Chapter 3
Entropy and Temperature

In phenomenological description (comparable to a kind of "wanted poster"), the entropy appears as a kind of "stuff" which is distributed in space, can be stored or transferred, collected or distributed, soaked up or squeezed out, concentrated or dispersed. It is involved in all thermal effects and can be considered their actual cause. Without it, there would be no hot and no cold. It can be easily generated, if the required energy is available, but it cannot be destroyed. Actually, entropy can be easily recognized by these effects. This direct understanding of the quantity S is deepened by a simplified molecular kinetic interpretation.

In addition to the *first law* of thermodynamics, a version of the law of conversion of energy (Sect. 2.3), the *second law* will be formulated in the following without recourse to energy and temperature. On the contrary, the absolute temperature can be introduced via energy and entropy. The *third law* is also easily accessible, and heat engines and heat pumps are analyzed after this introduction, without discussing process cycles, gas laws, or energy conversion processes. In closing, the entropy generation as a consequence of entropy conduction will be discussed.

3.1 Introduction

Misjudged and Avoided The central concepts of thermodynamics are *entropy* S and *temperature* T. While everyone is familiar with temperature, entropy is considered as especially difficult, in a way the "black sheep" among physicochemical quantities. School books avoided it totally in the past, introductory physics books often only "mention" it, and even specialists in the field like to avoid it.

G. Job, R. Rüffler, *Physical Chemistry from a Different Angle*,
DOI 10.1007/978-3-319-15666-8_3

But why is the subject of entropy avoided when it is actually something rather simple? It is just what is considered "heat" in everyday life (Fig. 3.1)!

Unfortunately, the name "heat" was given to another quantity (compare Chap. 24) which robbed S of its natural meaning, making S an abstract concept that is difficult to understand and deal with. Therefore, entropy could only be introduced abstractly, i.e., *indirectly* by integrating a quotient formed from energy and temperature, making it difficult to deal with. Furthermore, it is customary to interpret entropy atomistically as a measure of the probability of a certain state of a system composed of numerous particles. In chemistry, we must be able to infer our actions in the laboratory from atomistic concepts. In other words, we must be able to transfer the insight gained on one level to a different one as *directly* as possible. In the following we will demonstrate how to accomplish this.

Macroscopic and Microscopic View To illustrate this, we will characterize entropy at first by use of some of its typical and easily observable properties—similarly as already the energy. In the same way, a wanted person would be described by a list of easily distinguishable ("phenomenological") characteristics like height, hair color, eye color, etc. This group of characteristics is basically what makes up the person and his or her name is just an identification code for this group of characteristics. A "wanted poster" is an example for such a group of characteristics in strongly abbreviated form. Our intent is to design such a "wanted poster" for entropy that allows it to be defined as a measurable physical quantity. After that has been done, we will substantiate it by reverting to ideas actually foreign to macroscopic thermodynamics: particle concepts (atomistic concepts) usually only

Fig. 3.1 Entropy in everyday life: Generally stated, it is that which hot coffee loses when it cools down in a cup and what is added to a pot of soup to heat the food. It is what is generated in a hot plate, a microwave oven, and an oil heater. Entropy is also what is transported in hot water and distributed by a radiator. It is what is conserved by the insulating walls of a room and by the wool clothing worn by the body.

construed as thoughts. The idea of "entropy $\approx$ everyday 'heat'" is always kept in mind as an additional aid to understanding. After the phenomenological characterization we will discuss how a measure for entropy can be introduced, and that directly, meaning without recourse to other quantities (direct metricization) (Sect. 3.7).

3.2 Macroscopic Properties of Entropy

Thermal Effect Let us begin with the characteristics that are important in our everyday experience. Entropy can be understood as a weightless entity that can flow and is contained in everything to one extent or another. In physical calculations it represents like mass, energy, momentum, electric charge, and amount of substance a *substance-like* quantity, meaning that it is like the other quantities a measure for the amount of something which can be sought as distributed in space. Thereby, it is not important whether this "something" is material or immaterial, stationary or flowing, unchangeable or changeable. It can be distributed in matter, it can accumulate, and it can be enclosed. Entropy can also be pumped, squeezed, or transferred out of one object and into another one. The entropy density is high if a lot of entropy is accumulated in a small area and low if it is widely distributed.

Entropy changes the state of an object noticeably. If matter, for example, a piece of wax or a stone, contains little entropy, it is felt to be cold. If, however, the same object contains more or a lot of entropy, it can feel warm or even hot. If the amount of entropy in it is continuously increased, it will begin to glow, firstly dark red, then bright white, subsequently melt, and finally vaporize like a block of iron would, or it may transform and decompose in another way, as a block of wood might. Entropy can also be removed from one object and put into another. When this is done, the first object becomes cooler and the second, warmer. To put it succinctly: Entropy plays a role in all thermal effects and can be considered their actual cause. Without entropy, there is no warm and cold and no temperature. The obvious effects of entropy allow us to observe its existence and behavior quite well even without measurement devices.

Spreading Entropy tends to *spread*. In a uniform body, entropy will distribute itself evenly throughout the entire volume of the body by flowing more or less rapidly from locations of higher entropy density (where the body is especially warm) to areas where the body is cooler and contains less entropy (Fig. 3.2).

If two differently warm bodies touch each other, entropy will flow from the warmer one to the cooler one (Fig. 3.3).

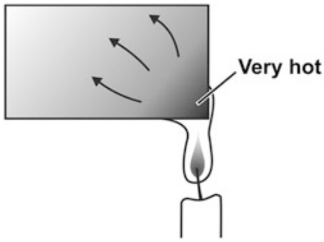


Fig. 3.2 Spreading of entropy within a uniform body.

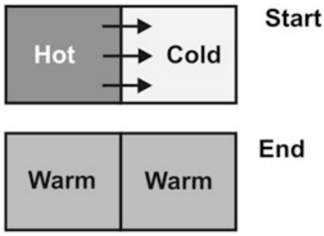


Fig. 3.3 Spreading of entropy from one body to another (entropy transfer).

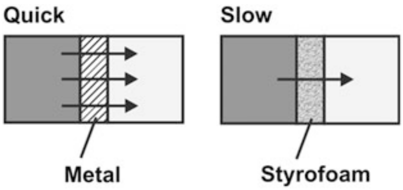


Fig. 3.4 Good and bad entropy conductors.

There are substances which conduct entropy very well, such as silver, copper, aluminum, and diamond, and others, such as wood, foamed plastic, or air, which only allow entropy to pass through them very slowly (Fig. 3.4).

Good entropy conductors are used to transfer entropy over a short distance. In order to overcome distances of decimeters and more—for example, for regulating the temperature of a room or an apartment or for cooling a motor—the conductivity is too small, the conductive transport of entropy—meaning the transport by conduction alone—is too slow. If one would like to transfer entropy from the furnace in the basement or the solar collector on the roof this has to be done convectively—meaning the entropy is transported by circulating water to the radiator and from there by circulating air into the room. To remove excess entropy out of a combustion engine, water is pressed through its cooling channels or air is blown over its cooling fins. If distances of meters and more are to be overcome like in industrial plants or even distances of kilometers like in the atmosphere or the oceans, convection is the dominant type of transport.

Bad conductors, however, are used to contain entropy. A vacuum acts like an especially good insulation. Entropy is also able to penetrate layers without matter by radiation, but this process takes place rather slowly at room temperature or below. This property is used in thermoses to keep hot beverages hot and cold

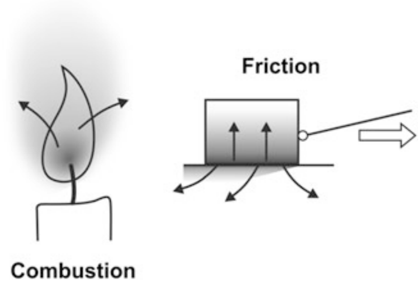


Fig. 3.5 Entropy generation: Locations where entropy was generated are generally noticeable by increased temperature.

beverages cold. Entropy transfer by radiation can be minimized by silvering the surfaces of the flask.

Generation and Conservation Entropy can be easily *generated*. For instance, great amounts of it are generated in the heating coils of a stove plate, in the flame of an oil burner, and on the surfaces rubbing together in a disc brake, but also by the absorption of light on a sunlit roof, in the muscles of a runner, and in the brain of a person thinking. In fact, entropy generation occurs almost every time something changes in nature (Fig. 3.5).

The most remarkable characteristic of entropy, however, is this: While it is generated to some extent in every process, there is no known means of destroying it. The cumulative supply of entropy can increase, but can *never decrease*! If entropy has been generated in a process, one cannot consequently reverse this process as one would rewind a film. The process is *irreversible* as one says. This does not mean, however, that the body in question cannot attain its initial state again. This may be possible by way of detours, but only if the entropy which was generated can flow out of it. If there is no such disposal available or accessible, because the system is enclosed by entropy-insulating (= heat-insulating or adiabatic) walls, the initial state is indeed inaccessible.

Laws of Thermodynamics Since it takes energy to generate entropy—which cannot disappear again—it seems as if energy is lost. This was the commonly held belief until the middle of the nineteenth century. Only in the second half of that century did the concept take hold that even under these circumstances, energy is conserved (compare to Sect. 2.3). Since then, this has been referred to as the *first law of thermodynamics* and is the basis of all teachings in the field of thermodynamics.

The statement that entropy can increase but can never decrease is the subject of the *second law of thermodynamics* which will be discussed in more detail in Sect. 3.4.

Let us conclude:

- Energy can neither be created nor destroyed (first law).
- Entropy can be generated but not destroyed (second law).

3.3 Molecular Kinetic Interpretation of Entropy

Atomic Disorder So what is this entity that flows through matter and, depending upon how much is contained in it, causes it to seem warm or hot to the hand? For more than two hundred years, one has attempted to explain thermal phenomena by the movements of atoms. The image is as follows: The warmer a body is, the more intensely and randomly the atoms oscillate, spin, and swirl—so the idea, the greater the agitation and the worse the *atomic disorder*.

In the particle view, the quantity called entropy is a measure of

- The *amount* of atomic disorder in a body
- With regard to *type, orientation, and motion* of the atoms, or more exactly, with regard to any characteristic which differentiates one group of atoms from another.

Two questions arise here:

- What does disorder mean regarding type, orientation, and motion of atoms?
- What is meant by amount of disorder?

To clarify the first question, one might consider a park on a sunny summer Sunday. There are children playing, a soccer game taking place, and joggers, but also people just resting or even sleeping—a mass of running, sitting, lying people without order to their distribution or motion (Fig. 3.6). The opposite would be the dancers in a revue—or soldiers marching in lockstep. In this case, position, motion, and dress are strictly ordered. Disorder grows when the motion becomes random, but it also grows if the orientation in rank and file is lost or the type of people becomes nonuniform. All three: randomness of type, orientation, and motion of the individuals cause the total disorder.

The same holds for the world of atoms (Fig. 3.7). Not only disorder in the type and distribution of atoms, but also disorder in their motion, which can be expressed in how *agitated* they are, makes an important contribution to entropy. In this sense, the atoms in a hot gas are similar to children romping in the schoolyard. Motions are completely free and without order, and therefore the agitation, meaning the disorder concerning motion, is great. The atoms of a crystal, in contrast, can be compared to tired pupils in a school bus. Motion is more or less limited to fixed locations, so the disorder and agitation stay small.

Amount of Disorder In order to get an impression of what is meant by *amount* of disorder, one might imagine a collection of, say, one hundred books at someone's home. A visitor comes, starts rummaging through the books, and makes a total jumble of them. Although the disorder appears great, the old order can be reinstated within a few hours. This means that even though the density of disorder is high, its amount is small. Compare this to just every hundredth book being falsely placed in a large university library. At first glance, there would appear to be almost no disorder. However, the amount of disorder, measured by the effort needed to

Fig. 3.6 Examples of groups of people becoming increasingly disordered in type, orientation, and motion.

