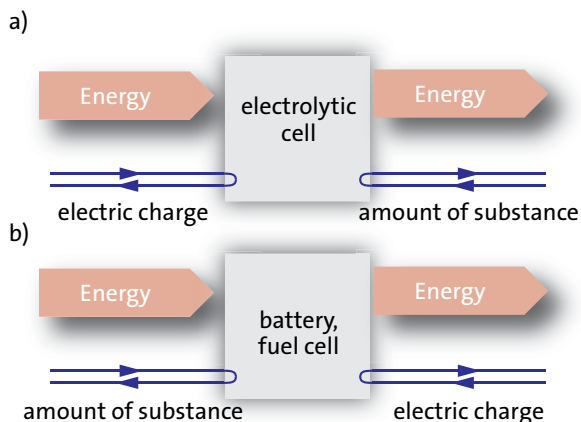
a)

b)

Fig. 6.17 Electrolytic cell (a) and battery (b)
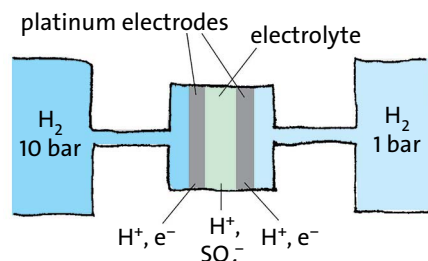

Fig. 6.18 Electrochemical cell. The chemical potential of the hydrogen is in the left reservoir higher than in the right one.

electron are separated from each other. The electrons cannot penetrate the acid. But could not at least the protons follow the chemical driving force and flow to the right? In fact, something that we already know will happen: at the very beginning, a small amount of protons will flow through the acid from the left to the right platinum electrode. An electrical potential difference emerges in the process that works as a driving force for the protons in the opposite direction. After a very short time, the two driving forces neutralize each other and the current of protons stops. There is electrochemical equilibrium for the protons. This means that the electric potential of the left half of the platinum electrode is lower than that of the right side.

Now it is easy to find a way from the left to the right for the electrons as well: we only need to connect the platinum electrodes with a copper wire.

| Most metals are conductors for electrons and insulators for protons.

(We have just seen platinum as an exception; it conducts both electrons and protons.)

This current of electrons can be led through any device that consumes electric energy, Fig. 6.19.

We could also have connected the two hydrogen reservoirs by a turbine. Then, the energy, that corresponds to the chemical potential difference, would have been tapped by the turbine, Fig. 6.20.

In fact, we have realized the hydrogen transfer from left to right in a different way: we led the two components of the hydrogen – protons and electrons – on different paths and tapped the energy in the wire.

However, the cell described in this section does not work well in practice as the platinum is not as good as a conductor for the protons as we have assumed.

A cell that is very similar to ours is the *concentration cell*. It uses the chemical potential difference of dissolved substances with different concentrations. Although concentration cells work, they have a very bad efficiency. The very good cells – car batteries, most cells in electric and electronic devices – take advantage of more complicated chemical reactions. A chemical reaction is also driven by a chemical potential difference. These cells are arranged in a way that the reactants are physically separated from each other. They can only come together if one of the substances is decomposed into electrons plus ions in or at an electrode. The ions go through the electrolyte, the electrons through the wire of the external electric current.
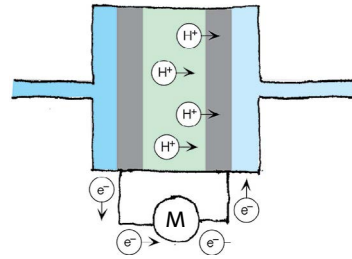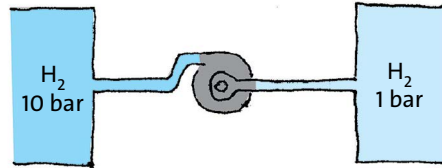

Fig. 6.19 The electric circuit is closed.

Abb. 6.20 The chemical potential difference can be used directly to drive a turbine.

It is not difficult to calculate the electric voltage that is created by our hydrogen cell. We look at the cell in a circuit that is not closed. The protons are then in electro-chemical equilibrium and we can apply equation (6.4). The sum

$$\mu + z \cdot F \cdot \varphi$$

must have the same value for the left and the right platinum electrode:

$$\mu_{\text{left}} + z \cdot F \cdot \varphi_{\text{left}} = \mu_{\text{right}} + z \cdot F \cdot \varphi_{\text{right}}$$

We name the potential differences

$$\mu_{\text{left}} - \mu_{\text{right}} = \Delta\mu, \ \varphi_{\text{left}} - \varphi_{\text{right}} = \Delta\varphi$$

We obtain

$$\Delta\varphi = -\frac{\Delta\mu}{z \cdot F}.$$

According to our logarithmic formula, the chemical potential difference is

$$\Delta\mu = R \cdot T \cdot \ln\frac{p}{p_0}.$$

With $p = 10$ bar, $p_0 = 1$ bar, $R \cdot T = 2\,500$ G, $z = 1$, $F = 96\,500$ C/mol we get $\Delta\varphi = 0.06$ V .

— **Exercise** ——————————

1. The hydrogen cell that we analyzed as an example creates a disappointingly low voltage. What would the pressure in the reservoir have to be to create a voltage of 1 V?

7   THERMAL RADIATION

7.1 Light has entropy

A hot body, e.g. a metal block, cools down by itself, its entropy flows to the environment – to the ambient air and to the surface on which it is located. We would now like to try to prevent this cooling process. We could think that this is very easy: we put the block into the vacuum, Fig. 7.1. There, the entropy could no longer escape through the air. In addition, we suspend it with thin threads that are only an insignificant thermal leak.

We make a peculiar observation: in spite of our precautionary measures, the vacuum jar starts to feel clearly warm and the block cools down (what we can experience as soon as we take it back out). In other words: both the entropy and the energy of the body have decreased. As neither one nor the other physical quantity can be annihilated, both must have escaped somehow from the block.

If you have doubts and think that the suspension is not perfectly heat-insulating: in principle, the block could also be brought into the outer space. Even there it would cool down.

Consequently, the entropy and the energy currents must be able to cross the vacuum by some invisible connection or by means of an invisible carrier. We discover what this carrier is when we heat up the block a bit more, i.e. as much as to make it glow. When it glows, it sends out what we all know: light. And light can go through the vacuum very well. By the way, it also traverses the 150 million kilometers between the Sun and the Earth, almost without any losses. But also when the temperature of the hot body is lower, so that
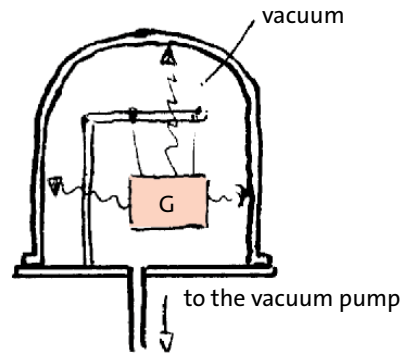
Fig. 7.1 A body is suspended in the vacuum. Although there is practically no heat-conducting connection to the environment, it cools down quickly.

it does not glow yet, it sends out some type of light, i.e. infrared light – electromagnetic radiation whose wavelength is longer than that of the visible light. We conclude that electromagnetic radiation has also entropy besides energy (we already knew that) – at least under the conditions of our experiment.

In fact, it is correct to make this restriction. You have probably already learned something about electromagnetic waves in the context of electrodynamics. But entropy was never mentioned there. The electromagnetic fields, that we analyzed in electrodynamics, were only a tiny selection of fields: they were very simple and their entropy content was zero. Hence, no wonder that we could not notice any entropy.

Electromagnetic fields (generally) contain entropy.

7.2 The light gas – thermal radiation

The plane sine wave is a particularly simple state of the electromagnetic field. As it carries no entropy, though, it is not interesting in the context of thermodynamics. There is another very simple state of the electromagnetic field, which is especially suitable for thermodynamic activities: the light-gas. It is, in turn, not very interesting in relation to electrodynamics since the distribution of the field strength is too complicated. The light-gas is important because we come across it very often in everyday life. To get an understanding of what a lightgas is, we should start with a thought experiment: we create a lightgas under very simple, albeit somehow unrealistic conditions.

But let's first get back to the common material gas. If we say of such a gas, which should be located in a recipient, that it has the temperature T and the pressure p, we assume that all parts of the gas are in *thermal* and in *chemical equilibrium* with each other. Such an *internal equilibrium* emerges in a material gas very quickly and by itself.