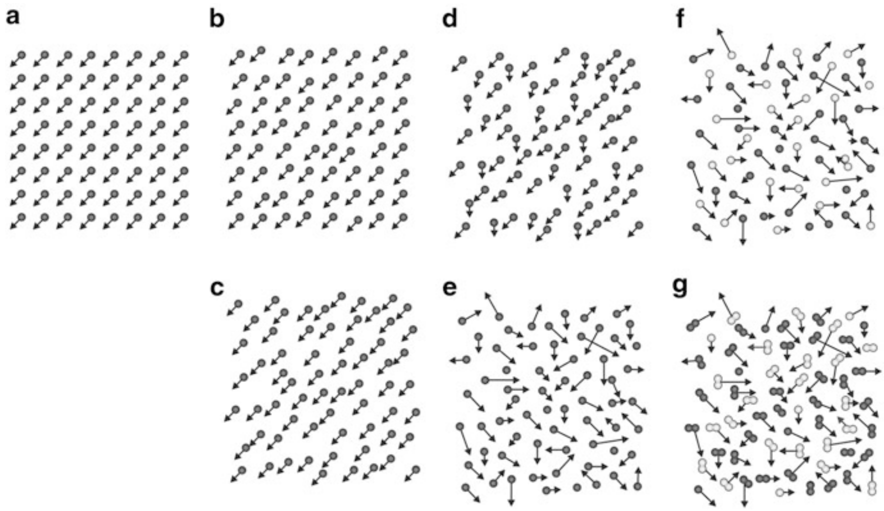


Fig. 3.7 An assembly of particles in states of increasing entropy: (**a**) Assembly is well ordered in every way, (**b**, **c**) Positions become increasingly perturbed, (**d**, **e**) Motion is increasingly disordered, (**f**, **g**) Particles become increasingly different (type, orientation, agitation, . . .). The *arrows* show magnitude and direction of momentum (and not of velocity) (This differentiation is important when the entropy of particles of different mass shall be compared.).

place all the books back in their rightful places, is much greater. The density of disorder is small, but the total amount of it is very great.

3.4 Conservation and Generation of Entropy

The atomic disorder in a warm object and, therefore, the entropy in it have remarkable and well-defined characteristics, some of which have already been mentioned. They will be described in more detail in the following.

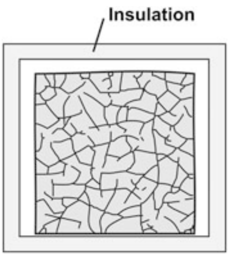


Fig. 3.8 Conserving entropy in a thermally insulated system. (Entropy is depicted by an irregular hatching in reference to the standard interpretation of entropy as atomic disorder. The amount of printing ink symbolizes the amount of entropy, the density of hachures, however, the entropy density. In objects made of the same material and in the same state of aggregation, a higher entropy density correlates with a higher temperature.)

Experiment 3.1 *Brownian motion*: Brownian motion is a tremulous, random movement of tiny particles distributed in a liquid (e.g., drops of fat in milk) or particles stirred up in a gas (e.g., smoke particles in air). This kind of movement can be observed under a microscope for indefinite amounts of time without it letting up.

Conservation The atomic disorder and agitation in a thermally insulated body which is left to itself remain undiminished for an unlimited amount of time. An object *contains* entropy—we can say—whose amount S cannot decrease if it is in a thermally insulating (adiabatic) envelope, because entropy cannot penetrate thermally insulating walls (Fig. 3.8).

The agitation manifests itself among others by the microscopically visible Brownian motion (Experiment 3.1). Therefore, it can be regarded not only as theoretically constructed but as directly observable.

The amount of entropy an object contains depends upon its state. Identical objects in the same state contain identical amounts of entropy. The entropy contained in an object that is composed of pieces is the sum of the entropies of

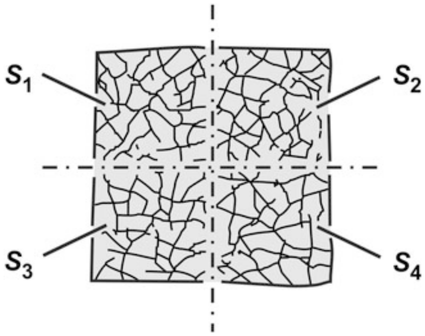


Fig. 3.9 Entropy as substance-like state variable ($S_1 \approx S_2 \approx S_3 \approx S_4$, and $S_{total} = S_1 + S_2 + S_3 + S_4$).

its parts. This is a direct result of the substance-like character of this quantity. In summary, it might be said: The entropy in an object is a *substance-like* (or *extensive*) quantity which—together with other quantities—determines its state (Fig. 3.9).

If a thermally insulated piece of matter, such as an iron block, is cautiously and slowly compressed with the help of a hydraulic press, or a gas in a cylinder with a piston (meaning the external pressure is only very slightly higher than the internal pressure of the confined gas), the interior agitation increases, and the motion of the particles becomes faster. This is easy to understand: An atom colliding with another particle moving toward it is hit like a tennis ball by a racquet and speeds backward. During compression, this process takes place simultaneously at innumerable interior locations so that agitation increases evenly overall. If the piece of matter is gradually relieved of pressure, the atoms quiet down, and it reaches its original state again. This is understandable as well, because the impact upon a receding particle lessens the rebound. No matter how often the process of compressing and subsequent releasing of tension is repeated, the original state of agitation is attained at the end—cautious action provided.

The atomic disorder in these types of *reversible* processes is conserved. Agitation is stronger in the compressed state—as mentioned, and motion, therefore, less ordered. At the same time, the range of motion for the atoms is decreased so that their positions are perforce more orderly than before. Therefore, it is plausible to assume that the extent of atomic disorder does not first increase and then decrease upon *cautious* compression and expansion, but remains constant (Fig. 3.10). This is an important fact that we should mention explicitly: Entropy is conserved in reversible processes.

Generation However, disorder in a thermally insulated body increases if the atomic structure is permanently disturbed. This can happen mechanically by simply hitting an object with a hammer, or more gently by rubbing two objects against each other. If an object can conduct electricity, an electric current can be sent through it. This means that electrons that have been accelerated by applying a voltage collide with the atoms. Another way would be the collision of fast particles

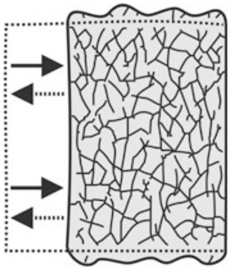


Fig. 3.10 Conservation of entropy during cautious compression and expansion (reversible process).

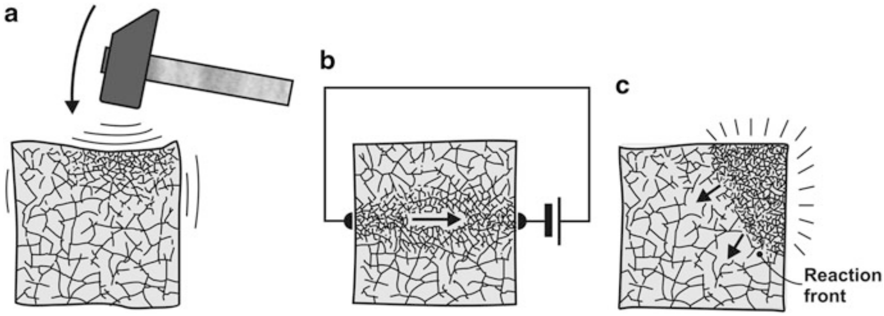


Fig. 3.11 Examples of entropy generation: (**a**) mechanically by hammering, (**b**) electrically by electron impact, (**c**) chemically by collisions of atoms shooting off in a reaction.

which have been formed by numerous chemical or nuclear transformations, irradiation by light, treatment with ultrasound, and many others (Fig. 3.11).

Entropy distributes more or less quickly over the entire body from the point where it is created. This process is also connected with the generation of entropy even if it is not directly obvious (see Sect. 3.14). All of these *entropy generating* processes are *irreversible*. If entropy was created in this way we will not get rid of it again, unless we could transfer it in the surroundings. But this is inhibited by the thermal insulation.

Entropy and Arrow of Time To sum up: In a thermally insulated system, entropy can increase but never decrease; at best its amount remains constant. As mentioned before, this is what the *second law of thermodynamics* states. We can also formulate: For a thermally insulated system entropy always increases for irreversible processes. It remains, however, constant for reversible processes. We can write in abbreviated form

$$\Delta S = S(t_2) - S(t_1) \underset{\text{rev.}}{\overset{\text{irrev.}}{\geq}} 0 \quad \text{for } t_2 > t_1 \text{ in a thermally insulated system,} \tag{3.1}$$

where t represents time. At the more, this is valid for a so-called *isolated* system that does not interact with the surroundings, meaning that it can exchange neither entropy nor energy or matter.

The inequality (3.1) obviously interlinks an increase in entropy with the direction of time. If $S(t_2) > S(t_1)$, then $t_2 > t_1$ has to be valid, meaning that t_2 indicates a later point in time, t_1, however, an earlier one. It seems that the second law of thermodynamics determines what is future and what is past.

3.5 Effects of Increasing Entropy

If the entropy and thereby the atomic disorder inside a piece of matter is continuously increased, certain external effects soon become noticeable.

Main Effect The main effect is that the matter becomes *warmer* (Fig. 3.12). To demonstrate this, entropy can be increased for example mechanically by strong hits with a hammer (Experiment 3.2).

Another way of formulating this effect: Of two otherwise identical objects, the one with more entropy is the warmer one. An object with no entropy is absolutely cold (Fig. 3.13).

As mentioned, entropy always moves spontaneously from warmer locations to colder ones (Fig. 3.14). When fast moving atoms collide with ones moving more slowly, they are themselves slowed while their collision partners speed up. As a result, the agitation and, therewith, the total disorder at the warmer locations gradually decrease while they continuously increase at the colder locations. In a homogeneous body, the process continues until the level of agitation is the same everywhere and the body is equally warm everywhere. This state is called *thermal equilibrium*.

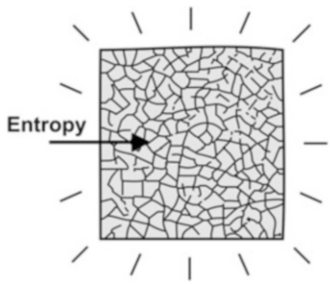


Fig. 3.12 Warming as the main result of increase of entropy.

Experiment 3.2 *Heating of metal by forging*: A block of copper having a volume of a few cubic centimeters will become so hot after about 15–20 strong hits with a heavy hammer that it will hiss when put into water. A strong blacksmith can even forge a piece of iron of similar size in a few minutes to red heat.

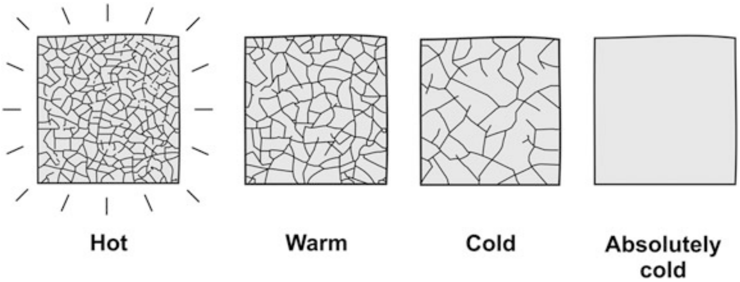


Fig. 3.13 Otherwise identical objects with different entropy content.

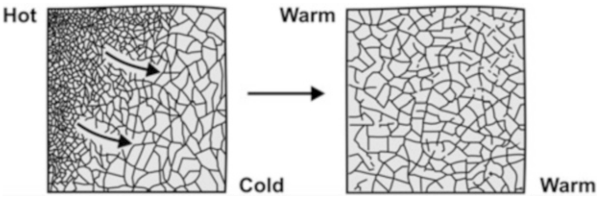


Fig. 3.14 Distribution of entropy in a homogeneous body.

Side Effects An increase of entropy can cause numerous side effects: Changes of volume, shape, state of aggregation, magnetism, etc., can result. Let us look at how a continuous increase of entropy affects a substance in general.

(a) Matter continuously *expands* (Fig. 3.15). This seems logical because moving atoms would need more space depending upon how strong and random their motion is. This process is called *thermal expansion*.

Experimentally, entropy can for example be increased by sending an electric current through the matter (Experiment 3.3).

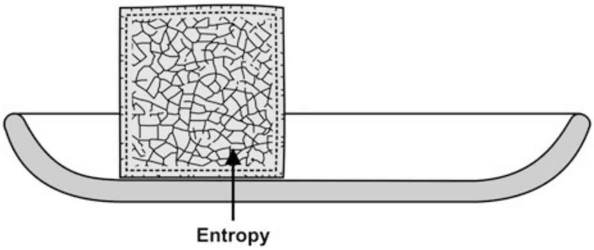
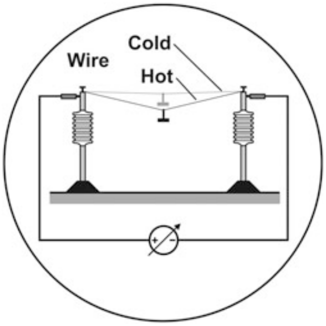


Fig. 3.15 Expansion due to the addition of entropy. The initial state is indicated by the *dashed line*.

Experiment 3.3 *Expansion of a wire caused by electric current*: A wire with a weight hanging from it lengthens noticeably when an electric current flows through it. The lowering of the weight can easily be observed. If the electric current is turned off, the entropy in the wire flows off into the air and the wire shrinks again.



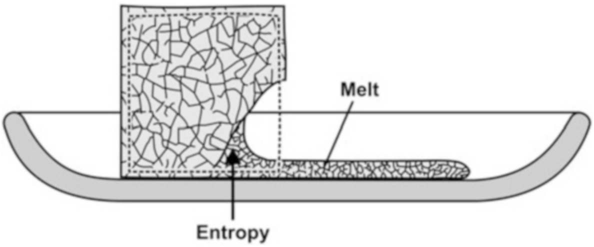


Fig. 3.16 Melting as an example of a change of state of aggregation with increasing entropy.

A substance that expands when entropy is added to it will, inversely, become warmer when compressed. This was mentioned in the previous section. Ice water is one of the few exceptions of volume decreasing with an increase of entropy. Therefore, it becomes colder ($< 0\,°C$) when compressed.

(b) The substance will finally *melt, vaporize,* or *decompose* (Fig. 3.16). This begins when the disorder and the motion with it reach a level where the atoms can no longer be held together by the bonding force in a lattice or particle union, but try to break out of them. A melt that has been produced in this way from atoms or groups of atoms that still hold together but are easily shifted against each other is much less orderly than a crystal lattice in which the atoms generally remained fixed in their places. This melt contains more entropy than the identically warm solid substance. As long as part of the solid substance is available, the entropy flowing in will collect in the resulting liquid so that the melting substance itself does not become warmer. When this happens, the main effect of entropy remains unnoticeable. If a substance changes completely at its melting point from solid to liquid state, the entropy inside it increases by a given amount. As we will see, this characteristic can be made use of to determine a unit for amounts of entropy.

Analogously, the vapor formed at the boiling point absorbs the additional entropy, preventing the boiling liquid from becoming hotter.

3.6 Entropy Transfer

Entropy and with it atomic disorder can also be transferred from one object to another. If two objects with variously strong particle motion touch each other, the agitation in one of them will decrease because of a slowing down of the atoms, while in the other, the opposite occurs. Figuratively speaking, the disorder flows from one body into the other. This process, as well, only continues until the agitation has reached the same level everywhere and thermal equilibrium has been reached (Fig. 3.17).

The thinner the surrounding walls are, the greater their area is and the better the substance of which such a wall is composed conducts entropy, the easier the entropy runs through the walls (Fig. 3.18). The correlation is similar to that of the current of electric charge through a wire (see Sect. 20.4).

Zero-Point Entropy All entropy capable of movement will escape an absolutely cold environment, meaning that any atomic motion comes to a standstill. This is the subject of the *third law of thermodynamics.* Entropy caught in a lattice defect is just about unmovable at low temperatures. It can therefore neither escape nor contribute

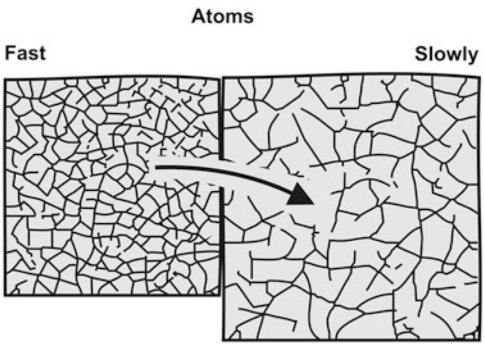


Fig. 3.17 Conduction of entropy from a warmer, entropy richer body where the atoms are moving fast to another cooler, entropy poorer one where the atomic motion is slow.

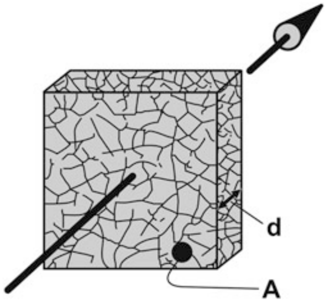


Fig. 3.18 Entropy current through a wall. The resistance which the wall imposes to the flux depends upon the thickness *d*, the area *A* through which the entropy flows, and the conductivity of the material.

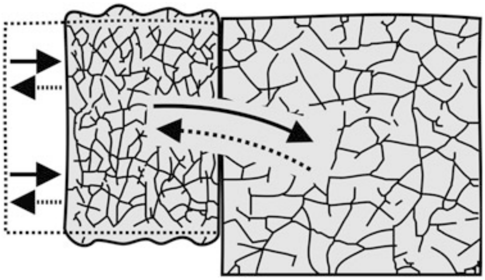


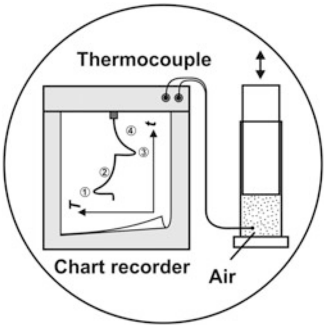
Fig. 3.19 Directed exchange of entropy between two bodies touching each other.

in any noticeable way to the warmth of an object. Whoever fails to leave a building or a park before closing is in danger of being locked in for the night. In this sense, the entropy stuck in the lattice defects can only escape as long as the particle motion is strong enough for the atoms to relocate. If the atomic motion in cold surroundings quiets down too quickly, the atoms do not have time to relocate into an ordered lattice structure, or to *crystallize*, as we say. The object then just solidifies into a more or less amorphous state. This unmovable entropy that does not flow off even in an absolutely cold environment is called "*zero-point entropy*." Therefore, we have to formulate the third law of thermodynamics as follows: The entropy of every pure (also isotope pure) *ideal* crystallized substance takes the value of zero at the absolute zero point. Only if the substance crystallizes ideally there is no spatial disorder and therefore also no residual "zero-point entropy."

Directed Entropy Transfer Let us now return to entropy transfer. Even when the atomic motion is equalized everywhere in the manner described above, it is still possible for disorder to pass from one object to another. It is only necessary to compress one of the objects to raise the agitation of the atoms, and the desired flow process takes effect. The more the object is compressed, the more disorder "flows out" (just like pressing the water out of a sponge). If the body is slowly relaxed, the atoms gradually quiet down and the disorder begins to flow back in (the "entropy sponge sucks up entropy") (Fig. 3.19).

These elastic expansion and compression effects can be especially well observed in substances that can be easily compressed such as gases (Experiment 3.4).

Experiment 3.4 *Compression and expansion of air*: If air is compressed with a piston in a plexiglass cylinder having a thermocouple built in, the atoms become accelerated making the gas warmer (phase 1). After a while, the gas cools down to its original value because it is not insulated from the cylinder walls (phase 2). The piston's expansion leads to further cooling (phase 3). Then, entropy begins to flow back in and the gas begins to warm up (phase 4). The more slowly this is done, the more the difference between the compression and expansion disappears.



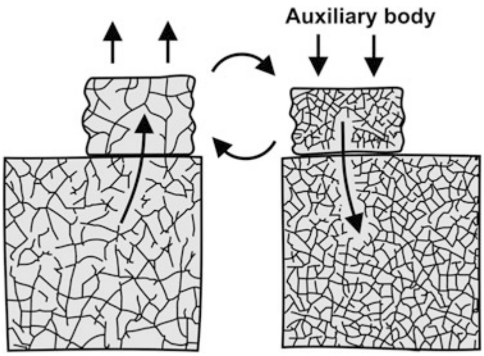


Fig. 3.20 Transfer of entropy with an auxiliary body. On the *left side*, the auxiliary body expands thereby absorbing entropy from the object. On the *right side*, it is compressed thereby adding entropy to another object.

As we have seen, entropy always flows spontaneously from an object with a higher level of agitation to one with a lower level. However, it is not difficult to make this happen in the opposite direction (Fig. 3.20). An *auxiliary body* is needed, a kind of "entropy sponge" which can easily be compressed and expanded. A gas contained in an expandable envelope is suitable for this purpose. When such a body touches an object and expands, it absorbs disorder from it. This absorbed disorder can now be transferred to any other object. The "sponge" is brought in contact with this second body and compressed. This process can be repeated at will, and as much entropy can be transferred as desired.

Ideal and Real Transfer Every refrigerator uses this principle to pump entropy from its interior into the warmer air outside, while the low-boiling coolant (operating as the auxiliary body) circulates in a closed circuit (Fig. 3.21). The entropy

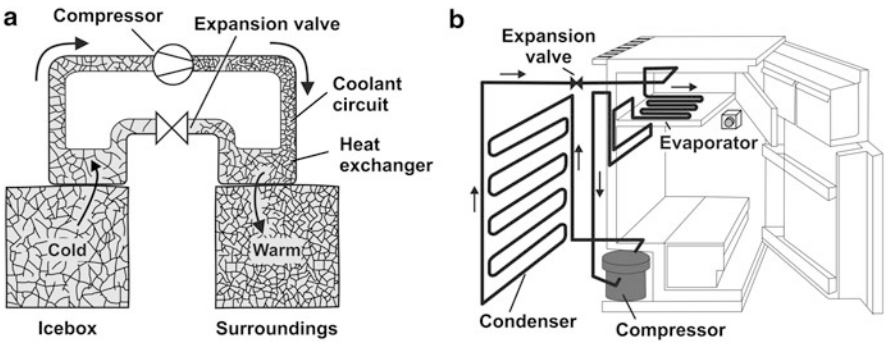


Fig. 3.21 (**a**) Principle of operation of a refrigerator, (**b**) Technical realization (according to: Leitner E, Finck U, Fritsche F, www.leifiphysik.de).

transfer takes place by the coiled pipe inside the refrigerator (heat exchanger) that is made of well-conducting material such as copper or aluminum. In older models, this coiled pipe is easy to see; in newer models, it is built into the back wall. The liquid vaporizes, taking up entropy in the process. The compressor sucks the gaseous coolant in and compresses it. The entropy is emitted into the air through the second coiled pipe that takes up most of the back of the refrigerator. This can be easily detected because the coil remains warm as long as the refrigerator is running. The coolant condenses, becoming a liquid again. Finally, the pressure of the liquid is brought back to the original value through an expansion valve, and the cycle is complete.

With skill and enough cautiousness during the compression and expansion processes, an (almost) reversible process can be attained where it is possible to keep the disorder during transfers from increasing noticeably. In this way, disorder is like a kind of substance that can be taken from one body and decanted into another. For instance, the entropy in a piece of chalk could be taken out of it and transferred to an ice cube. In the process, the chalk would cool down and the ice cube would begin to melt.

In summary, we have determined that the entropy content S of a body can basically increase in two ways: through the entropy generated inside it $S_{\mathrm{g(enerated)}}$ (cp. Sect. 3.4) and, as described in this section, by the entropy exchanged with the surroundings $S_{\mathrm{e(xchanged)}}$ (and that *conductively* by "conduction" in matter at rest, S_λ, or *convectively*, carried by a flow of matter, S_c):

$$\Delta S = S_g + S_e = S_g + S_\lambda + S_c. \tag{3.2}$$

3.7 Direct Metricization of Entropy

Selection of a Unit for Entropy The transferability of entropy opens up a possibility of measuring the amount of it in a body—at least theoretically. Measuring a quantity means determining how much more of it there is than its unit. Any amount

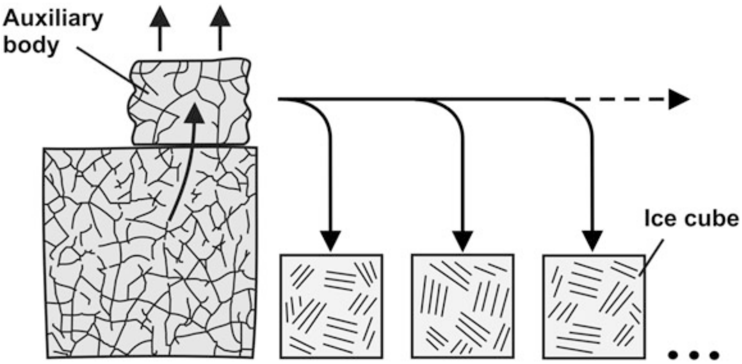


Fig. 3.22 Measuring entropy by counting ice cubes that melt when entropy is added to them.

of entropy can be used as the unit. For example, the amount needed to warm up a certain quantity of water by 1 °C (possibly from 14.5 to 15.5 °C), to evaporate a given volume of ether, or to melt an ice cube (Fig. 3.22). In order to accurately determine this unit, the size and state of the body in question must be exactly specified. For example, the ice cube would need to be 1 cm^3 in size, bubble-free, not undercooled, and the resulting water not be warmed up. However, instead of 1 cm^3, the somewhat smaller value of 0.893 cm^3 lends itself well because it yields exactly the amount of entropy that corresponds to the international unit. This unit has been fixed by a special method which we will come back to later. A certain amount of entropy contained in a body will be referred to as z units when z standard ice cubes can be melted with it. This procedure is comparable to the determination of the amount of harvested grain by using a bushel (Sect. 1.4) or that of an amount of water by scooping it out with a measuring cup.