Imagine that there are molecules in a recipient that are all moving with the same speed in the same direction, Fig. 7.2a. These molecules, of course, are not in an internal equilibrium. After a very short time, their movements will get into a muddle, though: the molecules move in all directions, they have the most different velocities, and the whole space of the recipient is filled evenly, Fig. 7.2b. The internal equilibrium has established. The molecules form a gas. Prior to this, we might have said that they form a beam.

Back to the light. We would like to fill light into a recipient. To be able to store it, the inner sides of the wall of the recipient must be ideally mirrored. Real mirrors are not an option because every real mirror absorbs a small portion of the light. After a short time, the light would have made so many reflections that nothing would be left of it anymore.

However, there is a problem: in our mirror box, no internal equilibrium can establish as the light particles (the photons) –in contrast to the molecules of a material gas– exchange almost no energy and no momentum among each other. They penetrate each other undisturbed. But there is a simple solution, at least in our thought experiment: we put a very small body K, which can absorb and emit photons of all frequencies, in the recipient. This small body ensures the formation of the internal equilibrium of the light. The body K should be small so that its entropy content can always be neglected in relation to the entropy content of the light.
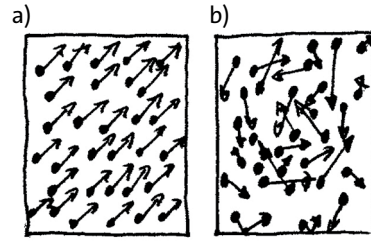
Fig. 7.2 (a) The molecules are not in an internal equilibrium. (b) After a short time, equilibrium has established.
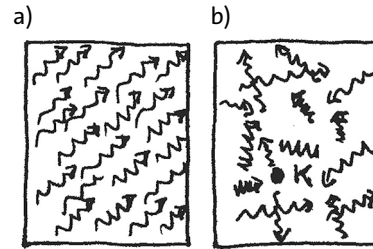
Fig. 7.3 (a) The photons are not in an internal equilibrium. (b) After a short time, the equilibrium has established.
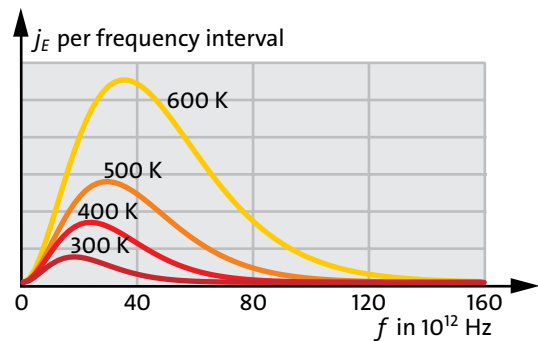
Fig. 7.4 Spectra of the light-gas for 4 different temperatures of the light source. Vertical axis: energy current density per frequency interval. Horizontal axis: frequency in units of 10^{12} Hz

Now we can make the same observation as for the material gas. We imagine that we bring light into a box. This light has a uniform direction and a single wavelength, Fig. 7.3a.

Light is absorbed and emitted by the small body K. The emitted light, however, has a different direction and a different wavelength than the absorbed light. Hence, the light in the box will spread in all directions, to all places and wavelengths after a very short time, Fig. 7.3b, and finally remain in this state. It will remain evenly spread to all directions, it will continue to fill the entire box, and – most remarkably – its spectrum

will not change anymore. It has now a uniform temperature, i.e. the same as body K. As soon as this is the case, K is no longer needed. The light that it emits and the one it absorbs are now equal.

The spectrum of the light-gas only depends on the temperature of the light, but not on the size or shape of the recipients. Figures 7.4 and 7.5 show the spectrum for different temperatures.

To examine light, it is convenient to use a light ray or a light beam. For this purpose, only a hole needs to be opened in the wall of the box so that the light can escape. Such light is called *thermal radiation*.

> Light-gas in a recipient:
> - The light is spread evenly in the entire recipient.
> - The light rays are evenly spread in all directions.
> - The spectrum only depends on the temperature of the light.

From our thought experiment you might conclude that a light-gas and thermal radiation are something very rare and very artificial since there are no boxes with ideally mirrored walls in reality.

In fact, however, thermal radiation can also be produced under more realistic conditions.

One possibility to create a light-gas with a uniform temperature is shown in Fig. 7.6.

Again, we have a recipient, but this one has walls that can absorb light of all wavelengths and that have a uniform temperature. In such a recipient, there is a light-gas that has the same temperature as the walls. While the photons in the light-gas of the thought experiment from Fig. 7.3b move back and forth in the box, they are constantly absorbed by the walls here, and the walls emit new photons that have the same spectrum as the absorbed ones so that the gas is not affected by the absorption and emission process.

There is also thermal radiation escaping from this box in case there is a hole. However, thermal radiation can also be created in an even easier way. Thermal radiation is constantly absorbed by the inner wall of the box from Fig. 7.6, and the same radiation is emitted. Hence, this means that a wall or the surface of a body, that can absorb light of all wavelengths and that has a uniform temperature, also emits thermal radiation, Fig. 7.7. Such thermal radiation is a very common substance: many bodies emit thermal radiation when they glow. The filament of a light bulb, the glowing coal in the barbecue, the flame of a candle, but also the Sun and the stars emit thermal radiation.
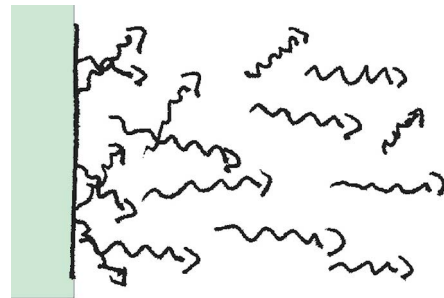
We would now like to highlight the results of our observations:
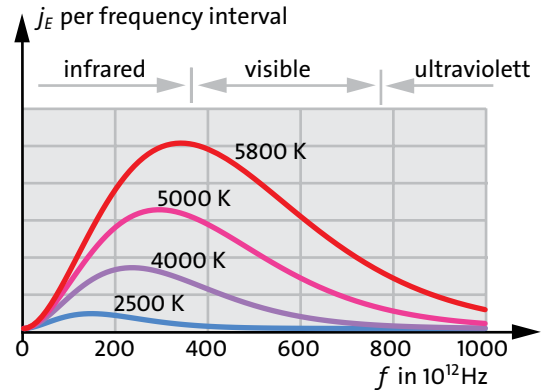
Fig. 7.5 Spectra of the light-gas for 4 different temperatures of the light source. The upper curve is equivalent to the sunlight (5800 K), the other one to a light bulb (2500 K).
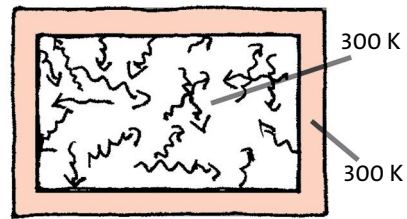
Fig. 7.6 The light-gas in this recipient has the same temperature as the walls.

Fig. 7.7 The surface of a body, that can absorb light of all wavelengths, emits thermal radiation.

> In each recipient, whose walls absorb light of all wavelengths, there is a light-gas.
>
> A body, that can absorb light of all wavelengths and that has a uniform temperature, emits thermal radiation.

We would now like to take a look at the spectra of thermal radiation, Fig. 7.4 and 7.5.

1. They are continuous spectra, i.e. the light contains contributions of all frequencies, albeit not the same amounts for the different frequency intervals.

The spectrum has a single maximum (in contrast to the spectra of fluorescent tubes that have many sharp peaks).

2. We compare the spectra of light sources with different temperatures: with a increasing temperature, the maximum shifts to higher frequencies. We find:

$$f_{\max} = 0.588 \cdot 10^{11} T \frac{\text{Hz}}{\text{K}} \tag{7.1}$$

Thus, the frequency that corresponds to the maximum of the spectrum is proportional to the temperature. Therefore, the temperature of the body can be read from the spectrum of the emitted light.

3. The energy current density j_E, i.e. the energy that is emitted per time interval and per area, increases strongly with the temperature. (The areas below the curves are an appropriate measure.) We obtain

$$j_E = \sigma \cdot T^4$$

with

$$\sigma = 5.67 \cdot 10^{-8} \text{ W/(m}^2 \cdot \text{K}^4)$$

We get a clear view of the implications of these laws by heating up a spike in the Bunsen burner flame. The spike glows red at moderate temperatures. With an increasing temperature, we can observe the following:
- The brightness increases strongly.
- The color of the light changes from red over yellow and orange to white.

> The spectrum of thermal radiation only depends on the temperature of the light source. The energy current increases with T^4. The position of the maximum of the spectrum on the frequency axis is proportional to the temperature.

— **Exercise** —

1. Calculate the frequency of the maximum of the spectrum of thermal radiation that comes from a light source with a temperature of 500 K. Compare with Fig. 7.4. What is the wavelength of the light that corresponds to the maximum?

7.3 Emission and absorption, black bodies

We come back to a remark from the previous section that you might have considered as somehow sec-ondary. To emit thermal radiation, a body must be able to absorb light of *all* frequencies (or equivalently all wavelengths). What does this mean?

Each photon with the frequency f_0 has an energy of $h \cdot f_0$. Here, h is the Planck constant:

$$h = 6.6262 \cdot 10^{-34} \text{ Js.}$$

To be able to absorb light with the frequency f_0, there must be a state that has the distance $h \cdot f_0$ from the ground state on the energy ladder, Fig. 7.8. However, if that is the case, it can also emit light of this frequency.

If the system (an atom, a molecule or a solid body) is in the ground state and if a suitable photon comes along, the photon is absorbed and the system passes into the excited state. If the system is in the excited state, it can return to the ground state through emission of a photon.

> A system that is able to absorb photons of the frequency f can also emit photons of the frequency f.

If a body can absorb light of *all* frequencies, it can also emit light of *all* frequencies.

To emit thermal radiation, a body must be able to absorb light of all frequencies. It may seem that this condition is never fulfilled because each body absorbs (and emits) only light of certain frequencies or frequency ranges. In fact, however, the condition does
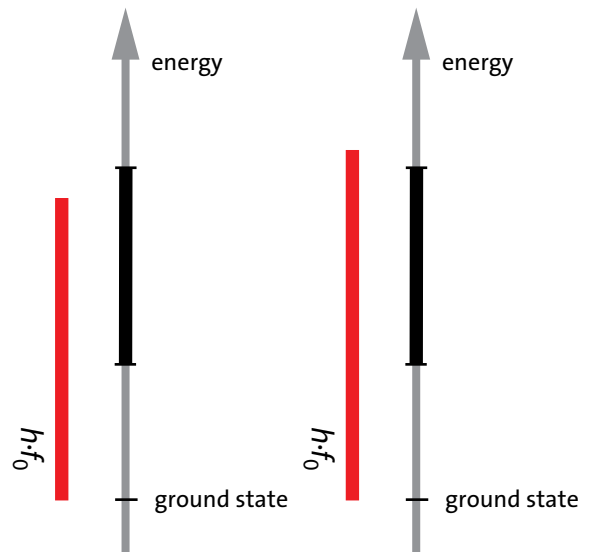
Fig. 7.8 Different energy ladders. The system with the energy ladder (a) can absorb and emit photons with the energy $h \cdot f_0$. The system with the energy ladder (b) cannot.

not to be taken as seriously as it is formulated here. In practice, a body only has to absorb in the spectral range in which the spectral function of Fig. 7.4 and Fig. 7.5 is clearly different from zero. This range varies depending on the temperature.

Glowing bodies

If a body can absorb at all wavelengths of the visible light, it starts to glow in red at approximately 525 °C. At approximately 1000 °C, the emitted light is yellow and from 1200 °C it is white. Hence, one can tell the temperature of a glowing body just by looking. The filament of a light bulb has a temperature of approximately 2500 °K. Fig. 7.5 shows that most of the light is infrared light at that temperature. This explains why light bulbs have such a bad efficiency .

We have concluded that a body only emits light that it can also absorb while it is heated up. Substances that are transparent or white do not absorb any light in the visible spectral range. Hence, they cannot emit in the visible spectral range either. Logically, they are expected not to glow either.

Put small samples of different materials in a hot flame that shines only slightly, e.g. the flame of a propane burner as it is used for brazing, Fig. 7.9. We recommend to try it with the following materials: iron, coal, silicon, white gravel stones, black gravel stones, silica glass, sapphire. Most of the samples glow. The piece of sapphire and the silica glass, in contrast, do not glow. The reaction of the white gravel stone depends on its degree of purity. If it is very white and pure, it does not glow. Possibly, some parts of it are contaminated. Those parts will glow.

Infrared radiation

Back to the absorbing materials. Even if the temperature of a body is not high enough to make it glow, it emits thermal radiation. In that case, practically the whole spectrum is in the infrared range and the radiation is invisible. But it can be felt. You certainly know some examples for this phenomenon. If you hold your hand over an active hotplate or closely to the bottom of an iron, you feel the infrared radiation. Also, a iron oven emits its entropy with thermal infrared radiation, Fig. 7.10.

Some ovens are built in a way to release as much entropy as possible through radiation; other oven types aim at spreading a maximum of entropy with hot air in the room to be heated by means of convection. The same applies for radiators of the central heating system. We distinguish between radiators and convectors. To make a heating system radiate well, it should
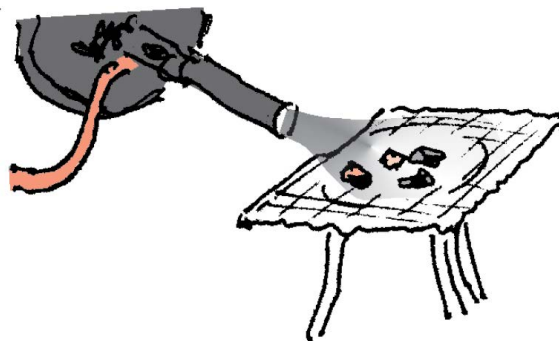

Fig. 7.9 Different small samples are heated up. Although all of them have the same temperature, some glow and others do not.
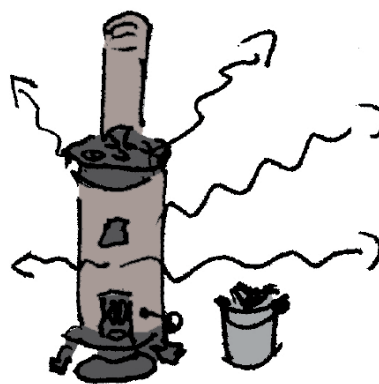

Fig. 7.10 The oven emits the entropy with infrared radiation.

–according to what we have learned so far– be black. In reality, however, most radiators are white. Do the heating system engineers lack physical knowledge? No, they don't. They know that the radiators only need to be "black" in the spectral range in which there is the biggest portion of the radiation, and this is the infrared range in the case of the radiator. In fact, a radiator painted in white is "black in the infrared range".

Emission and absorption at normal temperature

If our radiation laws are correct –and they are– a body does not only radiate when it has a high temperature, but also at low temperature, i.e. at any temperature except at $T = 0$ K. Also, each body around us radiates. The respective spectrum, however, is completely in the infrared range. This is one of the reasons for this light being invisible. (There is another reason, too.)

If we insert the normal temperature 298 K in equation (7.1), we will obtain for the maximum of the spectrum

$f_{max} = 17.5 \cdot 10^{12}$ Hz

This corresponds to a wavelength of 17 μm. Thus, the radiation maximum lies in the far infrared range.

But if all bodies with a normal temperature actually radiate, shouldn't they cool down due to the fact that they are losing energy and entropy? It is correct that all bodies radiate. But because *all* of them radiate, our environment is full of thermal radiation and each body that emits also absorbs this *environmental radiation.* Each body emits as much energy and entropy as it absorbs. Hence, the energy and the entropy accounts are balanced.

This shows the second reason why the infrared light of the environmental radiation is invisible. The same amount of light that is absorbed by our eyes is emitted by the eyes.

A body, whose temperature is lower than the ambient temperature, will slowly heat up, even if there is no heat-conducting connection to a warmer body. The temperature equilibration is due to the fact that it receives more entropy from the environment with the thermal radiation than it emits to the environment through its own thermal radiation.