Ice Calorimeter Instead of counting ice cubes, it is easier to use the amount of melt water produced as measure. A simple “entropy measurement device” can be built for this purpose. Melt water has a smaller volume than ice because of the anomalous behavior of the density of water and the decrease of volume can be measured. A bottle with a capillary on it and filled with a mixture of ice and water (ice-water bottle) (Fig. 3.23a) can then be used to show the change in volume. The lowering of the water level is simple to observe. Unintended entropy exchange can be avoided by using good insulation, and unintended entropy generation can be avoided by paying attention to reversibility.

This principle is also used by “Bunsen’s ice calorimeter” (Fig. 3.23b). The glass container is filled with pure water and the U-shaped capillary with mercury. The central tube is cooled to below the freezing point of water, possibly by pouring in ether and sucking off the vapor, so that an ice mantle is formed on it. Then the sample to be measured is inserted into it. The amount of ice melted is noted by the volume decrease indicated by the mercury in the capillary. If no entropy escapes, is exchanged, or is generated during the measurement process, the height difference in

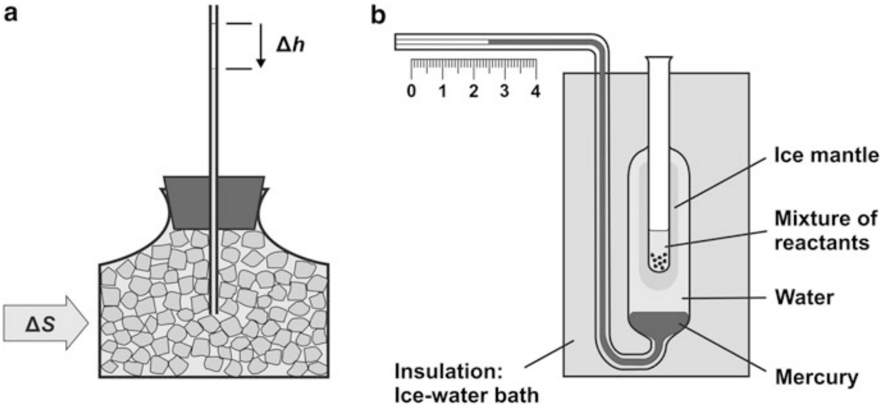
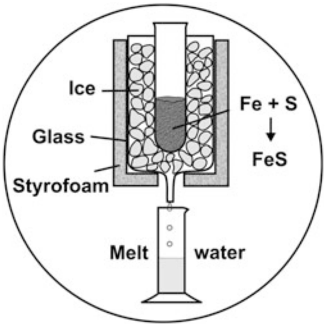


Fig. 3.23 (**a**) Principle of direct entropy measurement with the ice-water bottle, (**b**) Bunsen's ice calorimeter.

Experiment 3.5 *Measuring the entropy emitted during a reaction*: For example, the entropy emitted by the chemical reaction of iron and sulfur into iron sulfide can be measured by a simple ice calorimeter. A mixture of iron powder and sulfur powder is put into a test tube, and the test tube is subsequently placed in the calorimeter vessel filled with crushed ice. The reaction is initiated by a preheated glass rod or a sparkler. The melt water is collected in a graduated cylinder whereby 0.82 ml of melt water corresponds to the unit of entropy.



the capillary is proportional to the change of entropy in the sample or that of a reaction mixture, and the scale can be directly calibrated using entropy units.

Another way of determining the volume of the produced amount of water is to pour it into a graduated cylinder (Experiment 3.5).

Return to Macroscopic View The remarkable thing here is that this entire process has been developed using atomistic considerations, but the execution of it makes no use of them. Indeed, only macroscopic bodies are moved, brought into contact, separated, compressed, and expanded. Finally, ice cubes are counted. These are all manipulations that can be carried out when nothing is known about atoms. In order to have a well-directed approach, it is enough to remember the concept mentioned in Sect. 3.2 that all things contain a movable, producible, but indestructible something that generally makes the things warmer depending upon how much there is of it. What one actually imagines it is or what it would be called is unimportant when measuring or manipulating it. The German physicist Rudolf Clausius suggested calling it *entropy* in the middle of the nineteenth century, and the symbol S has been used for it ever since.

3.8 Temperature

Role and Definition Temperature and entropy are closely connected. While entropy is a measure of the amount of atomic disorder contained in a body, temperature describes how *strong* the atomic agitation, which means the intensity of random particle *motion*, is. Temperature is something like a level of agitation that is low when the atoms and molecules are gently oscillating and rotating. It is high when atomic motion becomes hectic and turbulent. The temperature in a body is therefore comparable to the strength of winds in the atmosphere with low values when the leaves rustle, but higher ones when the branches start swinging. Just as high winds can break branches or even whole trees, high temperatures can cause atoms to tear away from their bonds.

So how can temperature be defined? We will use the following statement as a basis: The more disorder is put into a body (meaning the more entropy there is), the higher the temperature will be in general. To generate entropy (or to increase the disorder in a body by the amount S_g), a certain amount of energy W must be expended. This is understandable considering that for example gas particles are accelerated, particle oscillations initiated, rotations increased, and bonds between atoms broken. The energy W needed will be greater depending on how many atoms are to be moved, and how many bonds torn. This means,

$$W \sim S_g.$$

Moreover, the warmer the body is, the more energy is needed. An example will show this. We imagine a body made up of some loosely and some tightly bound particles. Atomic disorder can be increased by breaking the particles and scattering the fragments. When the body is cold and the level of agitation low, the particles move slowly. Only the weakest connections break during collisions because very little energy is necessary to split them. Under such circumstances, it does not take much energy to increase the disorder by causing weak bonds to break by an increase in agitation. If agitation is already strong, the weakest connections will already have broken. If the disorder should be increased even more, the strong bonds left over need to be separated and this takes a lot of energy.

So now we know that increasing the entropy in a body takes more energy the higher the level of agitation is, meaning the warmer it appears to us. This fact can be used to make a general definition of temperature, a definition that remains *independent* of any thermometric substance (e.g., mercury or alcohol).

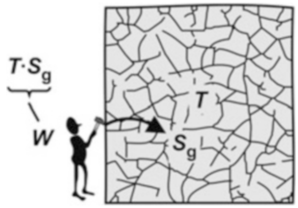


Fig. 3.24 Relation between the energy needed, the entropy generated, and the thermodynamic temperature.

This quantity is assumed to be proportional to the energy needed. It is called the *thermodynamic temperature* or *absolute temperature* and symbolized by the letter T:

$$W \sim T.$$

Because the more entropy that is generated the more effort is needed to generate it, the amount of energy used depends upon the amount of entropy created. Therefore, we define:

$$T = \frac{W}{S_g}. \tag{3.3}$$

The relation is clarified by Fig. 3.24.

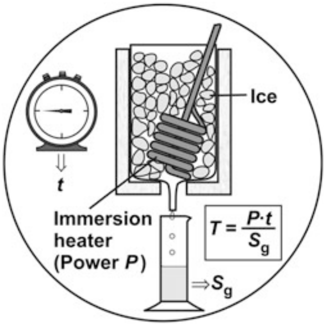
The entropy generated generally changes the temperature in a body, so when applying this definition, only very small amounts of entropy may be generated in order to be able to ignore the perturbation. The exact temperature value is obtained in the limit of infinitesimally small contributions of entropy:

$$T = \frac{dW}{dS_g}. \tag{3.4}$$

By the way, energy conservation guarantees that the energy W needed does not depend upon which method we employ to increase the entropy. In each case, T has a well-defined value.

Because energy and entropy are both measurable quantities independent of any atomistic considerations, the temperature T is also measurable. The zero point of the temperature scale cannot be arbitrarily chosen, meaning temperature can be determined in an absolute sense. From experience we know that entropy is only generated when energy is expended. No entropy is generated when energy is gained. From $W > 0$ and $S_g > 0$ (third law of thermodynamics) follows $T > 0$. Therefore, negative temperatures do not exist. As a concrete example, let us discuss the determination of the melting temperature of ice (Experiment 3.6).

Experiment 3.6 *Determination of the absolute melting temperature of ice*: We start with a beaker filled with pieces of ice into which an immersion heater has been inserted. When the immersion heater is switched on, entropy is generated in the heating coil by the collisions of electrons and then emitted through the metal casing to the ice. The ice melts and the volume of the resulting melt water shows us how much entropy has flowed into the ice. The amount of energy needed for generating the entropy can be determined from the power P of the immersion heater and the measured period of time t according to $W = P \cdot t$. The ratio of measured values of energy and entropy yields the temperature.



SI Unit The basic unit used in the SI system is not the unit of entropy, but the temperature unit called *Kelvin*, abbreviated to K. This was done by giving the melting temperature of pure airless water in a sealed container with pure water vapor (no air) above it a value, namely

$$T_0 = 273.1\underline{6}\ \text{K}. \tag{3.5}$$

This is based upon the so-called triple point of water, where all three states of aggregation (ice, water, water vapor) coexist and where pressure can be ignored. [When water is at the triple point, the pressure is fixed (see Sect. 11.5).] This odd numerical value is chosen so that the temperature difference between the normal freezing and boiling points of water is close to 100 units, as it is in the Celsius scale. For this reason, one Kelvin is one 273.16th of the thermodynamic temperature of the triple point of water. The zero point of the Kelvin scale lies at the absolute zero point which is indicated by an absence of entropy in the body. When one wishes to establish the relation between thermodynamic temperature T and Celsius temperature ϑ, it is important to be careful to set the zero point of the Celsius scale to the freezing point of water *at normal pressure*. This lies nearly exactly 0.01 K under the temperature of water's triple point, so that:

$$\frac{T}{\text{K}} = \frac{\vartheta}{^\circ\text{C}} + 273.1\underline{5}. \tag{3.6}$$

The Fahrenheit temperature scale used mostly in the USA can be converted into the absolute temperature scale in the following way:

$$\frac{T}{\text{K}} = \left(\frac{\vartheta_\text{F}}{^\circ\text{F}} + 459.67\right) \times \frac{5}{9}.$$

The unit of entropy is indirectly determined by the stipulation above [Eq. (3.6)] and our definition for T. The unit for energy is called Joule (J), and the temperature unit Kelvin (K), resulting in the entropy unit Joule/Kelvin (J K^{-1}). This is exactly the amount of entropy needed to melt 0.893 cm^3 of ice at the temperature T_0. The fact that entropy plays such a fundamental role in thermodynamics justifies giving it its own unit. Hugh Longbourne Callendar (Callendar HL (1911) The Caloric Theory of Heat and Carnot's Principle. Proc Phys Soc (London) 23:153–189) suggested naming it in honor of S. Carnot and calling it a "*Carnot*," abbreviated to $\mathrm{Ct} = \mathrm{J\,K^{-1}}$. Through his work with heat engines, the French engineer Nicolas Léonard Sadi Carnot (1796–1832) made important contributions to the development of thermodynamics.

3.9 Applying the Concept of Entropy

Molar Entropy We will look at some examples that give an impression of the values of entropy: A piece of blackboard chalk contains about 8 Ct of entropy. If it is broken in half, each half will contain about 4 Ct because entropy has a substance-like character. (Entropy is also generated in the breaking process, but this is so little that it can be ignored.)

A 1 cm^3 cube of iron also contains about 4 Ct, although it is much smaller. Therefore, the *entropy density* in iron has to be greater. If the amount of entropy in such a cube is doubled (by hammering, friction, or radiation, for example), it will begin to glow (Fig. 3.25). If the amount of entropy is tripled, the iron will begin to melt.

There is about 8 Ct of entropy in 1 L of ambient air. This is the same amount as in the piece of chalk. The reason that there is so little despite a volume more than 100 times as great lies in the fact that the air sample has far fewer atoms in it than the piece of chalk with its densely packed atoms. If the air is compressed to 1/10 of its original volume, it will become glowingly hot (Fig. 3.26).

This effect is utilized in pneumatic lighters to ignite a piece of tinder (flammable material) (Experiment 3.7), but also in diesel engines to ignite the fuel–air mixture. The compression must happen quickly because the entropy flows immediately from the hot gas into the cold cylinder walls and the gas cools down quickly.

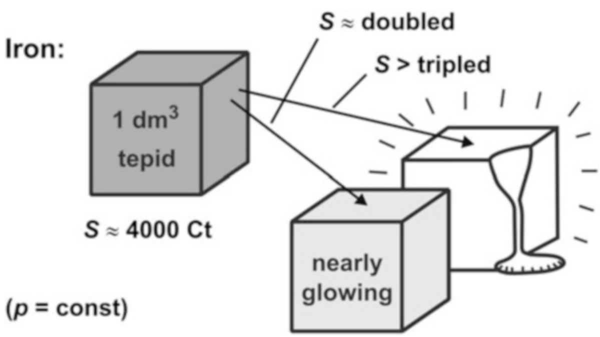


Fig. 3.25 The effects of raising the entropy content in a cube of iron with a volume of 1 dm^3.