The cosmic background radiation

It is the most perfect example for a light-gas. A short time after the Big Bang, a light-gas came into existence, which (in contrast to all the light on Earth that is immediately absorbed by some body) has already "lived" for more than 10 billion years. Its original temperature, however, was much higher than the one it has today: at its formation, its temperature was approximately 3 000 K, today it is not far away from the absolute zero point anymore; it is $T = 2.7$ K. The temperature decrease was due to a process that you already know from the material gases: the universe has expanded since its formation during the Big Bang. The entropy of the light in the universe has remained almost constant in the process. Just as the temperature of a material gas declines (at a constant entropy) during expansion, the temperature of a light-gas decreases when it expands (at constant entropy).

The Sun and other stars

Also the Sun and the other stars emit thermal radiation. Hence, it is not difficult to determine the surface temperature of these objects from the Earth: the spectrum is measured, and the temperature is directly derived from the position of the maximum. This is how the surface temperature of the Sun was found: it is ap-
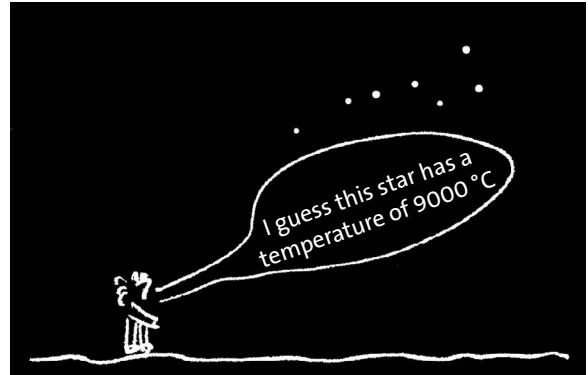
Fig. 7.11 The temperature of a thermal radiator can be estimated with the bare eye.

proximately 5800 K. At this temperature, the greatest part of the radiation consists of visible light. The surface temperatures of the other stars range from 3000 K to 20 000 K, Fig. 7.11.

Much higher are the temperatures inside the stars. Inside the Sun, where the nuclear reaction takes place and where the energy emitted by the Sun comes from, there is a temperature of 15 million Kelvin. On its way to the outside, which is around 500 000 km, the radiation must overcome a very high thermal resistance. This is why the big temperature difference has formed between the inside and the outside.

▬ Exercises ▬

1. The maximum of the spectrum of the star Sirius is at a frequency of $6.5 \cdot 10^{14}$ Hz. What is the surface temperature of Sirius?
2. There are electric radiators that emit the energy convectively by heating up the air directly; and there are others that emit their energy with thermal radiation. Most likely, you have already seen both types. Describe them.
3. Calculate the energy that the Sun emits per second. What is the energy current that reaches the Earth?
   Radius of the Sun: $7 \cdot 10^5$ km;
   radius of the Earth: 6371 km;
   distance between the Sun and the Earth: $1.5 \cdot 10^8$ km

7.4 Reversible and irreversible processes with light

A process in which entropy is created cannot run in a reverse direction, it is *irreversible.* The reversal would mean that entropy is destroyed, which is not possible. In this section we would like to examine a few processes that involve light in order to see if entropy is created or not.

In fact, there is no process in nature in which no entropy is created at all. However, there are processes in which very little entropy is produced. For example mechanical friction or electric resistance can be greatly reduced, so that the entropy creation is almost not perceived anymore. Is such a process reversible? Strictly speaking not. However, two processes can be implemented in which one process is almost the reversal of the other one. When we ask in the following whether a process is reversible, we actually only mean: is it strongly irreversible or is it only slightly irreversible?

Emission and absorption

A body whose temperature is not 0 K emits electromagnetic radiation. But this does not mean that its energy decreases because the body will generally absorb electromagnetic radiation at the same time. The energy balance depends on whether it emits more than it absorbs or vice versa.

We look at two bodies A and B that are arranged opposite to each other, Fig. 7.12. The body on the left has a higher temperature than that on the right:

$$T_A > T_B.$$

The energy that is radiated per time and per surface area from the left to the right is $\sigma \cdot T_A^4$, the energy radiated from the right is $\sigma \cdot T_B^4$.

For the net energy current we obtain:

$$j_E = \sigma \cdot (T_A^4 - T_B^4)$$

As more energy flows from the left to the right than from the right to the left, we have a net energy current from A to B, from the warmer to the colder body – as we expected. If T_A and T_B would be equal, there would be no net energy flow, neither from A to B nor from B to A.
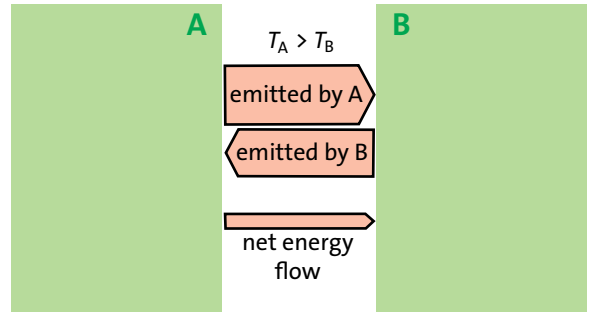
Now we assume that the net energy that flows from A to B is comes from the left side towards the surface, and that it flows away in B from the surface towards the right. The respective currents must be equal. Hence, we have
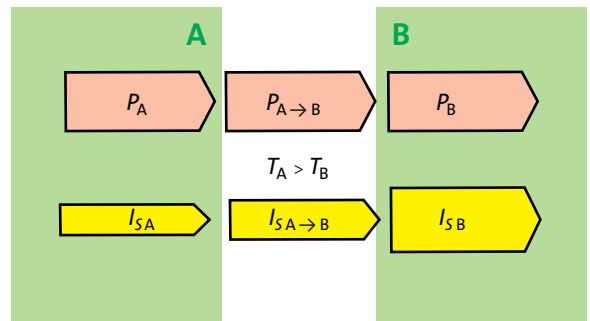
$$P_A = P_B \tag{7.2}$$

Now, we can express both P_A and P_B by the temperature and the entropy current:

$$P_A = T_A \cdot I_{SA}$$

and

Fig. 7.12 The energy current from A to B is greater than that from B to A. Hence, a net energy current is flowing from A to B.

Fig. 7.13 The energy current on the left is equal to that on the right. The entropy current increases while leaving A and entering into B.

$$P_B = T_B \cdot I_{SB}.$$

With equation (7.2) we obtain

$$T_A \cdot I_{SA} = T_B \cdot I_{SB}.$$

Since $T_A > T_B$ we conclude:

$$I_{SA} < I_{SB}.$$

The entropy current has increased on the way from A to B. Entropy was created in the emission-absorption process, Fig. 7.13. The entropy is created both while the energy leaves A and while it enters into B, but not on the way between A and B. It is difficult to tell how the process of entropy production is distributed between A and B. We will not analyze it in detail at this point. In cases where the temperature difference is very great, such as between the Sun and the Earth, the entropy production takes place almost completely in the absorption process.

You have probably noticed that the energy and entropy balance is the same as for the thermal current

through a heat conductor from a higher temperatur T_A to a lower temperature T_B. In both cases, energy flows together with entropy from the high to the low temperature, and additional entropy is created.

We summarize:

> Emission and absorption of thermal radiation
> - at the same temperature: no entropy creation; reversible process;
> - at different temperatures: entropy creation; irreversible process.

We look at an example in which body A is the Sun and body B the Earth. We are only interested in that portion of the energy-entropy current that arrives at the Earth.

The temperature of the Sun is

$$T_A = 5800 \text{ K},$$

and that of the Earth

$$T_B = 290 \text{ K}.$$

With

$$T_A \cdot I_{SA} = T_B \cdot I_{SB}$$

we get

$$I_{SB} = \frac{T_A}{T_B} I_{SA} = \frac{5800 \text{ K}}{290 \text{ K}} I_{SA} = 20 \cdot I_{SA}.$$

Thus, after the absorption of the light by the Earth, the entropy current is 20 times as great as before to the emission by the Sun.

Hence, the much greater part of the entropy that appears at the Earth through the sunlight is created during the emission and absorption process. In fact, most of the entropy is created in the absorption process.

As discussed earlier, processes in which entropy is created include: mechanical friction, electric currents flowing through resistances, chemical reactions.

The amount of entropy, that is created in all these processes everywhere on Earth, is still very small compared to the entropy that is created by the absorption of the sunlight.

A body that warms up in the Sun obviously receives entropy in some way. Now we know how: the greatest part of this entropy is created in the absorption process.

> The greatest part of the entropy that the Earth receives is created in the process of the absorption of the sunlight.

This process is essentially the same as when using a strong laser beam or an electron beam to heat something up, or when heating something in the microwave. Also in this case, entropy is produced when the laser beam, the electron beam, or the microwave beam hits the body to be heated up.

Reflection and refraction

Whenever light falls onto a mirror, a lens or a prism, it is reflected or refracted.

If a reflection process actually happened as shown in Fig. 7.14, it would be reversible. In reality, however, it is only almost reversible. We have already mentioned that a part of the light is always absorbed during reflection. Strictly speaking, the reflection process is therefore not reversible.

Also, refraction is almost reversible. The reason for the absence of complete reversibility is the fact that a part of the light that falls, for example, on a glass surface is always reflected, Fig. 7.15a. Fig. 7.15b shows the expected reversal of the process. Do you see that the picture illustrates an impossible process?

Just as we sometimes say in the context of mechanics: "we will neglect friction; we will assume that friction is so small that we almost don't notice it", it can
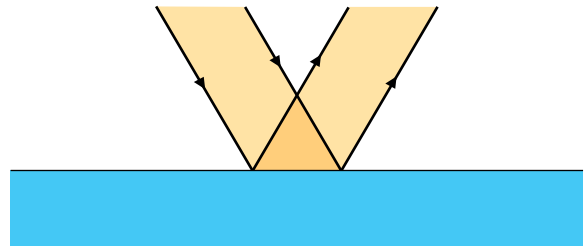

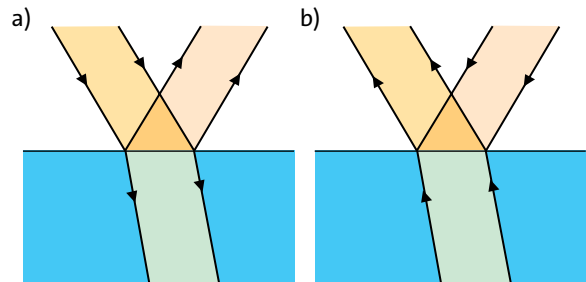**Fig. 7.14** Reflection is an almost reversible process.

Fig. 7.15 Refraction is an almost reversible process. (a) A part of the incident light is reflected. (b) The reversal is, strictly speaking, an impossible process.

often be assumed that the irreversibility does not hamper the processes of refraction and reflection. Hence, we can also say in this respect:

> Reflection and refraction of light are (almost) reversible processes.

Scattering

Scattering of light is the process in which a beam of light with a uniform direction is transformed into light that runs in many different directions.

Light is scattered on each white surface, be it on a sheet of paper or on a white wall, Fig. 7.16a.

Light is also scattered when it falls on a frosted glass plate. In this case, the scattered light does not only run in a backward, but also in a forward direction, Fig. 7.16b.

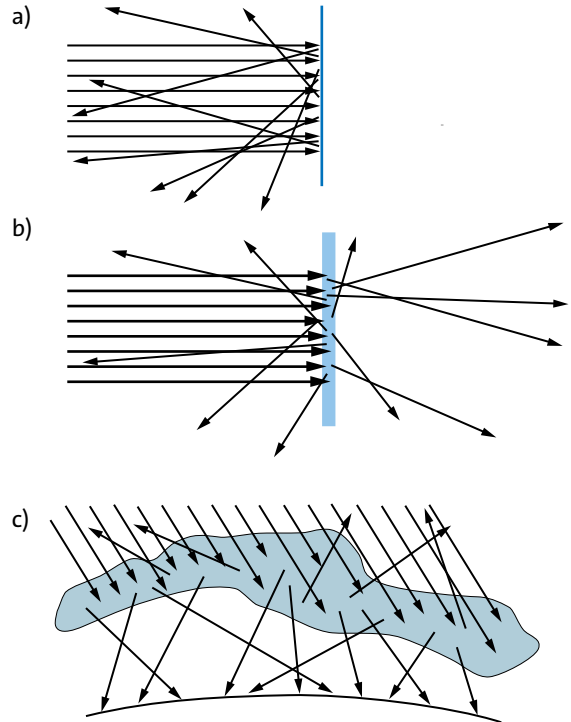A third example for scattering is shown in Fig. 7.16c. The light of the Sun falls on a layer of clouds.

In each of these examples, the incident light is different from the outgoing light in one substantial aspect: the angular range over which the outgoing light scatters is larger than for the incident light. Figuratively speaking, we could also say that during scattering, light "expands" into a larger angular range. This scattering is irreversible, similar to the expansion of a gas into the vacuum. Thus, entropy must have been created in the process of scattering. The scattered light has more entropy than the incident light.

The greatest part of the entropy that the Earth receives is created in the process of the absorption of the sunlight.

> Scattering of light is an irreversible process.

Fig. 7.16 Scattering of light (a) by a sheet of paper, (b) by a frosted glass a plate and (c) by a cloud

Exercises

1. (a) Sketch the Sun as it emits light to the space. Sketch the reverse process. Can we tell from the sketches whether one of the two processes is not allowed? (b) Sketch a body on Earth that absorbs sunlight. Sketch the reverse process. Can we tell from the sketches whether one of the two processes is not allowed?
2. Sketch a mirror and a light beam that is reflected by the mirror. Sketch the reverse process. Can we tell from the sketches whether one of the two processes is not allowed?
3. Discuss the scattering process that is caused by the frosted glass of a light bulb. Sketch a light beam that comes from the filament. The light bulb should be located inside a big, spherical lamp shade made of silk tissue paper. What happens to the light when it falls on the lamp shade?

8 ENTROPY CURRENTS IN THE GAS LAYERS OF PLANETS AND STARS

8.1 The troposphere

The air that surrounds the Earth is called *atmosphere*. The air becomes increasingly thinner towards the top. Hence, the atmosphere has no clear end. But when you move towards the top and when you have reached an altitude of approximately 12 km, 70 % of the air are located under you. This area, which contains the greatest part of the air and in which the most important weather processes take place, is called *troposphere*. The troposphere is our focus of attention in the following.

Chemical composition

4/5 of the troposphere is nitrogen and 1/5 is oxygen. Apart from that, it contains smaller quantities of other gases: water vapor, carbon dioxide and the inert gases argon, neon and helium. More accurate substance percentages are listed in Table 8.1. The values correspond to an atmosphere that does not contain any water. The water content can hardly be indicated as it varies very strongly. It does not only depend on the place on the surface of the Earth and on the weather, but also and above all on the altitude. We can keep in mind 1 % as a rough value. On the surface of the Earth, the water content can amount up to 4 %. In an altitude of 10 km, it is only a thousandth of this value. For the substances in Table 8.1, the percentage is independent of the altitude

Although CO_2 and H_2O only make up a small part of the overall amount of gas, these gases play an important role for the heat balance of the Earth.

substance	% amount of substance
N_2	78.08
O_2	20.95
Ar	0.93
CO_2	0.03

Table 8.1 Composition of the troposphere

Energy currents through the troposphere

The Earth receives energy with the sunlight. At the outer edge of the atmosphere, there approximately

$$j_E = 1368 \text{ W/m}^2.$$

This value is called *solar constant*. This radiation hits the Earth only from one side. If we imagine, that it spreads over the whole surface of the Earth an average of 342 W/m^2 will result. A large part of this light – 31 % – however, is irrelevant for the energy balance of the atmosphere: it is directly scattered back by the air, by clouds and by the surface of the Earth. What finally remains amounts to approximately

$$j_E = 236 \text{ W/m}^2.$$

This light is absorbed; most of it at the surface of the Earth, a smaller part in the atmosphere. We will not make a big mistake if we pretend that it is absorbed only at the surface of the Earth.

Although the light already brings entropy from the Sun, approximately 20 times more entropy is created in the absorption process.
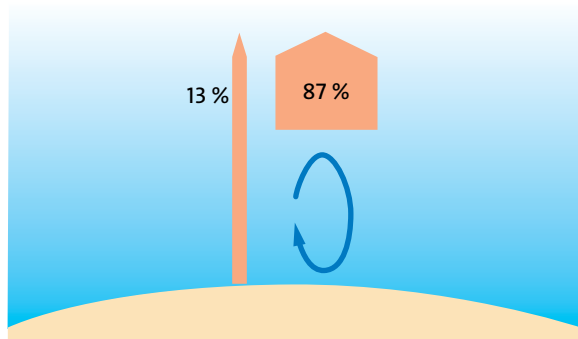
Fig. 8.1 The sunlight is absorbed by the surface of the Earth. Much entropy is created in the process. A small part of it is directly radiated to space with infrared light. The greater part moves convectively with the air to the upper side of the troposphere. From there, it is radiated with infrared light. The percentages refer to the energy.