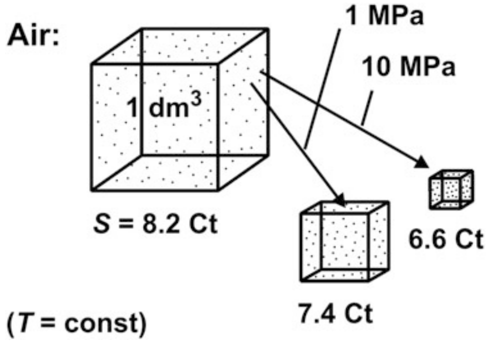
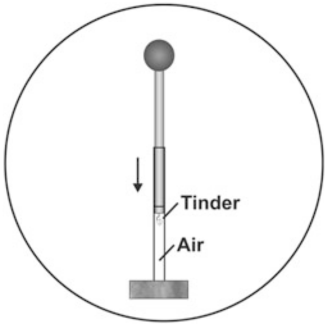


Fig. 3.26 Change of entropy content in air (1 dm^3) with rising pressure (The gas molecules are represented by *points*.)



Experiment 3.7 *Pneumatic lighter*: If the piston is moved down quickly and powerfully, the tinder (for example, a piece of nitrocellulose foil or a piece of cotton wool impregnated with a highly flammable liquid) bursts into flame.

1 L of gas loses almost 1 unit of entropy if it is compressed to 1/10 of its original volume. If the gas is compressed to 1/100 of its volume, one more entropy unit can be squeezed out of it.

Chemists tend to relate entropies to the amount of a substance, i.e., how much entropy is contained in 1 mole of the substance in question. This quantity is called *molar entropy*:

$$S_{\mathrm{m}} \equiv \frac{S}{n} \qquad \textit{molar entropy of pure substances.} \tag{3.7}$$

S and n symbolize the entropy and amount of substance of the sample. The formula or name of the substance is usually enclosed in parentheses, for example, $S_{\mathrm{m}}(\mathrm{Fe}) = 27.3\ \mathrm{Ct\ mol^{-1}}$.

Molar entropy depends upon both temperature and pressure. For this reason, an additional stipulation is necessary if the values are to be tabulated. In chemistry, one generally refers to *standard conditions,* i.e., 298 K (more precisely 298.15 K) and 100 kPa [this corresponds to room temperature of 25 °C and normal air pressure, so-called standard ambient temperature and pressure (SATP)]. For characterizing the standard values, we use the symbol $^{\ominus}$, so for example,

$$S_{\mathrm{m}}^{\ominus}(\mathrm{Fe}) = 27.3\ \ \mathrm{Ct\,mol^{-1}} \qquad \text{at 298 K and 100 kPa.}$$

Table 3.1 Molar entropies of some pure substances at standard conditions (298 K, 100 kPa).

Substance	Formula	$S_m^\ominus$ (Ct mol^{-1})
Graphite	C|graphite	5.7
Diamond	C|diamond	2.4
Iron	Fe|s	27.3
Lead	Pb|s	64.8
Ice	H_2O|s	44.8
Water	H_2O|l	70.0
Water vapor	H_2O|g	188.8

The value of ice was extrapolated from lower temperatures to 298 K

The values of some substances are listed in Table 3.1.

However, molar entropy not only depends upon the kind of substance in question, characterized by its content formula but also on the state of aggregation, as it is proved by the example of water. In order that the values are unambiguously given the aggregation state of the substance in question is added to the formula by a vertical stroke and the abbreviations s for solid, l for liquid and g for gaseous (cp. Sect. 1.6), for example, $H_2O|l$ for liquid water. Because we do not want to overload the expressions, we stipulate that the most normal case is meant if there is no further information. Therefore, H_2O generally symbolizes the liquid and not vapor or ice. Entropy also depends upon the crystal structure. Modifications can be indicated for example by their names like graphite, diamond, etc.

A rule to bear in mind is that, at the same pressure, temperature and particle number, the entropy of a body will be greater, the *heavier* the atoms and the *weaker* the bonding forces. Diamond, which consists of atoms that are rather light and very firmly linked in four directions, has an unusually low entropy per mole. Lead, on the other hand with its heavy, loosely bound atoms, is rather rich in entropy. The characteristics of iron lie somewhere in between; it has a medium value of molar entropy. Using the example of water, the table shows how entropy increases by transition from a solid to a liquid state and even more by transition from a liquid to a gaseous state.

Determining of Absolute Entropy Values How are the values in Table 3.1 actually determined? It would be possible to find the entropy content of a sample by "decanting" the entropy from it into the ice-water bottle with the help of an auxiliary body. However, this would require that each step be configured reversibly, as discussed in Sect. 3.7, so that the entropy cannot increase during transfer, and this is very difficult to accomplish in practice. The goal is reached more easily by taking a detour. First, all the entropy contained in the sample must be removed. Favorable circumstances would allow simply immersing the sample in liquid helium (4.2 K). With the entropy having flowed off, the sample would be just about empty of entropy. For very accurate applications, the sample would have to be further cooled to reduce the remaining entropy. However, the entropy from the disorderly distribution of isotopic atoms cannot be gotten rid of in this way. This value can be easily determined by other means. Afterward, the sample is thermally insulated, and

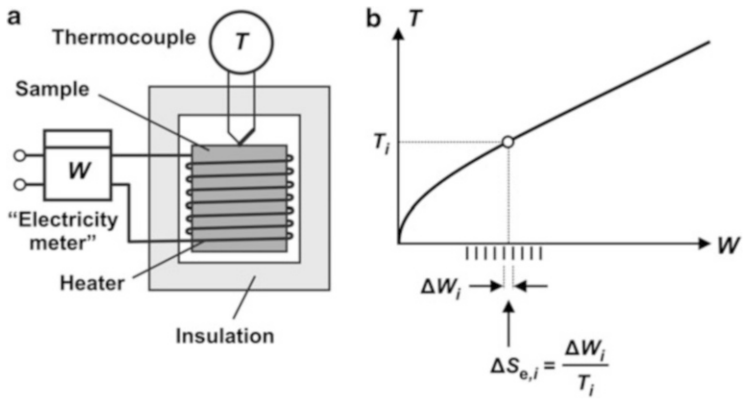


Fig. 3.27 Indirect measurement of entropy by heating up a sample previously cooled down to almost 0 K. (**a**) Measuring setup, (**b**) Corresponding experimental curve.

entropy is generated inside it in a controlled way. This might be done by electric heating (Fig. 3.27a). Energy consumption W and temperature T should be constantly measured (Fig. 3.27b) until the sample has attained the desired end temperature. The entropy generated during a small time span simply results from reversing the definition equation of temperature as the quotient of energy consumption and average temperature during this time period:

$$S_g = \frac{W}{T}. \tag{3.8}$$

The total amount of entropy contained in the sample at the end can be obtained by adding up all the amounts of entropy that have been generated over all time spans. To abbreviate, the symbol for summation $\sum$ will be used:

$$S_g = \sum_{i=1}^{n} \Delta S_{g,i} = \sum_{i=1}^{n} \frac{\Delta W_i}{T_i}. \tag{3.9}$$

The smaller the chosen time span, the more exact the result. If the time interval is allowed to approach zero, we have the definite *integral* (cp. Sect. A.1.3 in the Appendix):

$$S_g = \int_{\text{initial}}^{\text{final}} dS_g = \int_{\text{initial}}^{\text{final}} \frac{dW}{T} = \int_0^{t'} \frac{P(t)dt}{T}. \tag{3.10}$$

Because of the convention $S = 0$ at $T = 0$ for ideally crystallized solids (third law of thermodynamics), it is possible to determine not only differences but also absolute values of entropies and therefore absolute molar entropies as well. This determination is not only possible for substances in the state stable at 0 K but also for

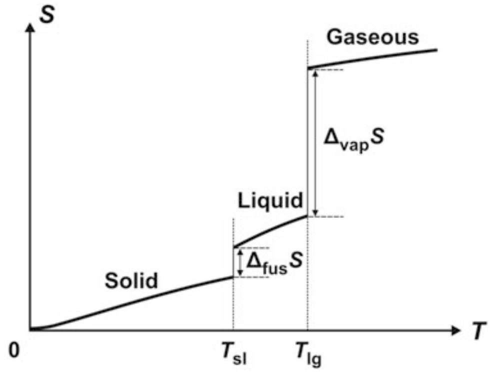


Fig. 3.28 Entropy of a pure substance as a function of temperature (without change of modification).

states which are formed during heating (other modifications, melt, vapor). The experimental curves $T = f(W)$ have horizontal parts when such phase transitions take place which means that energy is consumed, generating entropy without the temperature changing. If the resulting entropy content of a substance is plotted as a function of temperature (at constant pressure), we obtain the relationship shown in Fig. 3.28.

The entropy of a solid increases with an increase of temperature. It takes a jump at the *melting point* because the melting process causes the order of the solid to break and a noticeably higher disorder is produced in the liquid (see Sect. 3.5). Generally, we will symbolize the transition from the solid (s) to the liquid state (l) by the abbreviation s→l, the melting point therefore by $T_{s \to l}$ (the freezing point correspondingly by $T_{l \to s}$). Because melting and freezing points are identical for pure substances, we write in short T_{sl}. The change of entropy per mole of substance at the melting point is indicated as (*molar*) *entropy of fusion* $\Delta_{fus}S$. Subsequently, the entropy increases again up to the *boiling point* T_{lg}, at which point, another jump takes place [(*molar*) *entropy of vaporization* $\Delta_{vap}S$]. The entropy increases much more strongly during vaporization than during melting because disorder grows more strongly as a result of the transition from liquid to gas than from solid to liquid. We will deal in more detail with the entropy of fusion and of vaporization in Chap. 11.

Entropy Capacity Let us return again to the entropy content of a solid. As we have seen, it grows always with rising temperature. The curve is different for various substances, though. The increase of entropy per temperature increase is called the *entropy capacity* $\mathcal{C}$ in analogy to electric capacity $C = \text{charge } Q/\text{voltage } U$ (or if this is not constant, $C = \Delta Q/\Delta U$):

$$\mathcal{C} = \frac{\Delta S}{\Delta T} \quad \text{or for infinitesimally small changes} \quad \mathcal{C} = \frac{dS}{dT}. \tag{3.11}$$

The steeper a section of the curve, meaning the faster it rises at a given temperature, the greater the entropy capacity. The entropy content of a body is not generally proportional to temperature so its entropy capacity does not only depend upon the

Table 3.2 Molar entropy capacities of some pure substances at 298 K and 100 kPa.

Substance	Formula	$\mathcal{C}_m$ (Ct mol^{-1} K^{-1})
Graphite	C|graphite	0.029
Diamond	C|diamond	0.020
Iron	Fe|s	0.084
Lead	Pb|s	0.089
Ice	H_2O|s	0.139
Water	H_2O|l	0.253
Water vapor	H_2O|g	0.113

The value of ice was extrapolated from lower temperatures to 298 K

Table 3.3 Specific entropy capacities of some construction materials at 298 K and 100 kPa.

Substance	c (Ct kg^{-1} K^{-1})
Window glass	3.1
Concrete	3.7
Styrofoam	4.4
Wood (pine)	5.1
Particleboard	6.6
Wood (oak)	8.8

substance but, in general, also upon temperature. The pressure should be constant. This is important because a body can lose entropy during compression—like a sponge the absorbed water. Instead of $\mathcal{C} = \mathrm{d}S/\mathrm{d}T$, it is more correct to write

$$\mathcal{C} = \left(\frac{\partial S}{\partial T}\right)_p \quad \text{or even more detailed} \quad \mathcal{C} = \left(\frac{\partial S}{\partial T}\right)_{p,n}. \tag{3.12}$$

Because $\mathcal{C}$ is directly proportional to the amount of substance n, one divides it by n and obtains the *molar entropy capacity* $\mathcal{C}_m$:

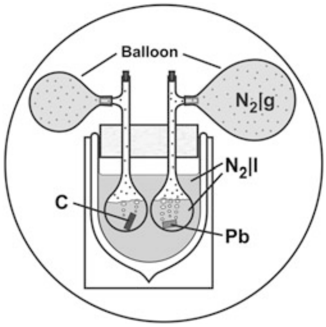
$$\mathcal{C}_m = \frac{\mathcal{C}}{n} = \frac{1}{n}\left(\frac{\partial S}{\partial T}\right)_{p,n}. \tag{3.13}$$

The values of some substances are listed in Table 3.2. Usually, the corresponding *molar heat capacities* $C_m = \mathcal{C}_m \cdot T$ are given in tables instead of entropy capacities. We will discuss the reasons for this in more detail in Chap. 24.