This entropy would now lead to a continuous warm-up of the Earth as a whole. However, this does not happen as the Earth also emits entropy, together with the respective energy. Its only possibility is the emission of electromagnetic radiation to the space: just as any other warm body, the Earth emits electromagnetic radiation. The maximum of the spectrum of this radiation is in the infrared range.

However, the troposphere is almost impermeable for such infrared radiation. Only in a pretty narrow range of the spectrum, the *atmospheric window*, it is transparent. This means that only a small part of the entropy is radiated directly by the Earth into space through the atmospheric window. The greater part first needs to move from where it is created, i.e. at the surface of the Earth, to where it is radiated: at the outside of the troposphere. From there, the atmosphere is tranparent for infrared light.

Hence, the Earth gets rid of its entropy, and consequently also of its energy, in two ways, Fig. 8.1:

- The smaller part – 13 % of the energy – is radiated directly into space through the atmospheric window.
- The remaining 87 % are first absorbed by the air, then transported to the upper side of the troposphere and only radiated there.

Hence, the troposphere works as a heat-insulating material. This heat-insulating effect is called *greenhouse effect*, because a greenhouse is also heated with sunlight. In fact, the existence of the heat-insulating effect on the Earth is more complicated than in case of a greenhouse.

In section 8.4 we will talk about the 87 % of the energy that are transported by the air. In 8.5 we will discuss the remaining 13 %. Before that, we need to analyze the general behavior of liquids and gases in the gravitational field.

The various processes taking place in the atmosphere are rather complex. Hence, we need to limit ourselves to the major aspects. We will therefore disregard the fact that the pressure and the temperature in the horizontal direction depend on the location. For the density, the pressure, the temperature, the energy current etc. at a given position on the surface of the Earth, we use the respective average values. We only take into account the dependence on altitude. Of course, we cannot describe wind, weather fronts and similar phenomena in this way.

Exercises

1. We stated that a square meter of the surface of the Earth receives an average of 236 W from the Sun. Calculate this value using the other indications in the text.
2. If the Earth had no atmosphere, it would have to emit entropy and energy directly with infrared radiation. What would be the approximate temperature of the surface of the Earth? If any numerical value is missing, make an estimate.

8.2 Stratification of liquids

We are interested in gases in the gravitational field that are heated from below. To understand them, we first need to examine a simpler system: liquids in the gravitational field.

Imagine a certain amount of water – in a recipient or in a lake, as you prefer – that has no uniform temperature. This water will stratify in a way that the water with the highest density is located at the bottom, and the water with a lowest density at the top. In general, colder water has a higher density than warmer water. Hence, the colder water will move towards the bottom, the warmer one rises to the top. The warm water "floats" on the cold water.

If such a stratification is disturbed by bringing the water with the higher density to the top, this water will dwindle down by itself. A stratification that emerges by itself is called *stable stratification*. As long as the denser water is still on top, the stratification is *unstable*. An unstable stratification passes to a stable one by itself, Fig. 8.2.
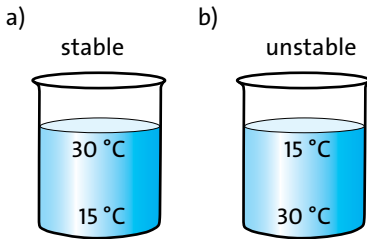
Fig. 8.2 (a) Stable stratification: the density of the water is lower at the top than at the bottom. (b) Unstable stratification: the density of the water is higher at the top than at the bottom.

An example for a stable stratification that you certainly know: on a sunny day, the water of a sea is clearly warmer on the surface than deeper in the water.

For water with a temperature between 0 °C and 4 °C, the density increases with growing temperature: warmer water is denser than colder water, Fig. 8.3. In the stable stratification, the colder water is now floating on the warmer one.

Hence, the temperature in a frozen pond increases towards the bottom, Fig. 8.4

We will now look at a third stratification type. It can be obtained through vigorous stirring of the water. You can imagine what will happen in the process: the temperature becomes uniform or *homogeneous*. There are no more preferred positions for the individual portions of water. If such a distribution of the water is disturbed, the water will not change its stratification anymore. This state is called *indifferent stratification.*

> *Indifferent stratification of a liquid:*
> - the density is the same at all depth levels;
> - the temperature is the same at all depth levels.
> *Stable stratification of a liquid:*
> - the density increases towards the bottom.
> *Unstable stratification of a liquid:*
> - the density decreases towards the bottom.

We will now ask what happens if water with a uniform temperature, i.e. indifferent stratification, is heated up. Thereby, we need to differentiate where the heating is done, i.e. at the top or at the bottom.

Let's look at the lake again. If the water temperature is homogeneous at first and then the Sun shines onto the water (of course from the top), the upper layers become warmer than the lower ones. The water passes from the state of indifferent to the state of stable stratification.
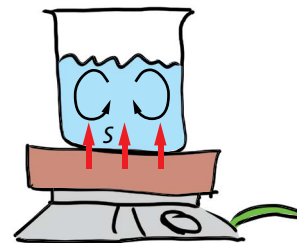
Next, we heat a liquid from below. There is also a well-known example for this process: the water in the pot on the hotplate, Fig. 8.5.
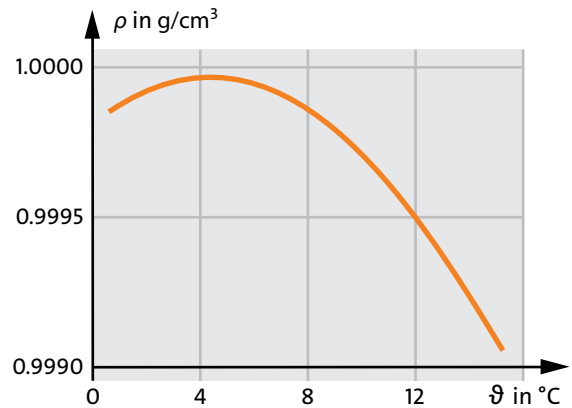
Fig. 8.3 Density of water as a function of the temperature. Below 4 °C, the density decreases again.
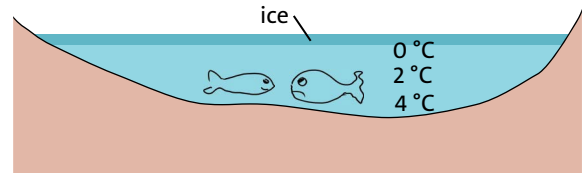
Fig. 8.4 Stable stratification: the water has a lower density at the top than the water at the bottom.

Abb. 8.5 Heating from below: there is convection. This "stirring" ensures an indifferent stratification.

Again, the temperature distribution is homogeneous at first. During the heat-up, entropy is supplied to the lower layers of the water. Thereby, the stratification becomes unstable and "tips over". The water from the bottom moves to the top, the one from the top moves to the bottom, convection starts. The convection then triggers a "stirring process" of the water. The stirring causes a homogeneous distribution of the supplied entropy. This ensures immediate equalization of the temperature differences caused by the heating.

> *Heating from below:*
> - a stable stratification results.
> *Heating of a liquid from above:*
> - convection sets in. The indifferent stratification is always restored.

You can verify these statements on your own.

1. Heating from below: a pot is filled with water and heated on the hotplate. Measure the water temperature in different depths carefully and without stirring.

2. The water is heated from above with an infrared lamp. It is sufficient to have a temperature of 35 °C to 40 °C at the surface of the water. Measure the temperature again carefully at the top and at the bottom. If you do not have a thermometer, you can simply dip your hand carefully in the water. If you have no infrared lamp, you can warm up the water from above in the oven in the barbecue mode. (Caution: the recipient must be heat-resistant. Be careful to avoid burning yourself.)

For water in the temperature range between 0 °C and 4 °C, the rules are as follows:

> Water between 0 °C and 4 °C
> *Heating from below:*
> - a stable stratification results.
> *Heating of a liquid from above:*
> - convection sets in. The indifferent stratification is always restored.

Exercises

1. Water of several different temperatures between 0 °C and 8 °C is gently brought into a recipient. We do not stir. What kind of stratification will result?
2. Explain the abovementioned mnemonic for water between 0 °C and 4 °C.

8.3 Stratification in gases

Many aspects are the same as for liquids, but others are completely different.

First, the experiments cannot be made in the classroom or in the laboratory. But nature itself represents a great laboratory instead. We only need to observe the processes that take place in the troposphere.

At first, we ask how the indifferent stratification looks like. How will the stratification look like if air is vigorously stirred? The troposphere of the Earth is always disarranged by the winds. Hence, it is in a state that can be regarded as an indifferent stratification for our purposes.

This state differs significantly from the indifferent stratification of a liquid. In the air, "stirring" neither leads to a constant density, nor to a constant temperature. Both density and temperature decrease in the upwards direction as we know. We will try to understand what happens during "stirring".
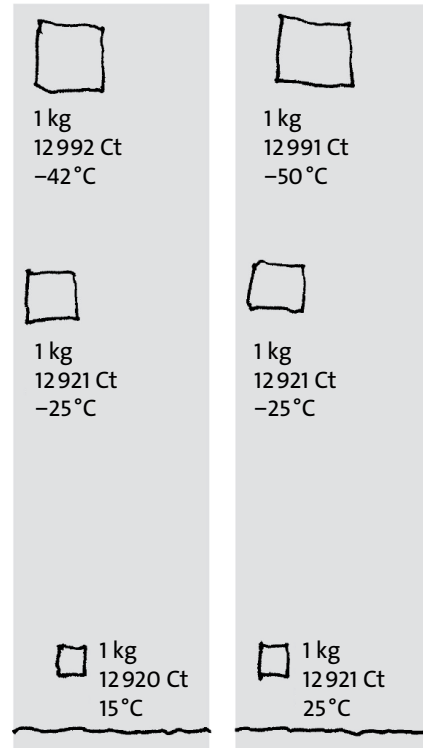
Fig. 8.6 (a) Different air portions of 1 kg contain different amounts of entropy at first. (b) Stirring leads to an equal distribution of the entropy among all air packages. The air packages that are located further up will then have a lower temperature than the ones further down.

We hypothetically divide the air into many small portions of equal size, Fig. 8.6. By equal size we mean: portions of the same mass (or equivalently the same amount of substance).

Let's first assume that the air has been heated very unevenly and unsystematically, so that the different portions of air contain different amounts of entropy. Stirring leads to a redistribution of the entropy among the air packages in a way that each portion, each kilogram of air has the end the same amount of entropy.

At the same entropy, however, an air portion that is located further up has a lower temperature than a portion further down. This is what we learned in section 2.5. Consequently, stirring leads to the formation of a temperature decline in the vertical direction.

This might look peculiar at first sight. Doesn't stirring have a balancing effect on everything? Stirring of the cake dough does not only result in a homogeneous composition, but also in a uniform temperature. Although eggs (from the fridge), flour (from the shelf) and butter (previously kept warm) had different temperatures at the beginning, the dough does not only

have a homogeneous composition, but also a uniform temperature after stirring. In case of the atmosphere, things are different. The temperature distribution does not become homogeneous.

But maybe this is not so peculiar after all. The pressure behaves the same way, and nobody is surprised about it: stirring – not only of air, but also of water – does not change the fact that the pressure remains higher at the bottom than at the top.

> *Indifferent stratification of a gas:*
> - the density decreases towards to top;
> - the temperature decreases towards the top.

The dependence of the temperature T on the altitude h at an indifferent stratification is though very simple, Fig. 8.7. It is a linear function:

$$T(h) = - a \cdot h + T_0$$

The factor a tells us how strongly the temperature decreases with the altitude. We refer to a as *temperature decline*. It depends on the gravitational field (the gravitational field strength g) and on the properties of the gas: on its molar mass and on its heatability. For waterfree air above the surface of the Earth, $a \approx 10$ K/km.

To apply the formula, the temperature T_0 at the zero point of the altitude needs to be set. As a zero point of the altitude, we choose for example the altitude of the sea level. Then, T_0 is the temperature at sea level.

In the next section, however, we will see that the formula is not yet useful for the real atmosphere. The reason is the water that is contained in normal air.

One question remains: what is a stable and an unstable stratification of a gas like? Just as for a liquid, we obtain a stable stratification out of the indifferent one by increasing the density at the bottom and reducing it at the top; or better: by increasing the density decline. For gases, an increase of the density decline comes with a reduction of the temperature decline, Fig. 8.7.
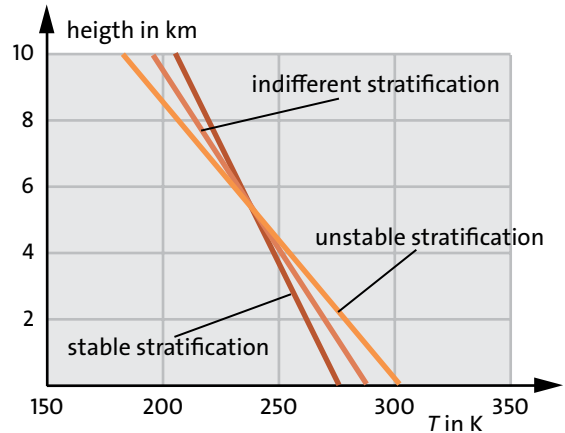
Accordingly, the stratification becomes unstable if the density decline is lower and the temperature decline higher than for the indifferent stratification.

> *Stable stratification of a gas:*
> - the density decline is greater, the temperature decline smaller than for the indifferent stratification;
>
> *Unstable stratification of a gas:*
> - the density decline is smaller, the temperature decline greater than for the indifferent stratification.

Fig. 8.7 Temperature as a function of altitude for water-free air. If the temperature decline is greater than in the case of the indifferent stratification, the stratification becomes unstable. If it is lower, the stratification is stable.

We now would like to heat up air, that at first is stratified indifferently, from below. Just as the stratification of water, the stratification of air becomes unstable, it tips over. Air from the bottom rises to the top and air from the top comes down. Convection sets in. Just as in the case of a liquid, convection is a stirring process. Through heating, we try to constantly disturb the even distribution of the entropy in the air. Convection, however, ensures that the entropy remains evenly distributed.

> *Heating of a gas from below:*
> - convection sets in. The indifferent stratification of the gas (evenly distributed entropy) is always restored.

▬ **Exercise** ▬

1. A room that is heated with a radiator in winter. Describe the way of the entropy. What is the temperature distribution? Is the stratification of the air unstable, stable, indifferent?

8.4 The convective energy transport through the troposphere

We already know the most important aspects of the 87 % of the energy transfer through the troposphere mentioned in section 8.1. The air is supplied with en-

8 ENTROPY CURRENTS IN THE GAS LAYERS OF PLANETS AND STARS

tropy from below, which is then moved convectively to the upper side of the troposphere. From there, it is radiated to the space with infrared light.

We must yet mention a trick that nature uses to charge the air with a maximum amount of entropy. (It is the same trick that engineers apply when they have to transport a large amount of entropy.) Water is vaporized on the surface of the Earth. As you know, much entropy is needed for vaporization. The water vapor mixes with the remaining air and is transported with it to a higher altitude. There, the water vapor condenses and raindrops are formed. In the process, the water returns the stored entropy to the nitrogen and the oxygen of the air. Although the water content of the air is low, see section 8.1, the water is sufficient to ensure a significant part, i.e. a third of the convective entropy transfer, to the top. The transfer of the remaining two thirds occurs on the "normal" way, i.e. through heating of the whole air including nitrogen and oxygen.

The fact that a phase transition takes place has a strong impact on the heatability of the air and hence on the factor a. For the troposphere of the Earth, we obtain an average of $a \approx 6$ K/km.

> Temperature in the troposphere as a function of the altitude:
> $$T(h) = -6 \text{ K/km} \cdot h + T_0 \qquad (8.1)$$

Of course, the formula is valid only up to a certain altitude. Beyond this altitude h_D, the air becomes permeable for infrared radiation. There, it releases the entropy, that it has absorbed further down, with electromagnetic radiation into space. In the process, it cools down and moves back downwards.

The temperature $T(h_D)$ in the altitude h_D adjusts in such a way that exactly the entropy that is supplied from below is released into space. With equation (8.1), we consequently obtain a higher temperature at the surface of the Earth.