In the field of engineering, entropy capacities are mostly related to mass. The result is the *specific entropy capacity* c. The specific entropy capacities of some common construction materials are given in Table 3.3. (Because the composition of the particular material can vary significantly, the given values are averages.)

The specific entropy capacity plays an important role for the "heat storage capacity" of a material. Therefore, it has for example consequences for the behavior of construction materials during heating such as wood in case of fire.

Experiment 3.8 *Vaporization of liquid nitrogen by graphite and lead*: If samples of equal amounts of different substances (possibly 0.1 mole of graphite and 0.1 mole of lead) are put into small flasks filled with liquid nitrogen ($N_2|l$) which are cooled in a Dewar vessel, an amount of nitrogen corresponding to the entropy capacity will evaporate, and the balloons will be inflated differently. Additionally, a considerable amount of entropy is generated; therefore the volume of the balloons is bigger than expected from the entropy exchanged. But the result remains qualitatively correct.



The effect of different entropy capacities of various substances can be illustrated by Experiment 3.8.

The entropy capacity depends not only—like the entropy—upon temperature and pressure, but also upon the conditions under which the substance is heated. A substance will absorb more entropy when it is allowed to expand freely than it would if its expansion were hindered. Depending on whether in most cases the pressure or more rarely the volume remains constant during the temperature increase, a different change of entropy content and therefore also a different entropy capacity can be observed. One characterizes the two different coefficients, if necessary, by indices: $\mathcal{C}_p$ and $\mathcal{C}_V$, respectively. If there is no index we always refer to $\mathcal{C}_p$.

3.10 Temperature as “Thermal Tension”

The atomistic image of entropy was given a short and qualitative description in this chapter. This was sufficient for introducing it. A formal version of the concept of entropy based upon this model would, however, be time-consuming. For the moment, referring to the particle image should just serve as an orientation. Phenomenologically or macroscopically, all the activities to be carried out in order to calculate quantities are well defined. The question arises here of whether or not these activities can be understood without recourse to the atomistic image. This has been hinted at in Sect. 3.7, and is, in fact, possible.

An image developed already in the eighteenth century seems especially simple. It imagines temperature as a kind of “pressure” or “tension” weighing upon entropy. However, at that time the word entropy was not used. One imagined a fluid like entity that warms a body, and considered it a kind of weightless substance comparable to electric charge. The temperature equalization of two bodies was described as a pressure equalization of this "heat substance" (caloric) in which this substance migrated from places of higher "pressure" to places of lower "pressure." If we accept this image, then it becomes obvious that energy is needed to generate entropy in a body against this "pressure" or "tension," or to force it into a body (comparable to filling a tire with air against an interior pressure p, or charging a body against its electric potential φ). The higher this "pressure" (the higher the temperature), the more energy is needed. The amount of energy also grows the more entropy is generated (S_g) or added (S_e). The following types of relations could be expected:

$$W = T \cdot S_g \tag{3.14}$$

and

$$W = T \cdot S_e. \tag{3.15}$$

We imagine the two entropies to be small, meaning

$$dW = T \cdot dS_g \tag{3.16}$$

or

$$dW = T \cdot dS_e, \tag{3.17}$$

so that the temperature will not change much as a consequence of the increase of entropy. Because we will discuss the energy exchange connected with the addition or removal of substances later on we suppose in this chapter that there is no convective exchange of entropy, $dS_c = 0$, meaning that the whole exchange takes place by "conduction," $dS_e = dS_\lambda$.

The first equation follows directly from the equation defining the absolute temperature if it is solved for dW. With help from the law of conservation of energy, the second equation follows easily from the first one. This law states that the same effect, no matter how it comes about, always requires the same energy. Whether a certain amount of entropy is generated in a body or added to it, the effect upon the body is identical. It expands, melts, vaporizes, or decomposes in the same manner. It must follow, then, that the energy needed for these processes must be the same.

3.11 Energy for Generation or Addition of Entropy

"Burnt" Energy Despite their similarity, the two equations above, $dW = TdS_g$ and $dW = TdS_e$, describe two rather different processes. Because entropy can increase but cannot be destroyed the process that generates it can only run in one direction and never in the other. As already mentioned, it is *irreversible*. The energy used cannot be retrieved (except indirectly). It is said that when entropy is generated and something is heated by it—noticeable such as in the heating coils of a stove plate or imperceptible when paddling in a lake—the energy needed is *devalued*, *wasted,* or "*burnt*," or that it gets *lost*. "Burnt" energy is found again in a state of random molecular motion. Statistically, it is distributed in tiniest portions over the innumerable oscillating and rotating atoms or groups of atoms. In view of these circumstances, one can speak of *dissipation of energy* instead of energy loss, waste, devaluation, etc. There are, as we have seen, plenty of terms to choose from depending upon which aspect is being emphasized. We will call the wasted and, therefore, no longer retrievable amount of energy that appears in the first of the two equations "*burnt*" *energy* $W_{\mathrm{b(urnt)}}$ (because of the close relation to the generation of entropy S_{g}):

$$\mathrm{d}W_{\mathrm{b}} = T\mathrm{d}S_{\mathrm{g}} \tag{3.18}$$

or summed up

$$W_{\mathrm{b}} = \int_{\text{initial}}^{\text{final}} T\mathrm{d}S_{\mathrm{g}}. \tag{3.19}$$

The fact that energy is needed to generate entropy does not mean that special efforts or equipment are necessary. Quite the contrary:

- In every process, a certain amount of dissipation of energy is unavoidable.
- Entropy is readily generated all the time and everywhere.

Just consider friction. On the contrary, special caution and devices are necessary to avoid this—such as ball bearings, lubricants, etc., in the case of cars.

The energy expended for generating entropy can come from inside a region itself, i.e., as if from an inner source. A compressed gas is an energy source that can be tapped. When a gas cools as it expands, the tapped energy W can be used to generate entropy S_{g}, which is then conducted back into the gas (along with W), making it warm again. In the ideal case, it will become as warm as it was at the beginning (Fig. 3.29). Entropy then appears to have been created without expending any energy. The total amount of stored energy in the system is exactly the same as at the beginning. Nevertheless, we can assume that *whenever* entropy is generated, it occurs at the cost of energy which might have been used more intelligently in

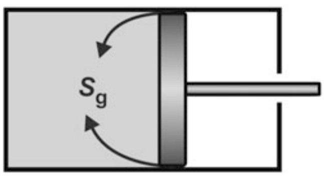


Fig. 3.29 A piston pushed out by gas enclosed in the cylinder. Entropy is generated by the friction between the cylinder and the wall. The entropy flows into the cooling gas, warming it up.

countless other ways. Energy that we can freely use is called *available energy* or *useful energy*. When referring to *energy production,* we actually mean available energy. This is also the case with so-called *lost* or *wasted energy*. The total amount of energy always remains the same, but it is of no use to us if we cannot draw it from its sources or if it disappears into sinks from where it is inaccessible.

Energy and Entropy Exchange In contrast to this, the second equation above, $\mathrm{d}W = T\mathrm{d}S_\mathrm{e}$, describes a process that is fundamentally reversible. When entropy S_e from one body is transported into another at constant temperature T, the energy $W = T \cdot S_\mathrm{e}$ is transferred with it. We will refer to this energy as W_e, if a differentiation from W_b seems necessary. The energy which was transferred returns to the original body again along with the entropy flowing back to it. This process is, therefore, *reversible*. The process described here corresponds to what is usually called *heat supply* and *heat removal*. Energy and entropy are exchanged together:

$$\mathrm{d}W_\mathrm{e} = T\mathrm{d}S_\mathrm{e} \tag{3.20}$$

or summed up

$$W_\mathrm{e} = \int_{\text{initial}}^{\text{final}} T\mathrm{d}S_\mathrm{e}. \tag{3.21}$$

In order to understand the importance of this equation, we will take a short detour to look at the development of the concept of heat. In the early days of the "science of heat" (thermodynamics), there were very diverse ideas about its nature. In the eighteenth century, heat was conceived of as a weightless "something" that heats things and could be exchanged between bodies. It was considered a kind of "heat substance" called caloric. The first successful qualitative and quantitative descriptions of effects such as heating and cooling, melting and evaporation, condensation and freezing were created based upon the concept of caloric at that time. Following the spirit of the time, it was assumed that this something could be neither created nor destroyed, just like chemical elements. In the nineteenth century, it became increasingly evident that this "substance" could actually increase indefinitely. When, however, energy appeared as a quantity that corresponded to the ideal of an entity that could neither be created nor destroyed, the view of things changed. From then on, "heat" was considered to be the energy transferred by random collisions of molecules, which could even penetrate seemingly rigid walls. This is exactly the energy described by W_e above that, even today, is usually symbolized by Q. When Rudolf Clausius introduced entropy S in the middle of the nineteenth century (under another name), neither he nor his contemporaries appear to have realized that he was only reconstructing the old quantity but with the new characteristic of being producible while remaining indestructible. Only later on, in 1911, did Hugh Longbourne Callendar allude to this fact.

Clausius derived a relation for determining the change of entropy ΔS in a body—an iron block, for instance—while it heats from a temperature T_1 up to T_2. We can find this relation much more easily. We can assume that T as well as $Q = W_e$ can be measured. T can be determined using suitably calibrated thermometers and Q can be measured calorimetrically. The entropy within a body can increase by generation or addition: $dS = dS_g + dS_e$ [compare with Eq. (3.2)]. If the addition of energy Q should be reversible, indicated by the index $_{rev}$, then $dS_g = 0$ and therefore

$$dS = \frac{dQ_{rev}}{T} \tag{3.22}$$

or correspondingly added up

$$S = \int_0^T \frac{dQ_{rev}}{T}. \tag{3.23}$$

In this way, Clausius defined the quantity entropy for the first time a century and a half ago.

Entropy plays an important role in all thermal effects. Along with temperature, it is the quantity that characterizes this field of study. Energy also plays its role, not only here but on (nearly) all stages of physical chemistry or physics. It is important but nonspecific. Although the exchanges of entropy and energy are so closely linked that it is not easy to clearly distinguish between their separate roles, it would be disastrous to mix them up. For this reason, we will avoid the word *heat* for any kind of energy, especially for the quantity Q, which we will no longer use. This word is the cause of grave misunderstandings that have been difficult to dispel. It leads us to believe that these energy-related quantities are the measure of what we imagine heat to be based upon our everyday experience. This does not really work and at the same time hinders the quantity S from being related to everyday life.

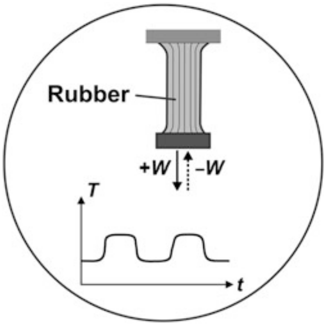
To improve understanding, we will contrast an entropy conserving process with one that generates entropy in two simple experiments. In order for an undesired exchange of entropy with the surroundings not to falsify the results, the samples must be well insulated, or the experiments must be carried out very quickly. Let us begin with the *entropy conserving* process, the expansion of rubber (Experiment 3.9).

The experiment can be adapted in a simplified manner to everyday life: We touch a thick rubber band with the upper lip and after waiting a short while for equalization of temperature, it is stretched quickly and powerfully and immediately pressed again against the upper lip. The band feels noticeably warm. When the stretched band is allowed to contract to its original length and then quickly pressed against the upper lip, there is a noticeable cooling.

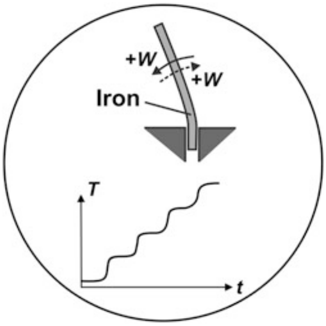
Bending an iron rod, however, is an example for an *entropy generating* process (Experiment 3.10).

Energy Exchange Along Different Paths In the systems we will be investigating, the exchange of energy will generally occur simultaneously along several paths rather than a single path. The simplest and most important paths are changes of volume V and entropy S. We were introduced to the relation between energy and

Experiment 3.9 *Temperature as a function of time in expanding rubber*: If a rubber band is expanded and then relaxed, the temperature that rises during expansion sinks again no matter how often the experiment is repeated. The energy expended at the beginning is retrievable. The temperature change $T(t)$ resembles a square wave. The process is reversible. Entropy is scarcely generated because the band is as cool at the end as it was at the beginning.