This temperature difference is much more significant at the surface of Venus. Among the planets of the Sun, Venus has the most interesting atmosphere. Although Venus has approximately the same size as the Earth, its atmosphere contains about 90 times more gas than the Earth, mostly CO_2. As a consequence, the pressure at the surface of Venus is 90 times higher than the pressure at the surface of the Earth, i.e. approximately 90 bar. This is why the troposphere of Venus is much thicker than that of the Earth. And hence, the temperature difference between the upper and the lower side of the troposphere is much higher than on

Earth. The temperature at the surface of Venus is approximately 730 K. Without the thick atmosphere it would be very cold on Venus.

— **Exercises** ═══════════

1. Estimate the temperature that the surface of Venus would have if Venus had no atmosphere.
2. Quito, the capital of Ecuador, is located right on the equator at an altitude of 2850 m above sea level. Estimate the temperature.
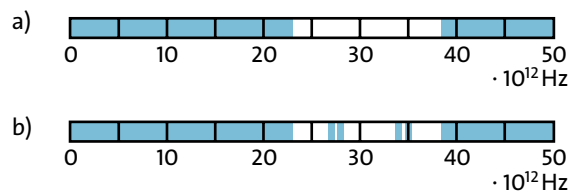
Fig. 8.8 Transparency of the troposphere in the spectral range in which the surface of the Earth emits (a) Normal air. (b) Air with CFC impurities.

8.5 The entropy transport through the atmospheric window

Fig. 8.8a shows for which kinds of light the troposphere is transparent. It shows the frequency range in which the Earth emits electromagnetic radiation. We can see that the atmospheric window is located between approximately $23 \cdot 10^{12}$ Hz and $38 \cdot 10^{12}$ Hz. Expressed in wavelengths: between 8 μm and 13 μm. The carbon dioxide and the water vapor are responsible for the absorption. Nitrogen and oxygen are transparent throughout the entire spectral range.

Although CO_2 and H_2O only make up a small part of the air, these gases play an important role for the heat balance of the Earth. Without them, there would not only be a window for the infrared light, but the atmosphere would be transparent in the whole infrared domain, and it would be much colder on Earth.

The radiation that goes through the atmospheric window is responsible for 13 % of the energy transfers that do not occur convectively. The infrared radiation, that is absorbed by the air, warms up the air and hence contributes to the convective transfer as discussed in the previous section.

8.6 The influence of greenhouse gases on the entropy transport through the troposphere

Gases are created through the different activities on Earth and released into the atmosphere. These gases can hamper the entropy transfer through the troposphere in two ways.

If gases absorb in the range of the atmospheric window, such as the chlorofluorocarbons (CFCs), the window becomes smaller, Fig. 8.8b. As a consequence, the temperature of the surface of the Earth increases until the evacuation of the entropy is ensured again. Both the convective evacuation and the radiation through the atmospheric window will increase if the temperature of the surface of the Earth rises.

However, the entropy evacuation is also hampered by gases that do not absorb in the atmospheric window, but in an area where the troposphere absorbs itself, e.g. through additional carbon dioxide. Carbon dioxide is created during combustion of coal and hydrocarbons, i.e. gasoline, diesel, jet fuel, natural gas, etc. It is evacuated into the atmosphere in very large quantities.

Starting from altitude h_D, the troposphere is transparent for any infrared radiation because practically all CO_2 is below h_D.

If the CO_2 content of the air grows, h_D will increase. The point at which emissions are released to space will rise. As h_D increases while $T(h_D)$ remains equal, the temperature at the surface of the Earth must rise. Fig. 8.9 shows how the straight $T(h)$ line moves as the CO_2 content of the air increases. We see: more CO_2 in the air means a higher temperature at the surface of the Earth.

Fig. 8.10 shows the CO_2 content of the Earth's atmosphere in the course of the last 200 years.

8.7 The heat transport in the Sun and in other stars

A star has quite something in common with the atmosphere of the Earth, more precisely: with the troposphere. To give a concrete example, we will look at the star "Sun" in the following.

Inside the Sun, in a region whose diameter is approximately 10 % of the radius of the Sun, a nuclear reaction is running in which entropy is produced. The
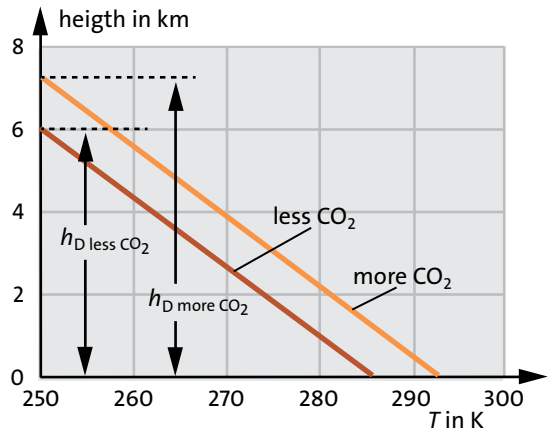

Fig. 8.9 The straight line $T(h)$ makes a parallel shift to higher temperatures as the CO_2 content of the air increases.

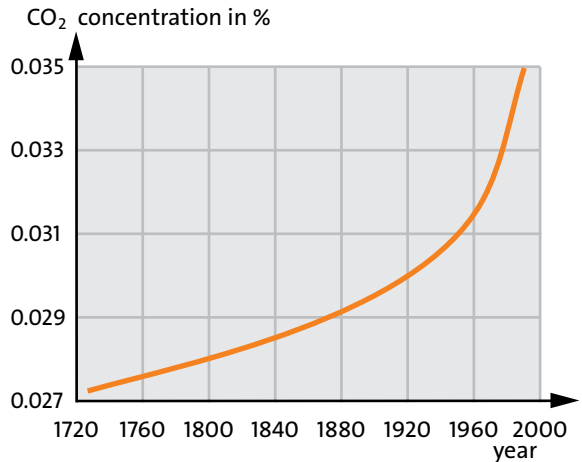**Fig. 8.10** CO_2 content of the Earth's atmosphere in the course of the last two hundred years.

temperature there is around 15 million K. The created entropy must be transported away to the outside. Therefore, it has to permeate the area of gaseous hydrogen outside of the reaction zone. On the outer surface of the Sun, whose temperature is approximately 6000 K, it is radiated away with the sunlight.

Just as for the troposphere of the Earth, we have a source of entropy inside, and the created entropy needs to be transported away to the outside through a gas in the gravitational field, Fig. 8.11.

We could expect the transfer to work the same way as in the troposphere. The gas would stratify indifferently. Through the heating from below, convection would emerge to ensure that the entropy would be transported to the outside and that the indifferent stratification would be maintained. However, this oc-
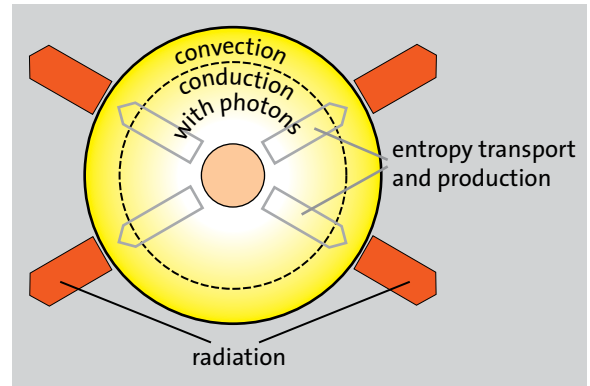
curs only in the outer tenth of the Sun radius. On the longer part of the way, something else happens.

The cause is that the gas of the Sun, contrary to the air of the Earth, is a good heat conductor. The heat conduction is ensured by light that is constantly absorbed and emitted.

To understand the consequences of this heat conduction, we make a thought experiment: the gas is vigorously stirred so that an indifferent stratification emerges. As we know, the indifferent stratification comes with a certain temperature deccline. In case of the Sun, this temperature decline, however, results in a strong entropy current because the gas is, as mentioned, a good heat conductor. This entropy current is greater than what is necessary to transport the entropy, that is created inside, away. Hence, the temperature difference in the gas layer decreases in our thought experiment until the entropy current has achieved the right value. As the temperature decline is now lower than the one that corresponds to the indifferent stratification, the resulting stratification is stable. There is no convection.

Fig. 8.11 In the Sun, the entropy created at the center must permeate a gas layer in the gravitational field. The heat conductivity of the gas, however, is so good that the gas remains stably stratified. Convection occurs only in the outer tenth of the radius of the Sun.

Exercise

1. Entropy is created on the way from the center to the surface of the Sun. By how much does the entropy current increase?