Experiment 3.10 *Temperature as a function of time in bending iron*: Bending an iron rod back to its original state (after previous bending) costs again energy, and therefore, the temperature rises in steps. This bending process is irreversible. Although the iron rod returns to its original position, it is now warmer. In this case, entropy is obviously being generated and the energy involved is used up. It is not retrievable.



volume in Sect. 2.5. If only infinitesimal changes dV and dS are considered, the following is valid:

$$\mathrm{d}W = \underbrace{-p\mathrm{d}V}_{\mathrm{d}W_{\rightarrow V}} + \underbrace{T\mathrm{d}S}_{\mathrm{d}W_{\rightarrow S}} \quad . \tag{3.24}$$

These kinds of equations, which describe the energy paths of a system, will be gone into in more detail in Chap. 9. At this point it will suffice to say that the increase of energy dW in our example is composed of one part $\mathrm{d}W_{\rightarrow V} = (\mathrm{d}W)_S$ in the V direction if all other parameters are kept constant (in this case it is only S) and a second part $\mathrm{d}W_{\rightarrow S} = (\mathrm{d}W)_V$ in the S direction, meaning at a constant V. In a graph of the function $W(V, S)$, the negative pressure $-p$ appears as the slope in the V direction and the temperature T as the slope in the S direction (Fig. 3.30). To visualize the foregoing: the slope of a mountainside m in the direction of north equals the increase of altitude Δh in this direction divided by the corresponding horizontal distance Δs in the same northerly direction, $m = \Delta h/\Delta s$ or more precisely, $m = \mathrm{d}h/\mathrm{d}s$ (compare Sect. A.1.2 in the Appendix). The following is correspondingly valid:

$$-p = \frac{\mathrm{d}W_{\to V}}{\mathrm{d}V} = \left(\frac{\partial W}{\partial V}\right)_S \quad \text{and} \quad T = \frac{\mathrm{d}W_{\to S}}{\mathrm{d}S} = \left(\frac{\partial W}{\partial S}\right)_V . \tag{3.25}$$

The increase of energy ΔW over longer paths, from location $P_1 = (V_1, S_1)$ in the (V, S) plane to a second location, $P_2 = (V_2, S_2)$, for example, can be found by adding up all the tiny segments along path $\mathcal{W}$. Curved paths can be approximated by zigzag curves made up of paraxial segments (dotted lines in the (V, S) plane in Fig. 3.30). In the case of infinitesimally small curve segments, the sum becomes an integral. For the increase $\Delta W = W(V_2, S_2) - W(V_1, S_1)$, we obtain:

$$\Delta W = \underbrace{-\int_{\mathcal{W}} p\mathrm{d}V}_{W_{\to V}} + \underbrace{\int_{\mathcal{W}} T\mathrm{d}S}_{W_{\to S}} . \tag{3.26}$$

$W_{\to V}$ is the resulting sum from all the segments running from right to left on the zigzag course, and correspondingly, $W_{\to S}$ results when all the parts along the segments running from front to back are added up. The path could be expressed in parametric form by assigning the coordinates of all the points being traversed $(V(t), S(t))$ as functions of a parameter such as time t.

In the cases we will generally be dealing with, ΔW is independent of the path, but the individual parts such as the mechanical $W_{\to V}$ and the thermal $W_{\to S}$ are not. This can most easily be seen when the paths from P_1 to P_2 along the outer edge of the

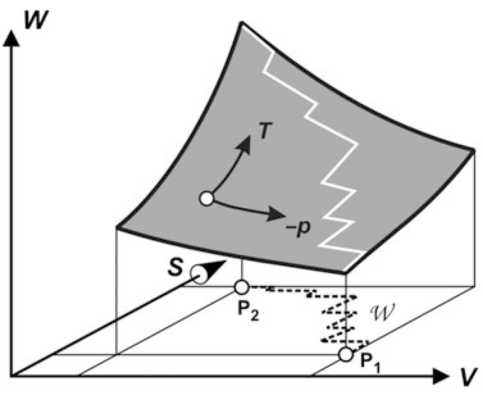


Fig. 3.30 Energy W as a function of volume V and entropy S.

gray surface are compared, first along the path on the left of the diagonal and then along the one on the right. The increase corresponding to $W_{\rightarrow V}$ on the left-hand path is small and the $W_{\rightarrow S}$ is correspondingly large, whereas it is just the opposite on the right-hand side.

If one knows that ΔW is independent of any path it takes, a lot of mathematical work can be saved by carefully choosing the path for determining ΔW. The arrows inserted for clarity's sake into the index above will generally be left out later on.

3.12 Determining Energy Calorimetrically

In Sect. 2.2 we discussed a method for measuring amounts of energy that resembles the one used since ancient times for quantifying lengths, time spans, and amounts of substance. This method involved dividing them into unit portions and then counting them. The unit portion we chose for energy was the amount necessary for stretching a so-called unit-spring. This method is easy to understand, but it is unfeasible because loss is unavoidable. The most common cause for energy loss is obstruction due to friction and the unwanted generation of entropy associated with it.

We can try to make the best of this and measure an amount of energy W by completely dissipating it and then determining how much entropy $S_g = W/T$ is generated at a given temperature T. The devices used for this are called "calorimeters," and we have already seen examples of them (Sect. 3.7). However, at this point we must be careful to neither lose any of the generated entropy nor to allow any addition from other sources. This is often the one viable method for measuring energy in chemical changes because it is nearly the only way of overcoming the ever-present inhibitions. We will come back to this later on. For now, we will begin with a mechanical example.

Let us suppose that we want to determine how much energy W is necessary to raise an object a distance h from the floor (Fig. 1.5). Instead of measuring W while the object is being lifted, we can find W while the object is being lowered, which we might do by drawing the rope over a braked hoisting drum connected to a calorimeter. An ice calorimeter could be used for this where the entropy generated (S_g) and the energy released ($W = T \cdot S_g$) in the brake shoe can be determined from the amount of melted ice. Theoretically, the energy released by expanding a spring, the impact of a thrown stone, the outflow of a compressed gas, or burning of a candle can be measured in this way.

Unfortunately, there is a hitch: latent heat, or rather, *latent entropy*. When an object is affected by compressing, stretching, electrifying, magnetizing, or by chemical alteration, it can become warm or cold even when no entropy is generated. Because of temperature differences, entropy begins to flow out into the environment or into the object from its environment making the amount of entropy in the object change. This process continues until temperatures are equalized again between the object and its environment. Such isothermal changes of entropy are called "latent entropies" ΔS_ℓ. The term "latent" was coined for caloric effects of this type in the eighteenth century. We will take a closer look at this concept in Sect. 8.7.

Every additional entropic effect interferes with measuring S_g. In mechanics, we have learned to overlook these effects because they appear to be totally meaningless. An example will make us realize that this impression is wrong. If we stretch a steel wire, it becomes colder, and when it is released, it warms up again. The change of temperature ΔT is small, only -0.5 K, even when the wire is extended to its limits. The wire needs to absorb entropy from its environment in order to retain its temperature. When the wire is allowed to shorten, the entropy flows back into the environment. In this case, the latent entropy is negative, $\Delta S_\ell < 0$. Energy W must be expended in order to expand the wire. We might determine W by allowing the expanded wire to snap back to its relaxed state in a calorimeter and measuring the generated entropy $S_g = W/T$. However, latent entropy greatly interferes with this because ΔS_ℓ is of approximately the same magnitude as S_g. If the stretching is small, it is even the dominant effect. In the calorimeter we measure the effects combined: $S_g - \Delta S_\ell = S_g + |\Delta S_\ell|$. Therefore, the procedure is only useful if it is possible to determine the latent entropy alongside the sum of the terms. In this example, it is easy to do because we can expand and relax the wire without noticeably generating entropy, so that $S_g \approx 0$ and therefore ΔS_ℓ can be determined using the same calorimeter.

In mechanics, energies are hardly ever measured directly, and certainly never calorimetrically. They are almost always calculated indirectly from measured or imagined forces and displacements. This is the preferred method because it is simpler to use and gives more exact results. In chemistry, though, things are different because to a large extent, one generally depends upon calorimetry. This gives the reverse impression that caloric effects are characteristics of transformations of substances and these types of processes cannot be properly described or understood without them. Fortunately, this impression is also false. We will return to caloric effects in Chap. 8.

3.13 Heat Pumps and Heat Engines

A *heat pump* like the one represented for example by the refrigerator described in Sect. 3.6 is a device that conveys entropy from a body of lower temperature T_1 to a body with a higher temperature T_2. The energy needed to transfer an amount of entropy $S_{t(ransfer)}$ can be easily found. It equals the energy $W_2 = T_2 \cdot S_t$ that is needed to press the entropy into the warmer body, minus the energy $W_1 = T_1 \cdot S_t$ that is gained when the entropy is removed from the colder body (Fig. 3.31):

$$W_t = (T_2 - T_1) \cdot S_t. \qquad (3.27)$$

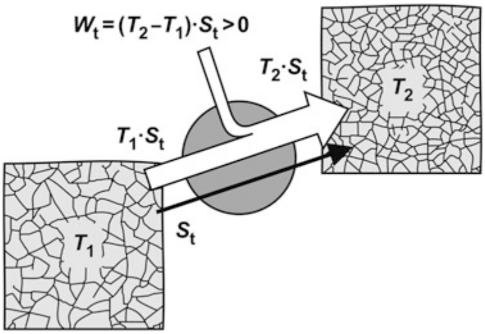


Fig. 3.31 Flow diagram of energy and entropy in an ideal heat pump (*gray circle*).

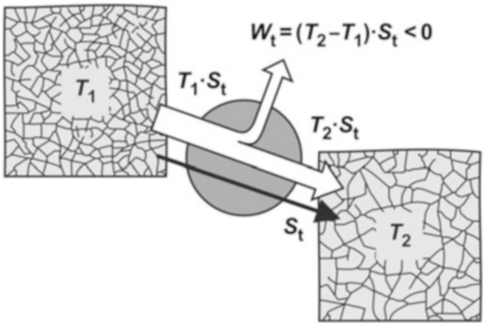


Fig. 3.32 Flow diagram of energy and entropy in an "ideal" thermal motor (heat engine) (*gray circle*).

Friction and other processes always generate some extra entropy in either smaller or larger amounts and this takes extra energy. The total amount of energy W_{total} becomes greater. The *efficiency* η of the device is expressed as follows:

$$\eta = \frac{W_t}{W_{\text{total}}}. \tag{3.28}$$

A *heat engine* or "thermal motor" (as an engine of this kind could be called following the language use in electricity) is the reverse of a heat pump. Energy is gained during the transfer of entropy out of a warmer body at temperature T_1 into a colder one with the temperature T_2 (Fig. 3.32). This energy can be calculated with the same equation that is used for finding the amount of energy needed for a heat pump. The only difference is that W_t is now negative because of $T_2 < T_1$. This means that W_t does not represent expended energy but energy gained, so-called *useful energy*.

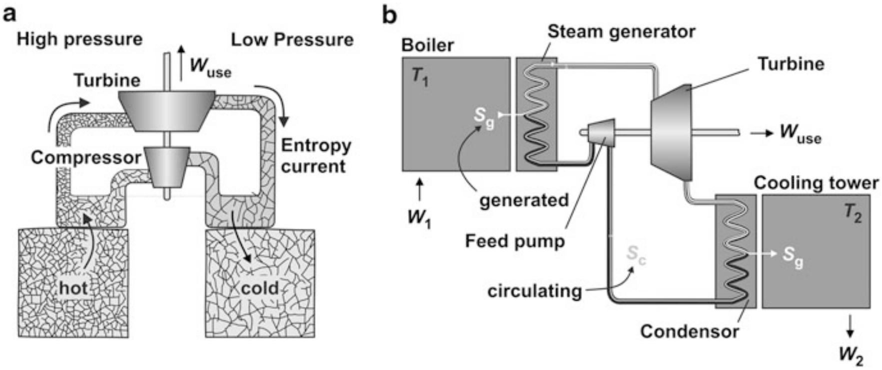


Fig. 3.33 (**a**) Possible inner setup of an "ideal" heat engine, (**b**) Simplified schematic diagram of a thermal power plant.

Figure 3.33 presents the possible inner setup of an "ideal" heat engine in more detail (Fig. 3.33a) as well as the strongly simplified schematic diagram of a thermal power plant (Fig. 3.33b). In the case of such a plant, the energy W_t ($= W_{use}$) is used which is gained during the transfer of entropy from the steam boiler to the cooling tower. The entropy itself is generated in the boiler by consumption of energy W_1.

When we use up energy W_1 to generate entropy S_g, we know that this is a one-way street with no return. Even so, we do not need to consider W_1 as completely lost. As we have seen in our example, if S_g is generated at the higher temperature T_1, it is actually possible to regain at least a part of W_1. A heat engine might transfer the entropy from a temperature of T_1 down to T_2, and ideally return energy $W_t = S_g \cdot (T_2 - T_1) < 0$ to us. In this case the quantity is counted as negative since energy is *released*. Entropy S_g cannot be destroyed so it must end up in some repository. If T_2 is the temperature of such a repository, then $W_2 = S_g \cdot T_2$ describes the amount of energy needed for this transfer, quasi the "fee" for use of the repository. Only W_2 can be considered to be lost but not W_1.

If it were possible to find a repository with a temperature of $T_2 \approx 0$, then $W_2 \approx 0$ and we would be able to recover W_1 almost completely. This energy would then be available for any type of use. It remains "undamaged" and retains its value while it is distributed over many atoms. It is neither really *lost* nor is it really *devaluated*. For this reason we will avoid using these expressions for their undesirable associations. The term "*burnt energy*" is actually much more exact because it simultaneously refers to two important aspects: the waste of useful energy and the heating associated with it.

A water mill works in exactly the same way as a thermal motor when water flows from a higher level to a lower one (Fig. 3.34). In this case, the entropy corresponds to the mass m of the water and the temperature corresponds to the term $g \cdot h$.

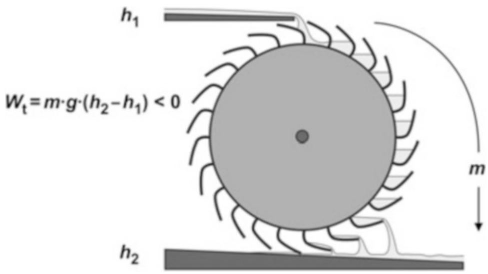
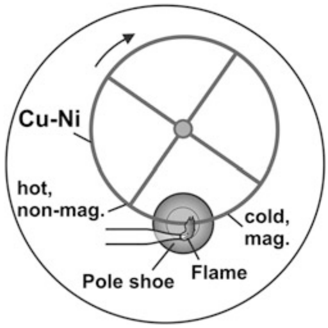


Fig. 3.34 Energy production by a water mill.



Experiment 3.11 *Magnetic heat engine*: When it heats up in the flame, the wheel flange (made of a CuNi alloy) loses in this part its ferromagnetism due to the low Curie temperature. (The Curie temperature is the temperature at which a ferromagnetic material loses its magnetism and becomes paramagnetic.) A force results which keeps the wheel in motion after a push-start. Because the left hot part of the heated wheel flange is less “magnetic” than the right cold part, the wheel flange is pulled from right to left in the area of the pole shoes.

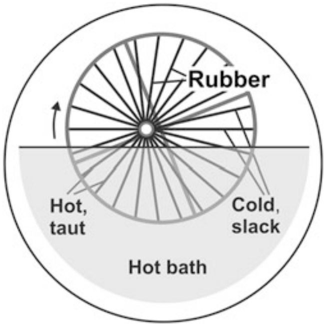
Another example would be a turbine operating between two water containers with different hydrostatic pressures. In electrodynamics the electric motor fulfills this role.

We try to direct the processes in nature in such a way that energy is left over which is freely available. By directing for example a rivulet over a mill wheel we cannot only grind corn but also pump water or drive a generator. *Free* means that the use is not predetermined. We will only say that energy is *set free* or *released* if we have the freedom to use it, even if it is just the freedom to “burn” it.

Some entropy is also generated in a thermal motor, a water mill etc., as a result of friction and other processes. This costs some of the energy W_t, so that the actual usable energy is smaller.

Finally, we will look at two examples of heat engines. Let us begin with the *magnetic heat engine* (Experiment 3.11).

The *rubber band heat engine* (Experiment 3.12) represents an alternative.



Experiment 3.12 *Rubber band heat engine*: While the wheel is centrally borne, the rubber bands pull at an eccentrically positioned wheel boss. Because the spokes are tauter after they are heated, the wheel begins to rotate and that from the right to the left in the *lower region*.

3.14 Entropy Generation in Entropy Conduction

We consider the flow of entropy through a conducting connection that we will call a "conducting segment," from a body with the higher temperature T_1 to another with the lower temperature T_2 (Fig. 3.35). We might imagine a rod made up of a material that conducts entropy well. It is insulated along its long side. One end is heated by a Bunsen burner, while the other is cooled by water. For the transfer of the amount S of entropy the energy $W = (T_2 - T_1) \cdot S$ is necessary. Its value is negative because of $T_2 < T_1$, meaning that the energy is released and has not to be expended. But where is the released energy? It cannot be stored anywhere, so it must have been used to generate entropy, it is "burnt," $W_b = -W$. The entropy S_g generated in the conducting connection must also flow—permanently increasing—down the temperature gradient to arrive finally at the cooler body with the temperature T_2. The amount S_g can be calculated from the released energy W_b:

$$S_g = \frac{W_b}{T_2} \tag{3.29}$$

with

$$W_b = -W = -(T_2 - T_1) \cdot S = (T_1 - T_2) \cdot S. \tag{3.30}$$

In the process of being conducted through a temperature gradient, entropy will increase according to set laws. This is a surprising but inevitable result of our considerations. The energy flowing to the cooler body is calculated according to

$$T_2(S + S_g) = T_2 \cdot S + T_2 \cdot \left[\frac{(T_1 - T_2)S}{T_2}\right] = S \cdot T_1. \tag{3.31}$$

Thus, it is exactly as much as the value $S \cdot T_1$ that is released by the hotter body. While the amount of entropy increases during conduction, the energy current remains constant. W_b represents the energy used up ("burnt") along the conducting

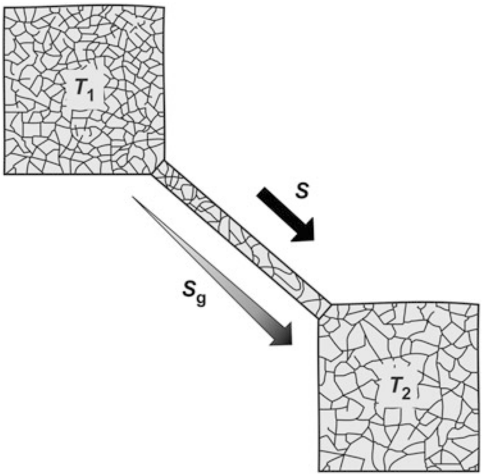


Fig. 3.35 Entropy generation related to the flow of entropy through a temperature gradient.

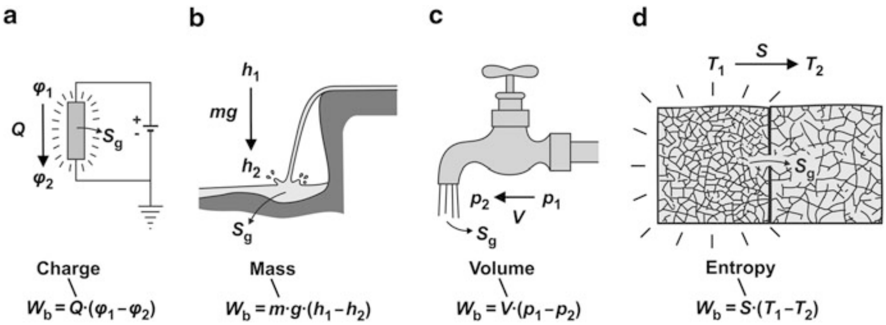


Fig. 3.36 Energy release and entropy generation for (**a**) a potential drop of charge, (**b**) a mass falling from a height, (**c**) a pressure drop of a volume, (**d**) a temperature drop of entropy.

segment. If an ideal heat engine were interposed here instead of the conducting segment, this energy would be useful energy. Here, this energy is not used and it becomes devalued while entropy increases.

Entropy conduction (Fig. 3.36d) can be compared to electric conduction (Fig. 3.36a). If an electric charge Q is forced through an electric resistor—from a higher to a lower potential φ—the resistor will become warm. This is a simple way of generating entropy which we encountered with the immersion heater in Experiment 3.6. The energy W_b released and completely "burnt" in this case results from a substance-like quantity that is pushed through the "conducting segment"—here the electric charge—and the drop of a potential—here the electric potential φ:

$$W_b = -(\varphi_2 - \varphi_1) \cdot Q = (\varphi_1 - \varphi_2) \cdot Q. \tag{3.32}$$

The entropy generated is calculated as W_b/T_2, where T_2 is the temperature of the segment. Using analogical reasoning, we can interpret the generation of entropy in

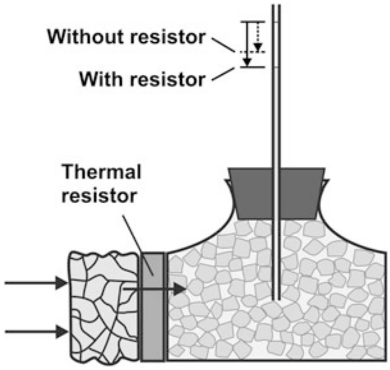


Fig. 3.37 Entropy generation by entropy exchange through a resistor.

entropy conduction as the result of the forcing of entropy through a "thermal" resistor. The temperature plays the role of a "thermal potential" and the entropy that of a "thermal charge" [Eq. (3.30)]:

$$W_b = (T_1 - T_2) \cdot S.$$

A vivid comparison is also that of a waterfall (Fig. 3.36b) where the released and "burnt" energy is found from the water mass m involved and the height of the drop, or more exactly, the drop of the "gravitational potential" $\psi = \psi_0 + g \cdot h$ where h represents the height above sea level:

$$W_b = (\psi_1 - \psi_2) \cdot m = m \cdot g \cdot (h_1 - h_2). \quad (3.33)$$

The amount of entropy generated can be calculated from the quotient W_b/T_2 where T_2 is the temperature of the effluent water. At last, let us mention an example from hydraulics, an opened water tap (Fig. 3.36c). Here, the pressure p acts as potential:

$$W_b = (p_1 - p_2) \cdot V. \quad (3.34)$$

There are two distinguishable steps that these processes all have in common:

1. Release of energy by a drop of a flowing "something" (characterized by a substance-like quantity) from a higher to a lower potential.
2. "Burning" of energy thereby generating entropy.

When entropy is conducted (Fig. 3.36d), this relation becomes a bit blurred because flowing and generated quantities have the same nature.

This type of entropy generation by forcing entropy through a resistor can be demonstrated experimentally (here as a thought experiment) (Fig. 3.37).

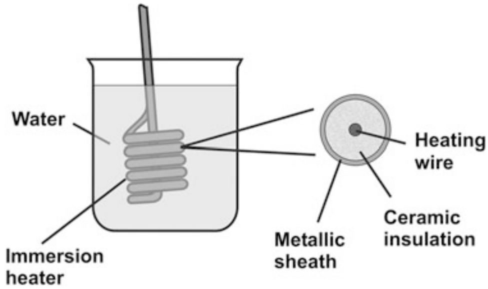


Fig. 3.38 Immersion heater in water. Magnified cross section (simplified) on the *right*.

- *Entropy flow without resistance*: If the auxiliary body is compressed, it remains cold because the entropy escapes into the bottle. The ice melts there, and the level in the capillary falls.
- *Entropy flow through a resistor*: If the same auxiliary body is compressed exactly as before, it will become warm because the entropy can only escape slowly through the resistor. It gradually seeps into the bottle and the capillary level falls even lower than before! Although the auxiliary body releases the same amount of entropy in both cases, the bottle shows more this time.

In closing, let us have a look at a concrete example, a 700 W immersion heater in water (Fig. 3.38). The heating wire should have a temperature T_1 of 1,000 K. Hence, in 1 s an amount of entropy S'_g of

$$S'_g = \frac{W}{T} = \frac{P \cdot \Delta t}{T} = \frac{700\,\mathrm{J\,s^{-1}} \times 1\,\mathrm{s}}{1{,}000\,\mathrm{K}} = 0.7\,\mathrm{J\,K^{-1}} = 0.7\,\mathrm{Ct}$$

is generated by the wire [see Eq. (3.8)]. At the surface, however, the immersion heater has the same temperature as the surrounding water. We suppose that the water temperature is $T_2 = 350$ K. Along the short path taken by the entropy S $(= S'_g)$ from the heating wire to the surface of the heater, an amount of entropy S_g of

$$S_g = \frac{W_b}{T_2} = \frac{(T_1 - T_2) \cdot S}{T_2} = \frac{(1{,}000\,\mathrm{K} - 350\,\mathrm{K}) \times 0.7\,\mathrm{Ct}}{350\,\mathrm{K}} = 1.3\,\mathrm{Ct}$$

is generated [see Eqs. (3.29) and (3.30)]. Therefore, an amount of entropy equal to $S_{total} = 2.0$ Ct flows into the water per second.